HIGHLY DISPERSED METAL SITES ON SEMICONDUCTOR SURFACE FOR SMALL MOLECULE ACTIVATION

Ehab Shaaban
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HIGHLY DISPERSED METAL SITES ON SEMICONDUCTOR SURFACE FOR SMALL MOLECULE ACTIVATION

BY

EHAB SHAABAN

M.Sc., Benha University, Egypt, 2015.

DISSERTATION

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in

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<table>
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<tr>
<td>CN</td>
<td>coordination number</td>
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<tr>
<td>DRIFTS</td>
<td>diffuse reflectance infrared Fourier transform spectroscopy</td>
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<td>EXAFS</td>
<td>Extended X-ray absorption fine structure</td>
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ABSTRACT

HIGHLY DISPERSED METAL SITES ON SEMICONDUCTOR SURFACE FOR SMALL MOLECULE ACTIVATION

By

Ehab Shaaban

University of New Hampshire, May 2023

Heterogeneous catalysts have been extensively used in various chemical transformations that have important ecological and economical relevance. The rational design of such catalysts, however, is still not effectively implemented due to the ambiguity that encircles their structure-activity correlations. The origin of synergetic effects which make the binary system (metal/metal oxide) distinct from the individual components continues to elude researchers.

In this work, binding and structural properties that emerge from metal/metal oxide interaction were investigated using in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and X-ray absorption spectroscopy (XAS). Different catalytic structures, including highly dispersed Cu sites on TiO$_2$, were prepared and characterized with spectroscopic techniques. These catalytic materials were studied in the activation of small molecules, including CO$_2$, CO, H$_2$O, and H$_2$.

XAS demonstrated that in the supported metal catalyst systems, the underlying support enables the deposited surface metal clusters to assume local structures that are different from the corresponding pure bulk metal or metal oxide. Such structures were found to be responsible for novel binding, redox, and optical properties in the binary catalyst.
In DRIFTS studies, carbon monoxide was utilized as a probe molecule to track the binding sites as other molecules are competitively adsorbed, and as the surface is brought gradually to operando catalytic conditions. The investigation revealed the existence of bifunctional active sites in which the metal sites catalyze the dissociation of CO₂ and H₂ molecules whereas interfacial sites (Cu⁺ and Ti³⁺, for instance, in Cu/TiO₂) bind and activate Lewis basic molecules such as H₂O and CH₃OH. Surface defects, such as oxygen vacancies often formed upon annealing in an oxygen-deficient atmosphere, could also play an important role in the activation of various reactant molecules.
I. INTRODUCTION

1.1 Artificial Photosynthesis through CO₂ Hydrogenation

Driven by the pressing environmental concerns and the mounting energy demands, extensive research has been implemented to find methods to harvest solar energy, as the most abundant, yet intermittent and diluted, sustainable source of energy. Solar energy could be harnessed, concentrated, and stored, either directly or indirectly, in chemical bonds which offers a promising research avenue for “artificial photosynthesis”. The photosynthesis process is generally perceived as using sunlight in converting water and carbon dioxide into carbohydrates and oxygen. However, it is important to notice that such transformation utilizes sunlight in the endergonic water splitting step only, where the hydrogen produced from the splitting is stored as NADPH (reduced form of nicotinamide adenine dinucleotide phosphate) to power the reduction of carbon dioxide in the dark cycle. So, water splitting can be seen as the main step of harvesting natural sunlight whereas CO₂ reduction is a way of H₂ storage.¹ The kinetically demanding CO₂ reduction necessitates the chemical and spatial separation of such reaction from water splitting since other more kinetically favorable reactions will be competing with CO₂.

About 80 percent of the world's energy is produced from burning fossil fuel and roughly 40% of the produced CO₂ is released to the atmosphere from point sources such as coal-fueled power plants. The recovery of CO₂ from the flue gases of these power plants is not a major technological problem, however, the utilization of the captured CO₂ in economical large-scale industries is the main challenge.²³ Recycling the captured CO₂ by reacting it with the solar-produced hydrogen to produce fuel could be implemented on an industrial scale to close the carbon cycle and facilitate H₂ storage.⁴ Hydrogen by itself can be used as a fuel since it burns cleanly and generates only heat.
and water, however, it has to be safely, efficiently, and economically stored due to its low volumetric energy density, the volumetric energy density of gaseous hydrogen at atmospheric pressure is 0.09 kg/m³.\(^5\) Utilizing CO\(_2\) as an H\(_2\) carrier facilitates the storage and distribution of the intermittent sustainable energy of the sun with the current infrastructure and helps to close the carbon cycle.

![Figure 1](image)

*Figure 1. Global CO\(_2\) emissions from energy combustion and industrial processes rebound back after slowing down due to the Covid-19 pandemic. Figure adapted for Reference \(^6\).*

### 1.2 Metal/metal oxide Catalysts

The hydrogenation of carbon oxides (CO\(_x\), including CO\(_2\) and CO) to various useful products, such as fuels, has been extensively studied on the surface of various heterogeneous catalysts, to solve both environmental and energy problems.\(^7,8\) Copper-based catalysts, for instance, demonstrated the ability to efficiently catalyze such hydrogenation reactions. Some of these catalysts have been already implemented in industry, as in the reverse water-gas shift reaction and methanol synthesis, see equations 1-3 and Figure 2.\(^8,9\)

\[
\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \quad (1)
\]
CO + 2H₂ ⇌ CH₃OH (2)

CO₂ + 3H₂ ⇌ CH₃OH + H₂O (3)

Despite the extensive research, there are substantial uncertainties on the mechanism and the role of active sites in COₓ hydrogenation that hamper the rational development of such catalysts. Generally, understanding the structure-activity correlations is the main challenge in heterogeneous catalysis. For this reason, the non-predictive or iterative approach was used to unveil significant discoveries such as the catalyst used for the synthesis of ammonia, the Haber-Bosch process, whose development required thousands of experiments before the nature of the active site was elucidated later thanks to the development of surface science.¹⁰ This lack of knowledge could be attributed to the paucity of experimental techniques that operate under the reaction conditions, the inherited non-uniformity in the heterogeneous catalysts, and the limited number of active sites among surface sites.¹⁰–¹²

Figure 2. Various industrial processes can be catalyzed synergically on metal/metal oxide catalysts. Molecules such as H₂, H₂O, CO, CO₂, and CH₃OH are activated on the surface of the catalyst either associatively or dissociatively.
Proposed mechanisms for reactions that are catalyzed by metal/metal oxide, including CO$_2$ hydrogenation, are either of dissociative nature, in which CO$_x$ species dissociate then hydrogenate to products, or of associative nature, in which H$_2$ atoms bind to CO$_x$ to form various intermediate species, Figure 2. Heated debate arises regarding (i) active sites that mediate these reaction steps and (ii) possible reasons behind the synergetic effects between the metal and the support.

In comparison to non-reducible supports, it is well-established that TiO$_2$ can significantly promote the activity and selectivity of different metals in the hydrogenation of carbon oxides and organic compounds containing polar groups such as carbonyl and nitro. Metals supported on TiO$_2$ showed enhanced activity in CO hydrogenation to methane at relatively low temperatures, approached RT when assisted with sunlight. In CO hydrogenation (Fischer–Tropsch reaction) TiO$_2$ was the most effective support to enhance metal activity and selectivity to C5+ products, enhancement can reach a 100-fold compared to other supports. The decline in activity was in the following order Co/TiO$_2$ > Co/Al$_2$O$_3$ > Co/SiO$_2$ > 100% Co > Co/MgO. The role of TiO$_2$ was dependent on the reaction under investigation, however, a general theme is that it provides Lewis acidic sites at the metal/TiO$_2$ interface, which activate polar molecules in the reactants or the intermediates. Observing Ti$^{4+}$ with in situ IR techniques as CO is adsorbed during CO oxidation to CO$_2$ at 120 K on Au/TiO$_2$ indicated that there is sequential delivery and the reaction of CO first from TiO$_2$ sites and then from Au sites, in contrast to what was believed before that only gold is involved in CO binding. Despite the paradigm shift presented in the previous article, the concept of TiO$_2$ involvement in activating CO during its oxidation on different M/TiO$_2$ catalysts and at higher temperatures was limited. It should be emphasized that the role
of Ti$^{3+}$ as CO binding sites has not been explored since it is not well differentiated from the adsorption sites of the supported metal.

Somorjai and his research group led pioneering investigations on the role of Lewis acidic interfacial sites in facilitating C-O bond dissociation during carbon oxides hydrogenation. It was suggested that the adsorbed CO is activated for dissociation with simultaneous C- and O-linking to the metal site and Lewis acidic oxide, respectively similar suggestion was introduced to explain CO$_2$ dissociation.

### 1.3 Synergetic Effects and Metal/metal oxide Interaction

Depositing metal on metal oxide doesn’t only enhance the dispersion and controls the morphology of metal sites on the high surface area of the support but also boosts the activity of the binary catalyst to orders of magnitude higher than the individual components, and also can steer the selectivity to specific products. To account for these synergetic effects, the formation of more active sites at metal/metal oxide interface, such as metals alloys, oxygen vacancies, and interfacial Lewis acidic sites were discussed. Other groups, however, proposed bifunctional mechanisms, in which metal and support coordinate tasks in the CO$_2$ hydrogenation reaction.

The observed synergy in heterogeneous catalysis itself should be a manifestation of one or more of the novel properties that could emerge from metal/metal oxide interaction in the binary system when compared to the individual component. These interactions have been discussed and reviewed before, and can range from an electronic charge transfer to a solid-state chemical reaction at the interface. It is well known in physics that electron transfer could occur from metal to semiconductor when they become in contact until the chemical potential in both solids has an equal value at equilibrium. Various visible light chromophores were used in photocatalysis using
metal-to-metal charge-transfer (MMCT) that exists between two different oxo-bonded metals in mixed metal oxides.\textsuperscript{48–50} Under mild reducing conditions, the metal-support interaction can lead to oxygen transfer from the metal oxides to the metal sites.\textsuperscript{51–56} Such sites were reported in different catalytic systems such as in Pt/CeO\textsubscript{2} (Pt\textsuperscript{+} and Ce\textsuperscript{3+}),\textsuperscript{54} Pt/TiO\textsubscript{2} (Pt\textsuperscript{+} and Ti\textsuperscript{3+}),\textsuperscript{55} Cu/CeO\textsubscript{2} (Cu\textsuperscript{+} and Ce\textsuperscript{3+}),\textsuperscript{56} and Cu/ TiO\textsubscript{2} (Cu\textsuperscript{+} and Ti\textsuperscript{3+}).\textsuperscript{57} Interestingly, studies showed that combining platinum group metals with ceria decreases the reduction temperature of ceria and that such temperature is inversely proportional to the work function of the used metal.\textsuperscript{58,59} Under stronger reducing conditions reducible supports may migrate to envelop the metal particle which affects the chemisorption properties of the latter for small molecules such as CO and H\textsubscript{2}, named as strong metal support interaction (SMSI).\textsuperscript{60} Extending reducing conditions to higher temperatures could trigger alloy formation at the metal/metal oxide interface.\textsuperscript{61–64}

Despite these achievements, there is still a lack of understanding of how metal-support interactions modify the structure of metal ions at both ends of the interface and how the new structure will affect the binding properties of such sites.

1.4 Open Coordination Sites

In homogeneous catalysts and metalloenzymes, catalytic activity usually starts with a coordinatively unsaturated transition metal site with empty orbitals to be able to bind reactants. Such sites can be occupied by an omnipresent species such as organic solvent or water, but such ligands should be labile under reaction conditions to allow binding and activating the reactants.

Investigating the structural and binding properties of surface sites in metal/metal oxide is crucial to understand how coordinately unsaturated sites get activated and bind different molecules.
1.5 Probe the Surface with IR Spectroscopy

All heterogeneous catalytic processes proceed by bond activation in adsorbed species. So adsorption of reactants from a reaction mixture on surfaces is of fundamental interest in surface chemistry, as it facilitates bond rearrangement in the adsorbed molecules.\textsuperscript{65} In the CO\textsubscript{x} hydrogenation reactions, CO can be considered not only as a reactant or intermediate but also as a molecular probe\textsuperscript{66,67} able to bind and distinguish between sites when combined with \textit{in situ} infrared spectroscopy.\textsuperscript{68}

Infrared spectroscopy is one of the most informative and efficient methods to investigate the properties of surface sites and reaction intermediates in heterogeneous catalysis.\textsuperscript{69–72} IR is usually measured through transmission mode; however, a more convenient alternative is diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The sample is used in a powder form under reaction conditions. The incident IR light striking the sample suffers multiples of reflections on the surface of the sample which produce diffusely scattered light over a wide area. The scattered light reaching the detector contains surface information since multiple absorptions take place as the beam diffuses on the sample surface, Figure 3.\textsuperscript{73}

![Figure 3. Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) diagram. IR beam passes through window CaF\textsubscript{2} to diffuse on the sample (powder) in the controlled atmosphere sample cell. The scattered beam is then collected using a parabolic mirror.](image-url)
DRIFTS studies have been used in various heterogeneous catalysis to identify adsorbate, such as intermediates in a given reaction, and to directly characterize the catalyst’s surface, such as surface hydroxyls or molecular metal species that have been installed on the surface. Another powerful approach to investigate the solid surface is to send a probing molecule to bind specifically to certain sites to characterize. Change in the IR signal after the gaseous probe molecule is adsorbed indicates the nature of the binding sites and the intensity of the absorbance can be used for quantitative analysis for different binding sites.

Analogous to the well-studied molecular metal carbonyl in organometallic compounds, CO molecule can interact with the metal or metal cation site on the surface to form surface carbonyls giving strong C–O vibration bands in the range 1800 to 2200 cm\(^{-1}\). The nature of the CO binding site affects the strength of the C-O bond thereby the carbonyl peak position. Once the gaseous CO (\(v_{\text{CO}} = 2143\text{ cm}^{-1}\)) is successfully adsorbed on the surface the carbonyl band either redshifts (classical metal carbonyls) or blueshifts (non-classical metal carbonyl).

M–CO bonds have a M←CO \(\sigma\) component, which strengthens the C-O bond and thereby increases the frequency, whereas some metals also back-bond to CO, M→CO \(\pi\) component, which weakens the CO bond and lowers its frequency. In the classical metal carbonyl region, usually carbonyls IR stretch above 2000 cm\(^{-1}\) are for metal with terminal CO structures, whereas below 2000 cm\(^{-1}\) are for bridged CO.

The ability of CO to identify surface sites and to assess their activity was widely implemented in CO oxidation, to develop catalysts for automotive emissions control, however, it was less explored in CO\(_x\) hydrogenation. Observing CO during CO\(_x\) hydrogenation offers a unique opportunity to observe both the reaction mechanism and the active sites produced from metal/metal oxide interaction at the interface.
The main challenge with probing the surface with CO, however, is the lack of an unequivocal assignment of adsorbed CO species and the various interpretation for the binding sites’ different behavior under different conditions. The lack of conclusive assignment of such peaks can be generally attributed to the complex factors that affect the stretching frequency of surface carbonyls, the lack of tools to describe minority surface binding sites, and the heterogeneity of the surface.

It is difficult to conclusively assign the CO stretch to a specific site on metal/metal oxide as the peak position is controlled by convoluted factors and the surface structure is not homogeneous or well-defined. The carbonyl peak position depends on the mode of CO bonding (poly and terminal carbonyl vs bridged carbonyl) and the type of M-CO bond, i.e. the σ vs π component which is dependent on metal electronic structure, and the chemical environment of the metal site, for instance, ligand types and the metal location at faces, edges or corners of the crystal. Assigning CO adsorption in metal/metal oxide surfaces can be guided with CO adsorption studies on single crystals of pure metal or oxide.

1.6 X-Ray Absorption Spectroscopy

X-ray absorption spectroscopy (XAS), also X-ray Absorption Fine Structure (XAFS), is a unique tool that can be used to extract quantitative chemical and structural information, at the atomic and molecular scale, about a selected element that is contained within a material. Such a technique is considered the only tool to drive local structural information around a metal site on a metal oxide support and thereby understand the structure-activity correlations in heterogeneous catalysis. The main advantage of XAS is that it is element specific and can be used in various conditions to
study different types of samples, such as solids, either crystalline or amorphous, liquids, and molecular gases.88

Figure 4. The basic configuration of X-ray absorption spectroscopy (XAS) indicates transmission and fluorescence modes.

The XAS experiments typically measure the absorption of X-ray upon illuminating the sample with high-brilliance X-ray radiation while increasing its energy. The energy is high and bright enough to efficiently eject core electrons from the atom, which is achieved using a synchrotron radiation source. The intensity of X-rays is usually tracked with ion chamber detectors, which is based on the ionizing characteristics of X-ray when it passes through a mixture of inert gases. XAS can be measured either in transmission and/or fluorescence mode and typically a reference metal foil of the same element as the analyzed sample to adjust for any drift in energy from monochromators, see Figure 4.

After illuminating the sample with X-ray radiation, the intensity of the incident beam exponentially decays according to Beer–Lambert law. However, when the energy of the incident radiation matches the excitation energy of the core electrons, a sharp jump in the absorption takes place, which is called the absorption edge. The fluorescence emission occurs after the ejection of the photoelectron when the absorbing atom de-excite as electrons in higher shells fill in the core hole. Figure 5 shows copper K-edge, as an example, located at 9.0 keV which corresponds to the
absorption of X-ray photons by 1s electrons of Cu cation. The rising part of the spectra, X-ray absorption near-edge (XANES), provides information about the oxidation state and coordination environment, and the initial part of the rise is called “pre-edge” and usually appears intense in atoms with tetrahedral geometries. 89,90

Figure 5. (a) Example of X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) of Cu K-edge XAS data for a Cu-based catalyst. (b) The EXAFS data in k (wavenumber) space for Cu K-edge extracted from the XAS spectrum shown in panel (a). 90

As the energy of the incident beam is further increased above the edge the ejected photoelectron starts to interact with surrounding atoms causing backscattering. The interference between the outgoing and the backscattered waves causes oscillations in the spectra due to constructive and destructive interferences. This part of the XAS spectra is called Extended X-ray absorption fine structure (EXAFS). The net sinusoidal wave carries information about the nature, number, and location of the neighboring atoms around the absorber. The produced wave can be described
mathematically with the EXAFS equation to obtain the local structural information for the absorbing atom. 91

XAS as a powerful and unique tool in structure characterization enabled untapped areas of research nonetheless there are certain limitations to such a method. Besides the requirement of a synchrotron facility, the main limitation of the XAS technique is that it averages the signal of the different species that exist in the sample, so the existence of multiple species from the same element could be challenging to analyze. 92,93 For this reason in metal/metal oxide catalysts it is not possible to target just interfacial sites with XAS as they are minority sites compared to the bulk metal or metal oxide.

1.7 TiO$_2$ a “Flagship” of Supports

Part of this introduction has been published and can be found here: Shaaban, E.; Li, G. "Probing active sites for carbon oxides hydrogenation on Cu/TiO$_2$ using infrared spectroscopy." Communications Chemistry 5 (2022): 1-9, https://doi.org/10.1038/s42004-022-00650-2.

As a “flagship” of reducible supports since the strong metal-support interaction (SMSI) was reported, TiO$_2$ attracted extensive research to explore its role in catalysis. 94,95 Understanding how the TiO$_2$ support affects the metal to modify its catalytic activity and selectivity can apply to other reducible supports. A common feature in a part of this research is that TiO$_2$ support significantly enhances the activity and the selectivity of metal catalysts in reactions that involve carbon monoxide, either as a reactant (in CO hydrogenation)$^{22-24}$ or as an intermediate (in CO$_2$ hydrogenation)$^{28-30}$. Mechanistic investigations pioneered by Somorjai and co-workers
highlighted the role of Lewis acidic interfacial sites, generated at the metal-titania interface, in facilitating C–O bond dissociation during carbon oxides transformation.\textsuperscript{22,31}

**Figure 6.** (a) Tetragonal structure of anatase, the experimental values for \( a, c, \) and \( d \) are 3.782, 9.502, and 1.979 Å. (b) Tetragonal structure of rutile. the experimental values for \( a, c, \) and \( b \) are 4.587, 2.954, and 1.976 Å. Red spheres represent oxygen and gray represents titanium.\textsuperscript{96}

Surface properties of TiO\(_2\) have been reviewed\textsuperscript{97,98} and binding properties have been studied with IR probing and temperature-programmed desorption techniques.\textsuperscript{99–101} Titanium dioxide predominantly exists either as anatase or rutile crystal structures, which are different arrangements of TiO\(_6\) octahedral units.\textsuperscript{102,103} Since the outermost layer at the surface of TiO\(_2\) crystal is coordinately unsaturated compared to the bulk it typically completes its coordination by water adsorption. The water could be dissociatively adsorbed to form surface hydroxyl groups, more than 12 kinds of OH groups were reported, or molecularly adsorbed. For this reason, the activation and pretreatment under certain atmospheres and temperatures before probing the surface dictate the extent and type of hydroxyl group coverage on the surface and thereby the numbers and types of coordinately unsaturated sites.\textsuperscript{104,105}
Infrared and temperature programmed desorption (TPD) studies showed that rigorous pretreatment for pure TiO$_2$ powder under a high vacuum and extended heating above 350 °C activates metallic Lewis acids for CO binding. In these infrared studies, multiple CO adsorption peaks were observed in the 2190-2179 and 2138-2121 cm$^{-1}$ for CO on Ti$^{4+}$ and Ti$^{3+}$, respectively. Such rigorous treatment was necessary to desorb the omnipresent surface water from these Lewis acidic sites to achieve CO adsorption at room temperature, once formed the Ti$^{3+}$-CO was stable up to 70 °C. There were limited available data for CO adsorption on pure copper and copper oxides.

The above discussion indicates that after certain pretreatment conditions, the titania surface can form coordinately unsaturated Ti$^{4+}$ and Ti$^{3+}$ which can bind CO molecules to form surface Ti carbonyl at room temperature. Analogous to the surface Ti carbonyls, molecular Ti carbonyls have been synthesized by various groups, and it was shown that the produced carbonyl IR signals cover a wide range of wavelengths depending on the number of the CO ligands and the charge of Ti cation.$^{113-116}$

### 1.8 Noble Metal-Based Catalysts

Copper-based materials have been used in various avenues of human life and their existence can date back to ancient Egypt$^{117,118}$ and are also of high relevance for the future. Cu-based catalysts are the ideal candidate to replace the noble metal counterparts to reduce the high cost of the catalyst. Supported copper catalysts have been used in different applications such as water splitting, CO$_2$ reduction, methanol production, the water gas shift, automotive exhaust pollution control, and preferential oxidation (PROX).$^{8,9,119-122}$
Copper oxide commonly exists as Cu$^+$ (Cu$_2$O) in a cubic structure with 2 coordination around copper in a linear geometry, or Cu$^{2+}$ (CuO) in a monoclinic structure with 4 coordination numbers around copper in an approximately square planar, see Figure 7. Supported copper sites are typically synthesized from a copper precursor in alkaline media along with the support. Depending on the conditions employed during synthesis, activation, and catalytic process, copper could exist as a dopant (substitute support cations), single surface site, cluster, or nanoparticle. The oxidation states are usually a distribution of species that is either more metallic (Cu$^0$ and Cu$^+$) or oxidized (Cu$^{2+}$/Cu$^+$) species.

Various groups investigated copper-based catalysts by probing the surface with CO adsorption IR spectroscopy to differentiate between copper species with different oxidation states, locations on Cu crystal (faces, terrace, and steps), or clusters with different morphologies, as discussed in references, including a recent review by Stacchiola. Generally, IR frequencies lower than 2100 cm$^{-1}$ are attributed to CO adsorbed on Cu$^0$ and higher frequencies between 2100-2140 cm$^{-1}$ are for CO adsorbed on Cu$^+$, while the existence of more than one peak in the latter range was arbitrarily attributed to Cu$^+$ in a cluster of different sizes. The assignment of carbonyl peaks

Figure 7. Unit cell crystal structure of (a) Cu$_2$O and (b) CuO. Red and brown balls represent oxygen and copper, respectively.
is not conclusive and often needs further investigation to understand the electronic and structural properties of such surface binding sites.

It is important when we discuss carbonyl peak assignment for CO adsorption on supported copper to shed light on *two experimental observations* to understand the origin of the CO binding sites. First, early CO adsorption IR studies on single crystal copper showed that no RT-stable surface carbonyl is formed and that low temperatures (80 K and less) were necessary to maintain the weak adsorption.\textsuperscript{130,131} The low CO adsorption temperatures are indicative of a reduced heat of adsorption, this is in contrast to supported copper sites which showed stable surface carbonyls at room temperature\textsuperscript{132}, the latter carbonyl is strongly bonded and stable against evacuation\textsuperscript{133} and thermal annealing as will be demonstrated later. No surface carbonyl was also observed in our study for CO adsorption at RT on polycrystalline copper metal, Cu\textsubscript{2}O, or CuO after different pretreatment conditions. This lack of adsorption has been also reported for CuO\textsubscript{x} in reference\textsuperscript{124}. The second observation is that copper single crystals showed RT-stable surface carbonyls IR peaks (at 2103, 2115, and 2148 cm\textsuperscript{-1}) *only* after introducing oxygen.\textsuperscript{134}

These two observations indicate how special the sites responsible for binding CO at RT are on copper-containing surfaces, and that oxidation state and crystal faces, or features (kinks, steps, and terrace) cannot alone explain some intriguing CO adsorption behaviors. With scanning tunneling microscopy (STM), it was demonstrated that exposing Cu(111) surfaces to oxygen forms different intermediate surface Cu\textsubscript{2}O ring structures.\textsuperscript{135,136} So, the observed carbonyl IR peaks produced upon CO adsorption on Cu\textsubscript{2}O/Cu(111) surface were attributed to special CO adsorption sites, in which CO molecule is confined inside a 7-membered oxide rings based on density functional theory calculations.\textsuperscript{135}
The formation of stable surface carbonyls only after exposing Cu(111) surface to O\textsubscript{2} and its absence on polycrystalline Cu\textsubscript{2}O and CuO could be attributed to the absence of previously suggested sub-nanometer cages\textsuperscript{,135} however, more investigation is necessary to further consolidate this understanding. Intriguingly, Cu (111) surface showed a certain pattern of catalytic activity that correlates with the formation of special binding sites upon oxygen introduction\textsuperscript{.135} Yates et al.\textsuperscript{137} demonstrated that the activity of Cu (111) surface for methanol oxidation reached a maximum at low oxygen coverage before deactivation due to the formation of bulk-like surface oxide.

Since the formation of RT-stable CO binding sites was enabled only after limited oxidation of Cu (111) which correlated well with the catalytic activity of the surface, as discussed above, it is important to consider other scenarios for the creation of the stable CO surface binding sites on Cu (111), other than the sub-nanometer cages\textsuperscript{135}. In the early stage of surface restructuring of Cu (111) before the oxide nucleate and thicken into Cu\textsubscript{2}O or CuO islands or continuous layers a heteroepitaxial growth of Cu\textsubscript{2}O on Cu crystal takes place\textsuperscript{.138–142} The crystal mismatch between the Cu metal substrate and the emerging Cu\textsubscript{2}O forces the latter to adapt the metal Cu spacings in the substrate. It was suggested that octahedral interstitial sites in FCC (face-centered cubic) Cu lattice become more favorable sites for subsurface oxygen\textsuperscript{.142} So, during the early oxidation, the oxo-copper surface site is forced to adopt a unique oxygenated structure that is different from both Cu\textsubscript{2}O and CuO. Such a site with a unique structure is probably the culprit in offering open coordination sites for binding CO upon exposing the Cu(111) surface to O\textsubscript{2}. The scenario proposed here better explains the presence of CO binding sites on oxidized copper metal crystal, and the absence of the same sites in pure oxides, which offer insights also into the origin of the stable CO adsorption created on the surface of supported copper.
Comparing CO adsorption properties of copper structures to Pt-group metal structures (such as ruthenium, rhodium, palladium, and platinum) reveals interesting similarities and differences. In contrast to copper metal structures, single and polycrystals of Pt-group metals showed stable CO adsorption at room temperature.\textsuperscript{143,144} Such a stable adsorption could deactivate the Pt electrode in fuel cells as traces of CO could poison the surface.\textsuperscript{145} The carbonyl stretch for CO adsorption on Pd and Pt metals can span from \(\sim 1800 \text{ to } 2100 \text{ cm}^{-1}\) depending on the CO mode of adsorption and location of adsorbing atom on the surface (faces and terrace vs step), where the highest frequency is for terminal CO and decrease as CO bridge to more than one surface atoms.\textsuperscript{143,146–148} In the scarcely available studies for CO adsorption on bulk oxides of Pt-group metal, no CO adsorption was observed at RT, and low temperature (e.g. 100 K) was necessary to enable CO adsorption,\textsuperscript{149–152} in intriguing similarity to copper oxides. Furthermore, introducing oxygen to single crystals of Pt-group metals produces high-frequency surface carbonyls (\(> 2100 \text{ cm}^{-1}\)), which was attributed to CO adsorption near oxygen-adsorbed atoms.\textsuperscript{153–155} The formation of high-frequency and RT-stable cationic metal carbonyls by Pt-group metal cations was also well-documented for MO\(_x\) (M= Ni, Pd, and Pt) sites on different supports and was attributed to cationic isolated sites (single atom site) and/or metal oxide clusters, it was suggested that reduction before CO adsorption will differentiate between both sites since the latter is more reducible.\textsuperscript{74,156,157}

The ability of certain metal structures (ultra-thin surface oxides over a single metal crystal and supported oxo-metal clusters, but not their bulk oxides) to produce stable cationic metal carbonyl raises a question regarding the catalytic activity of such structures. Structure-activity correlation aspects for one of the most-studied reactions, CO oxidation over well-define surfaces, as a single crystal, are still evolving.\textsuperscript{158} It was observed that most Pt-group metal model catalysts reached the mass transfer limit activity under specific conditions, high temperatures with high \(\text{O}_2/\text{CO}\) ratio
before they substantially deactivate upon further oxidation. The nature of this hyperactive surface was intensely debated as Frenken et. al suggested the formation of a specific type of surface oxide whereas Goodman et. al challenged this interpretation and emphasize the activity of oxygen-covered metal surface instead.\textsuperscript{155,159–163} Mainly the decrease or absence of IR CO adsorption signal during the system’s high activity\textsuperscript{164} was considered as evidence for the absence of surface oxide, whereas X-ray diffraction provided a confirmation\textsuperscript{160} for the surface oxide and the lack of carbonyl signal was justified \textsuperscript{162} by the too-short residence time of CO on the surface at such high activity. Recently, several reports demonstrated with \textit{in situ} scanning tunneling microscopy and surface X-ray-based techniques that before the single crystal surfaces of Pt-group metals form a thick inactive bulk oxide, other active surface oxides are epitaxially formed on the surface.\textsuperscript{165–169}

\textbf{1.9 Research Question and Approach}

From the previous discussion, section 1.8, we showed that the oxo-cation surface carbonyls that form on the surfaces of noble metal single crystals after mild oxidation as well as their oxo-clusters installed on other supports have a specific unique structure that is absent in bulk oxides of these metals. These oxo-cations metal carbonyls (O\textsubscript{x}M-CO)\textsuperscript{170,171} that appear at high frequencies, \(\sim\) 2100 cm\textsuperscript{-1} have been reported in various studies (Figure 8) as just a tool to distinguish between different oxidation sates of the supported metal cations. Here, however, it is hypothesized that the oxo-metal cation attains a unique structure as a result of the interaction with an underneath substrate which enables the formation of these surface carbonyls. Such structure could be similar to polyoxometalate in which highly coordinated oxo-cations of noble metal are stabilized in certain structures.\textsuperscript{172–176} This unique oxo-structure is likely the culprit of offering the open coordination to bind CO. And since in the CO binding over oxidized single metal crystal the support of the oxo-metal cation is the metal single crystals itself, the research of the epitaxial growth of the early layer
of oxide over the FCC (face-centered cubic) crystal structure of Cu or Pt-group metals can guide our understanding for the structure of these binding sites.\textsuperscript{138–142} The concept that the supported atoms/clusters/layers assume the lattice of the underlying substrate has been also discussed when ultrathin layers of noble metals were deposited on different metal single crystal support.\textsuperscript{177–179} This strained and pseudomorphic metal overlayer acquired new structural and electronic properties which were manifested as unique chemisorption properties, compared to their corresponding bulk metal.

Subjecting supported MO\textsubscript{x} clusters to oxygen deficient atmosphere would reduce the metal site, however, interfacial metal cations of the reducible supports, such as TiO\textsubscript{2}, could also change their coordination and oxidation state. These changes would occur before strong-metal support interaction takes place, i.e., before the reduced supports start to cover the metal particle.\textsuperscript{180} It is well documented that metals deposited on the surface of TiO\textsubscript{2} or generally reducible metal oxides, facilitate the reduction of the metal oxide upon thermal treatment under an oxygen-deficient atmosphere.\textsuperscript{51–56} So, in MO\textsubscript{x}/TiO\textsubscript{2} (M=Cu, Pt, Ni, etc.) it is likely to have metal cation carbonyl produced from Ti cations as well as MO\textsubscript{x} due to metal-support interaction. As mentioned earlier, pure TiO\textsubscript{2} \textsuperscript{106–110}, after rigorous pretreatment, showed the formation of stable surface carbonyl, Ti\textsuperscript{4+}-CO at 2190-2179 cm\textsuperscript{-1} and Ti\textsuperscript{3+}-CO at 2138-2121 cm\textsuperscript{-1} (Figure 8). Furthermore, molecular Ti carbonyls have been synthesized and displayed frequencies depending on the number of the CO ligands and the charge of Ti cation.\textsuperscript{113–116}
Figure 8. Summary of some CO adsorption studies indicating IR carbonyl stretching frequencies for different metal/metal oxides. TiO$_2$ typically shows high-frequency peaks (HF) below and above stretching frequency for gaseous CO. Doted rectangle indicates the HF peak region that could be assigned to reduced TiO$_2$ sites or oxidized metal sites.

The formation of cationic surface carbonyls exclusively on the metal/metal oxide binary system indicates the existence of coordinately unsaturated metal cations, either on the metal cluster, TiO$_2$, or both, with a specific structure that allows CO adsorption. Such Lewis acid species would coordinate the omnipresent water molecule from the atmosphere, so a necessary activation step will be required to observe surface carbonyls and competitive adsorption with water traces will be always observed after CO adsorption since the latter is a weaker Lewis base.$^{192}$ The water/hydroxyl ligand coordinated to such sites is more labile than the water/hydroxyl groups that exist on the plain support and the former can be driven off by activation, i.e. thermal annealing under inert gas or vacuum, under moderate conditions. Intriguingly, the change in coordination of the copper site
supported on zeolite was observed before with in situ XAS technique as copper loses water and coordinates CO.\textsuperscript{193–195}

To clearly understand the complex structure-activity correlation in metal/metal oxide catalysis, this correlation can be broken down into two layers of complication, the structure-binding properties, and binding properties-activity correlations. Using the XAS technique and in situ IR spectroscopy, respectively, structural changes and the novel binding properties that emerge from metal/metal oxide interaction have been investigated. The role of sites participating in M-O-Ti (M=Cu, Pt, Ni, and Ag) bond in catalysis, in H\textsubscript{2} generation and CO\textsubscript{2} hydrogenation, was investigated by monitoring the interaction of such sites with molecules taking part in the reaction, such as CO, CO\textsubscript{2}, H\textsubscript{2}, CH\textsubscript{3}OH, and H\textsubscript{2}O using in situ infrared spectroscopy. CO molecule, as a surface probe, was used to follow up the binding sites as other molecules are co-adsorbed and as the surface is brought gradually under operando catalytic conditions.

Since the XAS technique averages the signal of the analyzed element if it exists in multiple species (different oxidation state and local structure),\textsuperscript{92,93} it is not possible to investigate the electronic and structural changes that take place at interfacial sites, specifically on the support since most of the bulk metal oxide support are not interacting with surface clusters of the noble metal. This thwarts the implementation of one of the most powerful structure characterization tools in studying synergetic effects. To overcome a such challenge, different structures containing CuO\textsubscript{x} and TiO\textsubscript{y} centers were synthesized to enable the deduction of complementary information on the structural and electronic properties of Cu and Ti centers, see details of the structure in section 5.1.
II. SMALL MOLECULE ACTIVATION ON METAL/METAL OXIDE

Part of this chapter has been published and can be found here Shaaban, Ehab, and Gonghu Li. "Probing active sites for carbon oxides hydrogenation on Cu/TiO$_2$ using infrared spectroscopy." Communications Chemistry 5 (2022): 1-9, https://doi.org/10.1038/s42004-022-00650-2.

2.1 CO$_x$, H$_2$O and H$_2$ Activation on Cu/TiO$_2$

CO$_2$ dissociates at RT $^{57,196,197}$ or even at lower temperatures $^{198}$ on metals/metal oxide surfaces. Despite the activity of pure metal, in metal/metal oxide the interfacial sites, oxygen vacancies on the reducible support, were suggested to be the active sites that reduce CO$_2$ instead of the metal. $^{57,196,197}$ It was assumed that CO$_2$ is activated on TiO$_2$’s oxygen vacancies (Vo) to form CO$_2^-$ which will be destabilized by metal sites, such as Pt, Rh, Ir, and Cu, and this will result in the dissociation of CO$_2^-$, formation of CO on the metal, and healing of Vo. This healing mechanism was based on a weak correlation between the formation of a carbonyl IR peak and a decrease in an IR signal at ~1673 or 1640 cm$^{-1}$ that were ambiguously $^{199-202}$ ascribed to CO$_2^-$ $^{57,196}$ This limited role of the metal component in the catalyst is in contradiction with their active role, especially copper, as reductant and electron sink in CO$_2$ chemical conversion. $^{15,17,203}$ It is worth mentioning that Kong et al. $^{198}$ demonstrated with a combination of surface techniques that metal sites are the active reducing sites in the CO$_2$ dissociation over Ni/CeO$_2$. So, it’s crucial to reach a conclusive understanding of the nature and role of active sites in copper/TiO$_2$ as a model catalyst in CO$_2$ dissociation which can be in turn related to CO$_2$ and CO hydrogenation.

In the current study, *in situ* diffuse reflectance infrared Fourier transforms spectroscopy (DRIFTS) was employed to follow CO molecules as they bind to two disparate surface sites on Cu/TiO$_2$ at room temperature. The behavior of both sites was tracked, via monitoring carbonyl peak intensity
and position, as isotopically labeled $^{13}$CO$_2$ molecules dissociate and H$_2$O is introduced, and as conditions are changed to *in situ* hydrogenation conditions. Examining the disparities in their behavior under these conditions revealed novel information that dictated an assignment different from what was proposed previously in the literature. Such observations and discussion provide insights into the bi-functional role played by the metal sites and the interface during the CO$_x$ hydrogenation reaction.

### 2.1.1 Characterization of Cu/TiO$_2$ Catalysts

Highly dispersed copper sites were prepared on a TiO$_2$ surface following our published procedure, as described in the methods section. The presence of copper sites was confirmed with X-ray photoelectron spectroscopy (XPS), CO adsorption, and UV-vis spectroscopy.

The chemical states of copper sites on the Cu/TiO$_2$ sample were investigated by examining the Cu 2p and Cu LMM regions in the X-ray photoelectron and X-ray-excited Auger electron spectra, respectively (Figure 9). The catalyst was examined after hydrogen pre-treatment at 300°C for 1 hr (sample denoted as Cu/TiO$_2$-H$_2$), and after the reduced sample was annealed under Ar flow at 300°C for 1 hr (sample denoted as Cu/TiO$_2$-H$_2$-Ar). The XPS spectrum in the Cu 2p region indicates that Cu$^0$ and Cu$^+$ are the main species in the hydrogen-treated sample (Figure 9a). This is evident from the presence of Cu$^0$ and/or Cu$^+$ peaks at 932.2 eV (Cu 2p$_{3/2}$) and 952.0 eV (Cu 2p$_{1/2}$), and the absence of Cu$^{2+}$ satellite peaks that typically emerge in between those two peaks. It is difficult to distinguish between such species based only on the XPS spectrum in the Cu 2p region. Nonetheless, the Cu LMM region showed the characteristic peak for Cu$^0$ at 918.7 eV (Figure 9, a; in kinetic energy), and the amount of Cu$^0$ was estimated to be around 37% from spectral fitting (Figure 10).
Annealing the sample at 300 °C under Ar caused the copper speciation to shift more toward the cationic species, as the Cu$^{2+}$ and Cu$^+$ satellite peaks\textsuperscript{205,207} became more discernable (Figure 9, b). Cu$^{2+}$ was also detected in the Cu LMM region at 917.8 eV,\textsuperscript{206} along with Cu$^+$ and Cu$^0$ (Figure 9, d). Peak deconvolutions indicate that Cu$^{2+}$ is a minor component with around 10% peak area (Figure 10), which is consistent with the small Cu$^{2+}$ satellite peak in the XPS spectra. For pure CuO, the intensity of the satellite peak is typically $\sim$0.5 of the main Cu 2p\textsubscript{3/2} peak.\textsuperscript{207} The increase in the amount of oxidized species after annealing under Ar flow indicates that the TiO$_2$ support is likely reduced with copper metal to produce oxygen vacancies, as will be discussed in detail later.
Figure 10. Fitting Cu LMM X-ray-excited Auger electron spectra of (a) Cu/TiO$_2$-$\text{H}_2$ after the catalyst was pretreated at 300 °C under hydrogen for 1 hr; (b) Cu/TiO$_2$-$\text{H}_2$-$\text{Ar}$ after the hydrogen-treated sample was further treated at 300 °C under Ar. Reference $^{207}$ was used to guide this fitting.

To further probe the different copper sites, CO adsorption was conducted since the IR signals of surface carboxyls strongly depend on the oxidation states of the metal. The hydrogen-treated Cu/TiO$_2$ sample was loaded in the in situ diffuse reflectance cell in the air and purged with CO for 15 min at room temperature. Subsequently, gaseous CO was purged by flowing Ar prior to spectrum collection. Two carbonyl peaks at 2106 and 2058 cm$^{-1}$ are present in the spectrum (Figure 11) for CO adsorbed on surface Cu$^+$ and Cu$^0$ sites, $^{208,209}$ respectively, whereas on pure TiO$_2$ no strong carbonyl bands were observed under the same conditions. Diffuse reflectance UV-vis
spectra were also collected for the Cu/TiO$_2$ sample and pure TiO$_2$ (Figure 12). Unlike pure TiO$_2$ which shows adsorption only in the UV region, the Cu/TiO$_2$ sample possesses absorption in the visible region between 400 and 500 nm, due to Ti$^{IV}$–O–Cu$^I$ metal-to-metal charge-transfer, and ~600-800 nm for the d-d transition of Cu$^{2+}$.209

Figure 11. DRIFTS spectra of Cu/TiO$_2$ (blue) and TiO$_2$ (red) under CO flow for 5 minutes (solid lines) then after Ar purge for 1 minute (dotted lines).
2.1.2 Binding Sites and Source of the Unprompted CO

In order to probe surface sites responsible for CO\textsubscript{x} binding, the Cu/TiO\textsubscript{2} sample was pretreated in a Harrick Praying Mantis IR cell at various temperatures (100 - 400 °C) under constant Ar flow. After the sample was cooled down to room temperature under Ar, the IR cell was closed and the Cu/TiO\textsubscript{2} surface was monitored with \textit{in situ} DRIFTS. Despite the repeated washing for TiO\textsubscript{2} with H\textsubscript{2}O\textsubscript{2} (see the experimental section), there was always a slow and spontaneous CO formation on the surface of the pretreated Cu/TiO\textsubscript{2} sample at room temperature, as indicated by the carbonyl peaks associated with surface-adsorbed CO (Figure 14). The CO molecules could be produced from adventitious carbon on the surface of Cu/TiO\textsubscript{2}.\textsuperscript{211} However, in our study, it is likely produced from the recombination of surface oxygen and carbon species that have been formed during the pretreatment step. Heating the sample in this step should trigger the decomposition of carbonate-like species on TiO\textsubscript{2}.\textsuperscript{212,213} to produce carbon oxides which in turn dissociate \textsuperscript{214-220} on copper to form surface adsorbed oxygen and carbon, Figure 13. This is suggested also by the change in initial carbonate regions when the pretreatment temperature was increased, Figure 14.
Figure 13. Formation of carbon residue during thermal pretreatment and its re-oxidation when the sample cools down to RT.

At low temperatures pretreatments, 100 and 150 °C, a small fraction of adsorbed water was removed and only a low frequency (LF) CO peak was observed on Cu/TiO₂, Figure 14, a and b. On Cu/TiO₂ pretreated at 200 °C and higher, however, more water was removed from the surface and two distinct CO peaks were observed, the LF peak and another CO peak located at a higher frequency (HF), (Figure 14, c-e). Interestingly, the initial peak positions for both the HF and LF peaks showed a strong dependence on pretreatment temperatures. The onset peak position for both peaks is blue-shifted with the increase in the pretreatment temperature. Furthermore, with time after a given pretreatment, the HF peak initially increased in intensity and then decayed at the same wavenumber, whereas the LF peak appeared later and underwent similar changes in peak intensity but red-shifted until it fully decayed. For instance, on the sample pretreated at 300 °C, the HF peak appeared at ~2130 cm⁻¹ (vCO). The intensity of this peak increased gradually and then decreased while the LF peak started to emerge at ~2119 cm⁻¹ (Figure 14d). The LF peak slowly shifted to 2111 cm⁻¹ before its disappearance.
Figure 14. DRIFTS spectra of Cu/TiO₂ after activation at different temperatures. Carbonyl (a–e) and the corresponding carbonate (f–j) regions of Cu/TiO₂ as a function of time (10 min between spectra) after pre-treatment under Ar flow at (a, f) 100 °C, (b, g) 150 °C, (c, h) 200 °C, (d, i) 300 °C, and (e, j) 400 °C. Spectra were collected after the samples are cooled to room temperature. The carbonyl region demonstrates the change in intensity and position of two distinct CO binding sites, low frequency (LF) and high frequency (HF), on Cu⁺ and Ti³⁺, respectively. The corresponding carbonate region indicates the surface adsorbed water at 1620 cm⁻¹.

Both CO peaks showed different sensitivity to the residual adsorbed water that remained on the surface after different temperature pretreatments. Comparing the IR regions of surface adsorbed water, either molecularly adsorbed at ~1620 cm⁻¹ (Figure 14, f–j) or dissociatively adsorbed as hydroxyls at 3700-3000 cm⁻¹ (Figure 15)²²¹,²²² indicates that the HF CO peak emerges at lower water coverage compared to the LF peak, as can be seen from the initial spectra in h-j in comparison to f and g in Figure 14. This difference in sensitivity toward the residual water as a Lewis base indicates that the HF site is more Lewis acidic than the LF site. Furthermore, water
eventually re-accumulated on the sample surface with the extended time of data collection (up to a few hours in some experiments). The source of this water is the trace amount of adsorbed water that usually exists on the cold inner surfaces of the sample cell walls, a common issue in DRIFTS and other surface studies. In each experiment, the re-adsorption of water on the sample (Figure 14, h-j) was accompanied by the movement of the CO from the HF to LF sites (Figure 14, c-e). This indicates that the re-adsorbed water will eventually replace CO, since H₂O is a stronger Lewis base, on the HF site prompting CO migration to the less acidic LF site. More discussion is presented in section 2.1.4.

![Figure 15. Full DRIFTS spectra for Cu/TiO₂ with time at RT after pretreatment at 100 °C (a), 150 °C (b), 200 °C (c), 300 °C (d), and 400 °C (e). Solid lines are collected when the sample reached RT after activation and the dotted lines are collected at the end of the measurement (water vapor traces that diffuse from the cell walls are re-adsorbed). The dip around 3200 cm⁻¹ is an artifact due to spectral subtraction.](image)

The above observations indicate the presence of two disparate CO adsorption sites (HF and LF sites) on the Cu/TiO₂ surface. For metal catalysts supported on reducible metal oxides, it’s well documented that thermal treatment under an oxygen-deficient atmosphere triggers oxygen transfer
from the metal oxides to the metal sites at the interfacial region.\textsuperscript{51–56} Such interactions generate acidic interfacial sites as demonstrated in Pt/CeO\textsubscript{2} (Pt\textsuperscript{+} and Ce\textsuperscript{3+}),\textsuperscript{54} Pt/TiO\textsubscript{2} (Pt\textsuperscript{+} and Ti\textsuperscript{3+}),\textsuperscript{55} and Cu/CeO\textsubscript{2} (Cu\textsuperscript{+} and Ce\textsuperscript{3+}).\textsuperscript{56} Similarly, the thermal treatment of Cu/TiO\textsubscript{2} samples under inert gas flow leads to the formation of Cu\textsuperscript{+} and Ti\textsuperscript{3+} sites at the Cu/TiO\textsubscript{2} interface.\textsuperscript{57} Such Lewis acidic sites at the interfaces can bind to Lewis basic molecules such as H\textsubscript{2}O and CO. In the case of CO, the metal cations that possess a partially filled d-shell can back-bond to CO, resulting in IR stretch bands lower than 2143 cm\textsuperscript{-1}, where the IR band of gaseous CO locates.\textsuperscript{224} In accordance with the above discussion, the LF CO peak (2118-2111 cm\textsuperscript{-1}) observed in the spectra shown in Figure 14 can be attributed to the carbonyl stretching mode of CO adsorbed on the surface Cu\textsuperscript{+} sites.\textsuperscript{57,211} The adsorption site corresponding to the HF CO band (e.g. 2131 cm\textsuperscript{-1} on Cu/TiO\textsubscript{2} pretreated at 400 °C), however, is more acidic since it required higher pre-treatment temperatures and was more sensitive to water adsorption. More importantly, no progressive redshift was observed in the HF CO peak over time, suggesting that it is associated with a single adsorption site. For these reasons and based on previous theoretical\textsuperscript{225} and experimental\textsuperscript{106–110} studies, the observed HF peak can be assigned to CO adsorbed on oxygen vacancies (Ti\textsuperscript{2+}). Rigorous pre-treatment conditions (e.g. prolonged treatment at 450 °C under ultra-high vacuum) were often needed to create such CO adsorption sites on pure TiO\textsubscript{2} surfaces.\textsuperscript{106–110} In this present study, thermal treatment at 200 °C under Ar was sufficient to create oxygen vacancies on TiO\textsubscript{2}, due to the presence of surface Cu sites which facilitates the formation of such sites. It is worth mentioning that multiple studies demonstrated that metals supported on reducible metal oxides facilitate the formation of oxygen vacancies which get stabilized via metal/metal oxide Schottky junction.\textsuperscript{53,226,227}
2.1.3 Isotope Studies Using $^{13}\text{CO}_2$

To probe the roles of oxygen vacancies and surface Cu$^+$ sites in CO$_2$ dissociation, we carried out isotope labeling experiments where different amounts of $^{13}\text{CO}_2$ were introduced into the IR cell after Cu/TiO$_2$ was thermally treated at 300 °C and cooled down to room temperature under Ar. Formation of both CO isotopes, $^{12}\text{CO}$ from surface carbon residues and $^{13}\text{CO}$ from gaseous $^{13}\text{CO}_2$, on the HF/LF sites was monitored as a function of time and as the amount of $^{13}\text{CO}_2$ admitted was increased (Figure 16).

![Graphs](image)

Figure 16. $^{13}\text{CO}_2$ isotope labeling experiment. DRIFTS spectra of surface-adsorbed CO as a function of time on Cu/TiO$_2$ samples pretreated at 300 °C under Ar flow. Different amounts of $^{13}\text{CO}_2$ were present in the IR cell: a 0 bar, b 0.1 bar, and c 1 bar. To the right, the corresponding integrated CO peak areas are plotted as a function of wavenumber and time.
The presence of a relatively small amount of $^{13}\text{CO}_2$ (0.1 bar) led to the formation of $^{13}\text{CO}$ on Cu/TiO$_2$, as indicated by the appearance of the HF peak at 2082 cm$^{-1}$ (Figure 16b). The evolution of this peak follows the same pattern as the $^{12}\text{CO}$ HF peak at 2130 cm$^{-1}$, which gradually decayed while the LF peak started to develop. Both CO isotopes followed almost identical behavior in evolution, in terms of preferential adsorption on the HF sites and their migration to the LF sites. Increasing the pressure of $^{13}\text{CO}_2$ to 1 bar resulted in more surface-adsorbed $^{13}\text{CO}$ (Figure 16c). In the spectra collected immediately after the introduction of $^{13}\text{CO}_2$, the intensity of the $^{13}\text{CO}$ HF peak at 2082 cm$^{-1}$ is significantly greater than that of the $^{12}\text{CO}$ HF peak. This is likely because the amount of $^{13}\text{CO}$ produced from gaseous $^{13}\text{CO}_2$ is much larger than that of $^{12}\text{CO}$ produced from surface carbon. The increase in the onset relative amount of $^{13}\text{CO}$ as the amount of injected $^{13}\text{CO}_2$ increased confirms the occurring of dissociation whereas the relentless formation of $^{12}\text{CO}$ and its displacement to $^{13}\text{CO}$ from their binding sites supports that each of the CO isotopes originates from two opposing reactions on the catalyst as discussed earlier.

The presence of gaseous $^{13}\text{CO}_2$ inhibited the migration of CO adsorbed on oxygen vacancies (the HF peak) to surface Cu$^+$ sites (the LF peak), as shown by the comparison in Figure 16. In the absence of gaseous $^{13}\text{CO}_2$ (Figure 16a), the LF peak shifted from 2118 cm$^{-1}$ to 2111 cm$^{-1}$, and its maximum integrated area was slightly greater than that of the HF peak. Introducing a small amount of $^{13}\text{CO}_2$ (0.1 bar, Figure 16b) significantly reduced the amount of CO adsorbed on the surface Cu$^+$ sites, as shown by the relatively small integrated areas of the LF peaks (both $^{12}\text{CO}$ and $^{13}\text{CO}$). Further increasing the amount of gaseous $^{13}\text{CO}_2$ led to a nearly complete absence of the LF peak and slow decay of the HF peak (Figure 16c). These results suggest that the gaseous $^{13}\text{CO}_2$ competes with both CO isotopes during adsorption on the Cu$^+$ sites but not on the Ti$^{3+}$ sites. This is further
supported by previous studies demonstrating that CO\textsubscript{2} became strongly adsorbed as carbonates on oxidized copper sites\textsuperscript{214,228,229}.

### 2.1.4 Water Adsorption

As an omnipresent Lewis base, water molecules bind to the interfacial acidic sites on the surface of the Cu/TiO\textsubscript{2} catalyst. Since Ti\textsuperscript{3+} is a stronger Lewis acid than Cu\textsuperscript{+} and H\textsubscript{2}O is a stronger Lewis base than CO, the activation temperature required to desorb water from the Ti\textsuperscript{3+} was higher and CO was preferably adsorbed on such site compared to Cu\textsuperscript{+}. On Cu/TiO\textsubscript{2} samples with adsorbed CO, the re-adsorption of water will replace any adsorbed CO on the Ti\textsuperscript{3+} sites and then Cu\textsuperscript{+} sites, as discussed in section 2.1.2.

The role of water was further confirmed by purposely introducing water vapor in the middle of the rise of the HF CO peak. Spectra were collected for a Cu/TiO\textsubscript{2} sample at room temperature under continuous Ar flow after pretreatment at 300 °C. During the rise of the HF, the Ar flow was bypassed to flow above degassed water for 3 seconds then the Ar was switched back to the dry flow. As can be seen in Figure 17, the decay of the HF peak and the rise/decay of the LF peak occurred immediately after water introduction, in less than two minutes as compared to a few hours in the absence of dosed water.

The decay in the CO peaks was accompanied also by a rapid rise in the molecularly adsorbed water at 1620 cm\textsuperscript{-1} and hydroxyl peak at 3695 cm\textsuperscript{-1} (Figure 17, a and c). It is expected that the water molecules displacing CO from Vo are adsorbed dissociatively on such sites to produce free hydroxyl groups. However, locating such peak(s) is difficult since water re-adsorption on TiO\textsubscript{2} at RT after thermal pretreatment produces multiple dynamic hydroxyl peaks\textsuperscript{222}, i.e. peaks that keep shifting, morphing, and merging as a function of time and extent of water vapor, see Figure 18 for
hydroxyl peaks in Cu/TiO$_2$-300Ar sample. Here we noticed that among these dynamic hydroxyl peaks the 3695 cm$^{-1}$ could be due to water healing the V$_o$ in the vicinity of Cu. This peak instantaneously emerged in the Cu/TiO$_2$-H$_2$O sample directly when moisturized Ar was allowed to flow.

Figure 17. DRIFTS spectra upon introduction of water vapor. Changes in the (a) hydroxyl, (a) carbonyl, and (c) water regions in the DRIFTS spectra of Cu/TiO$_2$ before (blue, collected every 10 min) and after (red, collected every 33 s) the introduction of water vapor into the IR cell.

Multiple studies$^{222,230,231}$ showed that hydroxyl peaks around 3695 cm$^{-1}$ are for Ti$^{4+}$-OH peaks that were previously reactive defect sites (Ti$^{3+}$) but were filled dissociatively with adsorbed water. Figure 18 (c) represents the hydroxyl region around 3695 cm$^{-1}$ for Cu/TiO$_2$ -300Ar. It can be observed that the 3695 cm$^{-1}$ peak was absent, Ti$^{3+}$ sites exist, for a long time and then appear by the end of the spectra, when CO moved from the HF to LF binding sites (from Ti$^{3+}$ to Cu$^+$). Spectra
of the TiO\textsubscript{2}-300Ar sample showed that the 3695 cm\textsuperscript{-1} existed as an original peak\textsuperscript{222}, i.e. Ti\textsuperscript{4+}-OH existed before and after thermal treatment.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{hydroxyl_regions.png}
\caption{Hydroxyl IR regions at RT as a function of time for Cu/TiO\textsubscript{2}-300Ar, after pretreatment under Ar flow 300 °C. Complex ranges of hydroxyl peak emerge and disappear on the titania surface with time as water is reabsorbed.}
\end{figure}

\textbf{2.1.5 H\textsubscript{2} Admission}

In our study, introducing hydrogen at room temperature to activated Cu/TiO\textsubscript{2} either before or during the rise of CO on the HF site did not interrupt the behavior of surface adsorbed CO, either the rise CO adsorbed of the HF site or its transition to the LF site. Such behavior could be attributed to the inactivity of copper toward hydrogen at room temperature.\textsuperscript{232,233}

After pretreatment at 300 °C under H\textsubscript{2} flow, only the LF CO peak was observed in the DRIFTS spectra upon CO injection. However, upon a second pretreatment under Ar, both HF and LF CO peaks appeared (spectra not shown here for brevity). Likely, hydrogenic species formed on the HF
binding site upon hydrogen pretreatment are responsible for the absence of the HF CO peak. In line with these observations, CO adsorption on Cu/TiO$_2$ studies showed that the appearance of the HF peak required the application of delicate pretreatment conditions.$^{133,234}$ However, in such studies the HF site was assigned to different binding sites. For instance, thermal pretreatment with hydrogen precluded the formation of the HF peak, and re-oxidation with N$_2$O could not retrieve it.

Figure 19. a CO adsorption peaks under continuous CO flow over Cu/TiO$_2$ and as the temperature increases. The spectra were collected 10 min. after reaching the desired temperature. b Peak areas for the HF and LF CO peaks that were deconvoluted from a. c CO adsorption peaks at 275 °C under continuous CO flow over Cu/TiO$_2$, and as the flow was switched back and forth between Ar + CO and H$_2$ + CO.

When the H$_2$ pretreatment was followed with an evacuation step at the same reduction temperature, the HF peak was observed with even an enhanced intensity.$^{133,234}$ This intriguing behavior could
be attributed to the competitive adsorption of CO and H₂ on surface oxygen vacancies. This behavior was demonstrated previously, with different characterization tools, over Pt/TiO₂⁵⁵ and Rh/TiO₂²³⁵–²³⁸ catalysts. In such studies, it was concluded that the metal site facilitates the reduction of the titania support to produce hydrogenic species, which inhibited CO adsorption on titania.

To further investigate the role of the HF and LF CO binding sites in carbon oxides hydrogenation, those two peaks were monitored as the H₂ gas is co-adsorbed and as the temperature is increased to the reaction temperature. When the sample was purged with a mixture of Ar and CO at room temperature, only the LF CO peak was observed (Figure 19, a and b). As the temperature increased, the CO peak shifted gradually from the LF sites to the HF sites. Moreover, when the Ar flow in the gas mixture was replaced with an equal amount of hydrogen, the HF CO adsorption peak was not affected until the temperature reached 200 °C. At such temperature (and higher), a red-shift and a rapid decrease in the peak intensity were observed as H₂ was admitted (Figure 19, c) for H₂ and CO coadsorption at 275 °C. Starting at 275°C and above, the production of methane gas was observed. The CO peak intensity and position were partially retrieved again when H₂ and CO flow was switched back to Ar and CO flow. Such cyclic changes in the HF peak occurred whenever the flow was switched back and forth between Ar + CO and H₂ + CO. The observed ability of the HF site (Ti³⁺) to maintain CO binding at high temperatures and to interact with both H₂ and CO at different temperatures strongly suggests that such sites are the active centers in CO hydrogenation over Cu/TiO₂.
2.1.6 CO₂ Dissociation and Carbon Oxides Chemical Conversion

The observed disparities between the surface binding sites confirm the existence of bi-functional catalytic sites that can work collaboratively to catalyze CO₂ hydrogenation. Such bifunctionality enables heterogeneous catalysts to efficiently catalyze CO₂ conversion to higher hydrogenated products with one-pot synthesis.²³⁹,²⁴⁰ As discussed earlier, the introduction and dissociation of CO₂ affected only the LF site and the produced CO accumulated on the HF sites (Figure 20). Such observations confirm the role of the metal sites in the dissociative adsorption of CO₂. Multiple studies have demonstrated that CO₂ dissociation, a key step in CO₂ chemical conversion, takes place spontaneously on pure copper metal.²¹⁴–²¹⁸ It is worth mentioning that accumulation of the produced oxygen poisons the copper metal surface,²⁴¹,²⁴² which can be regenerated with hydrogen, based on redox mechanism²⁴³ in reverse water gas shift reaction. Moreover, studies of COₓ hydrogenation have demonstrated that surface copper sites can protect oxygen vacancies, the proposed active sites, from healing when CO₂ is introduced to a feed mixture of CO and H₂.⁴⁰

![Diagram](image)

*Figure 20. Schematic of competitive adsorption of CO with H₂O and CO₂. H₂O competes with CO on oxygen vacancies while CO₂ adsorbs on copper sites.*
The HF site demonstrated a higher affinity to bind CO even at high temperatures. This suggests that the oxygen vacancies will stabilize the CO produced from CO$_2$ dissociation occurring on the neighboring metal sites. And since hydrogenic species compete with CO on such sites upon H$_2$ introduction, it can be concluded that oxygen vacancies activate both molecules for the reaction. Calculations and experimental observation in multiple studies have confirmed the role of the oxygen vacancies during the conversion of syngas (or a mixture of syngas and CO$_2$) to methanol on reducible metal oxides and copper supported on reducible metal oxides.$^{21,40,45,226,244}$

The observed strong adsorption of water molecules on the acidic interfacial sites, which displace CO from HF binding sites, highlights the detrimental role of water on the interfacial active sites during the hydrogenation reaction. This is in line with the previous observations that water produced during CO$_2$ hydrogenation deactivates the Cu/metal oxide catalysts, and for this reason, CAMERE (Carbon dioxide hydrogenation to form methanol via a reverse-water gas shift reaction) process was implemented to minimize water percentage in the reaction mixture.$^{20}$ In such a process CO$_2$ was reduced first to CO then the CO was fed to another reactor for further reaction.

### 2.1.7 CO and CO$_2$ Adsorption at High Temperatures

The properties of interfacial binding sites in Cu/TiO$_2$ were also evaluated as the temperature of the catalyst was increased. To maintain tracking the sites and CO adsorption on the surface, CO+Ar was allowed to flow over the surface as temperature increased, and CO was negligible to the total Ar flow (400ml/min) to minimize the gaseous CO, Figure 21 (a). In another experiment, CO$_2$ was added to the flow over a fresh sample at around 80 ml/min, and Ar flow was adjusted to maintain the same total flow (CO+CO$_2$+Ar = 400 ml/min), Figure 21 (b). The temperature was increased to 300 °C then brought back to room temperature.
In the case of CO flow, there was a blue shift in peak position, then the peak intensity greatly decreased when the temperature reached 300°C, Figure 21 (a). In the presence of CO₂, the CO peak broadened when the sample temperature increased to 100°C, Figure 21 (b). At 300°C the CO peak had a much stronger intensity than the CO+Ar flow. After cooling down at room temperature two high-frequency peaks emerged at 2180 and 2165 cm⁻¹ in both experiments.

![Figure 21. In situ IR signal as a function of time for Cu/TiO₂ after activation and CO₂ injection at RT. CO was injected after the green curve](image)

The noticeable high intensity of carbonyl signal at higher temperatures in the presence of CO₂, relative to the RT adsorptions and compared to CO-only adsorption, indicate that the oxo-cations binding sites are more stable in the presence of CO₂, likely because oxygen produced from CO₂ dissociation replenish any reduction to the binding sites. The broadening in CO peaks in the
presence of CO$_2$ indicates that at high-temperature CO$_2$ interacts with the binding sites which causes its dissociation and the further oxidation of the binding sites. These observations would help in understanding the binding sites’ behavior during CO + O$_2$ reaction over supported copper. This is because CO$_2$ here is replenishing the surface with oxygen without the total consumption of the CO probing molecules. However, isotopic labeling to one molecule of the reactants, CO$_2$, and CO, is necessary to enable following the reaction.

2.1.8 CO Oxidation on Cu/TiO$_2$

Monitoring CO binding sites as O$_2$ is co-adsorbed and as the temperature gradually increases is important in studying the active sites in CO oxidation. As discussed earlier in section 1.8 of the introduction, O$_2$ adsorption on the surface of single crystal copper metal enabled the formation of stable high-frequency surface carbonyl at room temperature due to the formation of an oxo-cation with a specific structure.$^{134–136,245}$ Different studies highlighted the role of certain surface oxides, produced from the partial oxidation of noble metal surfaces, in the formation of a highly-active state in CO oxidation, in contrast to the inactive bulk surface oxide.$^{160,165–169}$ The decrease of the carbonyl signal for CO adsorbed on these surface oxides was attributed to the too-short residence time of CO on the surface at such high activity.$^{162}$ Since the formation of high-frequency carbonyls in Cu/TiO$_2$ was attributed to similar oxo-cations from the copper and/or TiO$_2$ it is important to clearly understand the role of these binding sites in CO oxidation.

Over activated (300 °C and Ar for 1 hour) Cu/TiO$_2$, Ar was allowed to flow at 500ml/min at different temperatures, and CO was allowed to flow at a low flow rate (around 1ml/min) to minimize gaseous CO signal, see black curves in Figure 22. The broad CO band can be deconvoluted to at least 3 peaks 2130, 2119, and 2107 cm$^{-1}$, the latter low-frequency component
declined as the temperature was increased from 150 to 200 °C. Replacing Ar flow with O₂, at different temperatures, blue curves in Figure 22(a-b), led to rapid consumption of the carbonyl peaks as the temperature increased. The gaseous FTIR for the outflow presented in Figure 23 indicates that more CO₂ is formed as the temperature increases, the DRIFTS outflow was connected to FTIR inflow, and 0.1 g of sample was used in DRIFTS. Carbonyl peaks were retrieved after switching to the Ar flow.

Figure 22. in situ DRIFTS spectra for CO oxidation with O₂ gas to CO₂ over Cu/TiO₂ inside DRIFTS cell at different temperatures (a) 150 °C, (b) 175 °C, and (c) 200 °C. (1) Ar (at 500 ml/min) was allowed to flow with CO (negligible flow through the oil bubbler) to allow CO adsorption and minimize gaseous CO in the IR signal. (2, blue) Ar was replaced with O₂ flow at the same rate. (3, red) O₂ flow was switched back to Ar.
Copper-supported catalysts showed high activity and selectivity in preferential oxidation (PROX) of CO to CO$_2$ in the presence of H$_2$. The PROX process is used to bring the CO levels below 50 ppm in the H$_2$ feed stream for proton exchange membrane fuel cells since even low CO levels can poison the Pt electrodes.$^{119,246}$ The ability of supported copper to catalyze PROX has been discussed before, especially over ceria. These studies showed that copper demonstrated unusual physical and chemical properties,$^{247,248}$ such as an oxidation state higher than CuO, and that interfacial sites are the active sites.$^{249}$

The results above indicate that metal oxo-cations produced from Cu-TiO$_2$ interaction are the active sites in CO oxidation. The higher frequency binding sites can bind CO at high temperatures and the CO is rapidly consumed upon the O$_2$ flow. Using CO and CO$_2$ co-flow, however, enabled monitoring the carbonyl of such sites since CO$_2$ will sustain CO molecules on the surface and replenish the oxygen of the oxo-cations as discussed earlier in section 2.1.7. This highlights the importance of supported oxo-cations in activating both oxygen and CO in CO oxidation.

Figure 23. Gaseous FTIR spectra for the outlet gases from in situ DRIFTS experiment during CO oxidation with O$_2$ gas to CO$_2$ over Cu/TiO$_2$ at different temperatures.
2.2 CO\(_x\), H\(_2\)O and H\(_2\) Activation on PtO\(_x\)/TiO\(_2\)

In contrast to the copper metal, Pt-group metals show stable CO adsorption at RT, and the carbonyl stretching can span from \(\sim 1800 - 2100 \text{ cm}^{-1}\) depending on the CO mode of adsorption and location of adsorbing atom on the surface, see 1.8 and Error! Reference source not found. Furthermore, similar to copper oxides, CO adsorption on the bulk oxides of Pt-group metal does not produce surface carbonyls unless a low temperature (100 K) is employed. The high-frequency (> 2100 cm\(^{-1}\)) and RT-stable surface carbonyls are only produced from thin oxide layers on a metal single crystal or supported PtO\(_x\) species. In the latter case, the peaks above 2143 cm\(^{-1}\) were arbitrarily assigned to Ti\(^{4+}\)–CO\(^{-}\)\(^{83,250}\) or Pt\(^{2+}\)–CO\(^{-}\)\(^{251}\). This demonstrates the role of the metal-support interaction in generating such binding sites. Here, interfacial binding sites produced from the interaction of PtO\(_x\) on TiO\(_2\) and their role in activating small molecules such as CO, H\(_2\), and H\(_2\)O were investigated.

Metal carbonyls on the surface of the 5wt%-PtO\(_x\)/TiO\(_2\) were observed upon CO injection at RT after the sample was activated under Ar flow at 300 °C for 1 hour, see Figure 24. A wide range of carbonyl frequencies was observed which demonstrates that a variety of species exist on the surface. The broad and low-frequency peak centered at \(\sim 1850 \text{ cm}^{-1}\) for bridged carbonyls indicate the existence of Pt metal particles. The carbonyl peak centered at 2086 cm\(^{-1}\) is for terminal CO adsorbed on Pt particles or a single atom site.\(^{143,146-148}\) The high-frequency carbonyl peaks at 2127 and 2186 cm\(^{-1}\) could be attributed to interfacial oxo-cations from Pt and/or Ti, which are difficult to be assigned conclusively. Introducing hydrogen in the middle of the CO rise, starting from the red curve in Figure 24, did not interrupt or change the continuous buildup of CO on the surface.

Reversing the order of adsorption (H\(_2\) first then CO) showed a completely different CO adsorption behavior, see Figure 25. After activation of fresh 5wt%-PtO\(_x\)/TiO\(_2\) sample under Ar flow at 300°C
for 1 hour, injecting H₂ gas at RT prompted an instantaneous rise in water adsorption peaks, hydroxyls, 3000-3500 cm⁻¹ and molecularly adsorbed water at 1620 cm⁻¹. Introducing CO gas afterward produced the carbonyl peaks characteristic of metallic Pt, and no higher frequency carbonyl was observed.

Figure 24. in situ DRIFTS spectra for CO-then-H₂ adsorption over PtOₓ/TiO₂ with time at RT after pretreatment at 300 °C under Ar flow, the cell was closed after the activation. Black to blue, CO adsorption with time (+2min) after CO injection (1 ìmoles, 10 ìL at10 PSIG) with a needle through a rubber septum. Starting from the red curve H₂ (70 ìmoles, 1ml at 10 PSIG) was injected with a needle, and no change in CO adsorption was observed.

The change in the CO adsorption behavior as the order of H₂ and CO injection is reversed reveals more information about the nature of the binding sites. The initial adsorption of CO prevents H₂ from being adsorbed on metallic Pt and thereby its spillover (H₂ dissociation on the metal site and migration of H atoms to the support) to oxo-cations at the interface, which maintained the high-frequency carbonyls due to CO adsorption on these sites, Figure 24. However, introducing H₂ first to the surface causes its dissociation on Pt metal particles via spillover²⁵²–²⁵⁴ to the oxo-cations on
the interface which causes water formation. The water molecules are adsorbed by Lewis acidic interfacial sites and thereby block these interfacial sites when CO is introduced later, see Figure 25.

Figure 25. in situ DRIFTS spectra for H2-then- CO adsorption over PtOx/TiO2 with time at RT after pretreatment at 300 °C under Ar flow, the cell was closed after activation. Starting from the red curve 70 µmol H2 (1ml at 10 PSIG) was injected with a needle through a rubber septum. Promptly after the H2 injection water accumulation started which precluded the formation of high-frequency after CO adsorption, 1 µmol of CO was injected after (a).

The behavior of CO biding sites over 5wt%-PtOx/TiO2 was also investigated at high temperatures to approach COx hydrogenation conditions. At 150 °C and above, the CO hydrogenation product could be observed as a methane IR peak at 3020 cm⁻¹ in C-H stretching region was obtained by the end of the reaction, see Figure 26. After activation and cooling down to 150 °C 1 µmol of CO was injected. Carbonyl peaks were similar to CO adsorption at room temperature however the peak at 2186 cm⁻¹ was absent, Figure 26 (2-4). Introducing 70 µmol of H2 of hydrogen caused a rapid loss of the carbonyl peaks and a dramatic upshift in the whole IR spectrum could be attributed to the
reduction of the TiO$_2$ support, Figure 26 (5). This substantial IR background upshift has been reported before and was attributed to H$_2$ dissociation over the metal site followed by atomic H spillover to the TiO$_2$ support. The trapped electrons from H in the TiO$_2$ conduction band cause this upward shift in the IR background.$^{221}$ This upshift was gradually decreased as the temperature cools down to RT and a methane peak was observed in the C-H bond stretch region. The downshift in the IR background could be attributed to the depletion in the concentration of conduction band electrons due to the adsorption of the produced water on the surface. Several reports studied the change in IR background as H$_2$ is adsorbed on reduced TiO$_2$ and showed that oxidation reverses the upshift caused by the reduction, it is important to note that atomic hydrogen was necessary to induce the upshift in pure TiO$_2$ otherwise high temperature and vacuum is required.$^{255,256}$

![Figure 26. In situ DRIFTS spectra for PtO$_x$/TiO$_2$: (1) At 150 °C after pretreatment at 300 °C under Ar flow for 1 hr. In a closed-cell after activation: (2-4) CO adsorption with time (+2 min) after CO injection (1 μmol, 10 μL at 10 PSIG) at 150 °C, (5) After injecting 70 μmol of H$_2$ (1 ml at 10 PSIG), and (6) After cooling back to RT.](image-url)
2.3 MO$_x$/TiO$_2$

The role of the TiO$_2$ support in creating interfacial binding sites by the interaction with supported NiO$_x$ and AgO$_x$ clusters was also investigated. Pure oxides, NO and Ag$_2$O, didn’t show any carbonyl peaks at RT after various treatments, only after in situ reductions at 300°C under H$_2$ flow NiO showed molecular Ni-carbonyl in the range 2060–1900 cm$^{-1}$.\textsuperscript{257}

![DRIFTS spectra](image)

Figure 27. In situ DRIFTS spectra for CO adsorption with time at RT after pretreating the sample at 300 °C under Ar flow, (a) nickel oxide deposited on TiO$_2$ (NiO$_x$/TiO$_2$), (b) NiO$_x$/TiO$_2$ after ex-situ reduction at 200 °C under H$_2$ flow, and (d) physical mixture of 10% NiO+TiO$_2$. (c) shows CO adsorption at RT for NiO$_x$/TiO$_2$ after in-situ reduction with H$_2$ at 300 °C. Note that pure NiO doesn’t form any surface carbonyls except when reduced at 300 °C and it shows low-frequency carbonyl for molecular Ni similar to (c).

Interaction between NiO$_x$ cluster and TiO$_2$ in 5wt% NiO$_x$/TiO$_2$ after activation, 300 °C under Ar flow, produced interfacial oxo-cations sites that bind CO to form carbonyl peaks at 2188, 2131, and 2113 cm$^{-1}$.
Figure 28. In situ DRIFTS spectra for CO adsorption over AgOx/TiO2 with time at RT after pretreatment at 300 °C under Ar flow. With time, water accumulation on the sample displaces CO(ads). Note that Ag2O doesn’t form any surface carbonyls.

Interfacial binding sites responsible for the high-frequency metal carbonyls were also produced from the interaction between the AgOx cluster and TiO2 in 5wt%-AgOx/TiO2 after activation, see Figure 28. Produced surface carbonyls have stretching frequencies at 2185, 2170, and 2129 cm⁻¹. Similar to the previously reported oxo-cations metal carbonyls, with time, water accumulation on the surface causes CO replacement on such Lewis acidic sites, as evident from the buildup of hydroxyl peaks and molecularly adsorbed water at 1618 cm⁻¹.

2.4 Summary

We have employed in situ DRIFTS to investigate surface binding sites produced from the interaction between TiO2 and supported MOx cluster ( M = noble metals such as Cu, Pt, Ni, and Ag). Results showed that only in binary systems this interaction enables the formation of interfacial oxo-metal cations with novel structures and binding properties that don’t exist in the corresponding pure bulk metal oxide. This was evident from the emergence of stable high-frequency metal cation carbonyls exclusively on the surface of binary catalysts. Such behavior was discussed along with
literature precedents on how the underlying support enforces unusual structures on overlayers of another metal or oxide, which cause an apparent change in the chemisorption properties of the overlayer.

CO adsorption was used to monitor the surface as the carbonyl peaks’ intensity and position were affected by the binding sites and the competitive adsorption of other molecules participating in the reaction. This study demonstrated the existence of bifunctional active sites in which the metal sites catalyze the dissociation of CO₂ and H₂ molecules whereas interfacial sites bind and activate Lewis basic molecules such as H₂O and CO molecules.

Introducing ¹³CO₂ at room temperature to a thermally activated Cu/TiO₂ catalyst produces a mixture of ¹³CO and ¹²CO that likely originated from ¹³CO₂ spontaneous dissociation and carbon residue oxidation, respectively. The ratio of ¹³CO/¹₂CO isotopes increased as the introduced amount of ¹³CO₂ was increased, however, with time ¹²CO eventually displaced ¹³CO on the catalyst surface.

Interfacial sites in Cu/TiO₂ catalyst gave rise to two distinct CO binding sites, Cu⁺ and Ti³⁺. The Cu⁺-CO spanned the range 2116-2111 cm⁻¹ whereas the Ti³⁺-CO (CO on oxygen vacancies) gave rise to a carbonyl peak at a single wavenumber in the range 2126 -2131 cm⁻¹, depending on the activation temperature employed. Being more acidic, the HF site (Ti³⁺) required a higher temperature (200 °C or higher) to relinquish adsorbed atmospheric water and showed more affinity to CO than the LF site (Cu⁺). Likewise, water adsorption on the surface prompted the migration of CO from the oxygen vacancies to the neighboring Cu⁺ sites. CO₂ admission, on the other hand, suppressed the LF CO peak area and limited the CO migration from the oxygen vacancies.
Hydrogenic species, formed from \( \text{H}_2 \) spill-over during pretreatment, prevented the formation of the CO HF peak at room temperature. However, this did not prevent the formation of the LF CO peak. Furthermore, the HF sites demonstrated the ability to interact with both CO and \( \text{H}_2 \) at high temperatures necessary to form methane.

On the Cu/TiO\(_2\) surface, the adsorption of CO was affected by the presence of other molecules in the hydrogenation reaction mixture, including CO\(_2\), CO, \( \text{H}_2 \), and H\(_2\)O. The observed disparities of carbonyl signals suggest the existence of bifunctional catalytic sites, in which metallic copper sites serve as CO\(_2\) dissociation sites, whereas the Cu\(^+\) and the oxygen vacancies bind the produced CO molecules for further reductions.

### 2.5 Methods

The MO\(_x\)/TiO\(_2\) catalyst was prepared via a simple precipitation method using metal salt (CuCl\(_2\), H\(_2\)PtCl\(_6\), NiCl\(_2\), and AgNO\(_3\)). P25 (TiO\(_2\), obtained from Evonik) was used as a support, and NaOH (Sigma-Aldrich, purity 99.99\%) as precipitating agent. To remove surface organic contaminants, 300 mg TiO\(_2\) was washed with 30 mL of 1:3 by volume solution of 30\% H\(_2\)O\(_2\) (aq, J.T. Baker, CMOS grade) in Milli-Q water, using sonication to disperse the powder and centrifugation to retrieve it. 5wt \% MO\(_x\)/TiO\(_2\) was synthesized from the aqueous solution of the metal salt and the required number of equivalences of NaOH in the presence of TiO\(_2\) dispersion. In some 5wt \% Cu/TiO\(_2\) samples NaOH was replaced with NH\(_4\)OH, however, this did not affect or change the binding properties if NH\(_3\) was completely removed by proper annealing. The resulting MO\(_x\)/TiO\(_2\) was separated by centrifugation, washed with Milli-Q water, and vacuum dried at room temperature overnight. Prior to infrared studies, the synthesized MO\(_x\)/TiO\(_2\) was annealed under a flow of \( \text{H}_2 \) for 3 hours at 300 °C in the tube furnace.
Additional pre-treatment of powder samples was done in a Harrick Praying Mantis diffuse reflectance IR cell attached to a Thermo Nicolet 6700 FTIR spectrometer. The catalyst in powder form was compressed in the sample holder and purged with Ar (99.999%) prior to thermal treatment at the desired temperature for 1 hour under Ar flow (400 ml/min). The sample was then cooled down to room temperature under continuous Ar flow before the IR cell was closed and spectra were collected. In the isotope experiments, specific amounts of gaseous $^{13}$CO$_2$ were introduced into the IR cell by using a syringe or flowing $^{13}$CO$_2$ briefly to produce desired pressure. Water vapor was introduced into the IR cell by using a bubbler with Ar flow. Typically, IR spectra were collected every 10 minutes, unless otherwise mentioned. UV-visible spectra were obtained on a Cary 50 Bio spectrophotometer. A Barrelino diffuse reflectance probe was used to collect UV-visible spectra of powder samples using BaSO$_4$ as a standard. X-ray photoelectron spectroscopy (XPS) investigations were performed with a KRATOS Axis Supra. Monochromated Al K$\alpha$ was used for the excitation of the photo- and Auger electrons. The binding energy scale was referenced to the C 1s at 285 eV. A glove bag was used to ensure that the hydrogen-treated sample is always kept under a dry atmosphere of either CO$_2$ or Ar during loading in the XPS instrument.

2.6 Acknowledgment

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III. CO₂ HYDROGENATION

Au and Pd metal nanoparticles in hierarchically porous TiO₂ for hydrogen generation and CO₂ reduction

3.1 Introduction

Because of the challenges in building an artificial complex catalytic system that can efficiently handle water oxidation and CO₂ reduction simultaneously, sacrificial electron donors (e.g. triethanolamine) are commonly employed in photochemical conversion of CO₂. However, such non-renewable amines could generate undesired byproducts and also protons which will compete with CO₂ for reduction. Green hydrogen can be used to replace these electron donors and reduce CO₂ to close the carbon cycle. CO₂ hydrogenation to carbon-based compounds, e.g. CO, CH₃OH, CH₄, and other hydrocarbons, can be envisaged as artificial photosynthesis since H₂ could be obtained first from the well-established technology of solar water splitting and subsequently used to reduce and recycle CO₂ into solar fuels.

Titanium dioxide is one of the most studied semiconductors and has been used extensively in photocatalysis due to its low cost and toxicity, and high chemical stability. Irradiating TiO₂ with light cause an electronic transition, the photoelectric effect in semiconductors, from the valence band (VB) to the conduction band (CB), which generates reductive electrons in the CB and oxidative holes in the VB. In pure TiO₂, however, these photogenerated-charge carrier suffers from a high recombination rate and thereby low utilization of absorbed light.

Utilizing metals as cocatalysts enhances the functionality of the TiO₂ by extending light absorption, enhancing reactant adsorption, and decreasing charge-carrier recombination. Different metal cocatalysts with various combinations and structure designs were investigated to bring about
different functions. For instance, some metal cocatalysts, such as Mn, Co, and Fe, can trap holes, whereas others are efficient at trapping electrons, such as noble metals. In CO$_2$ hydrogenation, Group 11 metals (e.g. Ag and Au) were found to be active under high temperatures and pressures (50 atm and 300 °C) to produce mainly methanol. Group 10 metals (e.g. Pd and Pt) on different support have been also investigated in CO$_2$ hydrogenation to methane at high temperatures (450°C and above).

Here we investigated heterogeneous hybrid catalysts containing Au and Pd metal nanoparticles (NPs) incorporated in hierarchically porous hollow TiO$_2$ (hTiO$_2$) for CO$_2$ hydrogenation. Plasmonic Au nanoparticles were loaded in the pores of titania to harvest visible light and convert photonic energy to energetic electrons and thermal energy for CO$_2$ activation. Loading Pd nanoparticles was also investigated in H$_2$ activation and production.

### 3.2 Results and Discussion

Hierarchically porous Au/hTiO$_2$ was synthesized based on the previously reported colloidal-amphiphile-templated growth method. The co-assembly of two templates, namely amphiphilic block copolymers (BCPs) and polymer-tethered Au NPs were used to grow mesoporous Au/TiO$_2$. The PEO-b-PTMSPMA (poly(ethylene oxide)–block–poly (3-(trimethoxysilyl) propyl methacrylate) was used as a micellization BCP template. Thiol-terminated PEO, produced from the esterification of PEO monomethyl ether with mercaptoacetic acid (PEO-SH), was used to cap the surface of Au nanoparticles (ca. 14 nm in diameter) through Au-S binding. Using these templates along with Ti precursors, see methods section 3.4, provided organosilane-containing colloidal templates that prevent the overgrowth of crystallinities and the collapse of the mesoporous structure. Before removing the silica structure with concentrated hot
alkaline solution the calcined powder was dispersed and Pd NPs were deposited, the catalyst was labeled as Au/hTiO$_2$-Pd. This synthesis method separated the metallic NPs and thereby prevented the alloying and sintering of Au and Pt NPs. hTiO$_2$ and hTiO$_2$-Pd were synthesized similarly without Au-Pd or Au NPs addition, respectively.

Au/hTiO$_2$-Pd showed uniform macropores and mesopores, with isolated Au and Pd NPs, see Figure 29. The pore size for macropores and mesopores are 387 nm and 17 nm, respectively, as shown in the dark-field STEM images. HRTEM showed the clear lattice structures of TiO$_2$(101), Pd (111), and Au(111). The isolated AuNPs and AuNPs were further confirmed by STEM-EDS mapping.

![Image](attachment:image.png)

**Figure 29. Structural characterization of Au/hTiO$_2$-Pd. (a-c) SEM, (d) TEM, (e, f) dark field STEM; (g) HRTEM images, and (h, i) STEM mapping of Au/hTiO$_2$-Pd**

Small-angle X-ray scattering (SAXS) patterns, Figure 30 (a), showed three clear scattering peaks, indicating the ordered structures of mesoporous TiO$_2$ frameworks. The XRD patterns showed the anatase phase of TiO$_2$ Figure 30 (b), no patterns of Au or Pd can be seen due to their low loading.
amount and small size. The N\textsubscript{2} sorption isotherms, Figure 30 (c,d), showed the typical hysteresis of mesoporous structures. Specific surface area (SSA) and other physical properties of samples are listed in Table 1. The hTiO\textsubscript{2} showed 127 m\textsuperscript{2}\text{g}\textsuperscript{-1} SSA whereas metal deposition causes a decrease in such value. The corresponding pore size was \~17 nm, in agreement with the size obtained from SEM images.

**Table 1. Specific surface areas, pore diameters, and pore volumes for different catalysts**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>SSA (m\textsuperscript{2}\text{g}\textsuperscript{-1})</th>
<th>Pore diameter (nm)</th>
<th>Pore volume (cm\textsuperscript{3}\text{g}\textsuperscript{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>hTiO\textsubscript{2}</td>
<td>127</td>
<td>16.6</td>
<td>0.29</td>
</tr>
<tr>
<td>Au/hTiO\textsubscript{2}</td>
<td>98</td>
<td>17.0</td>
<td>0.26</td>
</tr>
<tr>
<td>hTiO\textsubscript{2}-Pd</td>
<td>72</td>
<td>16.9</td>
<td>0.24</td>
</tr>
<tr>
<td>Au/hTiO\textsubscript{2}-Pd</td>
<td>77</td>
<td>16.8</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Figure 30. (a) SAXS, and (b) XRD patterns of different catalysts. (c) N\textsubscript{2} sorption, and (d) corresponding pore size distribution of different catalysts.
The optical properties were studied by measuring the absorbance spectra for powder samples in the UV-Vis region, 200 to 800 nm, see Figure 31. All the Au-doped TiO₂ samples exhibited improved absorbance spectra towards the visible region in the range 500 and 700 nm, associating with surface plasmon resonance absorption of gold.²⁶⁶

![Absorbance Spectra](image)

*Figure 31. UV-vis spectra and the optical band gap of catalysts.*

The catalytic activity of samples in CO₂ hydrogenation was evaluated using the DRIFTS cell in a batch reactor mode at 300 °C. Experiments showed that the photocatalytic activity component is trivial when the photothermal activity was measured, so only the thermal component was considered here. 50 mg of the sample was loaded in the cell and traces of KBr was dispersed on the surface to adjust the IR signal absorption. After activating the sample under a flow of Ar at 300 °C for 1 hour the cell was pressurized with a mixture of 10% CO₂ and 90% H₂ to 10PSIG. The in-situ DRIFTS measurements for hTiO₂, Au/hTiO₂, hTiO₂-Pd, and Au/hTiO₂-Pd samples are presented in Figure 32. Through a septum-sealed outlet, a sample was withdrawn using a gas-tight syringe to quantitatively analyses the gases in the cell headspace with an Agilent 7820 gas chromatography instrument equipped with a thermal conductivity detector (GC-TCD), see Figure 33.
For samples containing Au and/or Pd NPs, the CO gas was prominently produced in the beginning (IR peak at 2143 cm\(^{-1}\) in Figure 32 and filled-symbols curves in Figure 33), but with time CH\(_4\) gas (IR peak at 3020 cm\(^{-1}\) in Figure 32 and open-symbols curves in Figure 33) started to consistently accumulate. Meanwhile, the hTiO\(_2\) sample showed only a minor increase in the CO gas. Results showed that the Pd-containing catalyst had higher activity than Au/hTiO\(_2\).

![Figure 32. in situ CO\(_2\) hydrogenation for 300 °C inside DRIFTS cell with time at 300°C under 10 PSIG total pressure of CO\(_2\) and H\(_2\) mixture. CO\(_2\) was allowed to flow first at 300°C at 1 atm (using an oil bubbler to prevent air from backflow). The outlet valve was then closed and the cell was pressurized until the total pressure was 10 PSIG.](image)

CO\(_2\) hydrogenation could be accomplished in either a continuous flow fixed-bed reactor or batch mode reactor.\(^{267}\) Running CO\(_2\) hydrogenation in batch mode, however, allows following the change in the product composition with time. The initial rapid buildup in the CO gas then its deacceleration and consumption with time as the CH\(_4\) rises indicate that CO is a reaction
intermediate and product. This was further elucidated by following the reaction for a longer period in one of the trials, Figure 34. The CH₄ reduction continued to increase further as CO declined.

Figure 33. Quantitive measurements for CO and CH₄ produced from the CO₂ hydrogenation in DRIFTS cell as a batch reactor at 300 °C and 10 PSIG.

Figure 34. Analysis for CO₂ hydrogenation’s product over hTiO₂-Pd for a longer time, 4.5 hrs.
In \( \text{H}_2 \) evolution from 4:1 (vol/vol) water/methanol mixture under visible light irradiation and an Ar atmosphere, Figure 35, Au-containing samples showed higher activity than pure hTiO\(_2\) and hTiO\(_2\)-Pd. This could be attributed to the plasmonic effect that gold demonstrated in the visible region as discussed before.

![Graph](image)

**Figure 35.** Hydrogen generation under simulated sunlight using the visible light lamp. Catalyst was dispersed in a 4:1 (vol/vol) water/methanol solution.

### 3.3 Summary

Photothermal catalysis is a key process for the efficient and direct utilization of renewable solar energy. Here, the effect of loading two types of metal NPs into different pores of hierarchically porous oxide supports was investigated in CO\(_2\) hydrogenation and hydrogen generation processes. Au and Pd metal nanoparticles were doped onto mesoporous TiO\(_2\) through the evaporation-induced self-assembly (EISA) method. Pd-modified samples displayed enhanced catalytic activity toward CO\(_2\) reduction to methane at moderate temperatures, whereas the three-component
nanocomposites demonstrated enhanced photocatalytic hydrogen generation when irradiation with daylight bulbs. Based on the experimental results obtained, a plausible mechanism for CO₂ hydrogenation based on the dissociative route was discussed.

3.4 Methods

This was a collaborative project with Professor Jie He’s group at the University of Connecticut. They prepared mesoporous Pd, Au, and Au-Pd@hTiO₂ composites based on the co-assembly of two soft templates, namely amphiphilic block copolymers and polymer-tethered. Professor He’s group collected electron microscopy, XRD, BET, and UV-vis data shown in Figures 29-31.

Synthesis of hierarchically porous TiO₂ (hTiO₂):

The macro-meso TiO₂ was synthesized using PEO-b-PTMSPMA (poly(ethylene oxide) – block – poly (3-(trimethoxysilyl) propyl methacrylate) micelles (~20 nm) as the templates. Briefly, 0.8 mL of titanium tetrachloride (10 vol % in ethanol) and 0.54 mL of titanium isopropoxide were added into the 10 mL of PEO-b-PTMSPMA micelle solution (15 mg/mL) under stirring. Then 4 mL of PS suspension in ethanol (100 mg/mL) was added to the mixture. After stirring for 30 minutes, the mixture was poured into a petri dish, followed by evaporation at 40 °C for 24 hours and 100 °C for 12 hours. The obtained powder was calcined at 450 °C for 2 hours. The final macro-meso TiO₂ was obtained after washing with 2 M NaOH (50 °C) to remove the silica.

Synthesis of isolated Au and Pd NPs in hierarchically porous TiO₂ (Au/hTiO₂-Pd):

It was similar to the synthesis of hTiO₂, expect for the addition of PEO-modified Au NPs (14 nm) and post-synthesis of Pd NPs. Briefly, TiCl₄ and TIPO were added into the PEO-b-PTMSPMA micelle solution, followed by adding the PEO-modified AuNPs (1mg/mL in ethanol) and PS
solution in the mixture. After stirring for 30 min, the mixture was poured into a Petri to evaporate the solvent. The obtained powder was calcined at 450 °C for 2 hours (Au/hTiO₂). To grow the Pd NPs, Au/hTiO₂ was dispersed into water, followed by adding Na₂PdCl₄. After stirring for 30 min, the ice-cold NaBH₄ was added to reduce the Na₂PdCl₄ to Pd NPs. The Au/hTiO₂-Pd was obtained after washing the obtained powder with 2 M NaOH (50 °C) to remove the silica. The loading of AuNPs and Pd NPs are designed to be 1 wt% and 2 wt% respectively. hTiO₂-Pd was synthesis with the same loading technique using previously prepared hTiO₂.

**Photocatalytic H₂ evolution:**

10 mg of the catalyst was dispersed in a 4.0 mL mixture solution of 4:1 (vol/vol) water/methanol mixture under visible light irradiation. Prior to photocatalytic testing, the reaction solution was bubbled with Ar in the dark for 10 min. The solution was then irradiated with a halogen lamp equipped with a water filter. Light intensity reaching the solution was fixed at 200 mW/cm². The head space above the reaction solution was sampled with a gas-tight syringe at different time intervals for quantitative analysis using an Agilent 7820 GC equipped with a TCD detector.
IV. LOCAL METAL STRUCTURE IN HETEROGENEOUS CATALYSIS WITH XAS

4.1 Introduction

The dynamic relation between late transition metal particles with the underlying support under different reaction conditions has been intensively investigated because of its relevance to the catalytic activity. Depending on the nature of the metals in the binary system and the redox conditions the active state of the catalyst can be mixed oxides, metal/metal oxide, metal-reduced metal oxide, and alloy. When the support is a perovskite oxide (ABO₃, such as SrTiO₃, where the B cation, in 6-fold coordination, surrounded by an octahedron of anions O, and the A cation in 12-fold cuboctahedral coordination) the supported metal can substitute B-site. So, depending on the redox conditions the metal sites can either dissolve in the lattice to form mixed oxide in an oxidizing atmosphere or segregate to form metal particles under reducing conditions, such dual behavior in exhaust-emissions control systems was termed self-regenerating or smart catalyst. This doping-segregation has been used as a simple synthetic technique to control the properties of noble metal nanoparticles on perovskite supports and thereby tuning the catalytic behavior.

The segregation behavior of the dopant atom was found to be mainly dependent on the nature of the dopant atom and the choice of perovskite oxide. In this study the behavior of Au and Ni precursors to dope SrTiO₃ and then segregate to form metal nanoparticles under reductive conditions was examined with ex-situ X-ray absorption spectroscopy (XAS). The reductive segregation behavior of both elements was studied under different reductive conditions and dopant concentrations. Samples were synthesized with a hydrothermal method according to previous reports.
4.2 XANES and EXAFS data for Au-doped SrTiO$_3$

Studying the effect of reduction temperature employed during doping-segregation synthesis method on the dimensions and morphology of supported Au catalysts. As the reduction temperature increases, more Au atoms are expected to segregate from their position in the SrTiO$_3$ crystal to form metallic clusters.

Two Au doping percentages, 4 and 8 atomic percent (at.%) in SrTiO$_3$, were synthesized and then reduced at different temperatures, see table below. Ex-situ X-ray absorption data for Au edge were collected for these samples.

Table 2. As-prepared SrTiO$_3$ doped with 4 and 8 at.% reduced at different conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Doping level(at%)</th>
<th>Reduction T / °C</th>
<th>Reduction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>4</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>20</td>
<td>4</td>
<td>200</td>
<td>2h</td>
</tr>
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<td>21</td>
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<td>300</td>
<td>2h</td>
</tr>
<tr>
<td>22</td>
<td>4</td>
<td>400</td>
<td>2h</td>
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<tr>
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<td>4</td>
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<td>4</td>
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<td>2h</td>
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<td>300</td>
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<tr>
<td>28</td>
<td>8</td>
<td>400</td>
<td>2h</td>
</tr>
<tr>
<td>29</td>
<td>8</td>
<td>500</td>
<td>2h</td>
</tr>
<tr>
<td>30</td>
<td>8</td>
<td>600</td>
<td>2h</td>
</tr>
</tbody>
</table>

4.2.1 Result and discussion

XANES Au L$_3$ spectra for the as-synthesized samples showed a strong white line that arises from the high density of d-holes in the Au, see Figure 36 for 4 and 8 % Au doped SrTiO$_3$. This is consistent with the rich oxygen environment around Au as demonstrated by the Au-O1 shell in the
EXAFS spectra for both samples, Figure 38. The lack of Au-Au contributions in the EXAFS spectra, *vide infra*, indicates that isolated mononuclear gold sites were formed.

The fitting analysis for the fresh, unreduced 4 and 8% Au doped SrTiO$_3$ samples suggests that the first shell is for oxygen ligands with 3.1-3.3 coordination number ($\text{CN}_{\text{Au-O}}$) and 1.99 Å radial distance ($R_{\text{Au-O}}$), see Figure 39 and the structural parameters derived from EXAFS fitting listed in Table 3. The presence of an oxygen shell at this short distance indicates that the substitutional model in which Au replaces Sr in SrTiO$_3$ couldn’t be used in the fitting since the 1$^{st}$ oxygen shell is expected to be comparable to the Sr-O bond length (2.76 Å) in the SrTiO$_3$ structure. Model in which Au replaces Ti in the SrTiO$_3$ was considered to be unlikely due to the disparities in size between Au and Ti and due to the lack of reasonable good fit for the higher EXAFS shells.

![Figure 36. Au L$_3$ absorption edge XANES data for 4 and 8% Au-doped SrTiO$_3$ samples and Au foil. The as-synthesized samples showed strong white line absorption which rapidly shift close to Au foil upon reduction at 200 °C. Increasing the reduction temperature pushed the samples’ spectra closer to the Au foil.](image-url)
Improvements in fitting trials for higher shells were only viable when O (another O shell but at a longer distance), Ti, and Sr were introduced to the proposed structure, assuming that Au occupies surface sites as suggested by the weak intensity of the EXAFS higher shells. In the unreduced samples the Au-O₂, Au-Ti, and Au-Sr were located at 2.85-2.88 Å, 3.18-3.21Å, and 3.57-3.59 Å, respectively, see Figure 40 and Figure 41. The R_{Au-O₂} was found to be comparable to the 2.76 Å Sr-O bond in the SrTiO₃. This model suggests that Au is a monodispersed surface site coordinated to two sets of oxygen ligands at 1.99 Å and 2.85-2.88 Å, where the latter is a part of the SrTiO₃ structure. This was confirmed by the fact that the Ti shell in the samples was located at a similar distance from the absorber as the Sr-Ti distance (3.38 Å) in SrTiO₃, i.e. suggests that Ti is oxo-bonded to the Au site. Furthermore, the R_{Au-Sr} value suggests that Sr is also oxo-bonded to the gold site since the R_{Au-Sr} for the Sr shell (3.57-3.59 Å) was at a much shorter distance than the Sr-Sr distance (3.90 Å) in SrTiO₃. Additionally, this R_{Au-Sr} was the same as R_{Au-Sr} in the computationally derived crystal structure of SrAuO₃, 3.58 Å, which confirms the formation of the Au-O-Sr binuclear bond. Based on this discussion gold cation local structure could be envisioned as a surface oxo-gold site bonded either to terminal oxygens or bridging oxygen of Sr and Ti in SrTiO₃ crystal, Figure 37 (a) and (b), respectively.
As the samples were subjected to reduction at 200 °C and higher, a shift in the edge position toward Au foil occurred and the white line intensity greatly decreased, Figure 36. This indicates that cationic gold in the as-synthesized samples was predominantly reduced to zero-valent gold at 200 °C. EXAFS spectra for 4 and 8 % Au-doped SrTiO$_3$ samples as they were subjected to reduction at increasing temperatures are presented in Figure 38. The Au-O shell diminished and Au–Au shell emerged as the reduction temperature increased, note that the split in the Au–Au is attributed to
Ramsauer–Townsend resonance.\textsuperscript{279} Although Au-O shells in 4 and 8\% as-synthesized samples were of comparable intensity the Au-Au shell in the reduced 4\% Au samples have always a lower intensity at various reduction temperatures which indicates that the gold phase in the latter samples is more dispersed and has smaller Au clusters.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure39.png}
\caption{Coordination number and bond length produced from fitting EXAFS data for the first shell (Au-O) in the as-synthesized samples, and the Au-Au shell for samples after reduction at different temperatures and gold foil.}
\end{figure}

In the reduced samples, the \(CN_{\text{Au–Au}}\) and \(R_{\text{Au–Au}}\) in the gold cluster were dependent on Au loading percent, Figure 39, and EXAFS fitting parameters in Table 3. After the 200 °C reduction the \(CN_{\text{Au–Au}}\) for 4 and 8\% Au-SrTiO\(_3\) samples was around 7.7 ± 1 and 9.6 ± 0.8, respectively. Increasing reduction temperature causes a slight increase in \( CN_{\text{Au–Au}} \) in both of the Au loading. The lower
CN_{Au–Au} and the shorter R_{Au–Au} in the 4% sample confirm the higher gold dispersity and smaller Au cluster in the 4% Au-SrTiO_3 compared to the 8%.

**Figure 40.** EXAFS R space fitting for unreduced 4% Au-doped SrTiO_3 with different shells contribution.
Figure 41. EXAFS R space fitting for unreduced 8% Au-doped SrTiO₃ indicating different shells contribution.

Figure 42. EXAFS R space fitting for 200 °C reduced 4% Au-doped SrTiO₃.
Table 3. Structural parameters derived from $k^2$-weighted EXAFS curve fitting.

<table>
<thead>
<tr>
<th>No.</th>
<th>CN (a)</th>
<th>$\Delta E_0$ (b) [eV]</th>
<th>RÅ (c)</th>
<th>$\sigma^2$ [Å$^2$] (d)</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>Au-O1</td>
<td>3.1 ±0.4</td>
<td>1.99 ±0.01</td>
<td>0.001 ±0.001</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Au-O2</td>
<td>3.0 ±1.5</td>
<td>12.1 ±1.3</td>
<td>2.88 ±0.03</td>
<td>0.004 ±0.005</td>
</tr>
<tr>
<td></td>
<td>Au-Ti</td>
<td>1.1 ±0.6</td>
<td>3.21 ±0.04</td>
<td>0.006 ±0.001</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Au-Sr</td>
<td>1.0 ±0.1</td>
<td>3.59 ±0.03</td>
<td>0.004 ±0.0001</td>
<td>0.04</td>
</tr>
<tr>
<td>20</td>
<td>Au-O</td>
<td>0.5 ±0.1</td>
<td>2.00 ±0.04</td>
<td>0.010 ±0.005</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>7.7 ±1.0</td>
<td>5.5 ±0.7</td>
<td>2.84 ±0.01</td>
<td>0.014 ±0.002</td>
</tr>
<tr>
<td>21</td>
<td>Au-O</td>
<td>0.2 ±0.2</td>
<td>2.03 ±0.03</td>
<td>0.012 ±0.001</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>8.5 ±0.9</td>
<td>5.8 ±0.6</td>
<td>2.84 ±0.01</td>
<td>0.014 ±0.002</td>
</tr>
<tr>
<td>22</td>
<td>Au-O</td>
<td>0.2 ±0.1</td>
<td>2.05 ±0.03</td>
<td>0.001 ±0.006</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>8.3 ±0.8</td>
<td>5.7 ±0.6</td>
<td>2.83 ±0.01</td>
<td>0.014 ±0.002</td>
</tr>
<tr>
<td>23</td>
<td>Au-O</td>
<td>0.2 ±0.1</td>
<td>2.12 ±0.06</td>
<td>0.001 ±0.001</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>8.4 ±1.2</td>
<td>5.7 ±0.8</td>
<td>2.83 ±0.01</td>
<td>0.013 ±0.002</td>
</tr>
<tr>
<td>24</td>
<td>Au-O</td>
<td>0.2 ±0.1</td>
<td>2.11 ±0.04</td>
<td>0.001 ±0.003</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Au-Au</td>
<td>9.0 ±1.3</td>
<td>5.6 ±0.8</td>
<td>2.83 ±0.02</td>
<td>0.013 ±0.002</td>
</tr>
<tr>
<td>25</td>
<td>Au-O1</td>
<td>3.3 ±0.4</td>
<td>8.8 ±1.5</td>
<td>1.99 ±0.01</td>
<td>0.002 ±0.001</td>
</tr>
<tr>
<td></td>
<td>Au-O2</td>
<td>1.2 ±0.8</td>
<td></td>
<td>2.86 ±0.05</td>
<td>0.002 ±0.001</td>
</tr>
<tr>
<td></td>
<td>Au-Ti</td>
<td>0.9 ±0.5</td>
<td></td>
<td>3.19 ±0.04</td>
<td>0.005 ±0.001</td>
</tr>
<tr>
<td></td>
<td>Au-Sr</td>
<td>1.5 ±0.7</td>
<td></td>
<td>3.57 ±0.02</td>
<td>0.005 ±0.001</td>
</tr>
<tr>
<td>26</td>
<td>Au-Au</td>
<td>9.6 ±0.8</td>
<td>5.6 ±0.6</td>
<td>2.854±0.004</td>
<td>0.008 ±0.006</td>
</tr>
</tbody>
</table>

8% Au-STO unred. 200*
<table>
<thead>
<tr>
<th>Sample</th>
<th>Au-Au CN</th>
<th>Au-Au R</th>
<th>Au-Au Bond Length</th>
<th>Debye-Waller Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% Au-STO-300*</td>
<td>27</td>
<td>9.5 ±0.5</td>
<td>6.2 ±0.4</td>
<td>2.859 ±0.003</td>
</tr>
<tr>
<td>8% Au-STO-400*</td>
<td>28</td>
<td>9.4 ±0.6</td>
<td>5.8 ±0.5</td>
<td>2.853 ±0.003</td>
</tr>
<tr>
<td>8% Au-STO-500*</td>
<td>29</td>
<td>10.0 ±0.3</td>
<td>6.1 ±0.2</td>
<td>2.858 ±0.002</td>
</tr>
<tr>
<td>8% Au-STO-600*</td>
<td>30</td>
<td>10.5 ±0.7</td>
<td>5.7 ±0.4</td>
<td>2.857 ±0.003</td>
</tr>
</tbody>
</table>

(a) Coordination number. (b) Energy shift correction. (c) Bond length. (b) Debye-Waller factor.

* CN values for the Au-O shell in the reduced 8% Au-doped samples were less than 0.2, therefore CN and R values were not reported.

### 4.2.2 Summary

XANES and EXAFS spectra indicate that isolated mononuclear gold sites were formed in the as-synthesized Au-doped SrTiO$_3$ samples. The presence of a strong white line in XANES and the lack of Au-Au contributions in EXAFS supported this proposed structure. EXAFS fitting also showed that the Au site adapts surface oxo-structure that is connected to the SrTiO$_3$ structure through two oxo-binuclear bonding; Au-O-Ti and Au-O-Sr. Under reducing conditions, gold cations reductively segregate from such sites to form a metal cluster, the size of which is determined by the initial level of Au doping and the reducing conditions employed. After the 200 °C reduction, the cluster coordination number CN$_{Au-Au}$ for 4 and 8% Au doped SrTiO$_3$ samples was around 7.7 ± 1 and 9.6 ± 0.8, respectively. Increasing reduction temperature causes a slight increase in CN $Au-Au$ in both of the Au loading. The lower CN$_{Au-Au}$ and the shorter radial distance $R_{Au-Au}$ in the 4% sample confirm the higher gold dispersity and smaller Au cluster in the 4% Au-SrTiO$_3$ compared to the 8%.
4.2.3 Acknowledgment:

Data analysis described in this chapter was accomplished under the supervision of Professor Anatoly Frenkel (SBU-BNL) during a 6-month NSF-funded internship. This study was part of a larger collaborative project between Professor Anatoly Frenkel (SBU-BNL) and Professor Alexander Orlov (SBU). The raw data were provided by Professor Frenkel’s group.
4.3 X-ray Absorption Spectroscopy for Ni-doped SrTiO$_3$

Studying the effect of reduction temperature employed during doping-segregation synthesis method on the dimensions and morphology of supported Ni catalysts.

Two doping percentages, 4 and 8 at.%, of Ni in SrTiO$_3$, (Ni-STO) were synthesized and then reduced at different temperatures for either one or two hours, see Table 4 below. XAS data for Ni edge were collected for the reduced samples and in situ reduced samples.

Table 4. Ni-doped SrTiO$_3$ samples were synthesized with different loading and then reduced at different temperatures and time

<table>
<thead>
<tr>
<th>Number</th>
<th>Doping level(at%)</th>
<th>Reduction T / °C</th>
<th>Reduction time</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>200</td>
<td>2h</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>300</td>
<td>2h</td>
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<tr>
<td>5</td>
<td>4</td>
<td>400</td>
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<td>4</td>
<td>600</td>
<td>2h</td>
</tr>
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<td>11</td>
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<td>N/A</td>
<td>N/A</td>
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<tr>
<td>12</td>
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<td>200</td>
<td>2h</td>
</tr>
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</tr>
<tr>
<td>18(in situ)</td>
<td>4</td>
<td>600</td>
<td>2h</td>
</tr>
</tbody>
</table>

4.3.1 Results and Discussion

To understand the cluster formation process during Ni reductive segregation initial Ni local structure before the reduction was investigated. The as-synthesized samples are distinct from Ni
foil and NiO standards in XANES, Figure 43, and EXAFS, Figure 44, spectra. Such differences were maintained up to 200 °C reduction, however, at higher temperatures samples started to approach the Ni standard. The as-synthesized samples, in both 4 and 8% Ni-STO, showed higher Ni K-edge than the NiO standard, which suggests different oxidation states and chemical environments. After the 200 °C reduction, the samples’ Ni edge energy decreased but was still higher than the NiO edge, whereas at 300 °C and higher the edge became less than NiO and started to approach the Ni foil edge. Similarly, the intensity of the white line, that arises from the empty d shell in Ni cations, starts to drop only at 300 °C and higher.

The blueshift in the samples’ Ni edge dropped from 1.4 to 1.1 when the Ni loading percent increased from 4% to 8% and after reduction at 200°C, the samples shifted more towards NiO, see inset in Figure 43. Ni substitution to Ti⁴⁺ in the strontium titanate structure (SrTi₁₋ₓNiₓO₃) usually causes this blueshift in XANES Ni edge, however, the magnitude of the shift can be as large as 2.5 eV when a lower percent of Ni loading (3 mol%) and a much higher synthesis temperature (1500 °C) were used in the SrTi₁₋ₓNiₓO₃ synthesis.²⁸⁰,²⁸¹ The decrease in the Ni edge energy for the 8% Ni loading suggests an increase in the percent of unreduced Ni that doesn’t occupy Ti⁴⁺ substitutional sites since Ni has limited solubility in the strontium titanate crystal. Furthermore, since the solubility of Ni is also affected by the employed synthesis temperature, the energy shift in the 4% Ni-STO is still lower than the previously reported values²⁸⁰,²⁸¹ in which a high-temperature synthesis was employed. Assuming that the energy shift in the latter case corresponds to 100% of Ni loading in Ti⁴⁺ substitutional sites, the % of Ni⁴⁺_{sub} in the 4 and 8% Ni-STO samples can be estimated to be 56 and 44%, respectively, based on the relative energy shift.
Figure 43. XANES spectra were obtained for 4 and 8 % Ni-doped SrTiO$_3$ samples (as-synthesized and after reduction at different temperatures) and standard materials (Ni foil and NiO).

EXAFS spectra for the as-synthesized and 200°C-reduced samples, in both 4 and 8% Ni-STO, have generally similar shell locations but the 4% samples display differences in the shell magnitude, especially at longer bond distances. In comparison to the NiO standard, the oxygen shell in these samples was at a shorter bond distance whereas the 2nd shell is at a longer bond distance. Furthermore, their 2nd shell amplitude was much lower than NiO despite having comparable intensity in the 1st O shell.

Since XANES confirms the existence of Ni$^{4+}_{\text{sub}}$, the face-centered cubic structure of SrTiO$_3$ was implemented as a model for EXAFS fitting by replacing the central titanium with nickel. The CN$_{\text{Ni-Sr}}$ in this model was defined whereas other parameters were allowed to vary. Implementing this model for fitting the as-synthesized 8% Ni-STO unreduced, as an example for unreduced samples, gave reasonable fitting for oxygen shell, CN$_{\text{Ni-O}}$=6, and R$_{\text{Ni-O}}$=2.05 Å, see Table 5, however, fitting
the 2nd shell as Sr produced $R_{\text{Ni-Sr}} = 3.00 \, \text{Å}$ which is far shorter than expected; based on the model, $R_{\text{eff}} = 3.37 \, \text{Å}$, and previously reported values for $R_{\text{Ni-Sr}}$ in SrTi$_{1-x}$Ni$_x$O$_3$, 3.35 - 3.38 Å.

Figure 44. Comparison of $k^2$-weighted (K=2-8) EXAFS spectra for 4 and 8% Ni-doped SrTiO$_3$ samples (as-synthesized and after reduction at different temperatures) and standard materials (Ni foil and NiO).

In light of the previously discussed XANES observations on the existence of another oxidized, Ni phase fitting trials that involve Ti, using NiTiO$_3$ structure, and Sr shells were implemented. The best fit based on this model is presented in Table 7 for 8 and 4% Ni-STO samples, respectively. Figure 45 represents an example of such fit for the 8% Ni-STO unreduced Sample (#11). It is worth mentioning that including Ni- instead of Ti- with Sr in the fitting trials produced an unreasonably high Debye-Waller factor of ~ 0.03. Furthermore, including both Ni and Ti along with Sr gave a fit that excludes Ni, CN$_{\text{Ni}}$=0. Such observations are consistent with the low Ni
loading and suggest that the non-substitutional Ni\(^{2+}\) species are probably attached to titanium atoms on the surface of SrTiO\(_3\) rather than forming separate phases like NiTiO\(_3\).

Figure 45. \(k^2\)-weighted (K=2.5-11) EXAFS fitting in R space for the as-synthesized 8\% Ni-doped SrTiO\(_3\) sample #11) showing O, Ti, and Sr shells.

When the reduction temperature increased to 300 °C the as-synthesized samples showed significant reduction as indicated by the shifting in Ni absorption edge in XANES, Figure 43, which was accompanied in EXAFS by the emerging of Ni-Ni scattering shell as the Ni-O and Ni-Ti shells declined, see Figure 44 and Figure 46. Such changes were more dramatic in the case of 8\% Ni loading compared to 4\%. The percent of metallic Ni, from linear combination fitting analysis presented in Figure 47, and CN\(_{\text{Ni-Ni}}\), presented in
Table 6 and Table 7, were 87% and 10, respectively, in the 8 % Ni-STO-300, however, were 47% and 5 in the 4 % Ni-STO-300 sample.

As the reduction temperature was furtherly increased the % metallic Ni and \( \text{CN}_{\text{Ni-Ni}} \) gradually increased in the 4% Ni-STO samples until they reached 68% and 8 at 600°C, while the 8% Ni-STO samples did not display significant changes, were 89% and 11, respectively, see Figure 47 and 6. In these samples, the unreduced Ni is likely the residue of the Ni\(^{4+}\)\text{sub.} in the crystal, since Ni-Sr shell was still observed after the 600°C reduction. Considering the loading difference in 8 and 4 % Ni, the estimated remaining amount of Ni\(^{4+}\)\text{sub.} as a percent from the SrTiO\(_3\) ended up the same, 1mol%, after the 600°C reduction.

![EXAFS fitting](image)

Figure 46. \( k^2 \)-weighted (K=2.5-11) EXAFS fitting in R space for the 8 % Ni-doped SrTiO\(_3\) after reduction at 300°C ( #13) showing O, Sr, and Ni metal 1\(^{\text{st}}\) and 2\(^{\text{nd}}\) shells.

The surge that occurred in % of metallic Ni and \( \text{CN}_{\text{Ni-Ni}} \) after the 300°C reduction in both of the Ni loading could be attributed to the reduction of Ni\(^{2+}\) coordinated with Ti since the Ni-Ti shell
rapidly declined in comparison to the Ni-Sr shell. The formed crystals in this step can act as nucleation sites for the reduced Ni\textsubscript{4+} that will segregate from the crystal when the reduction temperature is furtherly increased. From these observations, it can be concluded that the initial Ni loading and the employed synthesis temperature control the amount of Ni\textsubscript{4+} in SrTiO\textsubscript{3} crystal, where Ni that exceeds this solubility limit is hosted by titanium atoms probably on the particle surface. The latter phase is more reducible and acts as nucleation sites for the Ni that segregate from the crystal as the reduction temperature increases.

Figure 47. The molar percent of reduced Ni phase in the 4 and 8 % Ni-STO as samples are subjected to different reduction temperatures using linear combination fitting.
Figure 48. Coordination number in the 4 and 8 % Ni-STO when as-synthesized samples are subjected to different reduction temperatures, fits were limited to Ni-O and Ni-Ni shells.

Table 5. EXAFS fitting parameters for 8% Ni-STO unreduced (#11) based on only SrTi$_{1-x}$Ni$_x$O$_3$ model

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>$\Delta E_0$ [eV]</th>
<th>R[Å]</th>
<th>$\sigma^2$ [Å$^2$]</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% Ni-STO</td>
<td>Ni-O</td>
<td>6.3 ± 1.7</td>
<td>2.05 ± 0.01</td>
<td>0.004 ± 0.003</td>
<td>0.04</td>
</tr>
<tr>
<td>8% Ni-STO</td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>-0.3 ± 2.2</td>
<td>3.00 ± 0.02</td>
<td>0.09 ± 0.002</td>
</tr>
</tbody>
</table>
Table 6. EXAFS fitting parameters for 8% Ni-STO samples (#11-16)

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>$\Delta E_0$ [eV]</th>
<th>R[Å]</th>
<th>$\sigma^2$ [Å²]</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>8% Ni-STO</td>
<td>Ni-O</td>
<td>$6.1 \pm 0.7$</td>
<td>$2.07 \pm 0.01$</td>
<td>$0.003 \pm 0.002$</td>
<td></td>
</tr>
<tr>
<td>unreduced</td>
<td>Ni-Ti</td>
<td>$4.4 \pm 1.3$</td>
<td>$3.2 \pm 0.9$</td>
<td>$3.19 \pm 0.01$</td>
<td>$0.002 \pm 0.002$</td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>$3.38 \pm 0.01$</td>
<td>$0.018 \pm 0.006$</td>
<td></td>
</tr>
<tr>
<td>8% Ni-STO-200</td>
<td>Ni-O</td>
<td>$9.0 \pm 8.0$</td>
<td>$0.0002 \pm 7.4$</td>
<td>$2.06 \pm 0.07$</td>
<td>$0.008 \pm 0.014$</td>
</tr>
<tr>
<td>(#12)</td>
<td>Ni-Ti</td>
<td>$6.3 \pm 8.3$</td>
<td>$3.14 \pm 0.13$</td>
<td></td>
<td>$0.01 \pm 0.04$</td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>$3.38 \pm 0.04$</td>
<td>$0.01 \pm 0.02$</td>
<td></td>
</tr>
<tr>
<td>8% Ni-STO-300</td>
<td>Ni-O</td>
<td>$1.1 \pm 1.0$</td>
<td>$2.03 \pm 0.07$</td>
<td>$0.001 \pm 0.002$</td>
<td></td>
</tr>
<tr>
<td>(#13)</td>
<td>Ni-Ni</td>
<td>$10.1 \pm 3.1$</td>
<td>$2.50 \pm 0.02$</td>
<td>$0.007 \pm 0.002$</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Ni-Ti</td>
<td>---</td>
<td>$2.49 \pm 0.01$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)*</td>
<td>$3.37 \pm 0.02$</td>
<td>$0.01 \pm 0.007$</td>
<td></td>
</tr>
<tr>
<td>8% Ni-STO-400</td>
<td>Ni-O</td>
<td>$0.9 \pm 0.7$</td>
<td>$2.02 \pm 0.06$</td>
<td>$0.001 \pm 0.001$</td>
<td></td>
</tr>
<tr>
<td>(#14)</td>
<td>Ni-Ni</td>
<td>$10.5 \pm 2.2$</td>
<td>$2.49 \pm 0.01$</td>
<td>$0.007 \pm 0.002$</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Ni-Ti</td>
<td>---</td>
<td>$2.49 \pm 0.01$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>$3.37 \pm 0.01$</td>
<td>$0.01 \pm 0.006$</td>
<td></td>
</tr>
<tr>
<td>8% Ni-STO-500</td>
<td>Ni-O</td>
<td>$1.1 \pm 1.8$</td>
<td>$2.02 \pm 0.04$</td>
<td>$0.001 \pm 0.001$</td>
<td></td>
</tr>
<tr>
<td>(#15)</td>
<td>Ni-Ni</td>
<td>$10.3 \pm 1.7$</td>
<td>$2.49 \pm 0.01$</td>
<td>$0.006 \pm 0.001$</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Ni-Ti</td>
<td>---</td>
<td>$2.49 \pm 0.01$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>$3.37 \pm 0.01$</td>
<td>$0.016 \pm 0.007$</td>
<td></td>
</tr>
<tr>
<td>8% Ni-STO-600</td>
<td>Ni-O</td>
<td>$0.8 \pm 0.9$</td>
<td>$2.03 \pm 0.08$</td>
<td>$0.001 \pm 0.006$</td>
<td></td>
</tr>
<tr>
<td>(#16)</td>
<td>Ni-Ni</td>
<td>$10.9 \pm 2.5$</td>
<td>$2.50 \pm 0.01$</td>
<td>$0.007 \pm 0.002$</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Ni-Ti</td>
<td>---</td>
<td>$2.50 \pm 0.01$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>$3.37 \pm 0.01$</td>
<td>$0.016 \pm 0.009$</td>
<td></td>
</tr>
</tbody>
</table>

* was defined whereas other parameters were allowed to vary
Table 7. EXAFS fitting parameters for 4 % Ni-STO samples (#2-10)

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>$\Delta E_0$ [eV]</th>
<th>R[Å]</th>
<th>$\sigma^2$ [Å$^2$]</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 % Ni-STO unreduced (#2)</td>
<td>Ni-O</td>
<td>4.0 ± 4.1</td>
<td>2.00 ± 0.3</td>
<td>0.001 ± 0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-O</td>
<td>2.6 ± 7.4</td>
<td>2.21 ± 0.004</td>
<td>0.001 ± 0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Ti</td>
<td>2.3 ± 5.3</td>
<td>3.19 ± 0.03</td>
<td>0.001 ± 0.002</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>3.38 ± 0.01</td>
<td>0.01 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>4% Ni-STO-200 (#3)</td>
<td>Ni-O</td>
<td>6.0 ± 7.1</td>
<td>-0.6 ± 17.4</td>
<td>0.001 ± 0.006</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>Ni-Ti</td>
<td>2.4 ± 8.7</td>
<td>3.11 ± 0.2</td>
<td>0.001 ± 0.006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>3.38 ± 0.06</td>
<td>0.019 ± 0.13</td>
<td></td>
</tr>
<tr>
<td>4% Ni-STO-300 (#4)</td>
<td>Ni-O</td>
<td>3.1 ± 1.3</td>
<td>1.3 ± 4.1</td>
<td>0.001 ± 0.001</td>
<td>0.04</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>5.5 ± 4.2</td>
<td>2.02 ± 0.04</td>
<td>0.006 ± 0.006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Ti</td>
<td>---</td>
<td>2.51 ± 0.03</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>3.37 ± 0.02</td>
<td>0.011 ± 0.006</td>
<td></td>
</tr>
<tr>
<td>4% Ni-STO-400-1h (#5)</td>
<td></td>
<td></td>
<td></td>
<td>High uncertainty in the fit</td>
<td></td>
</tr>
<tr>
<td>4% Ni-STO-500-1h (#6)</td>
<td>Ni-O</td>
<td>2.1 ± 2.0</td>
<td>-2.5 ± 6.9</td>
<td>0.001 ± 0.002</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>7.9 ± 8.4</td>
<td>2.02 ± 0.03</td>
<td>0.01 ± 0.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Ti</td>
<td>---</td>
<td>2.52 ± 0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>3.37 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>4% Ni-STO-600 1h (#7)</td>
<td></td>
<td></td>
<td></td>
<td>High uncertainty in the fit</td>
<td></td>
</tr>
<tr>
<td>4% Ni-STO-400 (#8)</td>
<td></td>
<td></td>
<td></td>
<td>High uncertainty in the fit</td>
<td></td>
</tr>
<tr>
<td>4% Ni-STO-500 (#9)</td>
<td>Ni-O</td>
<td>1.5 ± 1.4</td>
<td>-0.04 ± 6.9</td>
<td>0.001 ± 0.001</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>7.4 ± 5.2</td>
<td>2.00 ± 0.04</td>
<td>0.005 ± 0.006</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Ti</td>
<td>---</td>
<td>2.50 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>3.37 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td></td>
</tr>
<tr>
<td>4% Ni-STO-600 (#10)</td>
<td>Ni-O</td>
<td>1.6 ± 0.8</td>
<td>0.1 ± 2.3</td>
<td>0.001 ± 0.003</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Ni-Ni</td>
<td>7.8 ± 2.4</td>
<td>2.00 ± 0.04</td>
<td>0.007 ± 0.003</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Ti</td>
<td>---</td>
<td>2.50 ± 0.01</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Sr</td>
<td>8(Def.)</td>
<td>3.37 ± 0.01</td>
<td>0.01 ± 0.01</td>
<td></td>
</tr>
</tbody>
</table>
Table 8. EXAFS fitting parameters for *in situ* reduced samples (#17 and 18)

<table>
<thead>
<tr>
<th>Sample</th>
<th>CN</th>
<th>$\Delta E_0$ [eV]</th>
<th>R[Å]</th>
<th>$\sigma^2$ [Å$^2$]</th>
<th>R-factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Ni-O</td>
<td>1.5</td>
<td>-0.8 ± 6.6</td>
<td>1.95</td>
<td>0.01 ± 0.009</td>
<td>0.01</td>
</tr>
<tr>
<td>He at Ni-Ni</td>
<td>4.8</td>
<td>2.50 ± 0.04</td>
<td>0.002</td>
<td>± 0.007</td>
<td></td>
</tr>
<tr>
<td>Ni-Sr 8(Def.)</td>
<td>3.3</td>
<td>3.33 ± 0.05</td>
<td>0.004</td>
<td>± 0.004</td>
<td></td>
</tr>
<tr>
<td>(b) Ni-O</td>
<td>1.6</td>
<td>-3.4 ± 3.4</td>
<td>1.93</td>
<td>0.001 ± 0.003</td>
<td>0.01</td>
</tr>
<tr>
<td>H$_2$ at 400°C Ni-Ni</td>
<td>10.6</td>
<td>2.48 ± 0.02</td>
<td>0.010</td>
<td>± 0.002</td>
<td></td>
</tr>
<tr>
<td>Ni-Sr 8(Def.)</td>
<td>3.3</td>
<td>3.38 ± 0.02</td>
<td>0.005</td>
<td>± 0.003</td>
<td></td>
</tr>
<tr>
<td>(c) Ni-O</td>
<td>1.8</td>
<td>2.3 ± 3.6</td>
<td>2.05</td>
<td>0.001 ± 0.001</td>
<td>0.04</td>
</tr>
<tr>
<td>H$_2$ at RT Ni-Ni</td>
<td>8.4</td>
<td>2.52 ± 0.03</td>
<td>0.008</td>
<td>± 0.007</td>
<td></td>
</tr>
<tr>
<td>Ni-Sr 8(Def.)</td>
<td>3.6</td>
<td>3.38 ± 0.04</td>
<td>0.005</td>
<td>± 0.004</td>
<td></td>
</tr>
<tr>
<td>(a) Ni-O</td>
<td>1.4</td>
<td>0.5 ± 4.6</td>
<td>2.02</td>
<td>0.007 ± 0.005</td>
<td>0.01</td>
</tr>
<tr>
<td>He at Ni-Ni</td>
<td>7.6</td>
<td>2.51 ± 0.03</td>
<td>0.006</td>
<td>± 0.004</td>
<td></td>
</tr>
<tr>
<td>Ni-Sr 8(Def.)</td>
<td>3.6</td>
<td>3.36 ± 0.05</td>
<td>0.015</td>
<td>± 0.012</td>
<td></td>
</tr>
<tr>
<td>(b) Ni-O</td>
<td>1.9</td>
<td>-2.2 ± 5.3</td>
<td>2.00</td>
<td>0.001 ± 0.001</td>
<td>0.03</td>
</tr>
<tr>
<td>H$_2$ at 600°C Ni-Ni</td>
<td>7.2</td>
<td>2.49 ± 0.03</td>
<td>0.010</td>
<td>± 0.005</td>
<td></td>
</tr>
<tr>
<td>Ni-Sr 8(Def.)</td>
<td>5.3</td>
<td>3.33 ± 0.08</td>
<td>0.016</td>
<td>± 0.008</td>
<td></td>
</tr>
<tr>
<td>(c) Ni-O</td>
<td>1.9</td>
<td>-3.4 ± 5.6</td>
<td>2.02</td>
<td>0.001 ± 0.001</td>
<td>0.02</td>
</tr>
<tr>
<td>H$_2$ at RT Ni-Ni</td>
<td>8.2</td>
<td>2.49 ± 0.03</td>
<td>0.006</td>
<td>± 0.005</td>
<td></td>
</tr>
<tr>
<td>Ni-Sr 8(Def.)</td>
<td>5.6</td>
<td>3.36 ± 0.04</td>
<td>0.014</td>
<td>± 0.012</td>
<td></td>
</tr>
</tbody>
</table>
Figure 49. Effect of reduction time (1 vs 2 hrs reduction time for % Ni-doped STO at different temperatures).

Given that most of the edge shift in the 4 % samples occurred at 300°C and then slightly increased afterward, the energy edge shift as the reduction time was increased from 1 to 2 hours at different temperatures has a subtle effect, especially as reduction temperature increases.

There was considerable noise in the EXAFS region in some samples (5, 7, and 8), especially at higher energy. Limiting the K range to 2 - 8 helped to align the Ni scattering peaks in these samples with the Ni foil, however, it did not show a specific trend.

*in situ* reduced samples (17 and 18)

*Ni K-edge in situ reduction data for Ni-doped STO samples at 400 and 600°C also suggested incomplete Ni reduction. Both samples did not reach the edge of the Ni standard, as expected
600°C was closer, and there are still white lines in the samples, see linear combination fitting graph, Figure 47.

Figure 50. XANES spectra for 4 % Ni-doped SrTiO$_3$ samples during in situ reduction at 400 (a-c) and 600 °C (A-B): samples were purged first at RT under He and then under H$_2$ at indicated temperature and finally cooled to RT under H$_2$
Figure 51. $k^2$-weighted (K=2-10) EXAFS spectra for 4 % Ni-doped SrTiO$_3$ samples during *in situ* reduction at 400 (a-c) and 600 °C (A-C): samples were purged first at RT under He and then under H$_2$ at indicated temperature and finally cooled to RT under H$_2$.

Supporting information

The molar fractions of the reduced Ni phase were obtained using a linear combination fitting analysis. The as-prepared samples, sample 2 for the 4% series and sample 11 for the 8% series, were used as a reference for the unreduced Ni, and Ni metal foil was taken as a reference for the reduced catalysts.

Examples of linear combination fitting:

![Linear combination fitting for Sample 12.](image)

Figure 52. Linear combination fitting for Sample 12.
Figure 53. Linear combination fitting for Sample 13

Table 9. Linear combination fitting detailed table:

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Weight (Ni)</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 3, 200 °C_2h</td>
<td>0.027311</td>
<td>0.004345</td>
</tr>
<tr>
<td>Sample 4, 300 °C_2h</td>
<td>0.469917</td>
<td>0.009406</td>
</tr>
<tr>
<td>Sample 5, 400 °C_1h</td>
<td>0.493796</td>
<td>0.007811</td>
</tr>
<tr>
<td>Sample 8, 400 °C_2h</td>
<td>0.607962</td>
<td>0.007554</td>
</tr>
<tr>
<td>Sample 6, 500 °C_1h</td>
<td>0.495933</td>
<td>0.015177</td>
</tr>
<tr>
<td>Sample 9, 500 °C_2h</td>
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<td>0.005477</td>
</tr>
<tr>
<td>Sample 7, 600 °C_1h</td>
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<td>0.008672</td>
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<tr>
<td>Sample 10, 600 °C_2h</td>
<td>0.675305</td>
<td>0.007312</td>
</tr>
<tr>
<td>Sample 12, 200 °C</td>
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<td>0.004407</td>
</tr>
<tr>
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<td>0.868279825</td>
<td>0.001888</td>
</tr>
<tr>
<td>Sample 14, 400 °C</td>
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<td>0.003551</td>
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<tr>
<td>Sample 15, 500 °C</td>
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<tr>
<td>Sample 16, 600 °C</td>
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<td>0.003408</td>
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<tr>
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<td>0.016427</td>
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<tr>
<td>Sample 17 in situ H₂ 400 °C then RT</td>
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<tr>
<td>Sample 17 in situ He 400 °C</td>
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<tr>
<td>Sample 18 in situ He 600 °C</td>
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4.3.1 Summary:

X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) spectra revealed that Ni substitutes Ti in the SrTiO$_3$ perovskite structure (Ni$_{\text{sub}}^{4+}$). The initial Ni loading and the employed synthesis temperature, however, control the amount of Ni$_{\text{sub}}^{4+}$ in the crystal, where Ni that exceeds the solubility limit is forming Ni-O-Ti linkage probably on the particle surface. The latter phase is more reducible and thus acts as a nucleation site for the Ni that segregates from the crystal as the reduction temperature increases.

XANES spectra indicated that the Ni$_{\text{sub}}^{4+}$ in the as-synthesized Ni-SrTiO$_3$ causes a blue shift in the Ni absorption edge when compared to the NiO standard. The shift from the NiO increased from 1.1 to 1.4 eV when the Ni loading dropped from 8 to 4 mol %, respectively, however, it was less than the maximum reported shift $^{280,281}$ for SrTi$_{1-x}$Ni$_x$O$_3$ that was synthesized with lower Ni loading at much higher temperature (3 mol% Ni-SrTiO$_3$ that was synthesized at 1500 °C produced 2.5 eV edge difference between NiO and sample). This suggested that when the solubility of Ni in the B-sites of SrTiO$_3$ exceeds under specific synthesis conditions another lower oxidation state Ni phase coexists at different sites. EXFAS fitting analysis for the as-synthesized samples also revealed that in addition to the Ni-Sr shell, which usually exists at 3.38 Å due to Ni$_{\text{sub}}^{4+}$ phase, another shell for a Ni-Ti at 3.2 Å coexisted. The latter shell suggests Ni substitution in the A site but with a lattice distortion due to ions mismatch$^{283}$ and with the substitution occurs at terminal surface layers of the particle, since such phase has a lower oxidation state and higher reducibility.

The Ni cations in the as-synthesized resisted reduction up to 200°C, however, at 300°C there was a redshift in the absorption edge, growth in the Ni-Ni shell, decrease in white line intensity and Ni-O shell, and a large drop in Ni-Ti shell. The 4% sample showed gradual reduction as the
reduction temperature was furtherly increased. In such a sample, the percent of metallic Ni and Ni-Ni coordination number increased to 47% and 5, respectively, when reduced at 300°C and then showed a gradual increase to 68% and 8 as the reduction temperature reached 600°C. In contrast, the percent of metallic Ni and the Ni-Ni coordination number in the 8% sample largely increased (87% and 10, respectively) at the 300°C reduction, and both values were not much affected by the further increase in the reduction temperature.

4.3.2 Acknowledgment:

Data analysis in this chapter was accomplished under the supervision of Professor Anatoly Frenkel (SBU-BNL) during a 6-month NSF-funded internship. This study was part of a larger collaborative project between Professor Anatoly Frenkel (SBU-BNL) and Professor Alexander Orlov (SBU). The raw data were provided by Professor Frenkel’s group.
V. STRUCTURE-BINDING-ACTIVITY CORRELATIONS IN Cu-Ti STRUCTURES

5.1 Introduction

The region at which metal and metal oxide (or two oxides) converge is of great interest in catalysis since it is responsible for the unique properties, termed synergetic effects in the catalytic properties,\(^{37-39}\) which do not exist in either of the individual components of the catalyst. As mentioned earlier in section 1.3, these metal/metal oxide interactions can range from an electronic charge transfer to a solid-state chemical reaction at the interface.\(^{43,44}\) For instance, the interactions cause metal-to-metal charge-transfer (MMCT) between the two different oxo-bonded metals at the interface of the photocatalyst\(^ {48-50}\) and the formation of Lewis acidic interfacial metal sites with unique properties in thermally driven catalysis.\(^ {51-56}\) Reports showed that supported noble metals can decrease the reduction temperature of reducible supports based on the metal’s work function.\(^ {58,59}\)

Despite these achievements, there is still a lack of understanding of how metal-support interactions modify the structure of metal ions participating in the oxo-bond at the interface and how the new structure will affect the binding and redox properties of such sites.

From the previous discussion on the differences between the binding properties of supported metal sites compared to pure components, sections 1.7, 1.8, and Error! Reference source not found., it was concluded that the underlying metal oxide lattice may force the above metal cluster(s) to assume an unusual structure that is probably the reason for offering novel open coordination site for probing molecules such as CO. Furthermore, the ability of metal cluster also to change the redox properties of the underlying support could also facilitate the formation of coordinately unsaturated binding sites on the reducible support under oxygen deficient atmosphere.
To attain a profound understanding of the local structure-binding properties correlations as well as their catalytic properties in CuOₓ-TiO₂ catalyst, different Cu-Ti structures were synthesized to enable the investigation of the local environment of both metal ions on the interface with X-ray absorption spectroscopy (XAS). These structures were synthesized to overcome the limitation of XAS as an averaging characterization technique⁹²,⁹³ and the heterogeneity of measured metal in the sample, as the interfacial sites represent only minority sites in metal/metal oxide catalyst. Using the XAS technique and in situ IR spectroscopy, respectively. The CO molecule, as a surface probe, was used to follow up the binding sites as other molecules are co-adsorbed and as the surface is brought gradually under operando catalytic conditions for the H₂ generation. Structural changes and the novel binding properties that emerge from metal/metal oxide interaction have been investigated. It was envisaged that such different structures will provide complementary information that is not viable in one structure. The structures included conventional (Cu/TiO₂) and inverted (TiOᵧ/CuO) catalysts, and Cu-TiOₓclusters on SiO₂, see Figure 54. In each case, the element edge of the supported cluster is analyzed. The effect of ex-situ reduction on the cluster’s structural and electronic properties as they interact with the underlying support was also studied. The binding and optical properties of such structures were studied to examine their correlation to catalytic activity. The grafting of Ti⁴⁺ centers on CuO and SiO₂ was accomplished using titanocene dichloride (TiC₅₂Cl₂). This precursor was used instead of TiCl₄ and Ti(OR)₄ since the latter two precursors have a noticeable tendency for oligomerization. The cyclopentadienyl ligands in titanocene dichloride protect the oxophilic titanium atom and thereby a stable well-spaced single-atom titanium site is obtained. The cyclopentadienyl ligands in titanocene dichloride protect the oxophilic titanium atom and thereby a stable well-spaced single-atom titanium site could be obtained.⁹⁴
5.2 XAS for Cu and Ti centers

5.2.1 CuOₓ - TiOᵧ interactions (Cu edge)

Cu K-edge X-ray absorption near edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) spectra of supported copper samples, which were annealed in air at moderate temperature, showed unique spectra compared copper oxides standards, Figure 55. All in-air oxidized samples and CuO standard contained a common weak pre-edge peak in XANES spectra at 8976 eV, see insets of the region (I) in Figure 55. Such absorption is attributed to the 1s→3d transition that usually appears in copper compounds with unfilled 3d subshells and lacks in Cu (0) and Cu(I) compounds with 3d¹⁰ electronic configuration. The rising edge of samples containing supported CuOₓ, however, did not show the shoulder at ~8984 eV, region (II), which does exist in
CuO, Figure 55. (a) and (c). Furthermore, in the CuO$_x$ samples the white line intensity, region (III), was at a much higher intensity and the post edge (region IV) was also distinct compared to the standards. The shoulder at the rising edge, ascribed to the 1s $\rightarrow$ 4p transition, is attributed to the splitting of the 4p orbitals in the CuO square planner structure.$^{193,194}$ So, the intense white line and the absence of the shoulder in the rising edge in the supported CuO$_x$ samples imply that the copper center is highly coordinated with the oxygen in the framework of the support and adsorbed water/OH groups.$^{193,194}$

The high oxygen-coordinated copper structure was also manifested in EXAFS spectra, Figure 55. In the supported CuO$_x$ samples, the intensity of the first oxide shell Cu-O was much higher than the Cu-O shell in the standard oxides. In contrast, the 2$^{nd}$ shell was at a lower intensity and shorter distance, compared to CuO. This corroborates with XANES and suggests that most of the absorber ion is located on the surface where the 1st shell is a mixture of oxygen from the support and the water/OH groups whereas the weak higher shells are from the atoms in the support side.

**The ex-situ in-air high-temperature oxidation** at 800 °C for CuO$_x$/TiO$_2$ sample (CuO$_x$-TiO$_2$-800Air) causes the formation of a weak 1s $\rightarrow$ 4p shoulder, region (II), in XANES, Figure 55. (a). This indicates that the highly coordinated copper is a meta-stable phase on the surface of titania, however, high-temperature oxidation could lead to minor phase separation and formation of CuO. This highly coordinated phase emerged as a minor phase in the equimolar mixture of CuO-TiO$_2$ that has been treated in the air at 1000 °C, XRD demonstrated that CuO and TiO$_2$ (rutile) phases co-existed in the sample. This was evident from the increase in the white line and the light blue shift in the Cu edge position in the XANES spectra of the sample, Figure 55. (e).

**Reducing the samples** under ex-situ conditions, 250 °C under H$_2$ flow, demonstrated that the highly oxygenated copper sites can reversibly assume this structure upon its exposure to the
atmosphere as suggested by XANES and EXAFS spectra, Figure 55. (a) and (b). Under the same reducing conditions, however, pure CuO and samples with mixed copper oxide phases (bulk-like and highly coordinated copper cations) were fully or partially reduced, respectively. For instance, the CuO-TiO₂-800Air-250H₂ sample showed a partial reduction for copper species as demonstrated by the redshift in the Cu edge in XANES and the decrease in Cu-O shell in EXAFS, Figure 55. (a) and (b).
Figure 55. Cu K-edge XANES and EXAFS spectra for Cu-Ti structures as samples were subjected to different ex-situ pretreatments: (a, b) CuOₓ deposited on TiO₂ before and after they were reduced for 1 hour at 250 °C under H₂ or annealed at 800 °C in the air then reduced, pure CuO was reduced under the same conditions for comparison; (c, d) CuOₓ and TiOₓ on SiO₂ surface, with a different deposition order, before and after reduction at 250 °C H₂ flow, CuOₓ deposited on SiO₂ was measured for comparison; and (e, f) equimolar mixture of CuO and TiO₂ annealed in air at 1000 °C or annealed then reduced at 250 °C under H₂ flow.
In titania-supported copper the weakening or the absence of region (II) shoulder, for $1s \rightarrow 4p$ transition that typically exists in CuO due to the splitting of the $4p$ orbital in its square planar geometry, suggested that the copper center exists in a symmetrical geometry, it was proposed that Cu exists in an octahedral environment as it substitutes Ti in the TiO$_2$ lattice.\cite{285} Multiple reports observed a similar weakening of Cu$^{2+}$ shoulder, in copper-zeolites catalyst, which was attributed to the high coordination of Cu where oxygen is supplied by a combination of framework oxygens and water molecules or OH groups.\cite{193,286} Interestingly, in situ XAS studies showed that thermally dehydrating of similar systems at increasing temperatures under vacuum or inert gas led to a progressive gaining of the Cu$^{2+}$ shoulder (region II) and a decrease in the white line, due to the loss of water molecules from the Cu$^{2+}$ coordination sphere.\cite{286} Such process was reversed when water then O$_2$ were introduced to the samples. Therefore, the copper metal center over TiO$_2$ likely assumes the highly coordinated octahedral structure of the underlying Ti center. This surface structure can explain the CO adsorption after the sample is subjected to dehydration as it will offer open coordination to CO. The changes in copper edge as water is desorbed and CO is adsorbed have been also studied in copper-zeolite catalyst and it was suggested that the copper center is in tetrahedral coordination.\cite{195}

**5.2.2 TiO$_y$-CuO interactions (Ti edge)**

In the Ti K-edge XANES, Figure 56(a, c, and e), samples and standards can be compared in terms of three groups of features: the pre-edge region (I), on-edge region (II), and above-edge region (III). The pre-edge region (I) contains $A_1$, $A_2$, and $A_3$ features, and their intensity and position are sensitive to the valency, coordination, and symmetry of titanium ion.\cite{287-289}
Analogous to supported CuOx, supporting TiOy clusters over CuO or CuOx-SiO2 gave distinct XANES, and EXAFS spectra compared to the standard titanium oxides, see Figure 56 (a-d). The pre-edge region in these samples showed a dominant A2 feature which is higher in intensity and lower in energy (at 4971 eV) than the corresponding feature in anatase and rutile. The dominant pre-edge shared among the samples, at 4970.8 eV in Ti-edge XANES spectra is characteristic of tetrahedrally coordinated Ti center in titanium silicate. Furthermore, the prominent on- and post-edge features that exist in rutile and anatase are completely absent in the samples. In EXAFS spectra, Figure 56 (b) and (d), the lower intensity and shorter distance of the oxygen first shell in the samples as well as the insignificant contribution from higher shells corroborate with XANES data and confirm that the Ti center is undercoordinated, in comparison to bulk oxide.

The in-air high-temperature oxidation for the TiOy-CuO sample (Figure 56 (a) and (b), TiOy-CuO-800Air) triggered structural rearrangement around the Ti center. This was demonstrated in the loss of the high-intensity pre-edge feature in XANES spectra, the shift in the first oxygen shell to a longer distance, and the emergence of higher shells in EXAFS. This made the spectra significantly similar to the rutile standard except for the 2nd shell, which shows up at a shorter distance, Figure 56b. So, the high-temperature treatment triggered phase separation and agglomeration of TiOy into a bulk-like structure which indicates that TiOy clusters above CuO are a meta-stable phase.

The ex-situ reduction of the TiOy-CuO sample also triggered significant structural change around Ti, as copper is reductively segregating from Cu-O-Ti bonds. In the XANES spectrum, the prominent pre-edge peak declined however the spectrum was still different from the standard oxides. In the EXAFS spectrum, the first oxygen shell moved to a higher distance while the higher shells emerged at lower intensities compared to the standards. The ex-situ reduction of TiOy-CuO-800Air showed minor structural rearrangement around the Ti center because phase separation was
already triggered by the initial high-temperature oxidation. In comparison, under-coordinated Ti centers over CuOx-SiO2 resisted structural changes after reduction, see EXAFS and XANES spectra in Figure 56 (c-d).

Figure 56. Ti K-edge XANES and EXAFS spectra for Cu-Ti structures as samples were subjected to different ex-situ pretreatments: (a, b) TiOx deposited on CuO before and after they were reduced for 1 hour at 300 °C under H2 or annealed at 800 °C in the air then reduced; (c, d) CuOx and TiOy on SiO2 surface, loaded in a different order, before and after reduction at 250 °C H2 flow. The latter Cu-Ti structures correspond to the same samples in Figure 55. (c-d) whereas here Ti-edge was measured.

The above observation highlights the role of supports in stabilizing/enforcing specific Ti structures and the disparity in the behavior of this structure after subjecting the catalyst to redox conditions due to the different redox behavior of the support.
5.3 Optical and binding properties

Chromophores in photosensitizers capture sunlight light to induce electronic transition which can be used in photochemical applications. The chromophores can be classified into ligand-to-ligand charge transfer (LLCT), metal-to-ligand charge transfer (MLCT), and ligand-to-metal charge transfer (LMCT). In MMCT, electrons are excited from donor metal centers (e.g., Mn$^{II}$, Fe$^{II}$, Co$^{II}$, and Cu$^{I}$) to acceptor metal centers (e.g., Zr$^{VI}$, Ti$^{IV}$, and V$^{IV}$) which can extend the optical absorption from UV to visible regions. This transition occurs through bridging ligands such as oxygen in oxo-bridged heterobinuclear units in heterogeneous catalysts, which offer more durable structures for light harvesting. The transition was mainly monitored with UV-vis diffuse reflectance spectroscopy.

From the above discussion, it can be concluded that metal/metal oxide interaction could lead to the formation of oxo-bridged heterobinuclear units that sensitize the catalyst for visible light absorption. However, here a discussion will be furnished on how such interactions are affecting the binding properties of the binary system. The effects of the metal/metal oxide interaction on the binding and structural properties of the binary system, in comparison to these properties in the individual components, would deepen our understanding of the synergetic effects in such systems.

Supporting CuO$_x$ clusters on the rutile and anatase phases of TiO$_2$ produced the surface carbonyl characteristic for CO bonded to oxo-metal cations after standard activation procedures, 300 °C under Ar flow, Figure 57 (a) and (c). In the rutile case, the surface carbonyls were at higher frequencies compared to the anatase sample. Introducing moisturized Ar to the DRIFTS cell of the CuO$_x$/TiO$_2$ (rutile) sample causes the shift of the carbonyl peaks to lower frequencies. The corresponding UV-vis DRS of the samples, Figure 57 (b) and (d), showed the absorption
characteristic of MMCT in Cu-O-Ti, which usually extended from 400 up to 600 nm.\textsuperscript{48} Similarly, CuO\textsubscript{x}/TiO\textsubscript{2} (P25), the binding properties were detailed in 2.1.2, demonstrated an increase in the visible absorption in such region, Figure 58 (a), as the sample was subjected to higher temperature annealing that improve that interaction.

Reducing CuO\textsubscript{x}/TiO\textsubscript{2} (P25) sample showed a dramatic change in the optical properties of the catalyst, Figure 59 (b), however, such changes were largely reversed with time as the sample reacted with air. To induce similar changes in the optical properties in pure TiO\textsubscript{2}, reduction at 600 \degree C was necessary Figure 59 (c). The reduction-induced changes in the optical properties of CuO\textsubscript{x}/TiO\textsubscript{2} were likely from TiO\textsubscript{2} reduction since copper reductive segregation and then oxidation is expected to cause different optical, Figure 59. This was in line with the upward shift reported before, section 2.2, in the IR background due to the reduction of TiO\textsubscript{2} with H\textsubscript{2} spilled over from metal sites.\textsuperscript{221}

\textbf{Figure 57.} CO adsorption DRFTS for (a) 5\texttext{wt\%} CuO\textsubscript{x}/TiO\textsubscript{2} (rutile) and (c) 5\texttext{wt\%} CuO\textsubscript{x}/TiO\textsubscript{2} (anatase) at RT after activation at 300 \degree C under Ar flow for 1 hr. Corresponding UV−vis diffuse reflectance spectra for the same sample compositions are presented in (b) and (d), respectively, at RT after pretreatment in the air at increasing temperature, 100-500 \degree C.
Figure 58. UV–vis diffuse reflectance spectra for (a) 5wt%CuO/TiO$_2$ (P25) sample at RT after pretreatment in the air at increasing temperature, 100-500 °C, (b) 5wt%CuO/TiO$_2$ (P25) at RT in the air with time after pretreatment in H$_2$ at 300 °C and cooled down to RT under H$_2$ atmosphere, and (c) pure TiO$_2$(P25) after pretreatment in H$_2$. DRIFTS cell was just used as a reactor to treat the sample under different atmospheres.

Figure 59. UV–vis diffuse reflectance spectra for various pure oxides. Note that annealing rutile sample above 800 °C in the air causes a further redshift in the band gap.
A physical mixture of pure CuO and TiO$_2$ (rutile, anatase, or P25) readily form metal carbonyls upon annealing the mixture to induce interaction, Figure 60, note that none of the pure oxides can form surface carbonyls under similar conditions. Upon increasing the annealing temperature more intensity of surface carbonyl increases which indicates stronger interaction between the two oxides.

Heating a mixture of 10wt% CuO and TiO$_2$(P25)—higher percent of TiO$_2$ was used to decrease optical absorption—in the air at increasing temperatures also increased the absorption in the 400-600 nm visible region due to the formation of Cu-O-Ti which is responsible for MMCT in this region, Figure 61. Furthermore, it was observed that annealing the sample above 600 °C caused the transformation of the anatase phase component in P25 into rutile which is evident from the redshift in the band gap.

Figure 60. CO adsorption DRFTS data at RT for various 50-50 mol% CuO-TiO$_2$ physical mixtures after pretreatment at increasing annealing temperatures under Ar flow for 1 hr. (a) 50mol%CuO/TiO$_2$(rutile), (b) 50mol%CuO/TiO$_2$(P25) and (c) 50mol%CuO/TiO$_2$(anatase).
Figure 61. UV−vis diffuse reflectance spectra at RT for 10wt% CuO/TiO$_2$ (P25) oxide mixture after annealing in air at increasing temperatures—200, 400, 600, 800, and 1000 °C (a–e).

Deposition of TiO$_2$ clusters on CuO enabled the formation of surface carbonyls over CuO, Figure 62 (a). The TiO$_y$/CuO inverted catalyst showed surface carbonyls after low loading of TiO$_y$ clusters (0.1 wt.% nominal composition), and as loading increased the peak blue shifted and broadened.
UV-vis DRS for the same samples, Figure 62 (b), showed a limited absorption in the UV region for TiO_y clusters due to the high absorption of CuO support.

![Diagram](image)

**Figure 62.** (a) CO adsorption DRFTS for inverted catalyst (TiO_y/CuO) with increasing loading of TiO_2 at RT after activation at 200 °C under Ar flow for 1 hr. (b) corresponding UV–vis diffuse reflectance spectra for same samples compositions.

CuO_x and TiO_y clusters were anchored on the surface of SBA(SiO_2) in different orders to gain more insight into the effect of Cu-Ti interaction on the optical and binding properties of the catalyst, Figure 63 and Figure 64, respectively. UV-vis DRS for TiO_y/SiO_2 showed a significantly higher band gap than bulk anatase and rutile which indicates that the TiO_y exists as isolated clusters in tetrahedral coordination.²⁹⁸ The latter observation is in line with the Ti edge XAS data of the sample, see section 5.2.2. Loading CuO_x on the TiO_y/SiO_2 leads to the broadening of the absorption to the visible region. Reversing the order of the deposition to CuO_x then TiO_y clusters showed that there is an increase of the adsorption in the 400-600 nm region due to the formation of Ti-O-Cu.
Figure 63. UV−vis diffuse reflectance spectra at RT for SiO$_2$ (SBA) after loading 5wt % of CuO$_x$ and TiO$_y$ in different orders, for instance, 5wt % of TiO$_y$ loaded over 5wt% CuO$_x$/SiO$_2$ and vice versa.

CO adsorption on CuO$_x$/SiO$_2$ produced surface carbonyls centered at ~2100 cm$^{-1}$ which is displaced gradually around the same wavenumber with H$_2$O(g) in moisturized Ar. Upon TiO$_y$ deposition on the sample, a high-frequency carbonyl at ~2131 cm$^{-1}$, as well as a shoulder at ~2113 cm$^{-1}$ were observed. With competitive adsorption with water, the higher frequency carbonyls were replaced and the lower frequency carbonyl gradually redshifted to 2103, Figure 64 and inset (h-m).

For TiO$_y$/SiO$_2$ surface carbonyls were only observed after CuO$_x$ deposition, Figure 65. The carbonyl band was centered at 2131 cm$^{-1}$ and decreased to 2117 cm$^{-1}$ with competitive adsorption with water.
Figure 64. CO adsorption DRFTS with time at RT after activation at 300 °C under Ar flow for 1 hr for 5wt%CuOx/SiO2 before (blue) and after (red) TiOx loading. (a-f) and (g-m) represent spectra after activation then saturation with CO and competitive adsorption with water with time. The inset represents the carbonyl region of the two samples after subtracting the initial spectrum after activation.
Figure 65. CO adsorption DRFTS with time at RT after activation at 300 °C under Ar flow for 1 hr for CuO\textsubscript{x}/TiO\textsubscript{2}/SiO\textsubscript{2} before (blue) and after (red) introducing moisturized Ar to the cell.

5.1 Interfacial binding sites during H\textsubscript{2} generation

Interfacial binding properties of the bi-nuclear oxo-bond (Cu-O-Ti) in CuO\textsubscript{x}/TiO\textsubscript{2} were studied with \textit{in situ} DRIFTS as the catalyst was subjected to H\textsubscript{2} generation conditions, in the presence of CH\textsubscript{3}OH, water, and UV illumination. At RT and after activating the sample at 300 °C under Ar flow for 2 hrs, Figure 66 (a), the catalyst of the coordinately unsaturated sites produced from CuO\textsubscript{x}-TiO\textsubscript{2} interaction was earmarked with the adsorption of CO probing molecules, Figure 66 (b). Surface carbonyls were observed initially at a high frequency and then gradually broadened as CO saturates and fills different sites on the interface, inset of Figure 66 (a-b). Upon introduction of methanol introducing methanol causes a replacement of the high-frequency oxo-metal carbonyls started to occur until CO was shifted from 2126 to 2080 cm\textsuperscript{-1}, Figure 66 (b-c). C-H bond stretch for methanol adsorbed on the interfacial sites and other plane TiO\textsubscript{2} surfaces was observed in the
~3000 cm\textsuperscript{-1} ranges. No changes were observed in the spectrum after shining UV on the sample for 10 minutes at this point, the spectrum is not shown for brevity. Introducing water afterward cause an increase in OH bending/stretching IR peaks at 1620 and 3000-3500 cm\textsuperscript{-1} and suppressed the methanol on the surface, as evident from the lower C-H bond stretch frequency. This is direct evidence that water is preferentially adsorbed (than methanol) on the new coordinately unsaturated Lewis acidic metal sites that emerge for the interaction between CuO\textsubscript{x} and TiO\textsubscript{2}. This can better explain the isotopic labeling experiments\textsuperscript{299} that showed the preferential reduction of protons from water rather than methanol.

Illuminating the sample at this point with UV light causes a significant increase in the IR absorption background, Figure 66 (e). This substantial IR background up-shift is usually attributed to the reduction of TiO\textsubscript{2} support and a measure of the concentration of conduction band electrons.\textsuperscript{221,255,256} The upshift was also observed in the IR background for PtO\textsubscript{x}-TiO\textsubscript{2} during the thermal reduction under H\textsubscript{2}, see section 2.2. Injecting oxygen into the cell through the rubber septum causes a rapid depletion of the conduction band electrons as evidenced by the decrease in the IR background, Figure 66 (g), however, it slowed down as it approached the initial spectrum, Figure 66 (h). The increase in the IR background was also observed in pure TiO\textsubscript{2} in the presence of methanol and water and UV light, see Figure 67. This indicates that only in the presence of metal sites these conduction band electrons can be used to reduce water molecules to produce hydrogen.
Figure 66. in situ DRIFTS to investigate active sites “with CO marking” during H₂ photocatalytic generation from H₂O(\text{g}) and CH₃OH(\text{g}) over CuOₓ/TiO₂. (a) at RT after pretreating the sample at 300 °C under Ar flow, (b) after CO adsorption (to mark the active sites), (c) CH₃OH(\text{g})/Ar flow, (d) H₂O(\text{g})/Ar introduction, (e) illuminating with UV-Vis, and (f) and (g) after introducing O₂ for 1 and 30 minutes, respectively.
5.2 Hydrogen Generation

Recent reports on H₂ evolution from water catalyzed with CuOₓ/TiO₂ emphasized the importance of reversible and cooperative interaction between copper and the neighboring titanium center during the photoactivation cycle. In this study, electron paramagnetic resonance (EPR) and UV-vis DRS elucidated, along with density functional theory (DFT) calculation, the formation of Ti³⁺ under the moderate conditions of the reaction, for instance, very strong absorption in the visible region occurred under photocatalytic conditions, similar spectra were obtained earlier after the thermal reduction of CuOₓ/TiO₂ samples under hydrogen in Figure 58 (b). Furthermore, it was revealed that although methanol is typically used as a sacrificial reagent, CH₃OH + 2hv_B⁺→CH₂O +2H⁺, the isotopic labeling proved that evolved molecular hydrogen originates from water protons rather than methanol, which was attributed to statistical considerations. Despite such advances there is a lack of understanding of the detailed correlations between the catalytic activity and the
binding properties of the oxo-bridged binuclear units, such as Pt-O-Ti or Cu-O-Ti, at the interface of the catalyst.

The effect of increasing the interaction between TiO$_2$ (P25) and CuO in their equimolar mixture by increasing the thermal annealing temperature on the hydrogen generation activity was investigated, see Figure 68. The individual pure components did not show photocatalytic activity toward H$_2$ generation. Mixing TiO$_2$ and CuO and increasing the temperature of annealing from RT to 300 °C, see method 5.15.1, largely increased the catalytic activity, 50% CuO-TiO$_2$-(RT), (120 air), and (300 air) in Figure 68. Annealing the sample at 800 °C or higher, however, led to the complete loss of H$_2$ activity, and a trial to reactivate the catalyst via reducing the sample under H$_2$ at 300°C was not successful, 50% CuO-TiO$_2$-(800 air), (1000air) and (1000air-300H$_2$) in Figure 68.

The catalytic activity of deposited CuO$_x$ clusters on TiO$_2$, 5wt% CuO$_x$-TiO$_2$, was also investigated after the sample was dried/annealed at RT (under vacuum, 24 hrs), 120 °C (air, 5hrs), 300 °C (air, 3hrs), 800 °C (air, 1hr) or 1000 °C (air, 1hr), Figure 68. It can be observed that the sample dried at 120 °C CuO$_x$-TiO$_2$ showed the highest activity, however, further drying the samples led to decreasing the activity at 300 °C then total deactivation if annealed at 800 °C or higher. It was observed that reducing the sample under hydrogen slightly decreased the activity rather than increase it.
Figure 68. Photocatalytic $H_2$ generation performance with irradiation time for CuO$_x$-TiO$_2$ (CuO$_x$ deposited on the surface) and 50%-CuO$_x$-TiO$_2$ (physical mixture) samples that were annealed in air at different temperatures or annealed then reduced under hydrogen flow. The activity of pure compounds Cu$_2$O, CuO, and TiO$_2$ was measured under the same conditions as a control experiment.

The above observations show that the photocatalytic activity depends on the chemical state of the co-catalyst, the band gap of the photocatalyst, and the interaction between both of the components. The initial increase of the catalytic activity in the binary systems as drying/annealing temperature increases indicates that the interaction between CuO and TiO$_2$ enhances the activity. The decrease in the activity or the total deactivation could be attributed to the change in the band gap observed at high temperatures, section 5.3, as the inactive rutile phase starts to form. It is well documented that the anatase phase is higher in photocatalytic activity than the rutile phase and several investigations implemented methods to prevent anatase transformation at high temperatures.$^{301-303}$ Interestingly, the high catalytic activity that has been reported before, could be due to maintaining the anatase crystallinity at high temperatures during metal loading.$^{300,304,305}$
5.2.1 Effect of etching pretreatment on hydrogen generation

To enhance the photocatalytic activity in H₂ generation surface treatment of the catalysts with ammonium hydroxide and peroxide mixture (APM) was investigated since such treatments affect TiO₂ phases and surface.³⁰⁶-³⁰⁹ In this study, CuOₓ, and PtOₓ on TiO₂ (P25, which contain a mixture of anatase and rutile with an Anatase/Rutile ratio of 4.85)³¹⁰ samples were treated with APM, with an increasing volume of the mixture.

5.2.1.1 H₂ generation with CuOₓ/TiO₂

Supported oxo-copper cluster on TiO₂ (5wt%CuOₓ-TiO₂) samples were treated with an increasing amount of APM, 5-20 ml for 1hrs, see methods section 5.1 for the experimental details. Produced samples were tested for H₂ generation in the liquid (H₂O+CH₃OH)/ solid (CuOₓ-TiO₂) or gas (Ar+H₂O(ads.)+CH₃OH(ads.)/solid (CuOₓ-TiO₂) photocatalysis. Furthermore, the effect of in-air thermal annealing for the sample treated with the highest peroxide concentration was investigated. Figure 69 showed that photocatalysis with CuOₓ-TiO₂ in the liquid/solid phase predominantly produced H₂ from water reduction²⁹⁹ and traces of CO were observed, the latter could be produced from formate since methanol was used as a sacrificial electron donor.³¹¹ Increasing the peroxide concentration during sample pretreatment largely increases the photocatalytic activity for H₂ generation. Increasing in-air thermal annealing temperature causes also an enhancement in the H₂ production, however, this trend was reversed when the annealing temperature reached above 400 °C, Figure 69.
Figure 69. Hydrogen generation (top-left) and CO formation (top-right) with time from 20% volume of methanol in water solution catalyzed by CuO/x/TiO2 and illuminated with Hg lamp. The effect of increasing the volume of H2O2 in the NH4OH (10ml)+ H2O2(x ml) mixture (used to increase % of anatase in TiO2 in the catalyst) and increasing of annealing temperature (to decrease % of anatase )on the catalytic activity of CuO/x/TiO2 were studied. Similarly, photocatalytic activity was measured for CuO/x/TiO2-20ml sample after in-air annealing at increasing temperatures.

Photocatalysis utilizing CuO/x/TiO2-20ml-400 °C in the gas/solid phase reaction without methanol produced only traces of H2 and CO, Figure 70(a). However, after bubbling Ar gas through the 4:1 (vol/vol) water/methanol solution mixture and the activity dramatically improved by 26 and 28 times for CO and H2, respectively, Figure 70 (b). The large increase in CO production in gas-solid photocatalysis likely occurred due to the larger percent of methanol on the surface which allows methanol to compete with water on the Lewis acidic metal sites.
Figure 70. Hydrogen generation with time from gas-solid catalysis using CuOx/TiO2-20ml-400 °C dispersed on quartz wool and illuminated with a Hg lamp. The effect of using only water vapor (left) and water vapor+ methanol(right) was studied.

### 5.2.1.2 H₂ generation with PtOₓ/TiO₂

Samples with supported PtOₓ cluster on TiO₂ (2wt% PtOₓ-TiO₂) were tested also for H₂ generation after pretreatment with an increasing amount of APM, 5-20ml for 1hrs. The effect of in-air thermal annealing for the sample treated with the highest peroxide concentration was investigated, see Figure 72. Photocatalytic activity in liquid (H₂O+CH₃OH)/ solid (PtOₓ-TiO₂) phase reaction showed that activity in hydrogen generation increases as the catalyst was pretreated with an increasing amount of hydrogen peroxide, Figure 71. Increasing the in-air thermal annealing temperature also increased the catalytic activity which indicates that thermal annealing likely increases the interaction between PtOₓ and TiO₂, Figure 71. Similar to supported copper, using PtOₓ/TiO₂ in gas (Ar + H₂O(ads.) + CH₃OH(ads.))/solid photocatalysis causes a large increase in CO production, Figure 72. This can be attributed to larger concentrations of methanol on the sample surface since the Ar gas will carry more methanol (more volatile) than water from the methanol-water bubbler to the sample.
Figure 71. Hydrogen generation (left) and CO formation (right) with time from 20% volume of methanol in water solution catalyzed by PtO\textsubscript{x}/TiO\textsubscript{2} and illuminated with Hg lamp. The effect of increasing the volume of NH\textsubscript{4}OH+H\textsubscript{2}O\textsubscript{2} (used to increase % of anatase in TiO\textsubscript{2} in the catalyst) and increasing of annealing temperature (to decrease % of anatase) on the catalytic activity of PtO\textsubscript{x}/TiO\textsubscript{2} was studied.
Figure 72. Photocatalytic activity for hydrogen generation using PtO$_x$/TiO$_2$-400°C with gas-solid reaction, in presence of CH$_3$OH(g) and H$_2$O(g).

The effect of increasing the amount of APM on the anatase and rutile phase was studied with XRD, Figure 73. It was revealed that the percent of the anatase phase increases as the amount of APM increases. Percent of anatase was calculated from the relative intensities of the first diffraction peak of the two phases. In pure TiO$_2$ (P25), the measured % of anatase was ~ 90.5%. Upon treatment with 20 ml of APM, this percent slightly increased to 90.9% for CuO$_x$/TiO$_2$-20ml, however, it increased to 94.6 and 98.1% in the case of PtO$_x$/TiO$_2$-20ml and TiO$_2$-20ml. So, the enhancement in the photocatalytic activity with APM treatment could be largely due to the increase in the anatase phase since it is the more active phase as discussed earlier and as documented in literature . 306–309
Figure 73. XRD data indicating the effect of treating TiO$_2$-based samples with 20ml of NH$_4$OH+H$_2$O$_2$ on the ratio of anatase to rutile in TiO$_2$. Rutile phase peaks are noted with “R” whereas the remaining peaks are for the anatase phase.

5.3 Summary

Interfacial sites have been considered the origin of the synergetic effects in metal/metal oxide heterogeneous catalysis. Being minority surface sites, however, thwarts the conclusive understanding of the structure-function correlations and thereby the rational design of new catalysts. Here, we investigated the interfacial binding sites that emerge upon the interaction between CuO$_x$ and TiO$_y$ clusters in variously designed oxo-structures, including conventional (CuO$_x$/TiO$_2$) and inverted (TiO$_y$/CuO) catalysts and CuO-TiO$_2$ physical mixture, as well as CuO$_x$-TiO$_y$ clusters on SiO$_2$. Such structures enabled the deduction of complementary information on the structural, optical, binding, and catalytic properties of Cu and Ti centers.

Cu and Ti edge XAS demonstrated that the CuO$_x$ and TiO$_y$ are surface metal centers that adopt a higher and lower coordinated oxo-structure, respectively, than the corresponding pure oxide. These coordinating oxygens are offered by the framework of the support and water/OH ligands.
This structure is not only responsible for sensitizing the catalyst in the visible region, through oxo-bridged binuclear chromophore (Cu-O-Ti), but also for offering open coordination Lewis acidic sites, upon dehydration, to reversibly bind other molecules such as CO and CH$_3$OH, as demonstrated by *in situ* DRIFTS. The emergence of surface metal carbonyl upon CO adsorption was dependent on the existence of TiO$_3$ cluster over the CuO surface and vice versa, which suggests that binding sites are offered by both metal centers participating in the oxo-bond.

This structure was manifested in XANES, with high intensity in the white line and absence of 1s → 4p shoulder in the Cu rising edge due to lack of 4p splitting, and EXAFS spectra, since Cu-O 1$^{\text{st}}$ shell had much higher intensity and the 2$^{\text{nd}}$ shell was distinctly different when compared to the reference oxides. Such oxo-structure affected the redox properties of the copper center where supported copper showed more resistance to reduction at 250 °C under H$_2$ flow. The same reduction conditions, however, fully reduced CuO to Cu metal. High-temperature treatment, 800 °C and above in the air, did not enhance Cu-Ti interaction, it triggered instead phase separation and the resultant samples showed less resistance to reduction.

Supported TiO$_y$ sites on CuO and CuO$_x$/SiO$_2$ were highly dispersed sites and less coordinated (4 or 5 coordination) compared to TiO$_2$ references, as evidenced by the dominant pre-edge peak, and the low intensity of the white line and the oxygen 1$^{\text{st}}$ shell in Ti-edge XAS. As copper is reductively segregated from the samples, significant structural changes occurred around the Ti center yet does still differ from anatase and rutile.

From both Ti and Cu edges it can be concluded that the difference in the oxophilicity between Cu and Ti forces the two metal centers at the interface to adapt a unique oxo-structure, where Cu is highly oxo-coordinated whereas Ti is less coordinated, compared to the reference oxides. This
unique local structure offers novel adsorption and redox properties for both centers compared to the corresponding individual components of the catalyst.

Carbonyl peaks appeared only after TiO₂ deposition over a sample containing CuO and a higher frequency carbonyl peak after TiO₂ deposition on Cu/SiO₂. This observation suggests that both Ti and Cu in the oxo-bond can bind CO.

The photocatalytic activity in hydrogen generation was primarily dependent on the energy of the TiO₂ band gap and the interfacial binding sites. This was evident from the lack of activity of various control samples in which catalysts without copper doping or with TiO₂ band gap higher and lower than the band gap of Anatase did not show activity.

### 5.1 Methods

**CuOₓ-TiO₂ and CuO-TiO₂ mixture.** The mixture was prepared by dispersing the TiO₂ and CuO in 100ml of water and sonicated for 15 minutes. The sample was retrieved with centrifugation and then dried at RT under vacuum for 24 hrs., labeled 50% CuO-TiO₂-RT. Samples from this mixture were heated in air at 120 °C (5 hrs), 300 °C (3 hrs), 800 °C (1 hr), or 1000 °C (1 hr). The 5wt% CuOₓ-TiO₂ were prepared from TiO₂(P25) dispersion and CuCl₂ in water. An equivalent amount of NaOH was added to precipitate Cu(OH)ₓ on the surface. The sample was retrieved with centrifugation and dried/annealed similar to the mixture.

**APM treatment.** 5-20 ml of the mixture containing 10 ml ammonium hydroxide and 20 ml of H₂O₂ was used to etch the rutile phase form 0.5 g of TiO₂ (P25) for 1 hr.

**Photocatalytic H₂ evolution.** 10 mg of the catalyst was dispersed in a 4.0 mL mixture solution of 4:1 (vol/vol) water/methanol mixture under visible light irradiation. Prior to photocatalytic testing,
the reaction solution was bubbled with Ar in the dark for 10 min. The solution was then irradiated with a Xenon lamp equipped with a water filter. Light intensity reaching the solution was fixed at 100 mW/cm². The headspace above the reaction solution was sampled with a gas-tight syringe at different time intervals for quantitative analysis using an Agilent 7820 GC equipped with a TCD detector.
VI. CONCLUDING REMARKS

Spectroscopic techniques were extensively utilized to investigate surface sites of supported metal catalysts in my research described in this thesis. In particular, *in situ* DRIFTS was employed to investigate surface binding sites produced from the interaction between oxo-bridged heterobinuclear metal centers at the metal/metal oxide interface (Cu-O-Ti, for instance, in CuOₓ/TiO₂). Binary systems of MOₓ cluster (M = noble metal sites such as Cu, Pt, Ni, and Ag) over TiO₂ were also studied. Results demonstrated that the interaction enables the formation of oxo-metal cations with novel structures and binding properties that don’t exist in the corresponding pure bulk metal or metal oxide. This was evident from the emergence of stable high-frequency metal cation carbonyls exclusively on the surface of the binary catalysts.

Carbon monoxide was used as a molecular marker for the novel binding sites and the IR carbonyl peak intensity and position were used to understand the competitive adsorption of other molecules participating in catalytic reactions over the surface. This demonstrated the existence of bifunctional active sites in which the metal sites catalyze the dissociation of CO₂ and H₂ molecules whereas interfacial sites bind and activate Lewis basic molecules such as H₂O and CO molecules.

XAS demonstrated that the underlying support stabilizes the copper oxide cluster in a highly coordinated structure that is not viable in bulk oxides. It was demonstrated that such structures are responsible for offering open coordination on the Lewis acidic metal sites. Under reducing conditions, it was shown that the metal site also modifies the binding properties of the TiO₂ support. This was further supported by studying the structure and binding properties of TiOₓ deposited on CuO and when CuOₓ and TiOᵧ centers were loaded on SiO₂.
The effect of support on the reduction properties of the metal sites was also studied with XAS. The structure evolution in metal sites such as Au and Ni-doped/dispersed in/on SrTiO\textsubscript{3} during the reductive segregation of the Au and Ni centers was studied. It was demonstrated that the reduction properties of Ni sites depend on the location of the Ni sites in or on the crystal, the substitutional site has a higher oxidation state and is less reducible compared to surface sites. In the case of unfeasible substitution, the Au site adapts surface oxo-structure that is connected to the SrTiO\textsubscript{3} structure through two oxo-binuclear bonding; Au-O-Ti and Au-O-Sr. Under reducing conditions, gold cations reductively segregate from such sites to form a metal cluster, the size of which is determined by the initial level of Au doping and the reducing conditions employed.

For CO\textsubscript{2} hydrogenation, we demonstrated the importance of the interfacial Lewis acidic sites produced from metal/metal oxide interaction in stabilizing the CO intermediate. \textit{In situ} infrared spectroscopy in combination with isotope labeling revealed that CO molecules adsorbed on Ti\textsuperscript{3+} and Cu\textsuperscript{+} interfacial sites in CuO\textsubscript{x}/TiO\textsubscript{2} gave two disparate carbonyl peaks. Monitoring each of these peaks under various conditions enabled tracking the adsorption of CO, CO\textsubscript{2}, H\textsubscript{2}, and H\textsubscript{2}O molecules on the surface. At room temperature, CO was initially adsorbed on the oxygen vacancies to produce a high-frequency CO peak, Ti\textsuperscript{3+}–CO. Competitive adsorption of water molecules on the oxygen vacancies eventually promoted CO migration to copper sites to produce a low-frequency CO peak. In comparison, the presence of gaseous CO\textsubscript{2} inhibits such migration by competitive adsorption on the copper sites. At temperatures necessary to drive CO\textsubscript{2} and CO hydrogenation reactions, oxygen vacancies can still bind CO molecules, and H\textsubscript{2} spilled over from copper also competed for adsorption on such sites. These spectroscopic observations suggested the existence of bifunctional catalytic sites, in which metallic copper sites serve as CO\textsubscript{2} dissociation
sites, whereas the Cu$^+$ and the oxygen vacancies bind the produced CO molecules for further reductions.

The role of the interfacial sites in hydrogen generation was also studied with \textit{in situ} DRIFTS by marking these sites with CO probing molecules. It was demonstrated the Lewis acidic binding sites at the interface activate water molecules more than methanol. This explains the reason for the exclusive H$_2$ generation from water in the presence of methanol as revealed by previous isotopic labeling experiments.

Implementing XAS and DRIFTS tools in combination with different catalyst structures revealed the role of the interaction in creating sites with novel binding properties. This highlights the need for studying more metal/metal oxide systems preferably with \textit{in situ} tools that enable simultaneous XAS and DRIFTS measurements.
VII. LIST OF REFERENCES


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