In situ Imaging and Tracking of Reversible Metal-Support Interactions under CO2 Hydrogenation over a Cu@TiOx Core@shell Catalyst

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Article

Keywords:

Posted Date: January 24th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-2382852/v1
In situ Imaging and Tracking of Reversible Metal-Support Interactions under CO2 Hydrogenation over a Cu@TiOx Core@shell Catalyst

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Abstract

A combination of environmental-transmission electron microscopy (E-TEM), several in-situ techniques (XRD, PDF, XAFS, AP-XPS), and transient isotopic exchange analysis was used to explore links between the structural and chemical properties of a Cu@TiOx core@shell catalyst under CO2 hydrogenation conditions. The active phase of the catalyst involved an oxide/metal configuration, but the initial core@shell motif was disrupted. Images of E-TEM showed a very dynamic morphology, where the inverse oxide/metal configuration was substantially affected by the gas environment (CO2, H2, or CO2/H2) and the temperature of the system. At room temperature, CO2 was very reactive at the metal-oxide interface, producing big changes in its morphology. When the initial system was oxidized by reaction with carbon dioxide (CO2,gas → CO gas + O ads), the copper leached out and disrupted the titania shell. However, the core@shell structure was regenerated by hydrogen reduction at 150-250 °C. When oxidation and reduction occurred at the same time, under a mixture of CO2 and H2, the surface structure evolved toward a dynamic equilibrium that strongly depended on the temperature. At room temperature, the leaching of copper dominated, while, at 250 °C, the formation and development of an evolving Cu@TiOx structure prevailed. These morphological changes were linked to variations in metal-support interactions that were completely reversible with temperature or chemical environment and affected the catalytic activity of the system.
Nowadays, the trapping and conversion of CO\(_2\) is a major issue in environmental chemistry\(^1\)-\(^2\). Metal-oxide interfaces are frequently used for the conversion of CO\(_2\) into fuels and high-value chemicals\(^3\),\(^4\). There have been a lot of studies focused on identifying the active phase of metal/oxide catalysts that are active for the hydrogenation of CO\(_2\) to methanol\(^5\)-\(^8\). High-resolution transmission electron microscopy (HR-TEM) has been used to study the morphology of a powder Cu/ZnO/Al\(_2\)O\(_3\) catalyst after reduction\(^8\). The microscopy results showed that the active phase of the catalyst involved an inverse oxide/metal configuration produced as a consequence of strong metal-support interactions. In this article, we use environmental TEM to image the structural evolution of a Cu@TiO\(_x\) catalyst under CO\(_2\) hydrogenation conditions\(^8\). As in the case of Cu/ZnO/Al\(_2\)O\(_3\), we find an active phase with an inverse oxide/metal configuration, but, in addition, our E-TEM images show that there are large morphological changes for the catalyst depending on the chemical environment and that the effects of metal-support interactions are completely reversible.

The phenomenon of strong metal-support interactions (SMSIs) has received much attention in catalysis research since its discovery, as it has a significant impact on the structure of a catalyst, thereby determining its performance\(^8\),\(^10\)-\(^27\). For catalysts composed of a noble metal and a reducible oxide, the typical encapsulation of oxide on the metal particles can be induced by high temperature reduction\(^11\),\(^12\),\(^26\),\(^27\). As noble metals have a relatively high surface energy and work function, forming an oxide layer on the metal particles could lower the surface energy of the catalysts and stabilize the partially reduced oxide\(^13\),\(^14\),\(^26\),\(^27\). Different from Pt and Pd, late 3d transition metals like Co, Ni, and Cu have a lower surface energy and a work function as well as a weaker ability in H\(_2\) activation and dissociation. The tendency to induce a SMSI within a typical core(metal)@shell(oxide) structure is much lower. Typical SMSI cases are uncommonly reported\(^8\),\(^12\),\(^15\)-\(^18\), among which the most notable example is the inverse oxide/metal structure observed ex-situ in a reduced industrial Cu/ZnO/Al\(_2\)O\(_3\) catalysts\(^8\). In fact, the core(metal)@shell(oxide) structure in those systems could be much more fragile than the ones involving noble metals as the core metals have higher oxygen adsorption energies and oxide formation energies\(^19\)-\(^21\). Under oxidation conditions, the core metals in these systems could either form bulk oxides or mix into the shell overlayers\(^22\),\(^23\)-\(^27\). For these reasons, the structures of these systems under important catalytic redox conditions, such as the CO\(_2\) hydrogenation process, may be in a dynamic equilibrium of different configurations. A static picture about the structure of a working catalyst established from ex-situ imaging may be inaccurate or even misleading, when using structure-activity relationships for the optimization or design of catalysts. Depending on the nature of the metal and oxide combined in a catalyst, the effects of the metal-support interactions can be reversible\(^26\)-\(^27\). To the best of our knowledge, no E-TEM study has been published examining morphological changes and the reversibility of metal-support interactions under CO\(_2\) hydrogenation conditions.

In a recent work for CO\(_2\) hydrogenation on a Cu@TiO\(_x\) core@shell catalyst\(^24\), we observed typical SMSI effects, and TiO\(_x\) overlayers of a few atomic layers were found covering the surface of copper wires. Some copper particles leached out and were found on top of the titania shell\(^24\). In this study, we used
environmental TEM and a combination of several in-situ techniques (X-ray Powder Diffraction (XRD), Pair Distribution Function (PDF), X-ray absorption near edge structure (XANES), and ambient pressure X-ray photoelectron spectroscopy (AP-XPS)) to investigate links between the structural and chemical properties of the Cu@TiO$_x$ core@shell catalyst. Thanks to this multi-technique approach, a correlation between the evolving Cu@TiO$_x$ structure and its CO$_2$ hydrogenation activity curve is established. The observed behaviors are distinct from the classical noble metal core@shell structures where the dynamics are mostly observed in the shell part.$^{25-30}$ This work reveals the mutable nature of SMSIs that are completely reversible and change with variations in temperature and chemical environment.

**Results**

A Cu@TiO$_x$ core shell structure was found to epitomize the nature of the Cu/TiO$_x$ catalyst, which was synthesized by reducing a CuTi$_y$O$_z$ solid solution (Figure S1) using a published methodology.$^{24}$ Data for the structure and spatial composition of a freshly reduced sample are shown in Figures 1 and S2. Figure 1 shows the high-angle annular dark field (HAADF) images and energy-dispersive X-ray spectroscopy (EDS) in addition to electron energy loss spectroscopy (EELS) mapping from scanning transmission electron microscopy (STEM) on a freshly reduced sample, while Figure S2 highlights the corresponding low magnification images from TEM. Copper exists in two forms in the sample: as a nanowire encapsulated by a TiO$_2$ shell of about 50 nm thickness and as particles of 20-40 nm diameter on the surface of TiO$_2$. An amorphous layer can be observed on these particles (Figure S2) in the pre-reduced samples and after in-situ reduction, as observed with E-TEM (Figure S3).

Combined with the detailed EDS and EELS mapping for the Ti and O in the Figure 1g, 1h, the Cu@TiO$_x$ configuration was confirmed for the particles on the nanorods in a reduced sample. The spherical shape of copper particles indicates that it is thermodynamically favorable for the TiO$_x$ overlayer to bond to the low coordinated copper atoms in the less well-defined surfaces. Moreover, the bonding over the Cu/TiO$_x$ interface seems to depend on the valence state of Ti with some Ti$^{3+}$ species present in the sample (Figure S4). As the E-TEM data in Figure S5 shows, the spherical shape of Cu is preferred under H$_2$ at 450 °C which is just one of several possible shapes expected for these metal nanoparticles.$^{31}$ A similar phenomenon was observed in E-TEM images for the encapsulation of Pt with titania in the presence of H$_2$.$^{11}$

After annealing under H$_2$ at 450 °C, Ti$^{3+}$ was detected (Figure S4), and this cation is probably stabilized by bonding TiO$_x$ to atoms in the copper surface with a low coordination number and high reactivity.$^{32}$ Moreover, the observation of the spontaneous wetting of TiO$_x$ on the Cu surface at 450 °C under H$_2$ supports that the Cu@TiO$_x$ configuration is thermodynamically favorable under reduction conditions (Figure S3, S5), which is similar to the classical SMSI process.$^{9,11,34}$
Since the interface structure of Cu/TiO$_x$ is sensitive to the valence state of Ti, the stability of the core@shell structure under oxidation conditions was evaluated. The TEM images in Figure S6 were taken in situ under 0.2 mTorr of O$_2$ at 350 °C. Copper was oxidized and leached out to form Cu$_2$O (see Figure S6c) or a CuTi$_x$O$_y$ solid solution. It is worth noting that in the region where no Cu$_2$O or CuTi$_x$O$_y$ is observed, copper stays metallic (Figure S6c). The migration or leaching out of copper is facilitated by the stability of copper titanium oxide solid solutions, and is a consequence of metal(copper)-support(titania) interactions. After the oxidation process, the environment was switched to 10 mTorr of H$_2$ at 450 °C for 30 mins, and then a Cu@TiO$_x$ structure with a thinner shell was observed (Figure S7). The reversible change of copper distribution during oxidation and reduction is also supported by the AP-XPS data in Figure S8 where one can see clear changes in the oxidation state (peak position) and the intensity of Cu and Ti signals after sequential exposure to O$_2$ and H$_2$. In-situ studies with XRD and XAFS also pointed to reversible CuTi$_x$O$_y$ to Cu@TiO$_x$ transformations when switching from O$_2$ to H$_2$ exposure (Figure S1 and discussion below).

As mentioned above, it has been reported that a similar configuration, Cu@ZnO, is observed in an activated Cu/ZnO/Al$_2$O$_3$ industrial catalyst, which is an important benchmark for the CO$_2$ hydrogenation reaction. Considering the sensitivity of the Cu@TiO$_x$ structure to a reaction environment, investigating the surface dynamics of Cu@TiO$_x$ particles under CO$_2$ hydrogenation conditions should be helpful for understanding the behavior of similar copper-based core@shell structures, which were previously only
observed after an *ex situ* activation process. In a first step, we investigated the morphological changes that will follow after exposing a Cu@TiO$_x$ system pre-reduced in H$_2$ (Figure 2a) to 0.2 mTorr of CO$_2$ gas at 20 °C (Figure 2b-f). At room temperature, the adsorbate was very reactive and produced massive changes in the morphology of the catalyst. The partial dissociation of carbon dioxide (CO$_2$ → CO + O) led to the oxidation of copper. It appears that copper leached out as it was being oxidized. Meanwhile, the amorphous part became much thicker, while the metallic copper volume shrank with increasing reaction time. The images point to the coexistence of Cu, Cu$_2$O, TiO$_2$ and a CuTi$_x$O$_y$ solid solution. Carbon deposition was not likely as the produced CO typically does not dissociate on either copper or copper oxides. In experiments of AP-XPS, we did not see deposition of atomic carbon, but some surface carbonate species (CO$_x$) could be present in the system shown in Figure 2f. The dissociation of CO$_2$ on the Cu surface at room temperature may be promoted by the exposure of the Cu atoms with lower coordination numbers, due to the metal particle spherical

![Figure 2. E-TEM image sequence for the exposure of a pre-reduced Cu@TiO$_x$ catalyst (see Figures S3 or S5) to 0.2 mTorr CO$_2$ at 20 °C. “0 s” corresponds to the beginning of the E-TEM study. In part (e) are shown regions with Cu$_2$O(111), Cu(111) and Cu(200) orientations. The bars at the bottom of each image correspond to 5 nm.](image)
shape, and the existence of a Cu$^{\delta+}$/TiO$_x$ interface where metal-support interactions favor the oxidation of the copper component$^{33,36,37}$.

Experiments carried out under a mixture of H$_2$ and CO$_2$ showed morphologies (Figure 3) that were strongly dependent on the temperature of the system and reflected a balance between the reducing power of H$_2$ and the oxidizing power of CO$_2$. Figure 3a displays the morphology of a surface pre-reduced in H$_2$ that

![Figure 3. E-TEM image sequence taken at 250 °C with 20 mTorr of H$_2$ and CO$_2$ (p(H$_2$)/p(CO$_2$) ≈ 1). Initially, after pre-treatment in H$_2$, the sample was exposed to a 1:1 mixture of H$_2$ and CO$_2$ at 20 °C (image a). “0 s” corresponds to the moment when the temperature is rapidly raised from 20 to 250 °C. The amorphous overlayers are colored in the images (b-f). Zoomed in images from the sequence i to vi focus on the evolution of the leached out Cu$_2$O particle and image ii is taken from (d). The lattice spacing value of 0.25 nm and 0.30 nm is obtained in the measurements in the images ii and iv, whose corresponding lattice planes are determined to be Cu$_2$O (111) and Cu$_2$O (110). Scale bar = 5 nm.](image)

was exposed to a 1:1 mixture of CO$_2$ and H$_2$ at 20 °C. At room temperature, the role of H$_2$ was limited and eventually the system adopted a configuration with a morphology (Figure 3a) very similar to the one detected under pure CO$_2$ (Figure 2f). This morphology changed when the temperature of the system was increased to
250 °C where the splitting of H₂ and the reduction of the copper oxide component were faster. In Figure 3f, the sample morphology is not very different from that obtained under pure H₂ (Figures S3 and S5). It appears that as soon as Cu₂O is reduced, copper atoms quickly assimilate into the copper particles. After that, the system becomes a core@shell structure (Figure 3, 62 second). However, the evolution of the shell thickness is uneven, as amorphous shells disappear in some parts, while the thickness barely changes in other regions. This behavior is similar to the cases illustrated in Figures S3 and S5 when only H₂ was in the background. The morphological changes seen in Figure 3 were completely reversible with temperature, reflecting a balance between the reducing power of H₂ (high temperature) and the oxidizing power of CO₂ (low temperature). Furthermore, even when the ratio of H₂/CO₂ was increased by a factor of 50, the switch in the catalyst morphology was seen after cooling the sample to room temperature (Figure 4). It can be observed that Cu is oxidized and leach preferentially on some parts of the surface (regions 1 and 2 in the Figure 4), likely due to the defects on the oxide overlayers.

![E-TEM image sequence taken at 20 °C with 10 mTorr of H₂ and CO₂ (p(H₂)/p(CO₂) ≈ 50). The sample was initially exposed to the same H₂ rich feed at 250 °C (Figure S3). “0 s” corresponds to the moment when the temperature rapidly was dropped down from 250 to 20 °C. In part (e) are shown regions with Cu₂O(111) and Cu(111) orientations. Scale bar = 5 nm.](image)

**Figure 4.**

Since the E-TEM experiments were conducted under relatively low pressures, the situation under actual catalytic conditions could be different. To verify whether a comparable structure evolution of Cu@TiOₓ also occurs under CO₂ hydrogenation at 1 atm, *in situ* PDF, XRD and XANES measurements were carried out
where the sample was pre-reduced in H₂ and then exposed to a mixture of CO₂/H₂ at temperatures between 25 and 250 °C with several cycles of operation. The results of these experiments are summarized in Figures 5a and S9-S11. All the in-situ techniques point to the oxidation of copper and TiOₓ by CO₂ at RT and

**Figure 5** (a) Cu K edge *in situ* XANES measurements on a Cu/TiOₓ sample during the ramping process from 25 to 250 °C with a 7 °C /min ramping rate, under 12 sccm H₂, 4 sccm CO₂, and 4 sccm He. The temperature shows the average value during data collection. (b) The CO₂ hydrogenation activity was measured on a freshly reduced Cu/TiOₓ sample at 250 °C in a continuous experiment, composed of 10 cycles. In each cycle, the temperature is raised from room temperature to 250 °C, then kept at 250 °C for 5 h, and subsequently cooled down to room temperature in a reaction gas mixture of v(H₂): v(CO₂): v(N₂)= 3:1:1. (c-d) Reaction quotient of H₂+D₂=2HD calculated from mass spectrometry. H₂ (m/z=2), D₂ (m/z=4), and HD (m/z=3) evolution (sampling rate 500 ms) was measured in a H-D exchange experiment on freshly reduced samples. For each temperature cycle, the sample temperature was raised from 25 to 250 °C and then held at that temperature for 5 h before cooling down to 25 °C in 7.5% H₂, 7.5% D₂, and 5% CO₂ (balanced with Ar). (c) Data for Cu/TiOₓ. (d) Data for plain Cu nanowires.

reduction of Cu₂O and CuTiₓOᵧ by H₂ at 250 °C. A linear combination fitting (LCA) analysis of the XANES data showed that, at 250 °C under CO₂ hydrogenation conditions, copper cations were fully reduced, while 5-
10% of Ti$^{3+}$ was detected in the TiO$_2$. Thus, it appears that the E-TEM results and the in-situ characterization data at 1 atm match in the sense that copper gets oxidized during the cooling process and becomes reduced to the metallic state when the temperature is raised back to 250 °C. Therefore, while the time scale for the structural changes may vary, it is reasonable to assume that the transient configurations observed in the E-TEM images are representative for the morphological evolution under 1 atm.

Activity measurements were carried out for CO$_2$ hydrogenation and H$_2$-D$_2$ exchange (Figure 5b-d, S12 and S13). Under CO$_2$ hydrogenation conditions, CO was the only reaction product as a consequence of the reverse water-gas shift reaction (rWGS, CO$_2$ + H$_2$ → CO + H$_2$O). This is expected, since the catalytic measurements were done at atmospheric pressures where no methanol is produced.$^{3,24}$ In Figure 5c, in each cycle, the initial activity at 250 °C is large and then decreases with time. Moreover, when the activity is measured during multiple cycles following the same temperature program of cooling to RT and then heating to 250 °C, a stable pattern can be observed. A similar behavior was seen when the temperature was set at a final value of 350 °C (Figure S12b). The surface morphology generated by exposure to CO$_2$/H$_2$ at room temperature (Figure 3a or 4f) is probably the most active for the rWGS, but it is not stable at high temperatures. There is a change in the nature of the metal-support interactions, and this change affects the catalytic activity of the system. Furthermore, on the basis of our in-situ characterizations and the catalytic tests in Figure 5b, we can conclude that the metal-support interactions are reversible, depending on temperature and the chemical environment.

To gain insight into the factors that favor this reversibility, the transient behavior at the highest activity was investigated with a second reaction linked to CO$_2$ hydrogenation. A transient technique based on mass spectrometry was used to follow the hydrogen-deuterium exchange activity under CO$_2$ hydrogenation conditions, a process that usually is selectively catalyzed by metallic copper.$^{38-41}$ As the results in the Figure 5c and S13d show, the reaction quotient for the hydrogen-deuterium exchange reaction follows the same trend as the rWGS activity, essentially reaching a maximum when the temperature is raised to 250 °C, with a subsequent decrease thereafter. Thus, the surface sites that facilitate hydrogen-deuterium exchange are probably the ones that start the hydrogenation of CO$_2$ and both reactions are affected by the morphological changes in the catalyst.

An important difference is observed when comparing the results displayed in Figure 5c and 5d for the hydrogen-deuterium exchange on the Cu@TiO$_x$ catalyst and plain Cu nanowires (NWs) that were used as the core when depositing the titania shell.$^{24}$ The reaction rate is 2-3 orders of magnitude faster on the copper-titania interface, thereby highlighting the need for cooperative effects in a metal-oxide interface, as was also seen when analyzing results for plain CO$_2$ hydrogenation.$^{24}$ As Figure 5d shows, the H-D exchange activity on the plain Cu NWs does not rise to its maximum, until 0.5-1 hour after the temperature reaches 250 °C. As
it shows a consistent trend over three cycles, it is reasonable to propose that the increase of the H-D exchange activity is due to the production of metallic copper in the reduction of the CuO, generated during the cooling process. It is clear that the sites responsible for the catalysis in Cu@TiO, behave in a dynamic way, rapidly responding to changes in temperature and/or chemical environment. We performed experiments in which the Cu@TiO structure was activated in different ways (see Scheme 1 in the Methods section), but the catalyst always evolved to the same final state for a given set of temperature and pressure conditions (Figures 6 and S12).

![Scheme representing the surface evolution towards a steady state structure, starting from different Cu@TiO configurations, under CO$_2$ hydrogenation conditions. Scale bars in the TEM images correspond to 5 nm.](image)

**Figure 6.** Scheme representing the surface evolution towards a steady state structure, starting from different Cu@TiO$_x$ configurations, under CO$_2$ hydrogenation conditions. Scale bars in the TEM images correspond to 5 nm.

The E-TEM images displayed in Figures 2, 3 and 4 illustrate the substantial changes that can occur in the morphology of a metal-oxide system when exposed to the reactants during the hydrogenation of CO$_2$. Different changes are detected in the presence of O$_2$, H$_2$, CO$_2$ and CO$_2$/H$_2$ mixtures. These changes involve metal-support interactions that are reversible with gas composition and temperature. In the Cu@TiO$_x$ catalyst, the morphological changes associated with the oxidation and reduction of the copper component are affected by metal-support interactions and show clear differences with respect to those seen in plain copper oxide systems with E-TEM. Furthermore, during CO$_2$ hydrogenation, morphological changes are seen that have
not been detected previously in E-TEM images collected while exposing metal/oxide catalysts to either plain H₂ or under CO oxidation.¹¹,²⁷,⁴²,⁴⁴ These morphological changes may be responsible for the difficulties reported when establishing the active phase for catalysts used in CO₂ hydrogenation.⁵⁻⁸ The reversibility of metal-support interactions is a phenomenon that is rarely considered when dealing with the optimization and design of heterogeneous catalysts.²⁶,²⁷

Conclusions:

In-situ characterization methods highlight dynamic changes in the structural and electronic properties of a Cu@TiOₓ core@shell systems under H₂, CO₂ and CO₂ hydrogenation conditions. The nature of the metal-support interactions changes due to the opposite effects of H₂ and CO₂ on the physical and chemical properties of copper and titania. At room temperature, CO₂ was very reactive on the metal-oxide interface, thereby producing big changes in its morphology. E-TEM studies under a CO₂/H₂ mixture indicated that the Cu@TiOₓ core@shell configuration gradually evolved towards a dynamic equilibrium structure, which was temperature dependent. At 20 °C, the preferred catalyst structure had copper oxidized and leached out of the TiOₓ shell, while at 250 °C, a core@shell configuration with copper largely covered by TiOₓ was more favorable. The E-TEM observations matched the findings from catalyst activity measurements and an H-D exchange transient study. The highest rWGS activity was detected in a transient configuration with the largest exposed copper amount, before it evolved into a more thermodynamically stable structure wherein TiOₓ was spread out thereby covering the Cu surface. This study underscores the dynamic nature of the Cu@TiOₓ structure under CO₂ hydrogenation conditions wherein important insights into the transient configurations and the prevailing structure in the steady state cannot be extracted from conventional ex situ TEM images. Reversible metal-support interactions are essential for the good performance of the catalyst.

Materials and Methods

Catalyst preparation
The initial samples consisted of core@shell nanowires, generated using a published method.²⁴ The as-synthesized core@shell nanowires were treated in a reactor with 1 bar pressure with the following sequence: 1 h in 10 v% O₂ at 350 °C and then 1 h in 50 v% H₂ at 450 °C with a 10 °C/min ramping rate for heating and a 15 °C/min ramping rate for cooling. After treatment, the sample is referred to as “pre-reduced” throughout this paper.
Catalytic activity measurements

The catalytic performance of the materials was evaluated in a continuous-flow, fixed-bed microreactor at about 1 atm pressure. Around 1.2 mg of the Cu/TiOx sample were loaded in a quartz capillary of 1.1 mm OD and 0.9 ID. Before activity measurements, and after treatment in O₂, the sample was reduced at 450 °C under 50 v% H₂/N₂ (see above). For activity measurements at 350 °C, a total flow of 12 standard cubic centimeters per minute (sccm) was used, while a 2.5 sccm flow was utilized for measurements at a 250 °C reaction temperature.

In the experiments of catalytic activity and in-situ characterization, we followed the sequences labeled as path A or path B in Scheme 1. In path A, the sequence followed in most of our experiments, the sample was cooled to room temperature after pre-reduction in H₂, and then exposed to the reaction gas mixture and heated to high temperature for the catalytic tests. In path B, just used in a few tests, the sample was directly cooled to the reaction temperature after pre-reduction in H₂. The concentrations of the gas evolved were analyzed with a gas chromatography instrument (Agilent 7890A), equipped with both flame ionization and thermal conductivity detectors. The N₂ in the gas flow was used as the internal standard.

Scheme 1. Paths A and B followed in our catalytic tests. The main difference is in the final set of experiments where the sample was cooled down to room temperature (path A) or directly to the reaction
temperature tested (path B). Most of the activity measurements were done at 250 °C, with some at measurements at 350 °C.

**X-ray diffraction (XRD)**

The data were collected in the 17-BM-B beamline at the Advanced Photon Source (APS) in Argonne National Laboratory (ANL) using an area detector with an X-ray wavelength of 0.24012Å. The sample was loaded in a Clausen cell with a 0.9 mm ID and 1.1 OD quartz capillary. Rietveld refinements were conducted in the data analysis with the GSAS-II code.

**X-ray Absorption Spectroscopy (XAS)**

Most of the in-situ X-ray absorption fine structure (XAFS) spectra were collected at the 7-BM Quick x-ray Absorption Scattering (QAS) beamline of the National Synchrotron Light Source II (NSLS-II) at Brookhaven National Laboratory (BNL). Some of the XAFS traces were collected at the 8-ID Inner-Shell Spectroscopy (ISS) beamline of NSLS-II at BNL. In these characterization studies, powder samples were loaded onto aluminum foil and both the Cu K edge and Ti K edge spectra were collected in the transmission mode and calibrated with Cu and Ti foil as standards, respectively. A Nashner-Adler cell was used for the *in-situ* measurements. The XAFS spectra were analyzed using the Athena software. A k range of 2-12 Å⁻¹ was used for the Fourier transform of the Extended X-ray absorption fine structure (EXAFS) data.

In the linear combination fitting of the Ti K edge, done using Ti₂O₃ and anatase TiO₂ as standards, only the raising edge region was used, excluding the pre-edge feature. The feature in the pre-edge of the Ti K-edge relates to the 1s-3d transition. Without hybridization of the 3d and 4p orbitals, the feature is weak due to its electric quadrupole transition nature. Its intensity could be significantly affected by the extent of hybridization, which is strictly controlled by the symmetry of the Ti polyhedron. For a Ti atom of a certain valence state, the feature shape and profile could vary due to different geometries of the Ti polyhedron. By contrast, the feature in the raising edge region caused by the Ti 1s-4p transition could better reflect variations expected for different titanium valence states, due to the high intensity of its electric dipole transition moment.

**Ambient Pressure X-ray Photoelectron Spectroscopy (AP-XPS)**

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The ambient pressure X-ray photoelectron spectroscopy (AP-XPS) spectra displayed in Figure S4 were collected at the 23-ID-2 beamline of the National Synchrotron Light Source II at BNL. The standard Cu 2p3/2 binding energy (932.6 eV) was used for energy calibration. A lab-based AP-XPS was used to collect the data displayed in Figure S8. It consists of a SPECS AP-XPS chamber, equipped with a PHOIBOS 150 EP MCD-9 analyzer with an energy resolution of 0.4 eV. The Cu2+ was calibrated to 933.6 eV, and then Cu+ was used for Cu0 alignment.

**Pair distribution function (PDF)**

These data were collected using facilities at the 28-ID-2 (XPD) beamline in the NSLS-II. The X-ray wavelength was 0.187Å. The sample was loaded in a Clausen cell with a 0.9 mm ID and 1.1 OD quartz capillary. The distance between the sample and the 2D detector was 230 mm. The PDF data were analyzed using a program from the beamline.

**H-D exchange experiments**

The experiments were conducted using an experimental setup for transient kinetic studies located in the laboratory of the Catalysis Reactivity and Structure (CRS) group at the Chemistry Division of BNL. The system consists of a program-controlled gas handling system and a Hiden HPR-20 R&D triple filter mass spectrometer. In a typical experiment, a total flow rate of 12 sccm was used for 1.2 mg of sample.

**In-situ scanning transmission electron microscopy (STEM)**

The High-angle annular dark-field (HAADF) STEM data were collected on the FEI Talos F200X at the Center for Functional Nanomaterials (CFN) of BNL. The pressure was about 10^{-8} Torr during the heating experiments.

**Environmental transmission electron microscopy (E-TEM)**

The E-TEM images were collected on the FEI Titan 80-300 at the Center for Functional Nanomaterials (CFN) of BNL. The in-situ TEM sample was prepared by drop-casting suspension of pre-reduced Cu/TiOₓ in water onto a MEMS-based heating chip (through-hole chip of DENSsolutions Wildfire series).

All the E-TEM experiments were performed using Cu/TiOₓ samples that were pre-reduced in H₂ outside the microscope as done for the catalytic tests (see Scheme 1). Inside the microscope, the samples
were again reduced in H$_2$ before exposing them to O$_2$, CO$_2$ or a CO$_2$/H$_2$ mixture. To verify that the electron beam was not affecting the morphological studies, test images were collected on samples freshly exposed to the gases or on different places of a given sample.

**Data availability**

The data that support the findings of this study are presented in the article and Supplementary Information. Source data are provided with this paper. Any other relevant data are also available from the corresponding author upon reasonable request.
References


**Acknowledgement**

The work done at the Chemistry Division of BNL was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, and Catalysis Science Program under contract No. DE-SC0012704. J.A.R. and J.M. received funding from a DOE Office of Science Distinguished Scientist Fellow Award. X.C. and G.Z acknowledge the support by the National Science Foundation (NSF) under DMR 1905422. The Cu@TiO<sub>x</sub> core-shell nanowires, that inspired the current work, were initially produced in SSW's laboratory, supported by the U.S. National Science Foundation under Grant No. CHE-1807640. This research used resources of beamlines 7-BM (QAS), 28-ID-2 (XPD), and 23-ID-2 (IOS) of the National Synchrotron Light Source II, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Brookhaven National Laboratory under Contract No. DE-SC0012704. The QAS beamline operations were supported in part by the Synchrotron Catalysis Consortium (U.S. DOE, Office of Basic Energy Sciences, Grant No. DE-SC0012335). This research used resources of beamline 17-BM at the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science user facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. The morphology of the catalyst was studied at the Electron Microscopy Facility (FEI Titan 80-300 and FEI Talos 200x) of the Center for Functional Nanomaterials (CFN), which is a U.S. Department of Energy Office of Science User Facility, at Brookhaven National Laboratory under Contract No. DE-SC0012704.
**Author contributions**

J.A.R. conceived the general idea for the study, directed the project, and participated in the writing of most of the article. K.D. participated in the design and execution of all the experimental measurements and helped with the writing of the paper. X.C. was the main person in charge of collecting and analyzing the E-TEM images. J.M. participated in the XRD, XAFS, and catalytic studies. K.S. performed the synthesis of different catalyst configurations. N.R. performed the experiments with AP-XPS and analysis of these studies. W.X. performed XRD and PDF studies, helping with the analysis of the data. S.X. performed the full analysis of the XAFS data. N.M. performed the XAFS studies and helped with the catalytic studies. A.F. supervised the analysis of the XAFS data. G.Z. supervised the collection and analysis of the E-TEM images. S.W. helped to conceive the study, supervised the synthesis of the catalysts, and helped with editing the article. All the authors discussed the results and commented on the manuscript.

**Competing interests**

The authors declare no competing interests.

**Additional information**

**Supplementary information** The online version contains supplementary material available at ...

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