The Role of the Copper Oxidation State in the Electrocatalytic Reduction of CO$_2$ into Valuable Hydrocarbons


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ABSTRACT: Redox-active copper catalysts with accurately prepared oxidation states (Cu$^0$, Cu$^+$, and Cu$^{2+}$) and high selectivity to C$_2$ hydrocarbon formation, from electrocatalytic cathodic reduction of CO$_2$, were fabricated and characterized. The electrochemically prepared copper-redox electro-cathodes yield higher activity for the production of hydrocarbons at lower oxidation state. By combining advanced X-ray spectroscopy and in situ microreactors, it was possible to unambiguously reveal the variation in the complex electronic structure that the catalysts undergo at different stages (i.e., during fabrication and electro-catalytic reactions). It was found that the surface, subsurface, and bulk properties of the electrochemically prepared catalysts are dominated by the formation of copper carbonates on the surface of cupric-like oxides, which prompts catalyst deactivation by restraining effective charge transport. Furthermore, the formation of reduced or partially reduced copper catalysts yields the key dissociative proton-consuming reactive adsorption of CO$_2$ to produce CO, allowing the subsequent hydrogenation into C$_2$ and C$_1$ products by dimerization and protonation. These results yield valuable information on the variations in the electronic structure that redox-active copper catalysts undergo in the course of the electrochemical reaction, which, under extreme conditions, are mediated by thermodynamics, but critically, kinetics dominate near the oxide/metal phase transitions.

KEYWORDS: CO$_2$RR, Electrodeposited prepared copper oxides, In situ X-ray spectroscopy, Copper carbonate passivation layer, Charge transport limitation, DFT calculations, Electrocatalytically active reduced copper oxides

INTRODUCTION

Many solutions have been proposed to minimize the impact of CO$_2$ emissions, such as its sequestration or its chemical transformation into value added industrial products.¹² Among other technologies, the electrocatalytic route of energy conversion becomes of great importance because the electricity produced by renewable sources, like solar and wind, can be used to transform CO$_2$ into various chemical feedstocks.³⁴ In this direction, over the past decades, different materials capable of electrochemically reducing CO$_2$ in aqueous solution to...
produce hydrocarbons have been identified. Unfortunately, none of these materials are efficient and stable enough for practical use. 

Copper is unique in its ability to electroreduce CO₂ to hydrocarbons and alcohols in aqueous electrolytes, as was shown by Hori et al. However, the selective reduction of CO₂ into fuels is very challenging due to the multiple complex proton-coupled electron transfer steps that must occur. This complex network makes the cathodic CO₂ reduction reaction (CO₂RR) suffer from relative low current density (CO₂RR competes with hydrogen evolution), high overpotential (cathodic and anodic), and electrode deactivation/poisoning over time. Hence, the CO₂RR has been investigated using a multitude of copper based electrodes fabricated in many different ways including single crystals, oxide-derived copper (OD-Cu), nanowires, electrodeposited, plasma treated foils, nanoparticles, porous hollow fibers, shaped particles, mesopores, and dendrites. Nevertheless, the lack of detailed information on the electronic structure of these Cu surfaces during both the fabrication process and under the catalytic reaction makes it difficult to design more efficient and stable electrocatalysts. Herein, we report on the preparation of catalysts highly selective to C₂ hydrocarbon production and on the in situ monitoring of their electronic structure during preparation and electrocatalytic reaction. By tracking the electronic structure of the Cu catalysts, we were able to tune and precisely set the initial Cu redox state, such as Cu₀, Cu⁺, and Cu²⁺, by controlled applied potential protocols. Also, we traced the variations and modifications in the electronic structure (oxidation state) of the Cu catalysts during applied potential scans or steps and, in particular, under catalytic CO₂RR conditions. These experiments yielded unambiguous information on the catalyst redox processes governing the CO₂RR, as well as the nature of the active sites. In addition, the active/inactive and stable/unstable oxidation states depending on the applied potential and electrolyte were revealed.

**EXPERIMENTAL SECTION**

**Electrode Preparation.** The copper electrode was prepared by electrodeposition from 5 mM CuSO₄. The electrolyte was prepared by diluting 0.798 g of CuSO₄ (Sigma-Aldrich, anhydrous powder, 99.99%) in 1 L of Milli-Q water (18.2 MΩ) at room temperature (RT), 25 °C. The electrolyte was continuously saturated with pure N₂ gas by bubbling it through the electrolyte containing the copper salts. Therefore, the electrode was deposited at −0.5 V vs Ag/AgCl, yielding an overpotential deposition of copper in the oxidation state Cu⁺. After the electrodeposition, the electrolyte was changed to 5 mM KClO₄ in order to reduce the surface to Cu₀. The electrolyte was prepared by diluting 0.372 g of KClO₄ (Sigma-Aldrich, 99%) in 1 L of Milli-Q water (18.2 MΩ) at room temperature (RT), 25 °C. The electrolyte was continuously saturated with pure N₂ gas by bubbling. After that, the electrode was anodically polarized to produce Cu₀-, Cu⁺-, or Cu²⁺-like oxides that were used during the CO₂ electroreduction measurements and on the in situ monitoring of their electronic structure during preparation and electrocatalytic reaction. By tracking the electronic structure of the Cu catalysts, we were able to tune and precisely set the initial Cu redox state, such as Cu₀, Cu⁺, and Cu²⁺, by controlled applied potential protocols. Also, we traced the variations and modifications in the electronic structure (oxidation state) of the Cu catalysts during applied potential scans or steps and, in particular, under catalytic CO₂RR conditions. These experiments yielded unambiguous information on the catalyst redox processes governing the CO₂RR, as well as the nature of the active sites. In addition, the active/inactive and stable/unstable oxidation states depending on the applied potential and electrolyte were revealed.

**Calculation Methods.** DFT calculations were performed with the Quantum ESPRESSO package using the Perdew, Burke, and Ernzerhof (PBE) exchange correlation potential. Projector augmented-wave sets were taken from the PSLibrary using a plane-wave basis set with a kinetic energy cutoff of 30 Ry (300 Ry) for wave functions. We tested the role of dispersion corrections using the exchange-hole dipole moment (XDM) for both the clean Cu(111) and the Cu(111) with oxygen in the subsurface octahedral hole. On the clean surface, the activation energy was 1.68 eV with and without dispersion corrections, whereas, with subsurface oxygen, the activation energy was 1.54 eV with and 1.56 eV without dispersion corrections. Due to the small influence on barriers, we chose to ignore dispersion corrections in the main text. Calculations on metallic copper employed a k-point mesh equivalent to (12 × 12) for the (111) surface unit cell while those on Cu₂O employed a mesh equivalent to (2 × 4) for the (110) surface unit cell. In all cases, Marzari–Vanderbilt1 smoothing was used with a smearing parameter of 0.02 Ry. For the Cu(111) surface, we employed a 5 layer (2 × 2) surface unit cell slab with an in-plane lattice parameter of 5.15 Å. In the case of Cu₂O, a four layer (2 × 2) slab was used with in-plane cell parameters of 12.02 and 8.50 Å. In all cases, approximately 20 Å of vacuum was included to separate slabs from their periodic images and the bottom two layers were held fixed during ionic relaxation. MEFs were computed using the climbing image nudged elastic band method using 8 images for the metallic calculations and 16 images for those on Cu₂O. The transition states were converged when the force on the climbing image was less than 0.05 eV/Å and the energy change dropped below 10⁻³ eV.

**CO₂ Electroreduction Measurements.** CO₂ electroreduction measurements were carried out in a gas-tight H-cell separated by a Nafion anion exchange membrane (Selemion AMV, AGC Inc.). Both, the working electrode and counter electrode compartments were filled with 40 mL of 0.1 M KHCO₃ (Honeywell Fluka, 99.7%) and purged continuously with CO₂ (99.9995%, 20 mL min⁻¹). A KHCO₃ solution was prepared with ultrapure water and further prepurified with Chelex 100 Resin (Bio-Rad, 100–200 mesh). Prior to the measurement, the electrolyte was bubbled with CO₂ for 30 min to remove oxygen in the solution and saturate the solution. A platinum gauze (MatTeck,
3600 mesh cm$^{-2}$ was used as the counter electrode and a leak-free Ag/AgCl/3.4 M KCl electrode (Innovative Instruments, Inc.) was used for the reference electrode. The sample (Cu electrodeposited on Au mesh) was used as a working electrode and was contacted with a clamp wrapped by Kapton tape to avoid unwanted reactions. The sample was measured during CO$_2$RR at a constant potential for 1 h before changing to the next potential. The potentials were controlled with an Autolab potentiostat (PGSTAT 302N). The gas products were analyzed by online gas chromatography (GC, Agilent 7890A) every 17 min. CO, H$_2$, and hydrocarbons were separated by different columns (Molecular sieve 13X, HayeSep Q, and Carboxen-1010 PLOT) and quantified by a thermal conductivity detector (TCD) and flame ionization detector (FID). The reported Faradaic efficiency was calculated on the basis of the product distribution and current after 1 h of reaction at constant potential (see the SI for calculations).

## RESULTS AND DISCUSSION

The electrocatalysts were prepared and characterized using X-ray absorption spectroscopy (XAS) measured in fluorescence yield (FY) mode in an in situ electrochemical cell; the setup is described in the Supporting Information (SI). While in general XAS-FY are not analogous to the X-ray absorption cross section at the L$_{2,3}$ edges due to their sensitivity to distinct FY decay channels, these differences are negligible for Cu in oxidation states below 3$^+$. Thus, we will are free to compare XAS-FY to XAS and, as such, we will make no distinction between the two. The in situ XAS technique ensures an accurate direct correlation of the Cu redox state as a function of the applied potential, elapsed time, and electrolyte. Copper electrodes were electrochemically deposited from 5 mM of CuSO$_4$ (4.8 pH) at $-0.5$ V vs Ag/AgCl. The voltammetric profile of the electrodeposition of Cu is shown in Figure 1A as a function of the elapsed time. This process yields the electrodeposition of a stable oxy-hydroxide copper electrode (Cu$^+$), as the intense peak at 930.6 eV$^{27,28}$ in the XA spectrum indicates (highlighted in red). In order to minimize the impact of hydroxyl species on the electrodeposited copper electrode and to prepare a reproducible redox state, the deposited Cu electrode film was polarized cathodically in 5 mM KClO$_4$ (7 pH) to reduce Cu$^+$ to Cu$^0$, as shown in Figure 1B. The spectra collected as a function of applied potential confirm that the electrode reduces from Cu$^+$ (highlighted in red) to Cu$^0$ (highlighted in blue). This process is driven by the coupled ionic transport in solids in the presence of an applied electric field where the material acts as a solid-state electrolyte as well as a nonstoichiometric compound with mobile defects, like oxygen vacancies.$^{29}$ Diffusion is a slow process in solids; however, the existence of grain domains in our electrode facilitates diffusion due to the small grain size. Finally, after the electrochemical reduction of the deposited Cu film electrodes, the Cu oxidation state was deliberately controlled by linear sweep voltammetry (LSV) and concomitant recording of the X-ray absorption spectra at the Cu L$_{2,3}$-edges (Figure 1C). Stable Cu$^{2+}$ species were produced under anodic polarization where a significant amount of Cu$^+$ dissolves due to a local reduction of the pH.$^{27}$ This dissolution diminished the thickness of the electrodeposited material somewhat. Using the deposition and voltammetric post-treatment protocol above-described, Cu electrodes in controlled distinct redox states, such as metallic copper (Cu$^0$, highlighted in blue), cuprous (Cu$^+$, highlighted in red), or cupric (Cu$^{2+}$, highlighted in dark), were reproducibly/accurately prepared. The electro-synthesis also resulted in the formation of a continuous electrode film composed of polyhedral particles with well-defined facets, as shown in the SEM image in the inset of Figure 1A. The accuracy of the oxidation state of the electrochemically prepared Cu electrode was verified by...
Next, the electrocatalytic CO$_2$ reduction activity of the Cu$^{2+}$, Cu', and Cu$^0$ film electrodes was investigated using online gas chromatography. The catalytic product distributions as a function of applied electrode potentials for copper metal (Cu$^0$), cuprous-like oxide (Cu$^+$), and cupric-like oxide (Cu$^{2+}$) catalysts are shown in Figure S2, where the increase in the main peak at 930.6 eV is attributed to the reduction of Cu$^{2+}$ to Cu$^+$ and of Cu$^+$ to Cu$^0$, respectively, as proved by the XAS color maps in situ during negative potential scans. In the presence of a Cu$_2$O-free electrolyte (5 mM KClO$_4$) and Figure 3 (middle) (100 mM KHCO$_3$). Nevertheless, there was a slight decrease in the reduction potential peak position (in the LSV) ascribed to the transition from Cu' to Cu$^+$ at around −0.75 V vs Ag/AgCl (highlighted in green). It is related to a noticeable increase in the redox current, yielding a reduction wave in the LSV at −0.75 V vs Ag/AgCl.

(iii) Finally, the behavior of cupric-like oxide (Cu$^{2+}$) was elucidated during negative potential scans. In the presence of a Cu$_2$O-free electrolyte (5 mM KClO$_4$ saturated with N$_2$ gas), there were two reduction peaks at −0.2 V and −0.9 V vs Ag/AgCl related to the reduction of Cu$^{2+}$ to Cu$^+$ and of Cu$^+$ to Cu$^0$, respectively, as proved by the $in situ$ XAS color maps in Figure S1Cl. On the other hand, when cupric oxide was exposed to 5 mM KHCO$_3$ saturated in CO$_2$, the less cathodic reduction wave (at −0.2 V vs Ag/AgCl) in the LSV was suppressed (see Figure S1C2) due to the formation of highly stable/inert passivating copper carbonates. As a result of this passivation, copper remained in its Cu$^{2+}$ oxidation state until it was reduced directly to Cu$^0$ at around −0.7 V vs Ag/AgCl, showing the coexistence of Cu$^{2+}$ and Cu$^0$ species during the reduction process, which is expected under high cathodic polarizations in a basic medium according to the Pourbaix diagram.
the surface and cathodic reduction is suppressed, hindering charge transport, as shown in the upper panel of Figure 3. Note that the contact area of the working electrode is small in the in situ XAS electrochemical cell, yielding high electrode contact resistance. This resistance can be lowered by increasing the working electrode area, which is planned for future electrochemical cell designs. Meanwhile, it is not a problem for the employed cell to detect the reaction products during online GC or for the in situ EXAFS electrochemical cell, which uses a larger SiN window area as indicated in the SI. For completeness, the stability of the formed copper carbonate layer was investigated in an acidic environment (100 mM HClO4, 1 pH) as a function of time at open circuit voltage (OCV), as shown in Figure S3. These results indicate that the carbonate layer (probably azurite/malachite-like, Cu3(CO3)2−(OH)4/Cu2+CO3(OH)2) remains stable for a long time even under harsh acidic conditions, which effectively hinders the charge transport between counter and working electrodes. Comparing the LSVs for the different Cu oxides, it is obvious that the lowest overpotentials and highest currents are achieved with the metal-like oxides, CuO. On the other hand, Cu2+-like oxides show low currents compatible with severe charge-transport limitation effects.

In order to verify the formation of passivating copper carbonates, in situ EXAFS measurements at the Cu K-edge were performed under reaction conditions for the Cu− and Cu2+-like catalysts to obtain information about the metal−oxide (M−O) and metal−metal (M−M) bond distances. For the Cu K-edge measurements, each spectrum was collected at a fixed potential with an acquisition time of 1 h, comparable to the GC product analysis acquisition times. Figure 4A1 shows the EXAFS analysis of the Cu+−like oxide as a function of applied potential in 5 mM KClO4 saturated in N2. It is obvious that initially the dominant species is a Cu+ oxide with an M−O distance of around 1.65 Å. At increasing cathodic polarization, cuprous oxide underwent a reduction and the EXAFS spectra only show M−M distances (at around 2.5 Å), indicating the absence of any dominant oxide character at high cathodic polarization, in agreement with the Cu L2,3-edges. When the electrolyte is changed to 100 mM KHCO3, the behavior is similar; there is a dominant M−M distance at high cathodic polarization. However, a slight amount of oxygen remains with the characteristic M−O distance seen in Figure 4A2, which is ascribed to oxygen dissolved in the bulk and/or in subsurface of the material.

The cupric-like (Cu2+) oxide was investigated under the same conditions as the cuprous-like oxide, and in the presence of the CO2-free electrolyte, the same trends as those seen for Cu+ are observed. A prominent peak at 2.5 Å is ascribed to the M−M distance, as shown in Figure 4B1, as the catalyst is reduced to metal at high cathodic polarization. Exposing the Cu2+-like oxide electrode to a 100 mM HKCO3 electrolyte saturated with CO2, however, yields completely different behavior compared to the case of CO2-free electrolyte. When the electrolyte is saturated with CO2, there are two peaks under high cathodic polarization; see Figure 4B2. The M−M distance that evolves upon the electrode is reduced, and an M−O distance remains over the entire potential range. This lattice distance is ascribed to the copper carbonate species that hinder charge transport and dissociation of CO2 into CO, thereby preventing hydrogenation processes, in agreement with the Cu L2,3-edges measurements. Note that the structural changes observed in the EXAFS measurements are not observed in the XA spectra at high cathodic potentials (Figure 3), as we discussed previously. It is due to the fact that the working electrode area is smaller in the XAS cell than in the EXAFS cell, yielding a higher contact resistance, which hinders effective charge transport and saturates the potentiostat for the XAS cell.

Taking into account the discussed experiments, it is clear that the hydrogenation of carbon takes places when copper is mostly reduced, whereas the cupric-like oxide is most likely inactive. In situ X-ray spectroscopies, both XAS and EXAFS, indicate that surface copper carbonates generated on cupric-like oxide form a passivation layer that hinders charge transport, thereby making Cu2+ inactive in the cathodic reduction of CO2 into valuable hydrocarbons. As a result, Cu+ and Cu0 formation are required for activation. If the electrode is in the copper metal or cuprous oxide redox state, however, carbonate formation does not take place and the CO2 can be reduced, allowing its subsequent hydrogenation at higher cathodic potentials. While the nature of the hydrogenation products depends on the coverage of adsorbed intermediates—the first product evolved is C2H4 due to a dimerization process and finally CH4 evolves due to protonation effects on a proton rich surface—it is expected that a key reaction step in the CO2RR is the dissociation of CO2 into CO. The magnitude of this dissociation barrier will likely depend on the degree of surface oxidation and nature of surface defects. Therefore, we calculated the barrier associated with dissociative CO2 adsorption (CO2,ads → CO,ads + O,ads) on several copper catalysts, as shown in Figure S5, to test how the degree of surface reduction affects dissociative CO2 adsorption. As may be expected based on metallic surfaces,32 we found the activation energy for adsorption follows a Brønsted−Evans−Polanyi relation; that is, the CO dissociation barrier is linearly correlated with the heat of reaction (Eproduct − Ereactant) on different copper surfaces. (Note that, for simplicity, the dissociation barrier was calculated without a specific
assumption about the hydroxylation degree of the electrode and in the absence of electrolyte.) At 1.68 eV, the metallic surface had one of the highest barriers for CO₂ decomposition with an associated heat of reaction ($H_{\text{rxn}}$) of 0.93 eV, where the positive sign indicates the reaction is endothermic. The presence of subsurface oxygen generally lowers this barrier by decreasing the endothermicity of $H_{\text{rxn}}$. In particular, when oxygen is present in the subsurface tetrahedral holes, shown in Figure 5, Cu(111)/O₄tet $H_{\text{rxn}}$ drops to 0.77 eV with a concomitant drop in $E_a$ to 1.55 eV. This change can be ascribed to the stability of the linear Cu−O−Cu bond in the product state; see Figure 5. Similarly, when oxygen is present in the subsurface octahedral hole, Cu(111)/O₄oct(I) $E_a$ is 1.56 eV and $H_{\text{rxn}}$ is 0.83 eV. In this case, the decrease in $H_{\text{rxn}}$ relative to the clean surface is not due to linear Cu−O−Cu bonding in the final state but to the binding of CO to the Cu⁺ formed by the subsurface oxygen; see Figure 5. This can easily be verified by considering an alternative reaction path, Cu(111)/O₄oct(II), where the final state contains neither linear Cu−O−Cu bonding nor CO adsorption on Cu⁺. In this case, at 2.2 eV, $E_a$ is higher than on the clean surface due to the more endothermic nature of the reaction ($H_{\text{rxn}} = 0.83$ eV). Thus, an accumulation of subsurface oxygen is predicted to enhance CO₂ decomposition.

Similar, yet more dramatic, behavior can also be seen for the cuprous oxide surface. For this purpose, we chose to explore a Cu₂O(110) surface. On the pristine surface, the calculated $E_a$ is 4 eV with $H_{\text{rxn}} = 3$ eV due to the formation of extra oxygen on the surface, yielding a high-energy local CuO-like motif. However, introducing an oxygen vacancy on the Cu₂O(110) surface lowers $E_a$ to 1.20 eV with $H_{\text{rxn}} = 0.61$ eV, as in this case, the oxygen adatom formed during CO₂ decomposition can fill the lattice oxygen vacancy. These results are summarized in Figure 5, which shows $E_a$ plotted vs $H_{\text{rxn}}$, indicating that the most suitable structure for the effective dissociation of CO₂ is the metallic surface with dissolved subsurface oxygen or partially reduced metal oxides, with oxygen vacancies. Thus, these results indicate the copper electrode must be (partially) reduced to facilitate the dissociative adsorption of CO₂ to produce CO on copper catalysts takes places more readily on a nonstoichiometric copper surface, predicting the lowest barrier for CO₂ decomposition is on the non-

Figure 5. Calculation of the adsorption barrier and heat of reaction of different copper structures. The inset shows the $E_a$ vs $H_{\text{rxn}}$.

Figure 6. Performance resume with the Puorbaix diagram and the different copper oxide catalysts behavior found during the experiments and schematic of the catalyst activation–deactivation due to the formation of carbonates in Cu²⁺-like electrode.

DOI: 10.1021/acssuschemeng.8b05106
stochiometric oxygen-clean CuO surfaces. However, the Pourbaix diagram of copper predicts (see Figure 6) that the copper oxide is not stable under most of the cathodic potentials at different pHs, as the in situ XAS-EXAFS measurements proved, which is in the nature of the high overpotential observed in Cu catalysts under CO2RR conditions.

Thus, taking into account the discussed experiments and the calculations of the dissociation barrier of CO2 onto different copper surfaces, it is obvious that the hydrogenation of CO takes place when copper is locally reduced (and/or when oxygen vacancies are involved in the reaction), allowing the dissociative adsorption of CO2 onto the surface. In situ X-ray spectroscopies, both XAS and EXAFS, indicate that copper carbonates are generated on CuOx oxides, hindering effective charge transport due to the formation of a passivation layer. This layer can be eliminated at low pH conditions due to the introduction of an acidic electrolyte in the cell or by applying potential, if the contact resistance is not too high (i.e., the high contact resistance can be lowered, increasing the electrode area). Thus, CuOx is likely not active in the cathodic reduction of CO2 into valuable hydrocarbons due to its deactivation as a consequence of the formation of a passivating copper carbonate layer as shown schematically in Figure 6. Meanwhile, if the electrode is in the form of Cu+, it undergoes the dissociative adsorption of CO2 onto oxygen vacancies present on the surface until the HER is reached. Under HER, the Cu+ oxide is reduced to form Cu2+, due to the low stability of copper oxide under these conditions, as the Pourbaix diagram shows (Figure 6). After that, the first hydrocarbon product evolving is C2H4 due to a dimerization process and finally CH4 at higher cathodic potential due to protonation effects on a proton rich interface, indicating high selectivity to C2 for this type of electrode. A schematic with the activation and deactivation scheme of the catalyst surface induced by the formation of different intermediates is depicted in Figure 6 as well, which summarizes the overall process.

CONCLUSIONS

Redox-active copper catalysts were accurately prepared, yielding high selectivity to the C2 hydrocarbons formation during the CO2RR. The combination of in situ XAS/EXAFS, and GC product analysis provided direct evidence on the mechanisms governing the reduction of CO2 to industrially valuable C2 and C1 products on electrochemically prepared Cu electrodes with different initial redox states. It was found that the catalyst surface, subsurface, and bulk are affected by the presence of copper carbonates that inhibit the adsorptive dissociation of CO2. Instead, the key dissociative proton-consuming reactive adsorption of CO2 requires the formation of a reduced or partially reduced electrode. Once dissociative CO2 adsorption occurs, the hydrogenation of CO is controlled as a consequence of dimerization and protonation processes, yielding C2 and C1 valuable products, respectively.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b05106.

Additional supporting figures (Figures S1−S4) for the in situ reactions in 5 mM KClO4 (saturated in N2 gas) and 5 mM KHCO3 (saturated in CO2), dissociative proton-consuming reactive adsorption of CO2 on CuOx catalysts.

REFERENCES


