Supplementary Materials for

Highly active copper-ceria and copper-ceria-titania catalysts for methanol synthesis from CO₂

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Materials and Methods

AP-STM studies. Images of the CeO$_x$/Cu(111) surface under an environment of hydrogen were obtained with a SPECS™ Aarhus 150 HT STM (16). A Cu(111) single crystal (Princeton Scientific Corp) was cleaned by sputtering (Ar$^+$, 5 μA, 2 keV, 20 min) and annealing (700 K, 10 min) cycles in a chamber with a background pressure of 5×10$^{-10}$ Torr. Cerium vapor from a Triple Evaporator EFM 3T (Focus, Omicron Nano Technology) was deposited on the clean Cu(111) for 15 min at 600 K with a flux of 16.2 nA in 4.5×10$^{-7}$ Torr of O$_2$ (GTS-Welco, 99.9999% pure. In order to maintain high Ce oxidation states, the sample was oxidized for another 10 min and cooled down in an O$_2$ background (15). The as-prepared sample was transferred to a high pressure cell which locates inside of a SPECS™ Aarhus 150 HT STM. The STM cell was then sealed and filled with 1.5 Torr H$_2$ (GTS-Welco, 99.9999% pure) using a liquid nitrogen trap in the gas line.

AP-XPS and IRRAS studies. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) studies were performed at the Advanced Light Source in Berkeley, CA, at beam-line 9.3.2. A VG-Scienta R4000 HiPP analyzer was used (28). High purity of the gases was checked with an RGA and introduced via backfilling. Traps were utilized along gas lines to prevent contamination. The O 1s region was probed with photon energy of 700 eV and the C 1s, Cu 3s
and Ce 4d regions with a photon energy of 490 eV and energy resolution of 0.2-0.3 eV. Energy calibrations were performed with the Cu 3s signal for the Cu(111) sample.

Infrared reflection absorption spectroscopy (IRRAS) experiments were performed in a combined UHV surface analysis chamber and elevated-pressure reactor/IRRAS cell system (29). The surface analysis chamber is equipped with Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and temperature program desorption (TPD) techniques. The elevated-pressure cell is coupled to a commercial Fourier transform infrared (FT-IR) spectrometer (Bruker, IFS 66v/S) for IRRAS experiments. IRRA spectra were collected at 4 cm\(^{-1}\) resolution using a grazing angle of approximately 85° to the surface normal. All the IR spectra collected were referenced to a background spectrum acquired from the sample prior to exposure to CO\(_2\) and H\(_2\). The Cu(111) sample was cleaned by repeated cycles of Ar\(^+\) sputtering and annealing to 850 K. The CeO\(_{2-x}\)/Cu(111) system was prepared by vapor deposition of Ce metal in ~2×10\(^{-8}\) Torr of O\(_2\) at 550 K.

Tests of catalytic activity. The catalytic activity of the CeO\(_x\)/Cu(111) and Cu/CeO\(_x\)/TiO\(_2\)(110) samples was studied in a system which combines an ultrahigh-vacuum (UHV) chamber (base pressure \(\sim 5 \times 10^{-10}\) Torr) and a batch reactor (6,12,14,23,24). The sample could be transferred between the reactor and UHV chamber without exposure to air. The UHV chamber (base pressure ~ 5 \times 10^{-10} Torr) was equipped with instrumentation for X-ray and ultraviolet photoelectron spectroscopies (XPS and UPS), low-energy electron diffraction (LEED), ion scattering spectroscopy (ISS), and temperature-programmed desorption (TPD).

The CeO\(_x\)/Cu(111) and Cu/CeO\(_x\)/TiO\(_2\)(110) catalysts were prepared following procedures reported in the literature (14,23,24). In the tests of CO\(_2\) activation/hydrogenation, the sample was transferred to the reactor at ~ 300 K, then the reactant gases, 0.049 MPa (0.5 atm) of CO\(_2\) and 0.441 MPa (4.5 atm) of H\(_2\), were introduced and the sample was rapidly heated to the reaction temperature (500, 525, 550, 575 and 600 K). The walls of the batch reactor were covered with a special jacket to minimize the loss of heat. Product yields were analyzed by a gas chromatograph (7). The amount of molecules produced in the catalytic tests was normalized by the active area exposed by the sample. The reported rates for methanol synthesis correspond to steady-state conditions determined by plotting the yield of methanol versus the reaction time (6,7,12). In our experiments data were collected at intervals of 15 min up to total reaction times of 270 min. The kinetic experiments were done in the limit of low conversion ( < 5%).
**DFT calculations.** The CeOₓ/Cu(111) system was simulated using a model previously reported (14,15,30). It consists of a Ce₆O₁₃ cluster supported on a Cu(111) surface described by a 4√3 × 4√3 four layer thick slab (192 Cu atoms) and a vacuum region of 15 Å between repeated slabs. The Perdew-Wang 91 (PW91) functional (31) was used for the exchange-correlation potential. The effect of the core electrons on the valence states was represented with the projector-augmented wave (PAW) approach (32), as implemented in the Vienna ab-initio simulation package, (VASP 5.3) (33,34), with the valence states defined for each atom as Cu(3d,4s), Ce(4f,5s,5p,5d,6s), C(2s,2p), O(2s,2p), and H(1s) electrons, while the remaining electrons were kept frozen as core states. The valence electronic states are expanded in a basis of plane waves with a cutoff of 400 eV for the kinetic energy. In order to account for the strong localization of the Ce 4f electrons, a Hubbard-like U term was used, (GGA+U), according to the Dudarev et al. implementation, which makes use of an effective parameter U eff (35). We used a value U eff =4.5 eV taken from Fabris et al. (36) and satisfactorily used in our previous works dealing with supported cerium oxide particles (14,15,23,24,25,30,37). Calculations were performed at the Γ point of the Brillouin zone and, in the structural optimizations, only the two outermost layers of the Cu(111) slab together with the supported oxide and the adsorbed molecules were completely allowed to relax. The transition states were found by the climbing nudged elastic band method (cNEB).
Figure S1. Arrhenius plots for the reverse WGS and methanol synthesis on Cu(111), 0.2 ML of Cu on ZnO(000ı), a Cu(111) surface covered 20% by ceria, and 0.1 ML of Cu on a TiO$_2$(110) surface pre-covered 15% with ceria. In a batch reactor the catalysts were exposed to 0.5 atm of CO$_2$ and 4.5 atm of H$_2$. The reported values are steady-state rates measured at 600, 575, 550, 525 and 500 K.

Table S1: Apparent Activation Energies (Kcal/mol)

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Methanol synthesis</th>
<th>Reverse WGS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu/CeO$_x$/TiO$_2$(110)</td>
<td>7</td>
<td>6</td>
</tr>
<tr>
<td>CeO$_x$/Cu(111)</td>
<td>12</td>
<td>11</td>
</tr>
<tr>
<td>Cu/ZnO(000ı)</td>
<td>16</td>
<td>14</td>
</tr>
<tr>
<td>Cu(111)</td>
<td>25</td>
<td>22</td>
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</tbody>
</table>
Figure S2 Ce 3d XPS spectra collected before and after performing the hydrogenation of CO$_2$ on a CeO$_x$/Cu(111) surface. In a batch reactor the catalyst was exposed to 0.5 atm of CO$_2$ and 4.5 atm of H$_2$, at 500K, for 15 minutes.
Figure S3. IRRA spectra obtained (a) following the exposure of CeOₓ/Cu(111) to CO₂ and H₂ (1:9 – total pressure 10 Torr) at 500 K, (b) after evacuation of the high pressure (HP) cell at 500 K, and (c) after cooling down the sample exposed to CO₂ and H₂ (1:9 – total pressure 10 Torr) at 500 K under CO₂+H₂ and subsequent evacuation of the gases from the HP cell at 300 K. The spectrum (a) was collected in the presence of CO₂ and H₂ mixture at the indicated pressure at 500 K.
Figure S4

Figure S4. IRRA spectrum obtained following the exposure of CeO₂/Cu(111) to CO₂ and D₂ (1:9 – total pressure 10 Torr) at 500 K showing the presence of formates (DCOO⁻) and hydroxyls (OD⁻). This spectrum was collected in the presence of CO₂ and D₂ mixture at the indicated pressure at 500 K.
References


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