VIP Heterogeneous Catalysts

DOI: 10.1002/anie.201200903

Electronic Modulation of a Copper/Zinc Oxide Catalyst by a Heterojunction for Selective Hydrogenation of Carbon Dioxide to Methanol**

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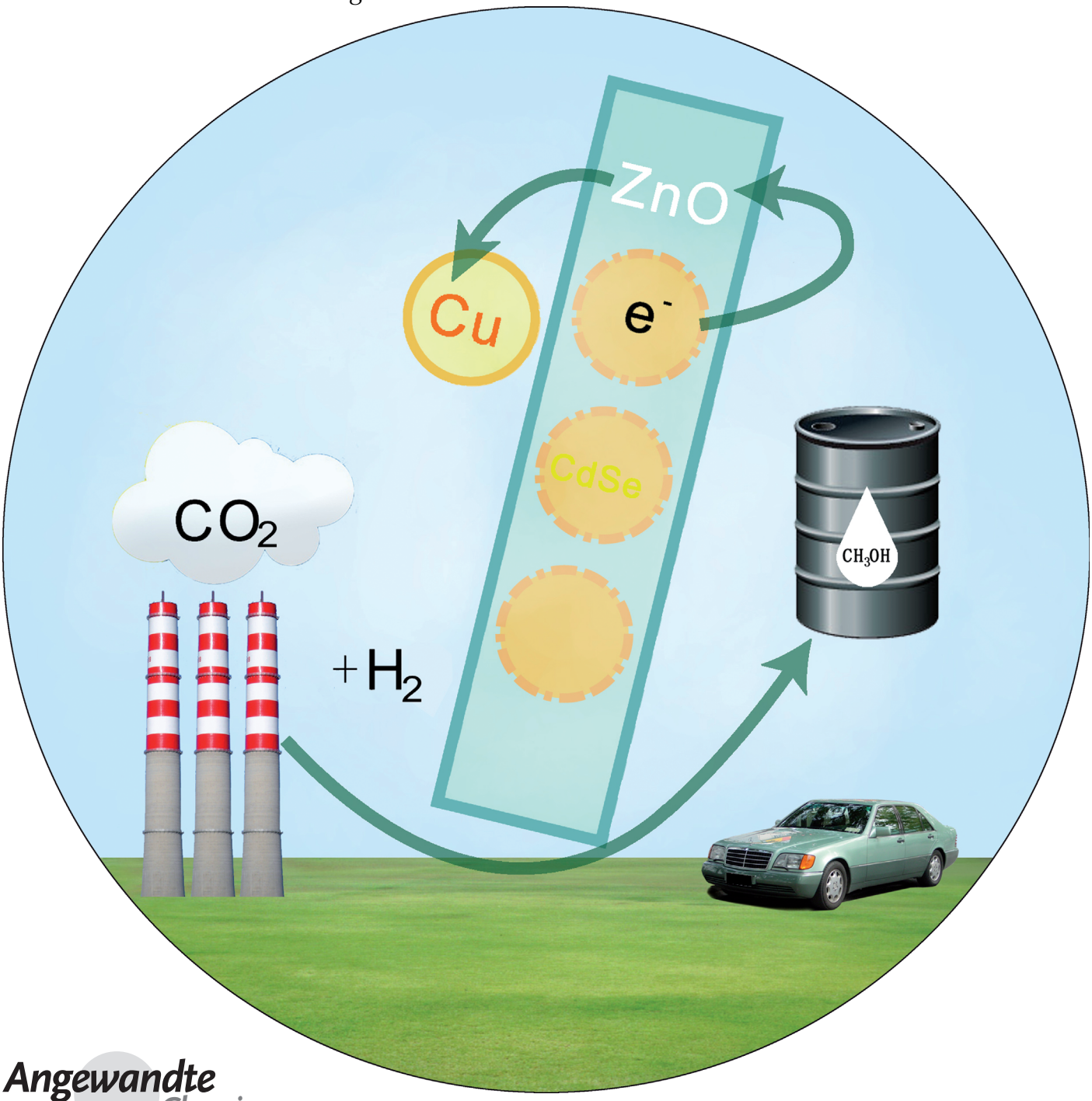

In the past decades, global warming caused by an increasing concentration of atmospheric carbon dioxide (CO_2) and the depletion of fossil fuels have received much attention by scientists and governmental agencies.[1,2] Catalytic conversion of CO_2 to liquid fuels or other valuable chemicals has a positive impact on these important environmental and energy issues.[3,4] In particular, the hydrogenation of CO_2 to methanol is very attractive because of its position as a high energy density liquid fuel and a key platfrom chemical (for manufacture of formaldehyde, methyl-*tert*-butyl ether, and acetic acid). The convenient production of hydrogen at large scale from renewable energy sources (solar energy, hydropower, biomass, or excess chemical heat) also supports this new green process.[5,6]

The majority of research on catalytic studies of CO_2 hydrogenation has been using modified industrial methanol catalysts for the hydrogenation of synthesis gas (CO/H_2), which contained Cu and ZnO as the main components together with an alumina support and different modifiers.[7–9] Ni was recently claimed to display a higher turnover frequency than Cu.[10] Up to now, the exploitation of the catalyst is slow because of the lack of knowledge on both hydrogenation reactions and the fundamental understanding of the important material interactions in the catalyst formulation. Regarding the hydrogenation of synthesis gas many models have been proposed to define the active sites and the synergetic interactions of the copper and zinc oxide.[11] For example, ZnO is regarded to provide active sites for spillover hydrogen[12] or as a structure-directing support controlling the dispersion, morphology, and specific activity of the copper particles.[13] We have previously reported a significant shape effect of ZnO on the interaction with copper for the synthesis of methanol from hydrogenation of CO_2. The electron-richer polar (002) face containing surface-terminated oxygen ions in the platelike ZnO nanocrystal showed a much stronger material synergy with copper than other crystal facets, which gave a higher selectivity (around 70%) towards methanol obtained from the hydrogenation of CO_2. On the other hand, the charge-neutral ZnO rod crystal surfaces (010, 110, and 101 faces) showed only a selectivity of around 40% towards methanol when they were physically mixed with copper particles of the same size.[14]

Here, we report, for the first time, a dramatic enhancement in the electron density of ZnO by encapsulating CdSe (electron rich quntum dot) into the ZnO rod as core–shell structure. Using ZnO rod/CdSe of controlled morphology as the model support for copper, a selectivity of 75% towards methanol production from hydrogenation of CO_2 was realized. The formation of heterojunctions between CdSe and ZnO rods promotes the electron transfer thermally at the Schottky–Mott junction between modified ZnO and Cu, which increases the methanol selectivity of the reaction. The procedure for preparing CdSe core–ZnO shell heterojunctions at different compositions (samples 1–5) can be found in the Supporting Information. The use of preformed CdSe nanoparticles followed by the growth of a ZnO rod material was adopted and verified by inductive coupled plasma (ICP) method.

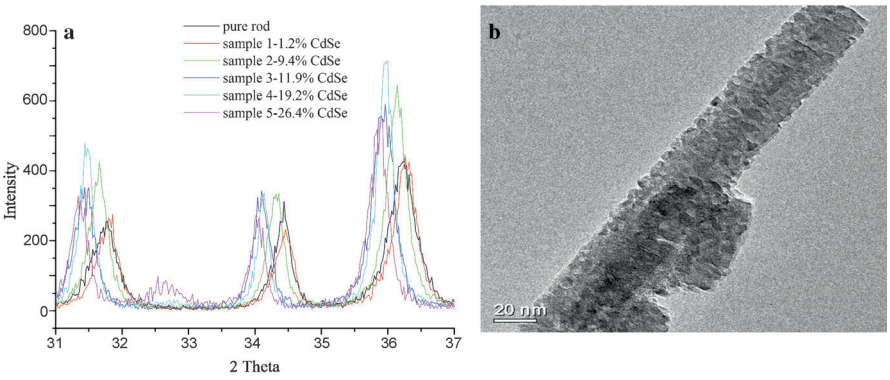

Figure 1. a) XRD of ZnO with and without CdSe heterojunctions; b) TEM image of around (4±1) nm CdSe particles embedded and decorated on large rod-shaped ZnO particles (sample 5).

The X-ray powder diffraction (XRD) data in Figure 1a confirm that all the samples show characteristic peaks of a rod-shaped crystalline wurtzite structure of ZnO without phase alternation (see also the Supporting Information). The diffraction peaks clearly shifted to a lower angle when the content of encapsulated CdSe was increased. However, no crystalline phase of CdSe (samples 1, 2, and 3) was observed, suggesting a good dispersion of CdSe within the ZnO matrix. CdSe also adopts the Wurtzite structure (27–29% lattice mismatch with respect to ZnO depending on the particular phases at the interface). The successful synthesis of a core–shell CdSe/ZnO structure has been reported.[15] However, we identified small CdSe phases at higher loadings (samples 4 and 5, see the Supporting Information). The lattice expansion (left shift) in the CdSe-modified ZnO samples can be attributed to the replacement of O^{2-} by Se^{2-} anions (Se^{2-} is larger than O^{2-}) at the extensive interface between the two phases (see the Supporting Information).

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[**] This research was supported by the NSFC (grant number 20903074) and the Fundamental Research Funds for Central Universities of China. TEM characterization was performed by the University of St Andrews (UK) through the EPSRC access scheme.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201200903.

High-resolution transmission electron microscopy (HRTEM) studies on the samples have been conducted. Rod-shaped ZnO particles were found (see Figure 1b). As seen from the HRTEM image of a typical area, the preformed (4 ± 1) nm CdSe nanoparticles were embedded and dispersed in the ZnO rod (Figure 2a). Our sequential synthesis method

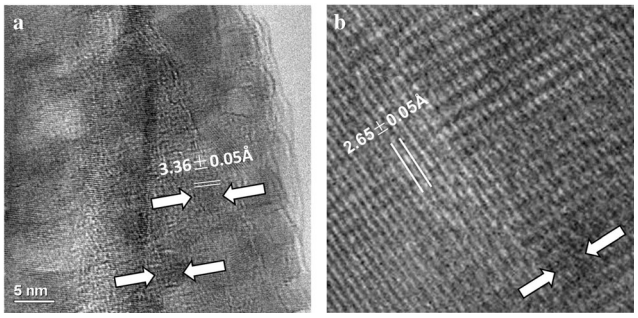


Figure 2. a) HRTEM image of ZnO rods showing the embedded CdSe nanoparticles with observed [002] fringes of (3.36 ± 0.05) Å; b) HRTEM of the material interface showing regions of wriggled [101] fringe lines of ZnO.

was successful in embedding CdSe, the electron promoter, into ZnO rod crystals. However, we observed that a small amount of CdSe decorated the ZnO rod surface, especially at the highest CdSe content of sample 5. Imaging at the interface (Figure 2b) showed some less defined regions with wriggled fringe lines, indicative of some substitution by anions.

Optical properties of the nanocomposites were characterized by photoluminescence (PL; Figure 3a). In all cases, the spectra show two bands: a luminescence band centered at 380 nm and a broadband in the region of 440–640 nm.[16] An obvious change for the broadband peak in the visible region is observed with the increasing content of CdSe. For samples 1, 2, and 3, the intensity of the visible emission decreases strongly. However, the signal begins to increase in sample 4 and the intensity of sample 5 reaches twice that of the pure ZnO rod. The visible emission is due to the exciton recombination at longer wavelengths originating from the presence of lattice imperfections (vacancies).[17,18] When a small level of CdSe was added into the ZnO lattice, it was expected that a small amount of the foreign Se^{2-} ions migrated to the region of the dangling bonds of ZnO which led to the reduction of the number of oxygen vacancies in the system. This accounts for the decreased intensity of the visible emission. However, the total number of vacancies introduced by both CdSe and ZnO lattice imperfections would increase if the doping concentration became excessive, resulting in a high probability of exciton recombination.[19]

The above experiments clearly demonstrate the presence of the intimate and extensive interface between the CdSe and ZnO rod phases at nanoscale created by our sequential growth technique, and also indicate some degree of anion exchange between the two phases. Therefore, investigation of the electronic interactions at the material interfaces is interesting because they are believed to play a key role in the methanol production.

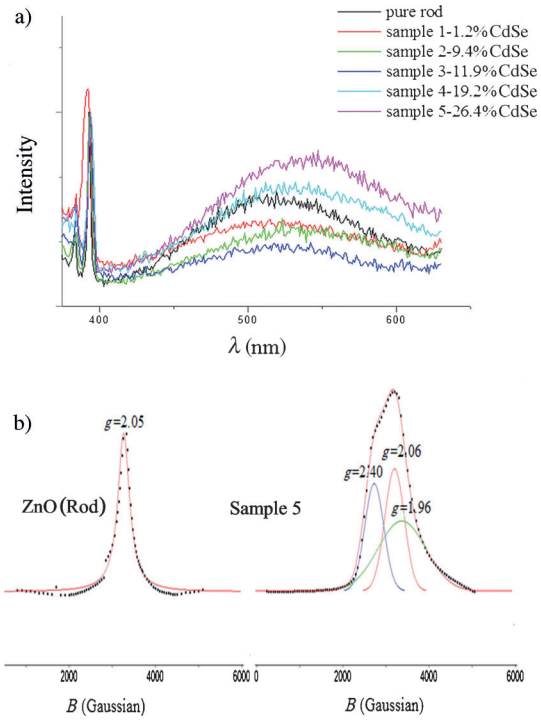


Figure 3. a) PL spectra of the rodlike ZnO without and with CdSe heterojunctions. b) Resolved and integrated ESR signal of ZnO rods (×100 signal; around 17 mg) and the CdSe/ZnO sample (sample 5; 40 mg).

Both the valence and conduction band positions of CdSe are at staggered higher-energy levels than those of ZnO, hence a type II heterojunction can form at the material interface.[20] This means excited electrons from the conduction band of CdSe can populate the conduction band of ZnO located at close proximity. We then determined the band gaps of ZnO and modified the ZnO rod samples by activating their valence electrons to populate the conduction band using diffusion reflectance spectroscopy (DRS; see the Supporting Information). The values of the band gaps were derived from the adsorption edges using the Tauc formula and are given in Table 1.

Table 1: Band gap values in (eV) of modified ZnO rods by DRS (Samples 1–5).

Samples	ZnO rod	S 1	S 2	S 3	S 4	S 5
Band gap	3.256	3.270	3.291	3.317	3.328	3.343

The DRS results show a progressive shift to shorter wavelengths at increasing CdSe loading. The increasing electron population to the lowest unoccupied "molecular" orbital (LUMO) of ZnO due to the presence of the CdSe phase in the vicinity resulted in the widening of the band gap of ZnO. Thus, excitation light source of shorter wavelength was needed to promote electrons to the increasing higher energy LUMO. When the CdSe content reaches 26.2%, the band gap of the ZnO rod opens up to 3.34 eV. This is similar to

the band gap value of electron-rich platelike ZnO (3.31 eV), which shows a much higher methanol selectivity than pure ZnO rods for the hydrogenation of CO_2 to methanol.[14] The electron richness in the conduction band of the plate ZnO is also observed by strong ESR signals associated with unpaired electrons trapped at defect sites (O_2^- with $g = 2.05$ and trapped electrons at shallow donor defect sites with $g = 1.96$).[14]

Figure 3b (left side) is the ESR spectrum of the ZnO rod showing a weak signal (low intensity) at $g = 2.05$, which indicates lower electron population in the conduction band.[14] Figure 3b (right side) is the ESR spectrum of sample 5, the ZnO rod modified with CdSe. Much enhanced ESR signals ($g = 2.06$ and $g = 1.96$) akin to platelike ZnO were observed, indeed showing the electron richness in the conduction band of the modified ZnO rod. A new peak at $g = 2.40$ was attributed to the electrons trapped at the significant CdSe defect sites.[21] The ESR results are in good agreement with both DRS and PL results, all providing strong evidence that the heterojunction increases the electron density of the ZnO rod.

It is essential to elucidate the interactions of copper with a range of modified ZnO samples of different electron densities for the CO_2 hydrogenation without the complication of a varying copper dispersion during the sample preparation. To achieve this goal, the same batch of preformed copper particles was physically mixed with each modified ZnO rod sample by a ball milling technique. Figure 4 clearly shows

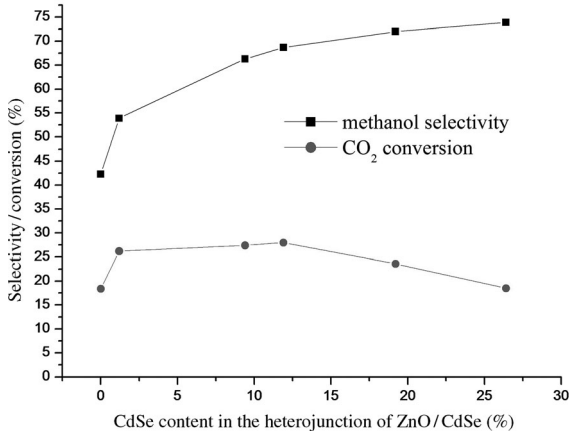
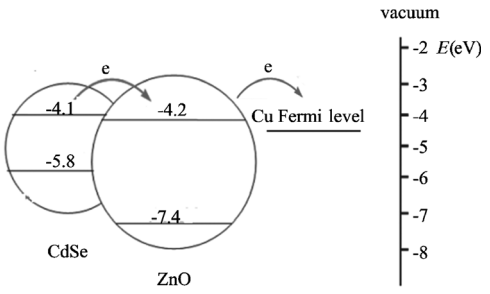


Figure 4. The influence of the CdSe content on the conversion of CO_2 and methanol selectivity of the synthesized catalysts (see the Supporting Information).

a progressive increase in the methanol selectivity from 40% of the undoped sample to about 75%, dependent on the CdSe content. It was found that the percentage of CO_2 conversion did not alter much until the appearance of CdSe on the surface of the ZnO rod at the two highest loadings (refer to TEM). Using pure CdSe and ZnO core–CdSe shell material (26.4% of ZnO) prepared by a reversed synthesis method as support materials only a small degree of CO_2 conversions without any methanol production was observed in both cases. Therefore, the catalytic results clearly show the importance of electronic interactions between the catalyst components at the interface.

It is well accepted that the metal–support interaction plays an important role in heterogeneous catalysis, which stems from either geometric or/and electronic perturbations between the two catalyst components. At present, a good selectivity (70–80%) at decent conversions can be obtained for both synthesis-gas and CO_2 hydrogenation reactions over empirically optimized co-precipitated Cu/ZnO-based catalysts. But, a further improvement in the catalyst performance without an in-depth understanding of the material interactions is difficult. Structure–activity relationships of the Cu catalysts for hydrogenation reactions of synthesis gas have been extensively studied with a variety of materials ranging from single-crystal model systems to industrial catalysts. Depending on the testing conditions, activity correlations with Cu dispersions[12] and lattice strain[22] on ZnO have been reported. However, the importance of electronic interactions is not easy to unfold, despite the fact that the direct contact of the two catalyst components is thought to establish a typical metal–semiconductor interface. The main difficulty of this research was the inability of controlling the morphology, structure, and interface of the two components. Herein, we attempt to alter the electronic characteristics of the ZnO support by a heterojunction within the ZnO particle of controlled morphology through a core–shell approach. There has been considerable interest in core–shell catalysts with good thermal stability and electron transfer.[23] A deep understanding of the material interactions, the electronic characteristics, and the catalytic performance can provide invaluable insight into the rational catalyst design for this important green hydrogenation process. Although there are some concerns regarding potential industrial applications of CdSe and the stability of the composites, the present study of this new model material clearly shows the fundamental and profound electronic effect of interactions in the catalyst.

Scheme 1 summarizes the influence of heterojunction-assisted electronic modulation of ZnO to promote Cu at a Schottky–Mott junction. The band positions are presented by bulk values[24] without information on the nanoscale. Nevertheless, there is a clear correlation between the activity and the electronic promotion, which renders the intrinsically poor methanol-selective ZnO rod surface to give an exciting high value which is higher than the value of electron-rich plate ZnO under conventional catalyst testing conditions by



Scheme 1. Electronic interactions of ZnO, CdSe, and Cu at heterojunctions.

thermocatalytic methods. Attempts to promote other ZnO surfaces and elucidate the charge-density effect on Cu for the methanol synthesis by both thermo- and photocatalytic methods[25] are in progress.

Experimental Section

CdSe was synthesized according to a reported method.[1] Cadmium nitrate ($Cd(NO_3)_2$) of analytical grade (Aldrich) was used. The Na_2SeSO_3 aqueous solution was prepared by refluxing Se powder in an aqueous Na_2SO_3 solution at 80 °C overnight. In 100 mL water $Cd(NO_3)_2$ (0.64 g) and sodium citrate (14.70 g) were dissolved to form a solution which was mixed with freshly prepared 0.1 M Na_2SeSO_3 (100 mL) and heated in a water bath at 60 °C for 15 min. The red precipitate was collected by centrifugation at 10000 rpm for 10 min, after which the supernatant was decanted and discarded. The solid was washed repeatedly with ethanol and water to remove surfactant and excess precursor. The synthesis of the core–shell CdSe/ZnO heterojunction was carried out using zinc nitrate [$Zn(NO_3)_2{\cdot}6H_2O$] (1.487 g) and NaOH (6 g) dissolved in 10 mL deionized water (the molar ratio of Zn^{2+} to OH^- was 1:30). Some preformed CdSe particles produced previously were dispersed in 100 mL ethanol which was added to the solution containing the Zn precursor. To the mixture was added EDA (5 mL) which was then transferred to a covered plastic container with a volume capacity of 250 mL. The reaction container was kept at room temperature under constant stirring until the red mixture turned white. The method for production of ZnO rods was based on Zeng's method.[2] After the synthesis a white crystalline product was centrifuged and washed with deionized water and pure ethanol. The precipitate was dried in an oven at 60 °C for 12 h. All the samples were calcined at 723 K for 2 h. The catalysts were prepared by mixing equal quantities of ZnO, Cu, and Al_2O_3 mechanically using ball milling. The preformed Cu particles were synthesized as follows: 0.8 g copper acetate dihydrate ($Cu(CO_2CH_3)_2{\cdot}2H_2O$) was dissolved in 60 mL ethanol and some $NaBH_4$ solution (0.4 g $NaBH_4$ in 10 mL ethanol) was added to the solution to reduce the Cu^{2+} ions. The black precipitate was collected by centrifugation at 5000 rpm for 10 min, after which the supernatant was discarded. The solid powder was washed repeatedly with ethanol and water. The precipitate was dried in vacuum at 100 °C for 2 h. Catalyst tests for the hydrogenation of CO_2 were carried out at a total pressure of 4.8 MPa using a tubular fixed bed reactor (12.7 mm outer diameter) with a catalyst weight of 0.3 g. The catalytic reactions were carried out under the kinetically controlled regime (lower than the thermodynamically predicted values). A CO_2/H_2 reaction mixture at a molar ratio of about 1/2.6 was fed at a rate of 20 stp mL min^{-1} (stp = standard temperature and pressure; $P = 101.3$ kPa, $T = 298$ K) through the catalyst bed. The reaction temperature was fixed at 513 K. Before each test, the catalysts were pre-reduced in situ at 553 K for 2 h under H_2 flow (20 stp mL min^{-1}). The products (methanol and CO) were analyzed by a calibrated GC equipped with a TCD detector. Details of the material characterization and equipment used can be found in the Supporting Information.

Received: February 1, 2012
Published online: March 14, 2012

Keywords: heterogeneous catalysis · carbon dioxide · heterojunctions · hydrogenation · methanol

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