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Room-temperature oxidation of reduced Cu/ZnO surfaces by lattice oxygen diffusion

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At room temperature in the absence of gas-phase oxygen, reduced Cu on Cu/ZnO extracts oxygen from the ZnO lattice to reoxidize the surface. After 120 min at room temperature, diffusion of lattice oxygen reoxidizes reduced Cu/ZnO to 3% of its completely oxidized state. When gas-phase oxygen is present, it promotes the partial reoxidation of the reduced Cu/ZnO surface at room-temperature.

KEY WORDS: room temperature; oxidation.

1. Introduction

The Cu/ZnO catalyst has attracted a great deal of research interest due to its promising potential in hydrogen production from methanol [1–13]. In addition, a substantial portion of previous work on Cu/ZnO catalysts focused on understanding MeOH synthesis, although the active sites and surface structures have not been identified. Several theories describe the interactions between Cu and ZnO, with most of them proposing a synergistic effect between Cu and ZnO phases. For example, one study [14] suggested that Cu, in the form of Cu^0, Cu^{+1}, or Cu^{+2}, is incorporated within the ZnO phase at interstitial and substitutional sites. Other studies proposed surface structures such as Cu on top of ZnO [15,16], ZnO on top of Cu [17–19], and formation of a Cu–ZnO alloy [20,21]. In addition, another study [22] proposed that no synergistic effect exists between Cu and ZnO and that Cu^0 alone provided the catalytic activity while ZnO stabilized the Cu surface area. Although the nature of the active sites is unclear, general agreement exists that the oxidation state of copper influences strongly the reaction behavior of the catalyst [11].

Although many studies have observed the dynamic nature of the oxidation state of Cu at reaction conditions [2,10,12,13,23–27], none of these studies reported any room-temperature changes in the catalyst. Topsøe and Topsøe [20,28] performed infrared spectroscopy studies by CO adsorption on 1–5% Cu/ZnO. After reducing the catalysts in 0.5% CO, 4.0% CO_2, 4.0% H_2 and balance Ar, the catalysts were cooled to room temperature and CO adsorption was performed. Although their results show that a Cu–Zn alloy formed at temperatures above 493 K, they did not report any changes to the surface at room temperature. Because, Jung *et al.* [29] have shown that CO and MeOH are capable of completely reducing CuO/ZnO while only the copper of CuO/ZnO will be reduced in H_2 up to 623 K [29], the catalysts studied by Topsøe and Topsøe were most likely reduced completely.

This study shows that reduced copper on Cu/ZnO surfaces reoxidizes partially by extracting lattice oxygen from ZnO at room temperature. This reoxidation process is important for researchers to consider when analyzing reduced Cu/ZnO catalysts that have remained at room temperature for several minutes. This study combines qualitative analysis using diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) with temperature-programmed hydrogenation (TPH) to quantify room-temperature reoxidation of reduced Cu/ZnO, CuO and ZnO catalysts. The effects of gas phase O_2 and the rate of lattice oxygen extraction were also investigated.

2. Experimental

2.1. Catalyst preparation

The Cu/ZnO catalyst was co-precipitated by combining a solution containing 0.5 mol sodium bicarbonate and 200 ml of water with another solution consisting of 0.05 mol of each copper acetate and zinc acetate along with 250 ml of water. A stir plate mixed the solution at room temperature for 2 h until a white precipitate formed. Subsequently, distilled water washed

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the precipitate until the effluent was colorless. The washed precipitate was dried overnight at room temperature followed by calcination at 723 K for 16 h. An x-ray diffractometer verified the presence of both copper and zinc oxide phases. Although at various times during experiments the copper of this catalyst was reduced to varying degrees, the catalyst will be referred to consistently as Cu/ZnO to differentiate it from the other two catalysts studied. Sigma-Aldrich supplied both CuO and ZnO and they were used as received.

2.2. Diffuse reflectance infrared fourier transform spectroscopy

A FTIR spectrophotometer (Thermo Nicolet 670) in conjunction with a Praying Mantis diffuse reflectance FTIR spectroscopy accessory (Harrick Scientific, DRP) collected infrared spectra. The DRIFTS accessory housed a reaction cell (Harrick Scientific, HVC-DRP) equipped with a heater, a sample cup to hold the catalyst, and a dome with windows that covered the sample. Oxygen traps reduced the O_2 concentration of He and H_2 gas streams to less than 1 ppm. Initially, the reaction cell heated the catalyst to 663 K in air for 15 min. The gas was then switched to approximately 7% H_2 in He and maintained for 30 min. Subsequently, cooling air cooled the reaction cell to 303 K, at which time a background was obtained. Omnic software (Thermo Nicolet Corporation) collected spectra at various time intervals.

2.3. Temperature-programmed reactions

The temperature-programmed reaction system consisted of approximately 60 mg of catalyst in a 7 mm I.D. tubular quartz reactor. A temperature-programmer, coupled with a Ni–Cr wire electric furnace, controlled the reactor temperature. A 0.5 mm chromel–alumel thermocouple, placed in the center of the catalyst bed, provided feedback to the temperature programmer. A Pfeiffer Vacuum QMS 200 quadrapole mass spectrometer monitored the reactor effluent directly downstream of the reactor. A computer interfaced with the mass spectrometer recorded multiple mass peaks simultaneously.

Before temperature-programmed hydrogenation (TPH), temperature-programmed oxidation of the catalysts created reproducible surfaces. The furnace heated the reactor to 663 K in approximately 20% O_2 in He. The reactor temperature was maintained for 15 min. When the reactor cooled to room temperature, approximately 7% H_2 in He flushed the reactor for 30 min. For some experiments, the gas was switched to 7% H_2 in He before the reactor was cooled in order to reduce the catalyst. One set of experiments on the reduced catalysts included the use of a switching valve to pulse 20% O_2 in He at room temperature into the reactor three times for 5 s each prior to TPH. The initial pulse was introduced at 5 min after the catalyst had reached room temperature. During TPH, the temperature controller increased the reactor temperature by 1 K/s to 663 K and maintained that temperature for a total heating time of 15 min. Calibration of water was performed after each experiment by injecting several pulses, each of a known amount of water, into the gas flow downstream of the reactor. Calibration provided the means to convert mass spectrometer signals to reaction rates. Integration of the areas under the reaction rate curves determined the amounts of desorption products.

3. Results and discussion

After Cu/ZnO was reduced by H_2 and cooled to room temperature, IR spectra were collected at various time intervals. Figure 1 shows that the surface of the reduced catalyst changed throughout the 10 h experiment. Specifically, a broad peak at 1200 cm^{-1} grew continuously. Figure 1 shows that this same peak dominates the spectra of oxidized Cu/ZnO, which suggests that the surface of Cu/ZnO oxidized as it remained in H_2 flow at room temperature. Spectra for fully oxidized Cu/ZnO did not drift. Note that all spectra displayed in figure 1 were referenced to a common reduced Cu/ZnO background. This experiment was then repeated on CuO and ZnO catalysts (not shown). The spectra for CuO did not change with time whereas that for ZnO drifted significantly, similar to Cu/ZnO. Thus, the reduction procedure appears to remove oxygen from both Cu/ZnO and ZnO and these surfaces reoxidize at room temperature. This reoxidation causes the spectra of the reduced catalysts to change with time.

For hydrogen-reduced catalysts, the reduction procedure created oxygen vacancies. After subsequent cooling to room temperature, a portion of the catalyst surface reoxidized by either lattice or gas-phase oxygen replenishing some of these vacancies. A subsequent TPH, performed after the reduced catalyst was allowed to reoxidize, should remove the *replenished* oxygen. Thus, performing TPH quantifies the extent of reduction and room-temperature reoxidation of Cu/ZnO, CuO, and ZnO simply by quantifying the amount of H_2O produced during TPH. Table 1 displays the total water production during TPH for both reduced and oxidized catalysts. The values listed are the amounts of water produced during TPH less the water produced in a control experiment in which a reactor containing only quartz wool was heated using the same procedure as that used in TPH.

3.1. Reduction of oxidized catalysts

Table 1 shows that oxidized ZnO, when heated to 663 K in H_2, produced 44 μmol/g-catalyst of H_2O, or about 0.4% of the total oxygen that the catalyst

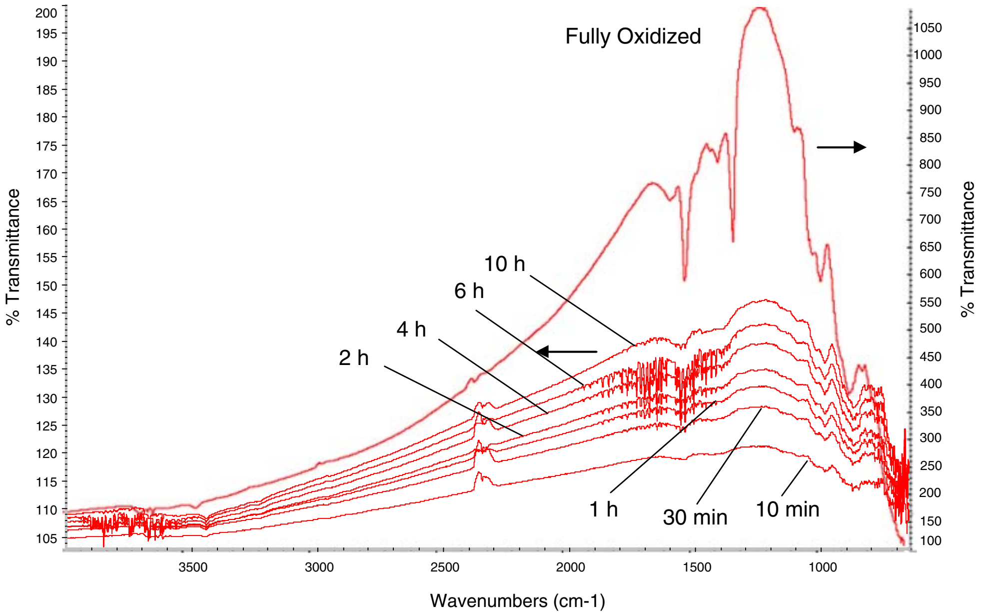

Figure 1. DRIFTS spectra of reduced Cu/ZnO for various times at room temperature in H_2 flow. Also included is the spectra of fully oxidized Cu/ZnO (secondary axis). All spectra were referenced to the same reduced Cu/ZnO background.

contained. The water production from TPH of CuO, in contrast, was two orders of magnitude greater than that of ZnO, indicating that the extent of reduction for CuO (about 15%) was much greater than ZnO. The relative ease of extracting oxygen from CuO was demonstrated by further experiments (not shown) in which heating to 423 K extracted nearly the same amount of oxygen as that shown in table 1, although over a longer time period. The oxidized Cu/ZnO catalyst lost one-fourth of the amount of oxygen contained in its fully oxidized form, which was approximately twice that of CuO.

During all TPH experiments, the mass spectrometer detected a consistent drop in the m/e = 32 signal, which indicates that an O_2 impurity was present in the reducing atmosphere. Calibration determined that the amount of O_2 in the reduction gas stream would only account for approximately 3 μmol/g-catalyst of H_2O produced during the TPH's listed in table 1. This amount of H_2O was accounted for in the values shown in table 1; note this correction only affected significantly the water produced from reduced CuO.

3.2. *TPH of reduced catalysts with and without room-temperature O_2exposure*

Table 1 shows TPH of reduced CuO (without O_2 pulse) did not produce H_2O, apparently because lattice oxygen that remained after reduction did not diffuse to the surface prior to or during the subsequent TPH. When O_2 was pulsed over reduced CuO at room temperature, subsequent TPH produced a small, although statistically significant amount of water.

The amount of water produced during TPH of reduced ZnO (table 1) was significantly greater than that for CuO and it was independent of O_2 exposure. That is, ZnO reoxidized at room temperature to the same extent both with and without gas-phase oxygen. The production of water in the absence of gas phase O_2 indicates that bulk oxygen of the catalyst diffused at a significant rate to replenish the removed surface oxygen. Because ZnO did not reoxidize to a greater extent after pulsing O_2 at room temperature (table 1), either ZnO does not readily adsorb O_2 from the gas phase, or the rate of bulk oxygen diffusion was great enough to replenish all of the oxygen vacancies that could have been filled with gas-phase oxygen.

The Cu/ZnO catalyst produced a four-fold greater amount of water than did ZnO without gas-phase O_2 exposure. Table 1 shows that for reduced catalysts, the amount of H_2O formed during TPH of Cu/ZnO was greater than the sum of CuO plus ZnO catalysts, indicating a significant interaction between the Cu and ZnO phases. Because table 1 shows that CuO reduces much more readily than ZnO, and Jung *et al.* [29] showed that the ZnO phase of Cu/ZnO will not be reduced *significantly* in H_2 at 623 K, the Cu phase of the reduced Cu/ZnO catalyst can be assumed to be significantly more reduced than the Zn phase. Also, because the amount of H_2O produced from Cu/ZnO was greater than that of pure ZnO and the oxygen in CuO does not diffuse rapidly enough to reoxidize this catalyst at room temperature, the relatively large production of H_2O from Cu/ZnO is most likely from the copper phase extracting lattice oxygen from ZnO. That is, bulk oxygen of the ZnO lattice apparently diffused to the reduced Cu phase either during TPH or while the reduced catalyst was held at room temperature before TPH. Figure 1

Table 1
H_2O Desorption amounts during TPH

Catalyst	Reduced and Held at Room Temperature (μmol/g catalyst)		Oxidized (μmol/gcatalyst)
	O_2 Exposure	No O_2 Exposure	
Cu/ZnO	180 ± 4	112 ± 6	5770 ± 310
CuO	3 ± 2	0 ± 2	3000 ± 600
ZnO	31± 2	30 ± 4	44 ± 16

confirms the results of table 1 by indicating that reoxidation of the reduced Cu/ZnO surface occurs at room temperature.

In contrast to ZnO, pulsing O_2 at room temperature increased dramatically the amount of water produced during subsequent TPH of Cu/ZnO. Moreover, the effect of pulsing O_2 was significantly greater for Cu/ZnO than it was for pure CuO (table 1). This also indicates substantial interaction between Cu and ZnO. That is, the effect of pulsing O_2 at room temperature was negligible for both CuO and ZnO, but significant for Cu/ZnO.

3.3. Temperature-programmed hydrogenation spectra

Figures 2–5 show the rates of water production during TPH after reduction of Cu/ZnO, CuO, ZnO, and for a blank reactor. The areas of these TPH spectra, less the amount of H_2O formed for the blank reactor, correspond to the amounts listed in table 1. Note that although the differences between spectra are generally small, several repeat experiments were performed and the differences were determined to be statistically significant as reflected by the confidence intervals in table 1. Figure 2 shows two H_2O desorption peaks during TPH of the blank reactor at 363 and 573 K; in one experiment of figure 2, O_2 was pulsed at room temperature prior to TPH. The two curves nearly coincide and the H_2O desorption amounts were not statistically different. The possible sources of this H_2O could be from the quartz wool used in the reactor, or H_2O adsorbed on tubing walls and fittings such as filters downstream of the reactor; during TPH, the heated gas stream exiting the reactor would drive off any H_2O adsorbed on fittings and tubing walls. This control experiment accounted for the effect of any H_2O impurity in the carrier gas because the amount of H_2O that formed during the blank TPH was subtracted from the TPHs of all catalysts. The top panel of figure 2 plots the TPH curves versus time rather than temperature, which shows that O_2 impurity in the H_2 flow produced a small amount of H_2O desorption as the reactor was held at the final TPH temperature. Similar behavior was observed for all TPH curves (figures 2–5), and accounted for in the table 1 values.

The TPH of reduced CuO, shown in figure 3, resembled that of the blank reactor. The spectra for TPH of reduced CuO after exposure to gas-phase O_2 may have developed a small additional peak at 493 K compared to TPH without exposure to gas-phase O_2.

Figure 4 displays three peaks at 363, 573, and 683 K (the maximum temperature of this experiment) during TPH of reduced ZnO. The first two peaks appear at the same temperature as those of the blank (figure 2). However, the H_2O desorption rate of the ZnO peak at 573 K was approximately twice that of the blank. Therefore a portion of the peak at 573 K was due to removal of oxygen from ZnO. The only effect of oxygen exposure on ZnO was that it may have increased slightly the peak at 573 K, but the effect was statistically insignificant.

The TPH of reduced Cu/ZnO without an O_2 pulse, shown in figure 5 , produced a broad H_2O desorption that started near 350 K and continued throughout TPH, and eventually increased near the maximum temperature of the experiment. Exposure of reduced Cu/ZnO to O_2 increased dramatically the amount of desorbed H_2O and produced additional low-temperature H_2O desorption peaks, most notably the two peaks at 480 and 535 K, which are absent from TPHs on both pure CuO and ZnO. The greater effect of the room-temperature O_2 pulse for Cu/ZnO suggests a promotional effect between Cu and Zn; the Cu/ZnO catalyst adsorbs O_2 from the gas phase more readily than either the Cu or ZnO catalyst alone. This is most likely due to the interface of Cu and ZnO phases creating new sites.

3.4. Time dependence of Cu/ZnO reoxidation at room temperature

Because pulsing O_2 at room temperature increased oxidation of Cu/ZnO but not that of ZnO, the time dependence of bulk oxygen diffusion was investigated for these catalysts. The reduced catalysts were held at room temperature for varying amounts of time between 5 and 120 min prior to TPH. Figure 6 shows the amounts of H_2O produced during TPHs of Cu/ZnO and ZnO. Figure 6 indicates that bulk oxygen diffusion does not reoxidize completely either Cu/ZnO or ZnO. After 120 min, bulk oxygen diffusion replaced 3% of the oxygen that the previous reduction procedure had removed from Cu/ZnO. The *rate* of oxygen diffusion decreased monotonically as shown in figure 6 and oxygen diffusion was not complete after 120 min at room

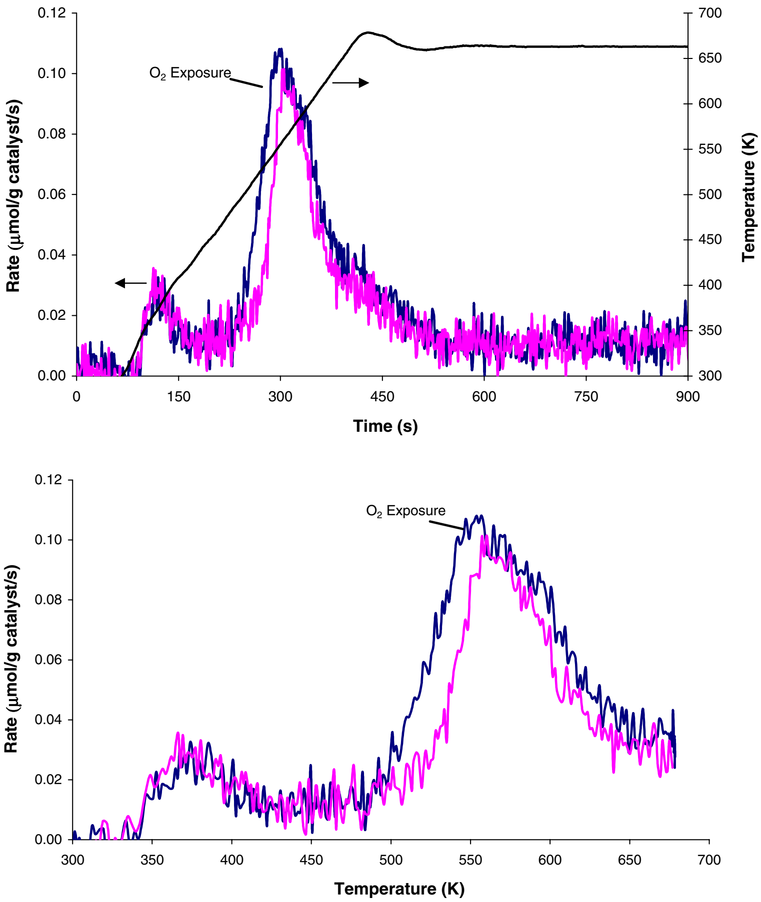

Figure 2. Temperature-programmed hydrogenation of a blank reactor containing only quartz wool with and without O_2 exposure. Spectra are plotted versus time (top panel) to show O_2 impurity in H_2 flow.

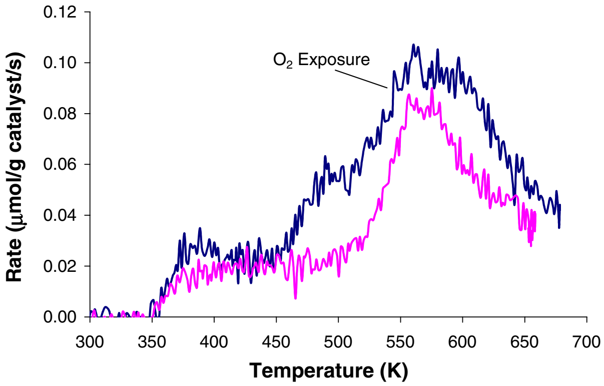

Figure 3. Temperature-programmed hydrogenations of reduced CuO catalysts with and without O_2 exposure at room temperature prior to TPH.

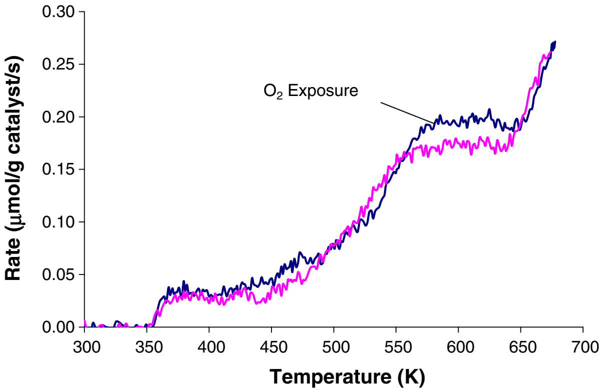

Figure 4. Temperature-programmed hydrogenations of reduced ZnO catalysts with and without O_2 exposure at room temperature prior to TPH.

temperature. For ZnO, approximately two-thirds of the oxygen removed by reduction had been replaced after approximately 10 min, and this extent of reoxidation did not change significantly thereafter.

The time dependence TPH agrees with DRIFTS experiments. Figure 6b plots the change in percent transmittance for the adsorption peak at 1200 cm^{-1} of Cu/ZnO with time at room temperature. The shape of the resulting curve resembles closely that of figure 6a. Both curves exhibit the same initial slope and begin to level off at approximately the same time. This similarity suggests that the reoxidation process occurred at about the same rate in both the DRIFTS and TPH studies.

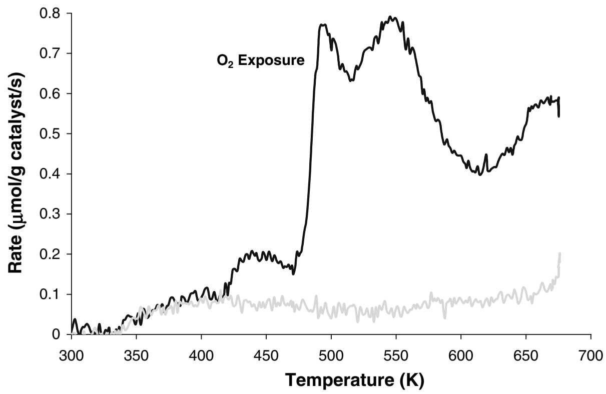

Figure 5. Temperature-programmed hydrogenations of reduced Cu/ZnO catalysts with and without O_2 exposure at room temperature prior to TPH.

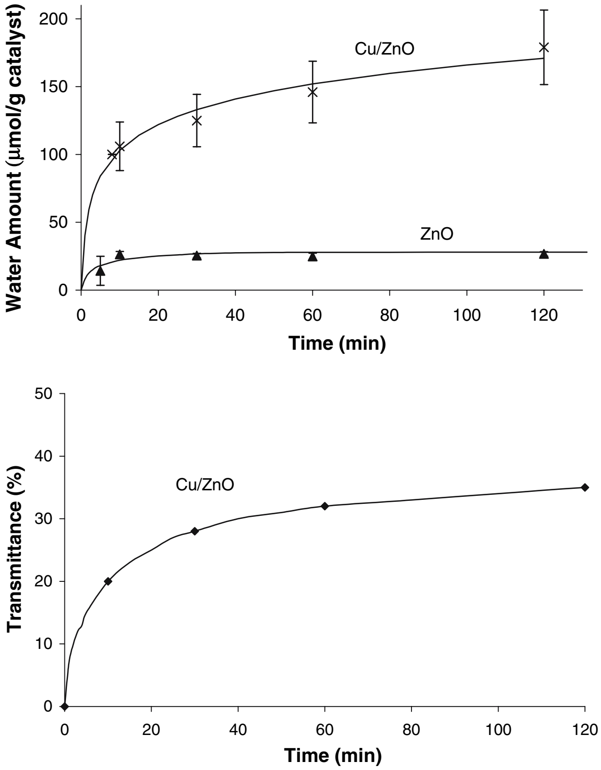

Figure 6. (Top Panel) Amounts of H_2O that desorbed during temperature-programmed hydrogenation of Cu/ZnO and ZnO after remaining at room temperature in H_2 flow for various times. The experiment was repeated in the DRIFTS reaction chamber and the change in percent transmittance of 1200 cm^{-1} peak is plotted.

Topsøe and Topsøe have shown the presence of a Cu–Zn alloy in reduced Cu/ZnO. Their reduction gas included CO, which has been shown to reduce both Cu and Zn. This study suggests that in a H_2 atmosphere, the initial step of the formation of a Cu–Zn alloy is reduced Cu extracting lattice oxygen from ZnO. Once all lattice oxygen is removed from ZnO, alloy formation is able to proceed. Hydrogen only reduces slightly the ZnO phase (as shown in table 1 for pure ZnO catalyst). However, it appears that ZnO reduction increases significantly due to the presence of the Cu phase.

4. Conclusions

After reduction in H_2, both ZnO and Cu/ZnO surfaces reoxidize at room temperature due to diffusion of lattice oxygen. The extent of room-temperature reoxidation of CuO was negligible. Gas phase oxygen did not increase the extent of reoxidation of ZnO but increased that of Cu/ZnO significantly. Interactions between the Cu and ZnO phases on Cu/ZnO allowed a greater extent of reoxidation of this catalyst compared to both pure CuO and ZnO catalysts.

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