The catalytic methanol synthesis over nanoparticle metal oxide catalysts

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Abstract

Several nanoparticle metal oxides were prepared and studied for the catalytic production of methanol from hydrogen and carbon dioxide. These catalysts include: ZnO, CuO, NiO, and a binary system CuO/ZnO. The catalysts were prepared through sol–gel synthesis and were found, via TEM and BET, to have high surface areas and small crystallite sizes. With this in mind, the catalytic production of methanol was studied at various temperatures in a flow reactor. The percent conversion and turnover numbers were calculated for each sample, and it was found that the nanoparticle ZnO, CuO/ZnO and NiO were much more active catalysts than the commercially available materials. The nanocrystalline CuO sample was found to rapidly reduce to Cu, where it lost all activity. The results suggest that the catalytic process is efficient for several nanoparticle metal oxide formulations, however, copper metal is not active, but small copper particles in a CuO/ZnO matrix is a very active combination.
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Keywords: Methanol synthesis; Metal oxide; Catalysts; Nanoparticles

1. Introduction

Nanocrystalline metal oxides prepared by sol–gel or modified aerogel procedures exhibit high chemical reactivities toward a variety of adsorbates, including acid gases, chlorocarbons, and polar organics including carbonyl compounds, insecticides, and chemical warfare agents (and surrogates) [1]. These high reactivities are due to high surface areas combined with unusually reactive morphologies [1].

To date, however, relatively little work has been reported where these nanostructured materials have been explored in classical catalytic processes. Herein we report on the relative catalytic activities of nanocrystalline ZnO, CuO, NiO, and intermingled CuO/ZnO materials for the catalytic reduction of carbon dioxide to methanol. The purpose is not to develop a new commercial catalyst for methanol synthesis, but to compare nanocrystalline forms of those oxides with conventional micro-polycrystalline materials.

Of course the choice of ZnO and CuO is based on their known properties as catalysts for partial reduction of carbon oxides. In fact ZnO, Cr_2O_3, CuO and combinations of these have received the most attention [2–8]. More recently copper metal particles supported on ZnO has allowed lower temperatures and pressures to be employed [9].
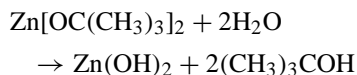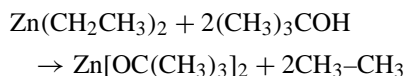
2. Experimental

2.1. Preparation of metal oxide samples

The reactions involved in the preparation are shown below.

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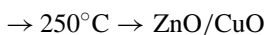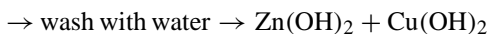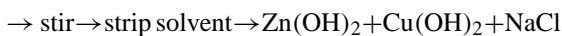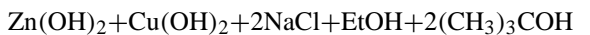fax: +1-785-532-6666.

(A) $Zn(OH)_2$ sol:

$$Zn(CH_2CH_3)_2 + 2(CH_3)_3COH$$
$$\rightarrow Zn[OC(CH_3)_3]_2 + 2CH_3-CH_3$$

$$Zn[OC(CH_3)_3]_2 + 2H_2O$$
$$\rightarrow Zn(OH)_2 + 2(CH_3)_3COH$$

(B) $Cu(OH)_2$ sol:

$$CuCl_2 + 2NaOH + EtOH \rightarrow Cu(OH)_2 + 2NaCl$$

$$\text{wash with water} \rightarrow Cu(OH)_2$$

Mix (A) and (B):

$$Zn(OH)_2 + Cu(OH)_2 + 2NaCl + EtOH + 2(CH_3)_3COH$$
$$\rightarrow \text{stir} \rightarrow \text{strip solvent} \rightarrow Zn(OH)_2 + Cu(OH)_2 + NaCl$$
$$\rightarrow \text{wash with water} \rightarrow Zn(OH)_2 + Cu(OH)_2$$
$$\rightarrow 250^\circ C \rightarrow ZnO/CuO$$

The preparations consisted of four main steps.

1. *Synthesis of the zinc hydroxide sol*. The chemicals used in the synthesis were directly from the company without further purification. In a glovebox 40 ml (0.040 mol) 1.0 M diethylzinc in hexanes (Aldrich) was added to a 500 ml round bottom flask. This was removed from the glovebox and placed under a head of argon gas, placed on a stir plate and cooled to 0 °C with an ice bath. A solution of 5.8 g (0.080 mol) *t*-butanol (Fisher) in 60 ml hexanes (Fisher) was added to the cooled diethylzinc solution via syringe. This solution was added over a time span so that the release of ethane was not extremely violent. Once the solution was completely added the ice bath was removed and the reaction was allowed to come to room temperature (about 25 °C). The reaction was then stirred at room temperature for 2 h. During this time the reaction mixture remained a clear colorless solution. A solution of 1.44 ml (0.080 mol) water in 140 ml absolute ethanol (McCormick) was then added to the reaction mixture. Once the solution was completely added the reaction was allowed to stir for an additional 2 h. The zinc oxide slowly formed a white colloidal solution.

2. *Synthesis of the copper hydroxide sol*. The chemicals used in the synthesis were directly from the company without further purification. Under argon 1.500 g (0.0112 mol) copper(II) chloride (Aldrich) was added to a 250 ml round bottom flask. This was dissolved with 70 ml absolute ethanol (McCormick) to form a clear green solution. 0.0224 mol sodium hydroxide (Fisher) was dissolved in absolute ethanol (McCormick) was added dropwise to form the copper hydroxide gel. The reaction was then stirred at room temperature for 2 h. During this time the reaction mixture forms a blue-green gel.

3. *Combining the zinc and copper sols*. The white $Zn(OH)$ sol was combined with the $Cu(OH)_2$ gel and mixed in a 1:1 molar ratio for 2 h to form a light blue–green sol. After the reaction was complete the argon line was removed and the reaction mixture was poured into a Schlenk tube. This was then connected to a vacuum line attached to a second liquid nitrogen trap. While stirring at 25 °C all of the solvent was condensed from the Schlenk tube to the second trap. After the solvent was removed the dry powder was filtered and washed with water to remove the sodium chloride. This left a dry, blue–green zinc oxide/copper hydroxide powder with a 90% yield.

4. *Conversion of hydroxides to oxides, and removal of residual solvents*. The dry hydroxide powder was placed into a Schlenk tube, connected to a flow of argon and surrounded by a furnace. The furnace was connected to a temperature controller, and it was heated at 250 °C for 15 min. After the heat treatment was complete the furnace was turned of and allowed to cool to room temperature.

Commercial copper oxide was purchased from Aldrich (CM-CuO). Commercial samples of the highest surface area ZnO available were purchased from Fisher (CM-ZnO-1) and Nanophase Materials (CM-ZnO-2).

2.2. Characterization of NC-ZnO/CuO

(1) *Brunauer-Emmet-Teller method (BET)*. BET methods were used to measure the surface areas of the ZnO/CuO samples. This was conducted using both Micromeritics Flowsorb II 2300 and

Quantachrome NOVA 1200 instrumentation. The samples were first outgassed at the desired temperature, and then allowed to cool to room temperature. Next they were further cooled to 77 K, and exposed to nitrogen (30% N_2, 70% He) where the adsorption of nitrogen molecules occurred. Here the amount of nitrogen adsorbed as a single layer was measured. From the number of molecules adsorbed, and the area occupied by each, the surface area was directly calculated.

(2) *Powder X-ray diffraction (XRD)*. For XRD studies the ZnO/CuO samples were heat treated under argon, directly before being placed onto the sample holder. The instrument used was a Scintag XDS 2000 spectrometer. Cu Kα radiation was the light source used with applied voltage of 40 kV and current of 40 mA. Two theta angles ranged from 20° to 85° with a speed of 2° per minute. The crystallite size was then calculated from the XRD spectra by using the Scherrer equation.

(3) *Infrared spectroscopy (FT-IR)*. These experiments were conducted on an RS-1 FTIR spectrometer from Mattson with a liquid nitrogen cooled MCT detector. Heat treated samples of NC-ZnO/CuO, CM-CuO and CM-ZnO were made into KBr pellets before IR analysis.

(4) *Thermogravimetric analysis (TGA)*. TGA was used to determine the weight loss of the ZnO/CuO during heat treatment. These studies were conducted under a nitrogen flow. To measure the weight loss the ZnO/CuO samples were placed onto a basket and heated at a rate of 10°/min from room temperature to 700 °C. The instrument used was a thermogravimetric analyzer TGA-50 from the Shimadzu Company.

(5) *Elemental analysis*. ZnO/CuO after heat treatment was transferred to glass vials, under argon atmosphere, and sent to Galbraith Laboratories for analysis. Elemental analysis was conducted for Zn, Cu, C, and H. The amount of oxygen was obtained by subtracting the sum of Zn, Cu, C, and H from 100.

2.3. GC Studies

The reactions of H_2, and CO_2 on various metal oxides to produce methanol were carried out to find the best conditions for catalysis, and to compare the various nanocrystalline metal oxides to each other, and to commercially available metal oxides. The reactions were conducted in a continuous flow reactor that was connected to a gas chromatograph (Varian Star 3600 CX). The U-tube which held the catalyst was made of Pyrex and connected between the gas mixture (certified gas mixture 0.99% ethane, 1.97% carbon dioxide, hydrogen balance) and an overfill valve. The overfill valve led to the column (Porapak Q), and a flow meter where when not sampling the gas flow can be monitored. A metal oxide sample was placed in the U-tube between two small plugs of aluminum-silicate wool. The reactor was then heated to the desired temperature. Gas injections (1.0 ml) were made through the overfill valve (150 °C) every 5 min. Any methanol coming off the sample, unreacted hydrogen and carbon dioxide, and the internal standard ethane was then sent via helium (30 cm^3/min) through the column (150 °C) to be separated. They were then detected by a thermal conductivity detector (200 °C) and peak areas recorded.

1. *Temperature dependent GC study*: The production of methanol from carbon dioxide and hydrogen was studied from room temperature to 500 °C, over a 0.9–1.1 cm bed length of catalyst. This was done for each sample to find the most favorable temperature for each oxide.

2. *Catalysis of methanol at pre-set temperature*: To better study the catalytic reactivity 0.9–1.1 cm bed lengths of each oxide were placed into the reactor and the catalysis was carried out at the most desirable temperature found for each oxide. The reactions were carried out for 2 h, and sampled every 5 min. Nanocrystalline CuO, NiO, ZnO, and ZnO/CuO were individually studied and compared to commercial brands. After reactions all of the samples were studied by XRD.

3. *Long-term GC study:* A long term GC study was conducted to see if over a relatively long time period activity would be lost. In this study the catalysts were placed into the reactor and the reaction was monitored over 3 days.

4. *In situ IR study:* An in situ IR study was carried out at room temperature on the ZnO samples. The catalyst was placed onto a tungsten mesh, and inserted into the IR cell [10]. The cell was then evacuated and background spectra were acquired, next 5 Torr of the gas mixture was allowed into the

cell for 2 h. After the 2 h the cell was evacuated and spectra acquired.

3. Results

3.1. Preparation of the zinc oxide/copper oxide

One objective was to prepare a ZnO/CuO sample with the highest surface area possible. Several experiments were conducted varying the amounts of water, stirring time and drying methods; and all were found to have an effect on the surface area of the resulting sample. Type of solvent employed was also important. Enough stirring time had to be allowed for hydrolysis, at least 2 h was necessary. However, the surface area was also found to decrease when long stirring times were used. Three drying methods were employed: (1) oven drying, (2) hypercritical drying using a high pressure autoclave, and (3) vacuum. In the example at hand, hypercritical drying was not successful since the organic solvents employed readily caused copper oxide reduction to copper metal. Overall, vacuum drying proved to yield the highest surface area materials.

3.2. Activation of the zinc oxide/copper oxide

The ZnO/CuO samples were heat treated under argon flow, or under dynamic vacuum, and the surface areas obtained were about the same for both methods. During heat treatment the surface area increases, then goes through a maximum, and above 250 °C decreases due to sintering.

3.3. Characterization of the zinc oxide/copper oxide samples

(1) *Brunauer-Emmet-Teller method (BET)*. Commercial ZnO is most commonly prepared by high temperature methods, and CM-1-ZnO typically had surface areas within the range of $2–4 m^2/g$, and CM-2-ZnO had surface areas of $16–20 m^2/g$. The CM-CuO sample had a surface area of $0.7 m^2/g$. NC-ZnO/CuO samples typically possessed surface areas within the range of $130–140 m^2/g$ after heat treatment at 250 °C.

Using BET it was also possible to obtain data on the pore structures. The average NC-ZnO/CuO sample after heat treatment possessed pores that were about 12 nm in diameter, held about $0.450 cm^3/g$ volume and were open at both ends.

(2) *X-ray diffraction*. From XRD we obtained diffraction patterns that showed the presence of small crystallites of both ZnO and CuO. However, the peaks were very broad compared with commercial more highly crystalline samples, as expected (Fig. 1). Interestingly, the crystallite sizes, as calculated using the Scherrer equation were in the same range for separate samples of NC-ZnO and NC-CuO (Table 1) [11]. The average crystallite size for NC-ZnO/CuO activated at 250 °C was found to be 5 nm (ZnO) and 8 nm (CuO), whereas the size for CM-1-ZnO was 41–45 nm, and CM-2-ZnO was 32–35 nm. It was found that when the NC-ZnO/CuO sample was heated to $\leq$200 °C only ZnO and $Cu(OH)_2$ species are observed, when heated to 300 °C the $Cu(OH)_2$ is converted to CuO, and when heated to 500 °C both the ZnO and CuO species become much more crystalline.

(3) *Infrared spectroscopy*. The heat-treated samples were ground with KBr, and pressed into pellets. IR spectra were taken after heat treatment at 100, 200, 300, 400, and 500 °C. A gradual loss of water and carbon dioxide was seen from 100 to 500 °C.

(4) *Thermogravimetric analysis*. By studying the weight loss under helium flow from room temperature to 500 °C, it was found to be continuous and gradual from room temperature to 500 °C. This indicates a gradual water/solvent loss, which is also supported by the IR data.

(5) *Elemental analysis*. Elemental analysis was conducted of NC-ZnO/CuO preheat-treated to 250 °C under argon flow. The results indicate the presence of some residual OH/H_2O as well as adsorbed CO_2, which are indicated by IR. There do not appear to be any residual OR groups, although some of the carbon may be present in the form of amorphous graphite. If CO_2 and surface OH are assumed to be the only adsorbed species, a formula $ZnO \cdot CuO(OH_2)_{0.016}(CO_2)_{0.11}$ fits the data (oxygen by difference).

3.4. Preparation and characterization of other metal oxides

The nanocrystalline (NC) CuO, ZnO and NiO samples used in this study were used as described earlier,
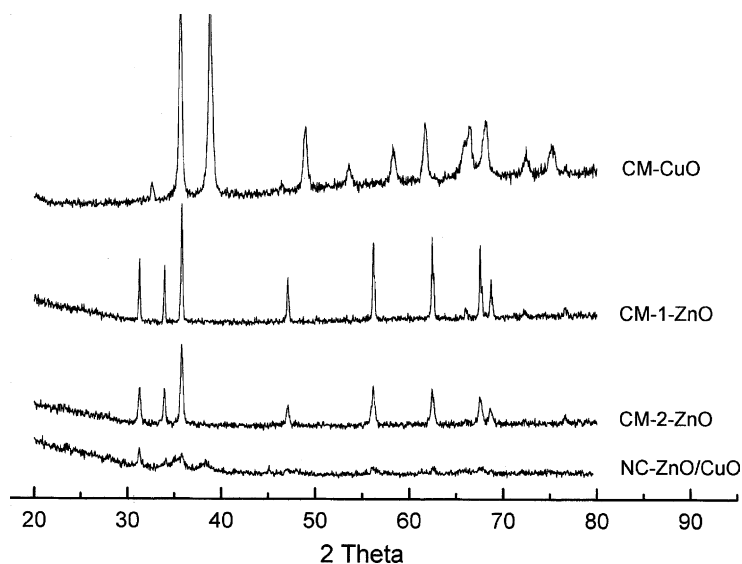
Fig. 1. XRD Spectra of CM-CuO, CM-1-ZnO, CM-2-ZnO, and NC-ZnO/CuO.

without additional treatment [1a,1b]. Because a detailed characterization has already been discussed for these oxides, only a brief summary will be given here to compare the oxides studied. Table 1 shows the surface areas, obtained via BET; crystallite sizes, obtained via XRD; and the pore volumes, and pore diameters of the NC samples and their corresponding CM samples. Surface areas ranging from 0.5 to 320 m^2/g, and crystallite sizes ranging from 4 to 59 nm can have a tremendous affect on how reactive a sample is. Pore volumes and diameters also play an important role by limiting the size, and amount of the adsorbate entering the pore structures.

3.5. Catalytic methanol production/GC studies

3.5.1. Temperature dependent GC study

The production of methanol from carbon dioxide and hydrogen was studied from room temperature to 500 °C, over a 0.9–1.1 cm bed length of catalyst. Table 2 show the amount of CH_3OH converted/CO_2 available for each sample at each temperature. As expected the catalysts became more active with an increase in temperature from room temperature to 450 °C, and had only a slight increase in activity from 450 to 500 °C. Fig. 2 shows a typical GC trace with peaks labeled, and the amount of CH_3OH

Table 1
Sample characteristics

Sample	Surface area (m^2/g)	Crystallite size (nm)	Pore volume (cm^3/g)	Pore diameter (nm)
NC-CuO	140	7.9	0.218	8.4
CM-CuO	0.53	56	0.004	31
NC-NiO	320	3.1	0.352	4.6
CM-NiO	1.2	59	0.004	15
NC-ZnO	130	3.9	0.101	11
CM-1-ZnO	3.9	44	0.012	13
CM-2-ZnO	20.0	33	0.0469	9.5
NC-ZnO/CuO	140	4–7	0.450	12

Table 2
The percent of CO_2 converted to CH_3OH at each temperature

Temperature (°C)	CM-1-ZnO	CM-2-ZnO	NC-ZnO	NC-ZnO/CuO
(a)				
25	0	0	0.90	0
50	0	0	1.20	0
100	0	0	1.60	0
150	0	0	2.30	4.70
200	0	0	10.3	13.2
250	0	0	12.1	21.3
300	0	0	17.4	30.5
350	0	0	21.3	36.5
400	0	13.0	32.7	51.3
450	0	29.5	37.1	58.6
500	0	30.0	37.9	58.9
	CM-CuO	NC-CuO	CM-NiO	NC-NiO
(b)				
25	0	0	0	0.70
50	0	0	0	1.50
100	0	0	0	2.30
150	0	0	0	8.30
200	0	0	0	17.9
250	0	0	0	20.0
300	0	0	0	46.2
350	17.8	0	0	51.0
400	42.1	0	0	59.4
450	73.7	0	0	64.2
500	73.9	0	0	64.5
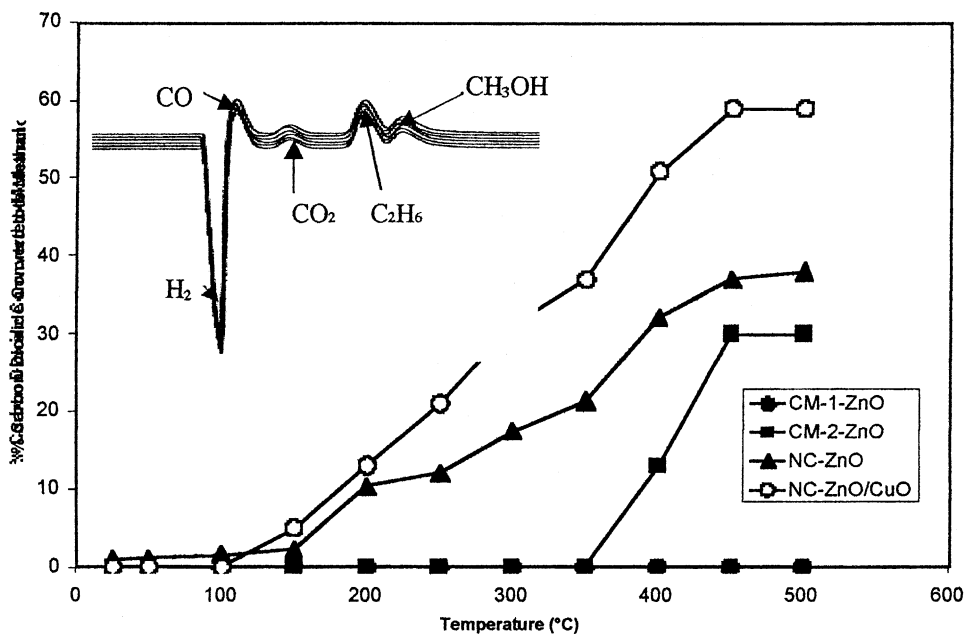
Fig. 2. The percent of CO_2 converted to CH_3OH vs. temperature for the ZnO samples.
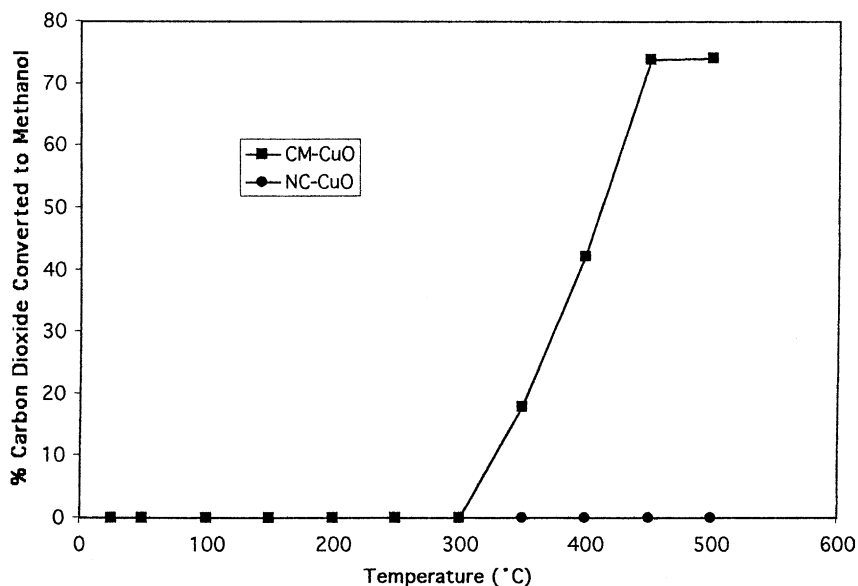
Fig. 3. The percent of CO_2 converted to CH_3OH vs. temperature for the CuO samples.

converted/CO_2 available vs. temperature for the ZnO samples. It can be seen that the CM-1-ZnO had no catalytic affect at any temperature. The CM-2-ZnO showed no activity until temperatures greater than 350 °C where it reached about 30% conversion and leveled off. The NC-ZnO, unlike the other samples, showed some activity at room temperature. This sample, like the others showed an increase in activity with temperature. Also note that the ZnO/CuO sample performed the best overall.

Fig. 3 shows the percent of CO_2 converted to CH_3OH for the CuO samples. The NC-CuO sample did not show any catalytic activity. However, the CM-CuO produced methanol at temperatures greater than 300 °C. Data from the synthesis confirms that the NC-CuO samples were reduced very easily to copper, much easier than the CM-CuO. The CM-CuO does not completely reduce to copper, which is most likely why the activity continues. Fig. 4 shows the percent of CO_2 converted to CH_3OH for the NiO samples. In the case of NiO both samples were reduced to Ni, but the CM-NiO showed no catalytic activity, whereas the NC-NiO showed great activity. For all samples studied, 450 °C was determined to be the best temperature, and significant increases in activities were not seen in going from 450 to 500 °C.

3.6. Catalysis of methanol formation at pre-set temperature

To better study the catalytic activity the catalysis was carried out at 450 °C. The reactions were carried out for 2 h, and sampled every 5 min. Nanocrystalline CuO, NiO, ZnO, and ZnO/CuO were individually studied and compared to commercial brands. Table 3 gives the percent of CO_2 converted to CH_3OH, and turnover numbers for the samples at their steady states. The turnover numbers indicate the molecules of methanol produced per second per site, based on final surface areas (and assuming all surface metal oxide moieties are active sites). It was found that the CM-1-ZnO, as expected showed no activity, and the CM-2-ZnO exhibited steady activity converting about 30% of the CO_2 to CH_3OH, which resulted in a turnover number of 2.1 molecules of carbon dioxide converted per second per site. The NC-ZnO showed activity converting about 40% of the CO_2 to CH_3OH, having a turnover number of 3.4. The NC-ZnO/CuO showed the best activity of all the ZnO samples converting about 60% of the CO_2 to CH_3OH, and having a turnover number of 87. It was observed that the CM-CuO, as expected, showed good activity converting about 74% of the CO_2 to CH_3OH, which
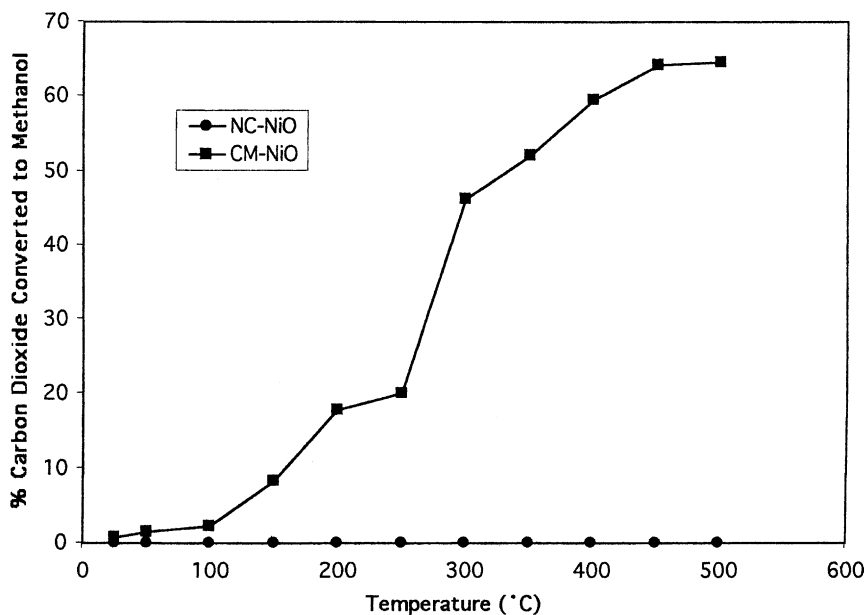
Fig. 4. The percent of CO_2 converted to CH_3OH vs. temperature for the NiO samples.

resulted in a turnover number of 50 molecules of carbon dioxide converted per second per site. The NC-CuO exhibited activity only in the beginning, and then loses all activity. It was found that the CM-NiO, as expected showed no activity, whereas the NC-NiO sample exhibited strong activity converting about 65% of the CO_2 to CH_3OH, which resulted in a turnover number of 17 molecules of carbon dioxide converted per second per site.

3.6.1. X-ray diffraction

XRD was used to study the solid catalysts after reaction. There was no spectral change observed in the ZnO samples. This is somewhat expected due to

Table 3
The percent of CO_2 converted to CH_3OH, and turnover numbers

Sample	CO_2 converted to CH_3OH (%)	Turnover number
CM-1-ZnO	0	0
CM-2-ZnO	30	2.1
NC-ZnO	37	3.4
NC-ZnO/CuO	59	87
CM-CuO	74	50
NC-CuO	0	0
CM-NiO	0	0
NC-NiO	64	17

the fact that ZnO is not easily reduced to Zn. However, in the cases of copper and nickel oxide we do see the metal peaks present. The XRD spectra for NC-ZnO/CuO showed that at least part of the CuO has been reduced to Cu.

3.6.2. Long-term GC study

A long term GC study was conducted to see if over a relatively long time period catalytic activity would be lost. In this study the catalysts were placed into the reactor and the catalysis was monitored over 3 days. This study was conducted at a lower temperature to reduce high temperature hazards, because the experiment could not be continually monitored. The experiment was conducted at 200 °C, the only samples that showed activity at this temperature were NC-ZnO, NC-ZnO/CuO, and NC-NiO, which were the samples of greatest interest. All three of the samples showed consistent activity, not as high a turnover number as at 450 °C, but consistent over the 3-day time period, Fig. 5.

3.6.3. In situ IR study

An in situ IR study was carried out at room temperature, in an attempt to identify any intermediate adsorbed species. The only three samples that showed
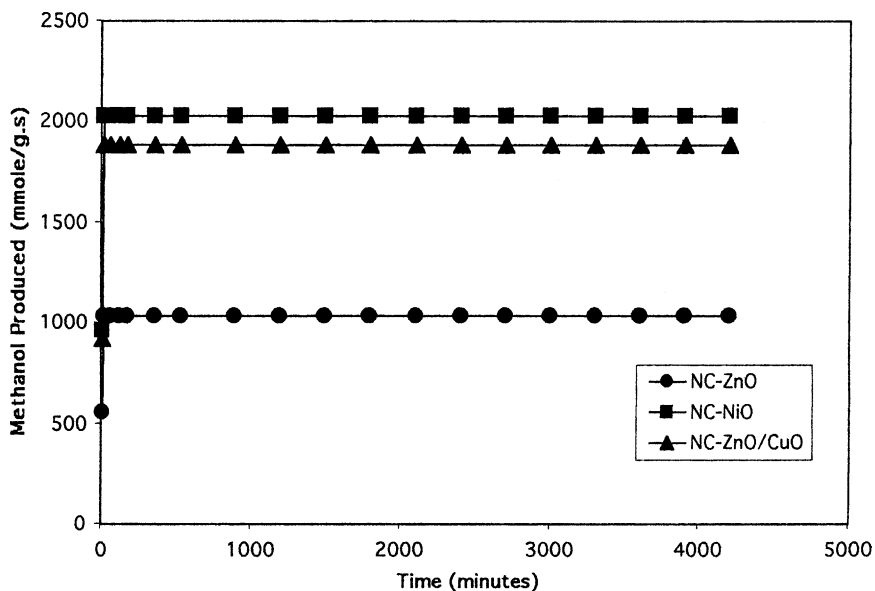
Fig. 5. Methanol produced (mmol/g s) vs. time for the nanocrystalline samples.
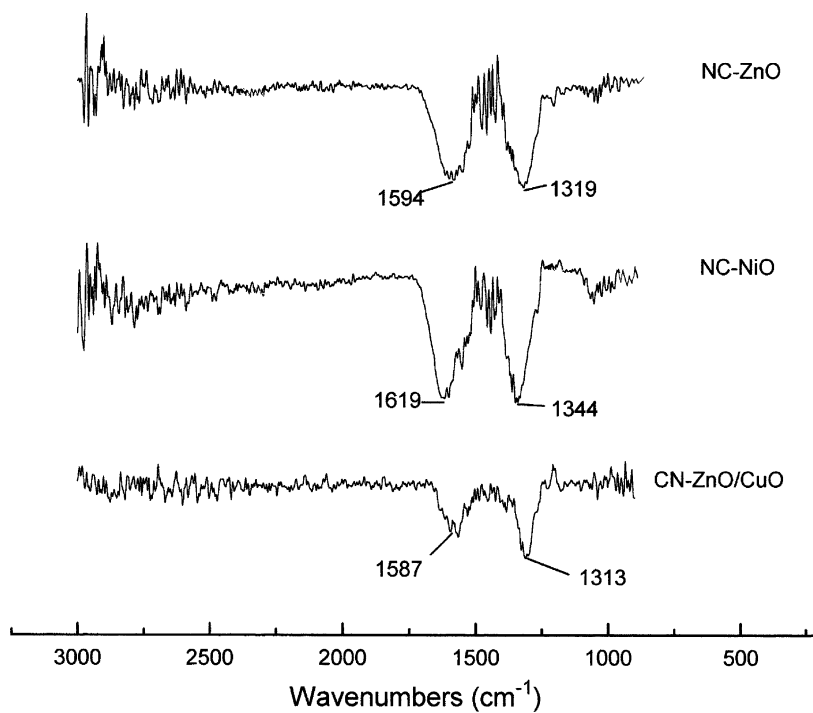

Fig. 6. In situ IR Spectra of samples exposed to CO_2/H_2 at room temperature, followed by evacuation of the excess CO_2/H_2. The peaks observed are due to formate intermediate species.

any signs of adsorption were NC-ZnO, NC-ZnO/CuO, and NC-NiO, this again is due to the lower temperature. Fig. 6 shows IR spectra of the three samples after 5 min of evacuation. Two characteristic peaks were seen in each of the samples at 1310–1340, and 1580–1620. These two peaks have been identified many times in literature and belong to the formate species [12–15].

In this study the methoxy species was not observed. It has been noted by many authors that the methoxy species is not usually observed, and this is believed to be because it is much more reactive than the formate species, and therefore only exists for a very short time [12–21].

4. Discussion

The binary intimate mixture ZnO/CuO is the most active catalyst for CO_2 conversion to CH_3OH at lower temperatures (150–300 °C). By combining zinc and copper sols, it was possible to produce a very high surface area intimately mixed nanocrystalline ZnO/CuO material. Comparison of this material with nanocrystalline ZnO, CuO, and NiO as catalysts in CO_2 conversion to CH_3OH, showed that all except the CuO samples were active at relatively low temperatures (150–300 °C). In the case of NC-CuO, rapid reduction to Cu metal occurred, completely deactivating this sample. Commercial samples were generally much less active, although at high temperatures (350–500 °C) CM-CuO did show good activity.

Operating at 200 °C, the NC-ZnO, NC-NiO, and NC-ZnO/CuO all showed long term activity over a period of 3 days. XRD indicated that the NC-NiO samples were partially reduced to Ni, and the ZnO/CuO was partially reduced to a Cu/ZnO/CuO composite. The best results were obtained overall with the ZnO/CuO system, and it seems likely that the presence of small copper clusters embedded in a ZnO-CuO matrix is the most favorable composition. A similar result was found for NC-NiO, where the active catalyst appears to be Ni clusters embedded in a NiO matrix.

It is clear that these nanocrystalline samples are active at the lower temperatures, whereas the commercially available micro-polycrystalline samples are not. At higher temperatures (450 °C, Table 3) the nanocrystalline samples generally exhibit higher turnover numbers, but CM-CuO was also quite active (based on final surface areas and assuming all surface oxide moieties are active sites).

Acknowledgements

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