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DIRECT ALCOHOL SYNTHESIS USING MODIFIED COBALT CATALYSTS: A PROGRESS REPORT

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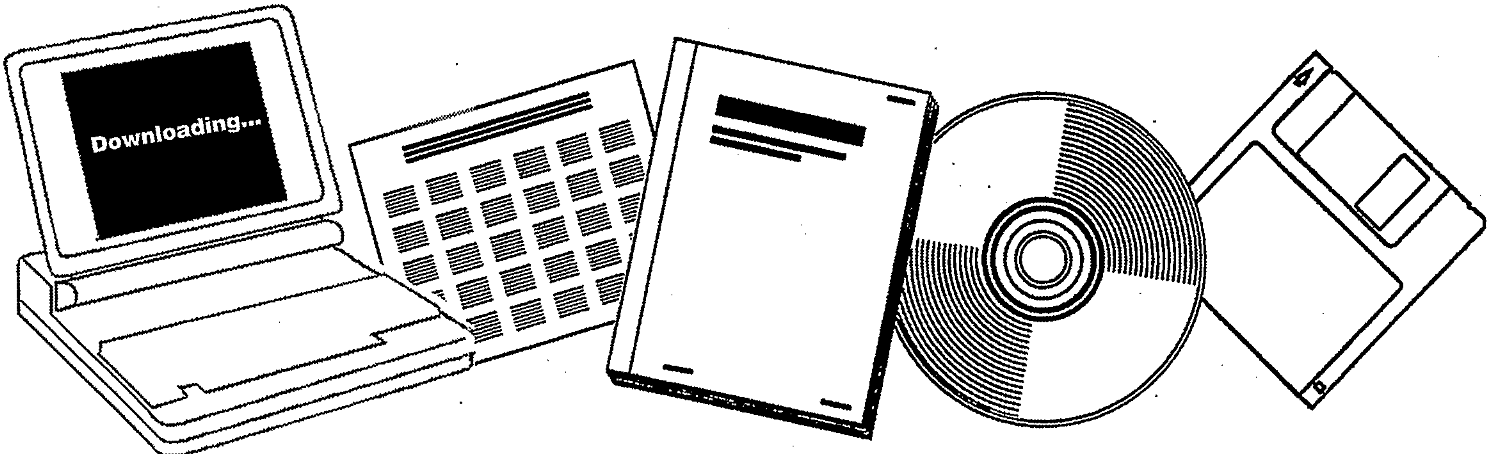

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Direct Alcohol Synthesis Using Modified Cobalt Catalysts

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Abstract

We describe the preparation, characterization, and kinetic activity measurements of a sequence of Cu : ZnO and Cu : Co : ZnO : Al_2O_3 catalysts for alcohol synthesis via CO hydrogenation. For binary Cu : ZnO catalysts prepared by various precipitation methods, methanol is the only reaction product and its rate of formation is proportional to the metallic Cu surface area of the catalysts. For Cu : Co : ZnO : Al_2O_3 : K catalysts, a Schulz-Flory-Anderson distribution of higher alcohols forms the major product group, with smaller amounts of hydrocarbons and methanol being formed in parallel. The overall yield of higher alcohols increases linearly with CO conversion, while the selectivity for hydrocarbon products increases slightly with conversion. The product alcohols do not undergo a significant degree of secondary reaction at the concentrations formed under these conditions. Temperature programmed desorption experiments using both H_2 and CO reveals the presence of distinguishable Cu and Co adsorption sites, with some limited evidence for interaction between sites. The overall results are consistent with a mechanism for higher alcohol synthesis that involves chain growth of a common surface alkyl intermediate at a surface-modified Co site, followed by a chain termination step which determines whether the final product desorbs as an alcohol or hydrocarbon.

Contents

Introduction

The phase-out of lead-containing anti-knock compounds from motor fuels is causing refiners to look for alternate methods to enhance octane ratings. One approach being explored is the addition of oxygenates such as alcohols or ethers as gasoline blending agents (1). The potential volume of this market has led to renewed interest in the manufacture of methanol and higher alcohols via synthesis gas derived from coal or natural gas (2,3).

Several types of catalyst have been studied for this reaction. These include alkalinized Cu/ZnO (4,5), sulfided Mo/Al_2O_3 (6,7), supported Rh or Pd promoted by any of several transition metals (8-12), and supported Co alloyed with a second transition metal (13-16). Of these, the Cu : Co bimetallic catalysts of the last group have received the greatest attention in the open literature with regard to progress toward commercialization. Courty et. al. have published results concerning the preparation and characterization of this type of catalyst (17), its activity and overall product distribution (12), and its incorporation in a 7000 bbl/day demonstration plant for higher alcohols synthesis (2).

We are presently studying the Cu : Co : ZnO : Al_2O_3 catalyst system at the fundamental level. Our goal is to ① understand how the Co, Cu, and alkali components of the catalyst interact to form active sites, and how ② reaction conditions influence the rate and selectivity of the reactions that occur at these sites. We ③ hope to express these results in the form of kinetic parameters that can be used for catalyst optimization and reactor design equations.

In this progress report, we summarize the results obtained under two sequentially running Department of Energy grants covering the current three year project period. The first of these grants ran for two years and was executed at the University of Minnesota. The results obtained during this period dealt primarily with methanol synthesis on binary Cu : ZnO catalysts and related adsorption studies. The second (and current) grant runs for one year and is being carried out at Louisiana State University. Results obtained under this grant deal primarily with the higher alcohol synthesis reaction on Cu : Co : ZnO : Al_2O_3 : K catalysts.

Experimental procedures

During the current three year project period we have achieved significant developments in our catalyst preparation and characterization procedures, as well as our capabilities for performing kinetic measurements. In the following section, we describe our new findings with regard to catalyst preparation and give a short summary of the remaining experimental techniques.

Catalyst preparation. Catalysts were prepared by co-precipitation, using starting solutions of 1.0 M aqueous $Cu(NO_3)_2$, $Co(NO_3)_2$, $Zn(NO_3)_2$, and $Al(NO_3)_3$, each of which were acidified with HNO_3 as needed to completely dissolve the salt. These solutions were mixed in the proportions needed to obtain the desired cation ratio in the final catalyst, and then precipitated using 1.0 M Na_2CO_3. Originally we followed the precipitation sequence used by Hermann et. al (18); i.e., the addition of the Na2CO3 solution to the mixed nitrates. This led to very low surface area materials in our hands, so subsequent catalysts were prepared by adding the mixed nitrates and Na_2CO_3 solution simultaneously into a well stirred beaker at 353K. The effect is to cause precipitation to occur at neutral rather than acidic pH conditions, which leads to a more uniform rate of deposition of the various cation species leaving solution (17).

The resulting precipitate is filtered, washed 5 times in hot water, dried for 12 hours at 383K, and calcined in air for 12 hours at 623K. An optional alkalinization step is included at this point, by loading the powder to the incipient wetness point with an aqueous solution of K_2CO_3 at the concentration needed to give the desired K loading in the final catalyst and repeating the drying step. The catalyst is then loaded into the reactor or the IR/TPD cell and reduced *in-situ* using a flowing 5 vol% H_2/N_2 gas mixture at 1 atm. Reduction is performed over 2 days, during which time the temperature is gradually increased to 563K.

Kinetic measurements. The high pressure (50 atm) kinetic measurements are performed in a Cu-plated stainless steel tubular microreactor. The typical reaction conditions were 50 atm, 563K, and $H_2/CO = 1/1$. Products were analyzed by gas chromatography (Hewlett Packard 5890 with 3393A integrator) using a Porapak T column with temperature programming and a TCD detector. Peak areas were calibrated by liquid injection of individual components.

A brief set of CH_2O hydrogenation experiments was performed in a separate Cu tubular microreactor with a dedicated gas chromatograph (Carle 311).

Adsorption, TPD, and IR measurements. Most of the IR and TPD experiments were performed in a dedicated sample cell designed for this purpose (19). The cell is UHV compatible to allow for controlled sample outgassing and volumetric dosing of adsorbates, as well as to permit the TPD experiments to be performed in the dynamic vacuum mode. A key feature of the cell is that the powdered sample is dispersed onto a Ag mirror, and the IR optical path is configured in a reflection - transmission mode. This permits the temperature of the thin layer of catalyst powder to be carefully controlled during the TPD experiment. The TPD experiments are performed using a quadrupole mass spectrometer with computer controlled data aquisition (e.g., multiple peak scanning, peak temperature determination, and area integration). The IR spectra are recorded using an Fourier transform IR spectrometer (Nicollet 60-SX).

During the second year we also assembled a flow adsorption apparatus to perform BET and O_2 chemisorption measurements. The BET area is determined by N_2 adsorption at 98K, as measured by integrating the decrease (or increase) of N_2 concentration in an N_2 : He mixture flowing continuously over the catalyst as it is cooled (or warmed) between 300K and 98K. The O_2 chemisorption uptake is determined by admitting pulses of O_2 to the sample at 98K, and measuring the decrease in pulse height during the first few pulses.

Results

In the following section we describe results of our research that have either appeared in print or have been submitted for publication.

Adsorption studies on binary Cu : ZnO catalysts (Year 1). The major result during the first year of the original grant contract was to complete our IR and TPD studies of H_2 and CO chemisorption on binary Cu : ZnO catalysts prepared by co-precipitation methods (20). These results were performed to allow us to next apply these techniques to the more complex Cu : Co : ZnO and Cu : Co : ZnO : Al_2O_3 catalyst mixtures.

The IR results show that CO adsorbs on reduced catalysts in several states which are distinguished by different vibrational frequencies. These lie in the range 2104-2067 cm^{-1}, which shows that the CO is adsorbed on both high and low Miller index Cu surface planes. The CO desorbs with a range of apparent activation energies between 10 to 16 kcal/mole. The lower limit of this range is comparable to values reported for desorption from low-index single crystal surfaces. When CO is adsorbed on pre-oxidized catalysts, the ν(C-O) band shifts to 2136-2210 cm-1 and the upper limit of the range of apparent desorption energies increases to 19 kcal/mole.

We also measured the H_2 desorption spectra from both reduced and oxidized forms of the catalysts. The apparent activation energy for desorption is 20-21 kcal/mole from reduced catalysts, and 26-27 kcal/mole from oxidized samples. Both values include an activation energy of several kcal/mole for the (reverse) adsorption step.

We next compared the amount of each gas adsorbed on the Cu component with the Cu surface area measured by irreversible O_2 chemisorption at 98K. The relative uptakes of all three gases correlated well for a variety of samples, in the ratio $CO : H_2 : O_2 = 9 : 2 : 10$. Thus reversible CO adsorption and low temperature O_2 chemisorption appear to give comparable measurements of the number of Cu surface sites, while H_2 appears to adsorb on only a fraction of the Cu surface.

Control experiments with Cu/ZnO catalysts prepared by impregnation and Cu/SiO_2 catalysts both gave similar results. Thus, we were unable to find any definitive evidence for adsorption on isolated Cu(I) sites that are unique to the co-precipitated Cu : ZnO catalyst. Instead, we suggested that the usefulness of the Cu : ZnO catalyst for methanol synthesis may instead be related to its ability to maintain a large area of high Miller index Cu sites.

Kinetic studies of Cu : ZnO catalysts (Year 2). During the second year of the original grant contract, we assembled a continuous flow, tubular microreactor for kinetic measurements at high pressure (21). The first set of experiments was to measure the CH_3OH synthesis activity for a series of binary Cu/ZnO catalysts. This allowed us to test the reactor and chromatographic analysis system for a simple reaction, before starting experiments with higher alcohol synthesis on multi-component catalysts. The literature debate over the nature of the active site in the binary catalysts had also intensified at this time.

In this work we studied a set of catalyst compositions with Cu : ZnO ratios between 20 : 80 and 80 : 20. In addition, we compared three catalysts with Cu : ZnO = 30 : 70 that were prepared by different co-precipitation procedures. The latter experiments, which were performed first, showed that catalysts with the highest Cu surface area are obtained when the precipitation step is done by simultaneous addition of the mixed Cu and Zn nitrate solution with the Na_2CO_3 solution. All of the remaining composition ratios were prepared using the simultaneous precipitation sequence.

In general, we found that the rate of CH_3OH synthesis correlates well with the measured Cu surface area. The BET area, the Cu surface area, and the CH_3OH synthesis activity all reach their maximum value at compositions between 20 and 40 mol% Cu. The activity reaches a maximum near 30 mol% Cu, in agreement with the results of Herman et. al. (18). However, the maximum is not as sharp as reported by those authors. Moreover, the CH_3OH activity changes in parallel with the Cu surface area, which is at variance with the results reported in (18). The slope of the correlating straight line fit is 0.04 +/- 0.013 gm CH_3OH / m^2 Cu / hr. This lies well within the range reported for other supported Cu catalysts; i.e., between 0.02 and 0.06 gm CH_3OH / m^2 Cu / hr (22).

We also performed H_2 and CO TPD experiments with this series of catalyst compositions. The peak temperatures for both adsorbates agreed very well with the results on the low surface area Cu/ZnO catalysts described above, which we attributed to adsorption on high index planes of Cu. In addition, there is no evidence for a CO desorption state above 350K. This appears to be in conflict with previous reports of irreversibly bound CO adsorption sites on co-precipitated Cu : ZnO catalysts (23).

These results are a promising indication of our ability to correlate activity with specific surface area. In the future, it would be useful to perform adsorption measurements on the same samples used for the kinetic experiments, immediately after they are relieved from reaction conditions.

Reaction kinetics of the CH_2O intermediate (Year 2). During this period we also studied the kinetics of CH_2O hydrogenation, in order to obtain further insight into the mechanism of kinetics the more complex CH_3OH synthesis reaction. These experiments were performed using reaction conditions of 1 atmosphere total pressure, with CH_2O being supplied to the reactor using a H_2 : He carrier gas mixture that had passed through a bed of powdered paraformaldehyde held at elevated temperature. Yield vs. temperature results (i.e., "light-off curves") showed that the conversion of CH_2O reached 100% at 400K on the Cu : ZnO catalysts, vs. 500K on pure ZnO. This confirms the essential role of Cu in these catalysts.

The key result of this work was to show that CH_2O reacts primarily to form CH_3OH and CH_3OCHO, instead of decomposing to CO or CO_2. This shows that the maximum barrier in the overall potential energy surface for CO hydrogenation to CH_3OH via the adsorbed CH_2O intermediate must be located between the CO and CH_2O species. This implies that hydrogenation of the adsorbed CH_2O intermediate cannot be the rate limiting step in CH3OH synthesis. Instead, the rate limiting step must be the formation of the adsorbed CH_2O intermediate. This step must involve hydrogenation of either a formyl or formate intermediate on the surface.

We also developed a mechanism and rate expression to account for the observed yield vs. conversion results for CH_3OH and CH_3OCHO. It appears that the surface is saturated with adsorbed CH_2O and CH_3O species that are in equilibrium with their gas phase CH_2O and CH_3OH counterparts. At low conversion the main reaction is hydrogenation of adsorbed CH_2O to produce new CH_3OH, while at higher conversion the bimolecular reaction between the two surface species takes over, producing CH_3OCHO as the main reaction product. The resulting rate expression for the conversion of CH_2O is zero order in CH_2O, while the rate expression for the formation of CH_3OCHO is first order in CH_3OH and negative first order in CH_2O.

Adsorption studies of Cu : Co catalysts (Year 2). The goal of our selective area chemisorption experiments is to determine the number of Cu and Co adsorption sites on these catalysts, whether these sites are segregated into domains of the respective pure metal or homogeneously distributed as a bimetallic alloy surface, and how the adsorption properties of the sites are influenced by their composition and morphology.

The most thorough set of adsorption experiments was performed with the 20Cu : 20Co : 20ZnO : $40Al_2O_3$ catalyst. A limited number of experiments with the corresponding K-promoted catalyst showed no qualitative difference in the peak temperatures for either H_2 or CO desorption.

For H_2 adsorption, the most informative set of experiments were those where the adsorption temperature was varied. All of the experiments gave nearly identical H_2 desorption peaks at 310K, which our earlier work showed can be assigned to H_2 desorption from a metallic Cu component. In addition, the experiments in which the H_2 adsorption step is performed above 300K produce a second peak around 450-500K. Both the peak temperature and integrated area of this peak increase with increasing adsorption temperature. This state is assigned to H_2 desorbing from the Co component of the catalyst, by analogy with the temperature dependent H_2 adsorption behavior reported by Zowtiak et. al. (25) for unpromoted Co/Al_2O_3 catalysts.

The amount of H_2 adsorbed on the Cu component is estimated to increase from 30 to 41 µmole H_2 / gram of catalyst over the range of adsorption temperatures from 300 to 450K. In contrast, the amount of H_2 adsorbed on the Co component increases to 54 and 87 µmole H_2 / gram catalyst when adsorption is performed at 390 and 450K, respectively. Thus there are substantially more H_2 adsorption sites on Co atoms than on Cu atoms. As noted above, however, only a small fraction of the total Cu surface sites adsorb H_2. This means that the total number of Cu sites may be larger than the number of Co sites.

The CO desorption experiments confirm this result. The major desorption feature is a well-resolved peak at 200K with a somewhat less intense shoulder extending to 300K. Desorption states over this temperature range were observed for the various binary Cu : ZnO catalysts discussed above, which leads us to assign the low temperature features on the present catalysts to desorption from Cu sites. A smaller peak is observed at 450K which we assign to CO desorbing from Co sites. The amount of CO desorbing from Cu sites is 125 μmole / gm catalyst when the adsorption step is performed at 200K, and decreases to 100 μmole / gm catalyst when adsorption is performed at 390K. Over the same temperature range, the amount of CO desorbing from Co sites increases from 19 to 62 μmole / gm catalyst. Thus the number of Cu sites is greater than the number of Co sites.

The IR spectra of adsorbed CO at 150K on this catalyst contain peaks at 2090 and 2060 cm^{-1} and a broad feature around 2000 cm^{-1}. The larger peak at 2090 cm^{-1} is assigned to CO adsorbed on high Miller index Cu planes, while the peak at 2060 cm^{-1} is consistent either with CO adsorbed on low index Cu planes or on highly dispersed Co atoms (26). As the sample is warmed the peaks at 2090 and 2060 cm^{-1} disappear by 300K, which confirms that they are associated with the low temperature peaks in the TPD spectra assigned to desorption from Cu sites. The remaining, broad feature shifts slightly and becomes well-resolved at 1974 cm^{-1}. As the sample is warmed further to 390K, the band shifts to 1956 cm^{-1}. The peak disappears completely at 590K. This temperature behavior is consistent with the high temperature peak in the TPD spectra, so that we may assign this lower wavenumber band to CO adsorbed on the Co component of the catalyst.

A more thorough analysis of the adsorption uptake results summarized here leads to estimated specific surface areas of 30 m^2 Cu / gm catalyst for the Cu component and 7 m^2 Co / gm catalyst for the Co component. The former result is similar to the Cu surface area in the binary Cu : ZnO catalysts discussed above. The ratio of H_2 and CO uptake on the Co component can be compared to results reported by Reuel and Bartholomew (26), which leads to the conclusion that the dispersion of the Co component is low on these catalysts.

Rate measurements of higher alcohol synthesis (Year 3). The kinetic experiments were done with the 20Cu : 20Co : 20ZnO : $40Al_2O_3$: 0.5K catalyst described above (26). We performed the experiments using a continuous flow, tubular microreactor operated at integral conversion. The reaction conditions were fixed at 563K, 50 atm total pressure, and H_2 : CO = 1 : 1. We obtained results in the form of yield vs. W/F measurements for each component in the product stream. (For the CO and H_2 components, the results take the form of conversion vs. W/F).

The rate of CO conversion at these conditions was 6 mmol CO / gm catalyst / hr. This is roughly two-thirds of the rate reported by Courty et. al. (13) for a Cu : Co : Zn : Al_2O_3 : Na catalyst at 563K, 60 atm total pressure, and H_2 : CO = 2 : 1 . This confirms that we are able to prepare active catalysts.

The selectivity can be analyzed in two ways; i.e., in terms of the functionality of the product molecules (e.g., methanol, higher alcohols, and hydrocarbons), and also in terms of the chain length distribution of products of a specific functionality. The rate of CH_3OH formation was 0.5 mmol / gm catalyst / hr, which is significantly lower than the value of 1.8 mmol / gm catalyst / hr reported by Courty et. al. (13). The overall selectivity for CO conversion into CH_3OH on our catalyst is about 8%, vs. about 20% for those authors.

We can also analyze our results in terms of the relative rate of CO hydrogenation to produce CH_3OH vs. the rate of CO dissociation to begin growing adsorbed hydrocarbon chains. These rates correspond to the selectivity factors γ and $(1-\gamma)$ defined by Sachtler (10). We obtain a value of $\gamma = 0.23$, vs. the value $\gamma = 0.065$ reported there for a promoted Rh catalyst at low pressure conditions.

The rate of CO conversion into higher alcohols is 3 mmol CO / gm catalyst / hr. This corresponds to a molar selectivity of about 50%, which is comparable to the values reported by Courty et. al. (13). The rate of formation of individual alcohols (i.e., C1-OH through n-C6-OH) could be analyzed on a Schulz-Flory-Anderson plot, which gives a value of $\alpha = 0.71$ for the chain propagation factor. This is larger than the value of $\alpha = 0.4$ reported by Sachtler (10) for his promoted Rh catalyst. It is also higher than the value of $\alpha = 0.45$ reported by Courty et. al. (13) for hydrocarbon products on their Cu : Co : Al_2O_3 catalysts.

We also observed that the selectivity toward higher alcohol products decreased at higher W/F values. Specifically, we found that the ratio of the yield of an individual higher alcohol to the yield of all products having longer chain length decreased from around 0.5 to around 0.25 over the range of W/F values studied. Using Sachtler's nomenclature, this corresponds to values of the selectivity factor for alcohol chain termination, β_i, that decrease from 0.33 to 0.20. These are similar to the values reported for the promoted Rh catalyst; i.e., $\beta_1 = 0.44$, $\beta_2 = 0.36$, and $\beta_3 = 0.21$ (10). One difference from the results for the Rh catalysts is that on our Cu : Co catalysts the values of β_i for individual alcohol chain lengths measured at a fixed value of W/F are closer together; i.e., the alcohol selectivity is less strongly dependent on chain length.

To obtain additional information about the reaction mechanism, we performed two groups of separate experiments. The first group was intended to help understand the decrease in alcohol selectivity noted above. We had previously observed that the alcohol selectivity is low during the first several hours on stream for a newly prepared catalyst. Since the reaction conditions provide a more strongly reducing environment than is used during the formal reduction step, this suggests that the catalyst is incompletely reduced when the reaction mixture is first introduced. To confirm the influence of the catalyst oxidation state, we deliberately oxidized a sample in flowing O_2 after measuring its steady-state activity and then re-started the reaction mixture. We found that the CH_4 yield was markedly increased and the higher alcohol yield decreased for a transient period of several hours. Additional work is needed to measure the magnitude of this effect quantitatively.

We also tested the earlier supposition that the reaction mechanism on these catalysts proceeds via the homologation of CH_3OH and subsequent alcohols. The results of adding either CH_3OH or C_2H_5OH to the reactant stream had a much smaller effect on the exit concentration of higher alcohols than did simply increasing the residence time. Although measureable rates of both bi-molecular condensation reactions and CO carbonylation reactions could be detected at high inlet alcohol concentrations, neither process contributes the major part of the chain growth mechanism at the present conditions. This result also confirms that the Cu : Co catalyst is not an example of a bi-functional catalyst system; i.e., CH_3OH that is produced on Cu sites does not subsequently undergo homologation at separate Co sites. Our results do not rule out CO insertion as the primary chain propagation step for surface intermediates, since the latter is postulated to involve surface alkyl groups.

Future needs

We have performed a number of experiments which now point the way for systematic study of the direct synthesis of higher alcohols on these multi-metallic Cu : Co catalysts. For example, we have identified both H_2 and CO chemisorption as techniques for distinguishing Cu and Co surface sites in these catalysts. Additional experiments using catalysts with different Cu : Co ratios are needed to determine whether any site interaction effects due to alloy formation can be resolved. The specific surface area measurements should also be correlated with catalyst activity and selectivity. Both measurements should be made using the same sample, preferably without exposing the sample to air between the kinetic measurements and the surface characterization. We have shown that the reaction mechanism proposed by Sachtler for CO hydrogenation on promoted Rh catalysts can also be applied to the reaction on Cu : Co catalysts. Further work is needed to obtain more accurate measurements of individual selectivity parameters, and to correlate these parameter values with changes in specific surface area and other physical properties of the catalyst.

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In print:

"Formaldehyde Conversion to Methanol and Methyl Formate on Copper/Zinc Oxide Catalysts"; Mueller, L. L.; Griffin, G. L. J. Catal. 105, 352 (1987).

"Temperature-Programmed Desorption and Infrared Study of CO and H_2 Adsorption on Cu/ZnO Catalysts"; Roberts, D. L.; Griffin, G. L. J. Catal. 110, 000 (1988).

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"Methanol Synthesis Activity of Cu/ZnO Catalysts". Pan, W. X.; Cao, R.; Griffin, G. L. J. Catal (Accepted 3/18/88).

"Direct Synthesis of Higher Alcohols Using Bimetallic Copper/Cobalt Catalysts". Cao, R.; Pan, W. X.; Griffin, G. L. LANGMUIR (Submitted 12/3/87).

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