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DIRECT ALCOHOL SYNTHESIS USING MODIFIED COBALT CATALYSTS: FINAL PROJECT REPORT COVERING THE PERIOD 7/15/85-7/14/87

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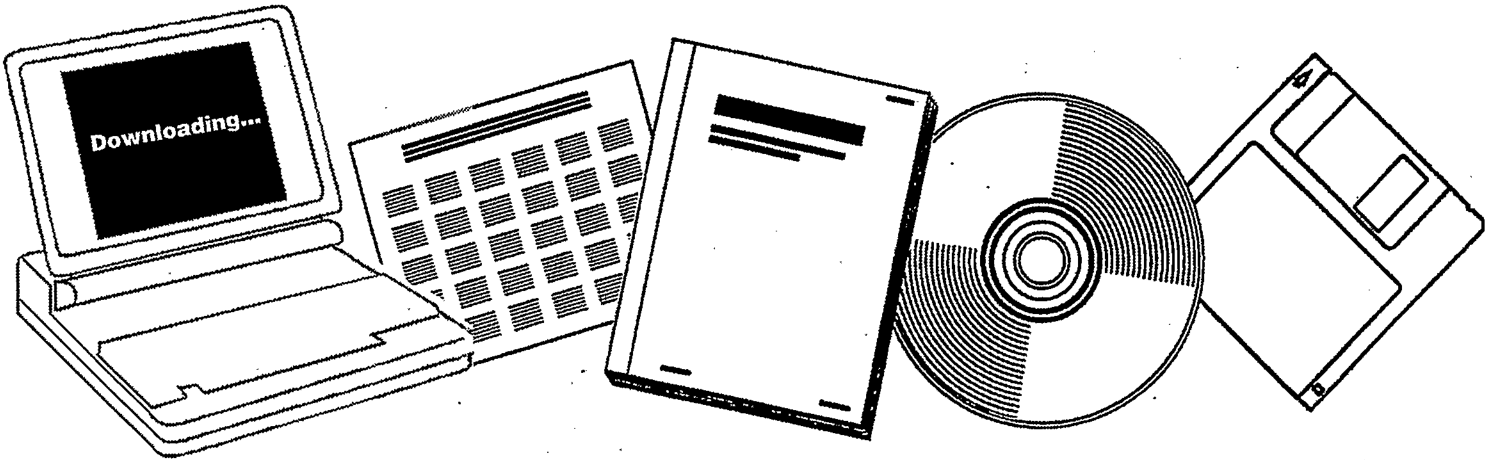

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MASTER

ABSTRACT

We have studied the preparation and characterization of mixed Cu-Co-ZnO catalysts, and tested the activity of these catalyst for direct synthesis of methanol and higher molecular weight alcohols. Our primary goal is to understand and control the factors which determine the selectivity of these catalysts. We have prepared a series of binary and ternary compositions using both sequential and simultaneous precipitation methods, both with and without alkali promoters. We have used temperature programmed desorption techniques to measure the concentration and adsorption energy of sites on the individual components of the catalyst surface, using H_2 and CO as adsorbates. Work completed to date has shown that both adsorbates are useful for correlating the CH_3OH synthesis activity of Cu/ZnO binary catalysts. Experiments have also shown that the CH_3OH synthesis activity of the binary catalysts correlates with Cu surface area, which in turn is sensitive to the precipitation method used to prepare the catalysts. We have also performed mechanistic studies which show that the rate limiting step in CH_3OH synthesis must be the hydrogenation of either the formyl or formate intermediate.

CONTENTS

INTRODUCTION

The direct synthesis of methanol and higher alcohols from CO-H_2 synthesis gas mixtures is potentially an important technology for maintaining this nation's supply of liquid transportation fuels (Courty, 1987). Despite the recent fall in oil prices, there is continued concern about the possibility of another United States "energy crisis" within the next decade (Hirsch, 1987; Basslev, 1986). Moreover, existing pressure on refinery octane capacity has led to increased use of a variety of oxygenated hydrocarbons as blending agents for enhanced octane numbers (Anderson, 1986; Othmer, 1985; Short, 1985; Kliagebiel, 1986).

Manufacture of the simplest oxygenated hydrocarbon, methanol, is a well-established technology (Meyers, 1984), although there continues to be discussion about both the catalyst and reaction mechanism (Klier, 1982) and the optimum commercial reactor configuration (Makihara, 1987). The Cu/ZnO based catalysts used for this process are capable of selectively hydrogenating the CO molecule to produce CH_3OH (e.g., with yields in excess of 99%), without allowing it to dissociate and react to produce CH4 or longer hydrocarbons. However, the attractiveness offered by the selectivity of the CH_3OH synthesis process is at least partially offset by regulations which limit the amount of CH_3OH that can be used in gasoline blends (Othmer, 1985). Thus there is also incentive to develop processes for the direct manufacture of longer chain alcohols, which can be blended into gasoline in higher concentrations.

The catalysts which have been studied to date for the higher alcohol synthesis reaction can be classified into four groups:

i) Alkali metal promoted Cu/ZnO catalysts which produce ethanol, n-propanol, and 2-methyl propanol, apparently via a base-catalyzed aldol condensation mechanism (Smith 1983);

ii) Sulphided Mo catalysts reported by researchers at Dow, which give C_2-C_5 alcohol selectivities of up to 70-80% (Dianis, 1987);

iii) Rhodium-based catalysts using either rare-earth oxide supports (Keim, 1987) or with various transition metal promoters (Sachtler, 1984; Bastein, 1987; Orita, 1984) which are relatively selective for C_2H_5OH synthesis;

iv) Alloy catalysts which contain cobalt in combination with one or more additional transition metals, and which yield a Fischer-Tropsch distribution of C_2-C_6 alcohols (Courty, 1987; Takeuchi, 1985; Holy, 1985; Lisitsyn, 1985; Fujimoto, 1985).

Of these four groups of catalysts, the system under development by IFP-RAPAD appears to be the closest to commercial development, having reached the level of a 7000 bbl/y demonstration plant in Chiba, Japan (Courty, 1987). The catalyst itself is a complex mixture which contains Cu, Co, Al or Cr, Zn, and an alkali metal. Although a number of results have recently been published concerning both the catalyst (i.e., its preparation, composition, morphology, activity, and selectivity) and its incorporation into an overall process design (Courty, 1983; 1987), the composition and structure of the active site(s) and the limiting factors in the preparation procedures which determine the concentration of these sites are still unknown. Thus it is likely that fundamental research in this direction can lead to improved preparation methods for the catalyst, and possibly to catalysts with either higher overall activity or selectivity.

A related question concerns the mechanism(s) of the alcohol synthesis reactions on these catalysts. The observed Schulz-Flory distribution of alcohol chain lengths suggests that the mechanism for chain growth is similar to that for conventional Fischer-Tropsch catalysts; i.e., the sequential formation of new C-C bonds by the repeated addition of a partially hydrogenated 1-carbon intermediate to a growing alkyl chain. Following a model described by Sachtler (1984), the selectivity to alcohol products is determined at the point of the chain termination step, which is postulated to be an insertion reaction with molecularly adsorbed CO. Some as-yet undetermined feature of the modified Co surface enhances the rate of this reaction, relative to simple hydrogenation.

In contrast, CO adsorbs molecularly on Cu surfaces, which means that CH_3OH is the largest hydrogenation product that can be produced on the Cu component of these catalysts. In order to design catalysts which will yield a increased ratio of higher alcohols to methanol, it will be helpful to understand the CH_3OH synthesis kinetics on both pure and modified Cu surfaces. Thus, mechanistic studies are also a useful part of our research program.

The basic strategy of our research is to correlate the preparation method, surface characteristics, and overall activity and selectivity for a series of catalysts, beginning with binary Cu/ZnO mixtures and progressing eventually to the complex Cu-Co-Al-Zn-alkali mixtures described above. Our progress during the past two years is described in section II of this document, which summarizes the results of three specific projects that have been submitted and/or accepted for publication.

II. RESULTS TO DATE

Adsorption studies of H_2 and CO. Our first project during the current year was a combined infrared - temperature programmed desorption study of H_2 and CO adsorbed on binary Cu/ZnO mixtures prepared by various methods. The information provided by this study includes the concentration of adsorption sites, the adsorption energies of the probe molecules on these sites, and the configuration and local environment of the infrared-active adsorbed species. The results of this study of the binary Cu/ZnO system are an essential pre-requisite for the studies of the more complex Cu-Co-ZnO and Cu-Co-Al-ZnO systems which we will perform during the coming year.

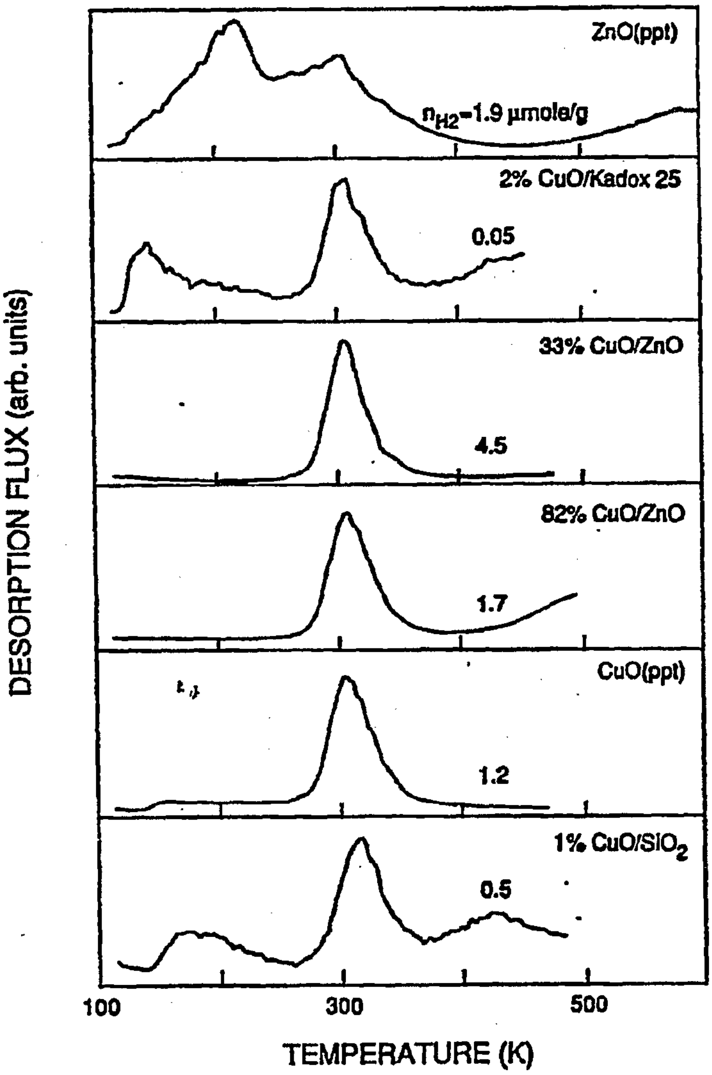
The IR-TPD studies were performed using a high vacuum IR cell which is attached to a gas handling system and computer-controlled mass spectrometer and data aquisition system. Using this system, we are able to adsorb volumetrically measured amounts of an adsorbate onto the sample, monitor the presence, configuration, and environment of the adsorbate (provided it has at least one IR-active vibrational mode), and measure the temperature and amount of adsorbate and/or decomposition products that leave the surface during the TPD experiment. As shown below, this combination of techniques has allowed us to separately measure the Cu and ZnO components of the binary catalysts.

H_2 desorption studies. A total of six materials are compared in this study. Four samples were prepared using the precipitation method described by Herman et. al. (1987). This consists of precipitation by dropwise addition of $NaCO_3$ solution to mixed $Zn(NO_3)_2$ and/or $Cu(NO_3)_2$ solutions, followed by filtering and drying of the precipitate, then calcining in air at 623K for 16 h, and finally reducing in flowing H_2 (1 atm) at 483K for 16 h. The four samples include pure ZnO, 33 wt% CuO/ZnO, 82 wt% CuO/ZnO, and pure CuO. The copper content of the mixed catalysts was confirmed using atomic absorption spectroscopy. The other two samples were prepared as supported metal catalysts: A 2 wt% CuO/ZnO catalyst was prepared by impregnating Kadox 25 ZnO (Gulf Western Natural Resources, B.E.T. area 10 m^2/g) with $Cu(NO_3)_2$ solution, drying, calcining, and reducing. A 1 wt% CuO/SiO_2 catalyst was prepared in a similar fashion using Aerosil 380 SiO_2 (Degussa, B.E.T. area 380 m^2/g).

The TPD spectra for H_2 on these six materials in their reduced state are shown in Fig. 1. The spectra are shown normalized to the same height; the actual H_2 uptake is indicated above each curve. The curve for ZnO (prepared by precipitation) shown at the top of the figure was obtained only after heating the sample above 600K to desorb H_2O. Spectra for all of the other samples could be obtained after a reduction step at 523K; if the ZnO sample was reduced only at this temperature, no H_2 adsorption occurred.

The desorption curve for ZnO is similar to that reported for H_2 desorbing from Type I sites on other ZnO samples (Griffin 1982b), with the major desorption peak occurring at 210K and a smaller peak occurring at 310K. For all of the copper-containing samples in the reduced state, the major H_2 desorption peak also occurs at 310K. Although this temperature is the same as the most stable H_2 state on ZnO, the peak at 310K on the Cu-containing samples can definitively be assigned to H_2 desorbing from the Cu component, for three reasons:

i) The lower outgassing temperature required to obtain H_2 TPD spectra on Cu catalysts is not sufficient to activate H_2 adsorption site on ZnO.



TPD SPECTRA OF 40 Torr H_2 ADSORBED ON REDUCED Cu CATALYSTS

Figure 1

ii) The presence of the 310K peak on the Cu/SiO_2 samples cannot be due to desorption from ZnO sites.

iii) If the Cu-containing catalysts are heated in O_2 in order to oxidize the Cu component, the temperature of the H_2 desorption peak in subsequent TPD spectra increases to 400K. In contrast, oxidation has no influence on the H_2 desorption spectrum of ZnO.

<u>CO desorption studies</u>. The TPD spectra of CO for the same catalysts are shown in Figure 2. The adsorption step is performed at 150K with a small background pressure of CO in the cell, followed by evacuation with the sample kept at 150K. This adsorption procedure saturates all of the CO adsorption sites that have binding energies greater than the heat of condensation of CO, while minimizing the contribution of non-specific, physically adsorbed CO to the TPD spectrum.

For pure ZnO there is no chemisorbed CO state unless the sample is pre-treated by outgassing at 673K (cf. the behavior of Type I adsorption sites discussed above). For Cu-containing samples, a broad desorption spectrum is observed which has resolvable peaks at 170K, 210K, and 280K. These temperatures correspond to desorption energies of 10, 12, and 16 kcal/mole, respectively, in agreement with our earlier published results (Roberts 1984). These energies are comparable to or slightly greater than values determined for CO adsorption on low-index planes of Cu single crystals.

The absence of any CO desorption states at significantly higher temperatures appears to be in conflict with earlier reports of exceptionally strong CO adsorption sites in co-precipitated Cu/ZnO catalysts (Klier 1982). We did observe that the upper temperature limit of the CO desorption spectrum increased to 330K if the Cu catalysts were oxidized before

TPD SPECTRA OF CO ADSORBED
ON REDUCED Cu CATALYSTS

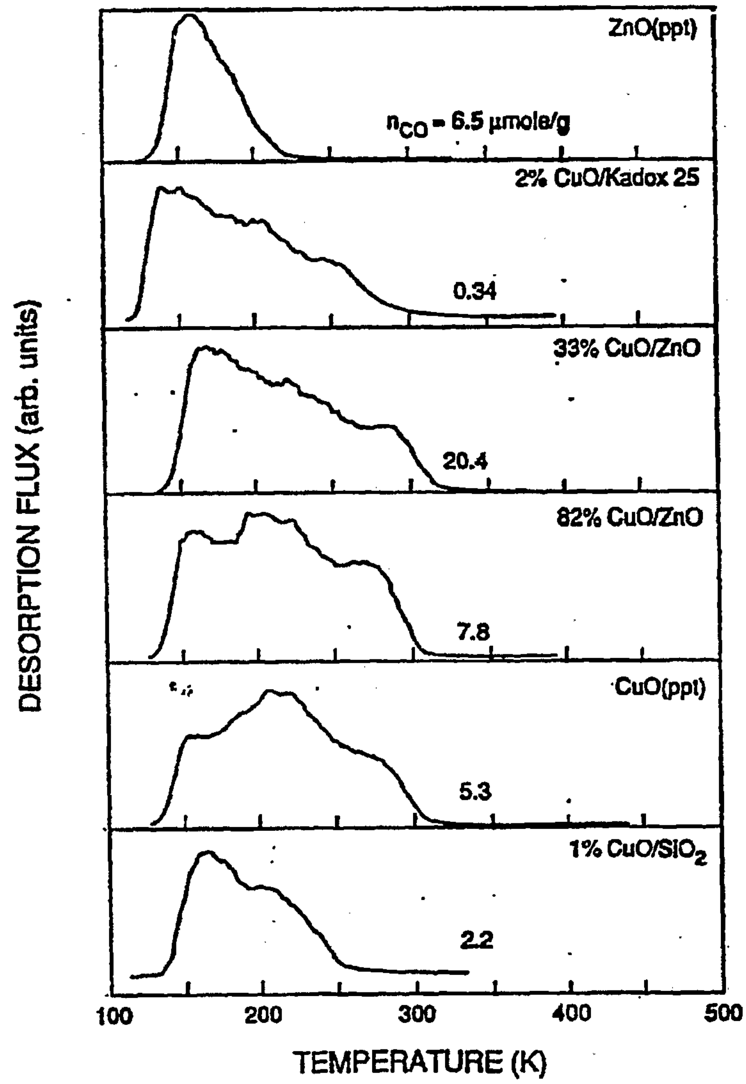


Figure 2

performing the CO TPD experiment. This highest temperature state is sufficiently stable to remain adsorbed for short periods at 300K, so that it may correspond to the strongly bound CO state reported by earlier authors.

Preliminary results for the cobalt-containing catalysts show the existence of a much more strongly bound CO adsorption state. This state desorbs at 500K, corresponding to a desorption energy of 24 kcal/mole. By comparison with the results for binary Cu/ZnO catalysts, it appears that this state can be assigned to the CO adsorbed on the Co component of the catalyst. During the coming year we hope to exploit this difference in CO binding energy to separately determine the surface area of the Co and Cu components in the ternary catalysts.

The IR spectra recorded before starting the TPD warm-up revealed the presence of several bands that could be assigned to CO adsorbed on various Cu sites. On reduced samples, the strongest band occurs at 2100 cm^{-1}, with weaker shoulders observed as low as 2065 cm^{-1}. Comparison with earlier studies of CO adsorbed on different Cu crystal planes and polycrystalline foils (Sheppard 1978) suggests a morphological model for Cu/ZnO catalysts in which the Cu is present as clusters which expose a significant fraction of high index crystal planes.

Finally, we compared the H_2 and CO uptakes determined from the TPD experiments with the amount of irreversible O_2 chemisorption at 98K (c.f., one of several conventional methods for determining Cu surface area in supported catalysts). The ratio of the adsorption stoichiometries is $H_2/CO/O_2$ = 1/4/4. The CO/O_2 ratio is consistent with earlier reports, while the H_2/O_2 ratio is surprisingly low. This suggests that only a small fraction of the high-index planes exposed on the Cu clusters in these catalysts may be active for H_2 adsorption.

II.2 CH_3OH synthesis activity of binary catalysts. Our second project during the current year was to measure the CH_3OH synthesis activity of the catalysts described above, as well as a second group of catalysts prepared using a modified precipitation procedure. These kinetic studies were performed in a high pressure plug flow tubular reactor which can operate up to 50 atm. Product composition was determined by gas chromatography.

Influence of preparation method. When the O_2 uptake measurements were performed for the catalyst series described above, it became apparent that the surface area of the Cu component in every sample was significantly lower than typically reported values. Therefore we experimented with two other preparation methods for making the binary 30 wt% CuO/ZnO catalyst. In one case, the precipitation step was effected by adding the mixed $CuNO_3$ + $ZnNO_3$ solution into well-stirred $NaCO_3$ solution (i.e., precipitation takes place at high pH), while the other catalyst was prepared by adding both solutions simultaneously to a well-mixed beaker (i.e., precipitation at intermediate pH).

The surface areas of the three 30 wt% CuO/ZnO catalysts produced by the different methods are compared in the first part of Table I, along with the rate of CH_3OH synthesis extrapolated to the inlet conditions. The BET surface of the catalyst produced by the original method is only 14 m^2/gm, while the two alternate methods lead to areas of 47 and 52 m^2/gm, respectively. An even more pronounced difference is seen in the Cu surface area, as determined by low temperature O_2 chemisorption. Using an assumed adsorbate coverage of 4.9×10^{-6} mole O_2 per m^2 of Cu, the Cu sur-

TABLE I

CH_3OH Synthesis Activity of Cu/ZnO Catalysts

Catalyst Composition	Preparation Method	BET Area (m^2/gm)	Copper Area (m^2/gm)	Initial CH_3OH Rate (gm/gm/hr)
I. Preparation method				
33:67	Low pH	14	0.9	0.07
30:70	High pH	47	26	0.8
30:70	Simultaneous	52	48	1.9
II. Composition				
20:80	Simultaneous	66	33	1.0
30:70	"	51	48	1.9
40:60	"	50	49	1.6
50:50	"	49	36	2.1
66:34	"	34	29	1.3

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30:70	"	51	48	1.9
40:60	"	50	49	1.6
50:50	"	49	36	2.1
66:34	"	34	29	1.3

face areas for these samples are 1, 26, and 48 m^2/gm, respectively. Differences are also apparent in the CH_3OH synthesis rate measured for each catalyst, with the samples prepared by precipitation at high or neutral pH showing much greater activity than the sample prepared at low pH.

The H_2 and CO TPD spectra measured for catalysts prepared using the alternate methods showed desorption peaks at the same temperatures as for the low surface area materials described in section II.1. This indicates that the various precipitation methods produce sites with similar adsorption properties, but in different concentrations.

Influence of composition. In view of the much greater surface areas obtained by the simultaneous addition method for the precipitation step, we decided to evaluate the entire range of useful Cu/Zn composition ratios. The surface areas of the new samples are listed in the second section of Table I. Both the BET surface area and the Cu surface area reach their maxima at a composition ratio somewhere between 30 and 40 at% CuO. For composition ratio greater than this, the Cu surface area calculated using the commonly assumed O_2 adsorption stoichiometry is quite close to the measured BET surface area. This suggests that the Cu component may actually "coat" the ZnO component of these catalysts, or else that a higher adsorption stoichiometry occurs on these high surface area catalysts. Additional work is needed to resolve this issue.

The synthesis activity of all of these catalyst is quite similar, in contrast to earlier results which suggested that activity shows a well-defined maximum at around 30 wt% CuO/ZnO (Klier, 1982). The values of the ratio of synthesis activity to Cu surface area for the five compositions listed in part II of Table I have an average of 0.04 ± 0.013 gm CH_3OH/m^2 Cu/hr. This agrees with the specific activity of 0.03 ± gm/m^2/hr reported by Chinchen et. al. (1986) for Cu-based catalysts using several different support materials.

II.3 Hydrogenation of CH_2O. The third project competed during the current year was a study of the hydrogenation kinetics of CH_2O. This study was performed to improve our understanding of the mechanism of the CH_3OH synthesis reaction. Numerous earlier studies have reported rate expressions for the reaction that contain a factor of $(P_{CO}P_{H2}^2)$ raised to some power (Denny, 1978; Saida, 1964), which has led to the suggestion that the rate limiting step is the addition of the final $H_{(a)}$ atom to the $CH_3O_{(a)}$ intermediate; i.e., the desorption of CH_3OH. However, Vedage and Klier (1982) reported that the C=O double bond in 1-propanal is hydrogenated much faster than CO (cf., the initial reactant in CH_3OH synthesis from syngas). We suspected that a similar result would hold for CH_2O hydrogenation as well, which would refute the suggestion that CH_3OH desorption is the RLS in CH_3OH synthesis.

Most of these experiments were performed using a separate 1-atmosphere reactor system assembled specifically for the CH_2O experiments. Hydrogen and helium from separate cylinders are mixed and fed through a CH_2O generator, which consists of a tube containing ca. 1 gm of paraformaldehyde powder. The generator releases a constant flux of CH_2O vapor when warmed slightly (ca. 368 K). The composition of the reactant stream before and after passing through the reactor was measured using a gas chromatograph. The inlet composition of the reactant mixture was P_{CH2O} = 0.3 kPa and P_{H2} = 101 kPa. Measured products included CO, CO_2, CH_3OH, CH_3OCHO, and CH_2O.

Measurements were performed using Kadox 25 and 1 wt% Cu/ZnO (Kadox 25) prepared by impregnation. The latter catalyst is about two orders of magnitude more active, confirming the dominating influence of the Cu component. Figure 3 shows the CH_2O conversion and CH_3OH and CH_3OCHO product yields as a function of temperature. The conversion rises sharply between 420 and 440K, which is almost 100K lower than the temperatures typically required for CH_3OH synthesis. This in itself does not prove that CH_2O hydrogenation cannot be the RLS for CH_3OH synthesis, since this result would have to be extrapolated to the CH_2O concentration expected under synthesis reactor conditions. However, the fact that only minor amounts (less than 10%) of the CH_2O decomposition products CO and CO_2 are produced is proof that CH_2O hydrogenation cannot be the RLS in CH_3OH synthesis at these conditions, based on the following reasoning:

The physical significance of the RLS for a sequential, reversible reaction mechanism at steady state is that it represents the elementary step whose forward and reverse rates are most dissimilar. This implies that the intermediate which is produced by the RLS will have a (reverse) decomposition rate which is slower than the forward rate of any subsequent elementary step. Since CO and CO_2 are produced in much smaller yields than either CH_3OH or CH_3OCHO, this means that CH_2O hydrogenation cannot be the RLS for either of the latter products.

Instead, we suggest that the RLS for CH_3OH synthesis will be the $HCOO_{(a)}$ hydrogenolysis step:

$$HCOO_{(a)} + 2\,H_{(a)} \dashrightarrow CH_2O_{(a)} + HO_{(a)} \qquad (1)$$

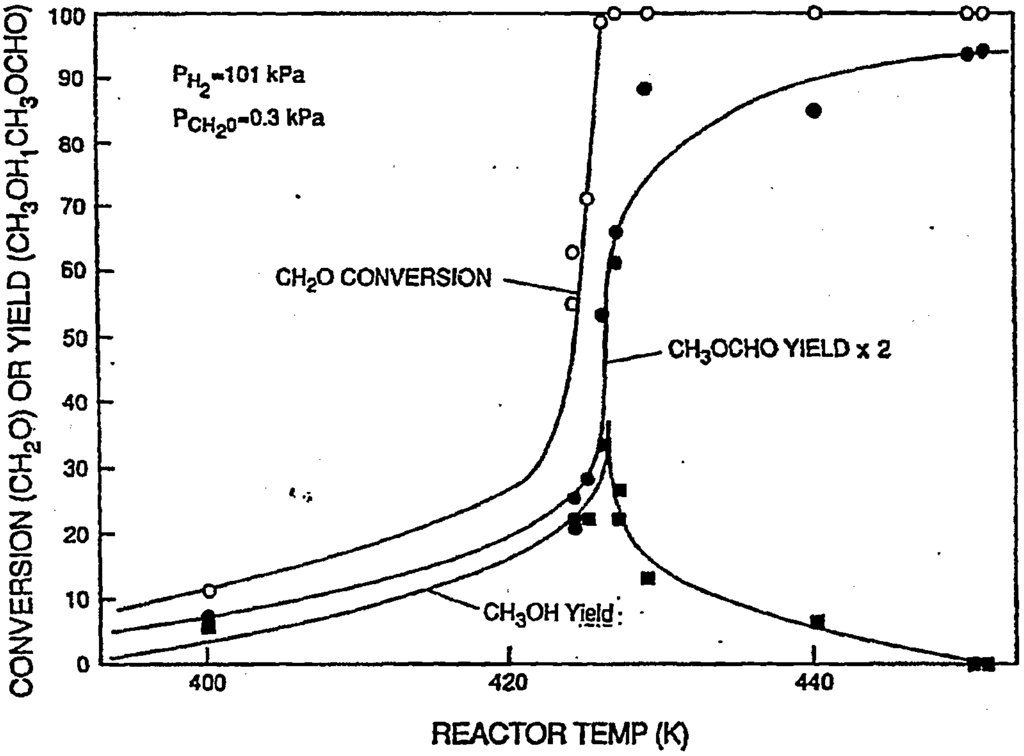
PRODUCT YIELDS DURING CH_2O HYDROGENATION: INFLUENCE OF TEMPERATURE
P_{H_2}=101 kPa
P_{CH_2O}=0.3 kPa
CH_2O CONVERSION
CH_3OCHO YIELD x 2
CH_3OH Yield
CONVERSION (CH_2O) OR YIELD (CH_3OH, CH_3OCHO)
0
10
20
30
40
50
60
70
80
90
100
400
420
440
REACTOR TEMP (K)

Figure 3

This suggestion is examined more carefully in our published discussion (Mueller 1987).

As a separate observation, the behavior of the CH_3OH and CH_3OCHO yields in Fig. 3 suggests that these species are respectively the primary and secondary products of a series reaction network:

$$CH_2O + H_2 \longrightarrow CH_3OH \qquad (2)$$

$$CH_2O + CH_3OH \longrightarrow CH_3OCHO + H_2 \qquad (3)$$

This was confirmed in a separate series of experiments in which the flow rate was varied. These experiments also showed that CH_2O conversion varies almost linearly with W/F_{Ao} up to 100% conversion, which implies that CH_2O conversion obeys zero order kinetics, and that the rate of CH_3OCHO production actually increases with decreasing CH_3OH concentration. The simplest reaction network that can reconcile these results involves the formation of competitively adsorbed $CH_2O_{(a)}$ and $CH_3O_{(a)}$ species which may undergo either direct hydrogenation or else bimolecular condensation. The simplified rate expressions that follow from this mechanism have the form:

$$r_1 = k_1 \qquad (4)$$

$$r_2 = (k_2 K_{Me}/K_F)\,(P_{Me}/P_F) = k_2'\,(P_{Me}/P_F) \qquad (5)$$

Parameter estimates of k_1 = 17 mole/gm/hr and k_2' = 70 mole/gm/hr were determined by regression analysis of the measured product yields using the integrated forms of equations 4 and 5.

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