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Alcohol Synthesis from CO/H_2 over $Co/Cu/ZnO/Al_2O_3$: *In Situ* Addition of CH_3NO_2

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A $Co/Cu/ZnO/Al_2O_3$ catalyst prepared by cobalt impregnation of a commercial methanol-synthesis catalyst was used to study the formation of alcohols from CO/H_2. The addition of cobalt selectively and significantly suppressed methanol formation without promoting the formation rates of higher alcohols. Co also poisoned the promoting effect of CO_2 on methanol formation, suggesting that the primary role of Co was to block the pathway for methanol formation from CO_2/H_2. The addition of nitromethane to $Co/Cu/ZnO/Al_2O_3$ suppressed the formation rates of all alcohols equally and produced substituted methylamines, probably by diverting the aldehydic intermediate for methanol formation. The equal suppression of C_1–C_3 alcohols observed during nitromethane addition suggests that the same intermediate was involved in the formation of methanol and higher alcohols over $Co/Cu/ZnO/Al_2O_3$. © 1995 Academic Press, Inc.

INTRODUCTION

Increased attention has recently been paid to the catalytic synthesis of higher alcohols from CO/H_2 over Co–Cu based catalysts (1–11). A fundamental understanding of the reaction mechanism is desirable from both an industrial and an academic point of view, but this is hampered by the complexity of the process, which involves multiple reaction pathways and various catalytic components. Different views on the mechanism of the formation of C_{2+} alcohols from CO/H_2 over this type of catalyst have been proposed in the literature, but a consensus has not been reached concerning either the reaction pathways (1–4) or the nature of the active sites (1–10).

The *in situ* addition of probe molecules has been demonstrated as a technique capable of providing important insights into catalytic reaction mechanisms in studies dating from the early 1950s (11–23). The probe molecule is added in an attempt either to generate the same surface species as the precursors or intermediates of the desired products or to react in a specific manner with active surface species. The pathway(s) through which the probe molecules or their fragments are incorporated into the products can then be deduced by analyzing the reaction products in the absence and in the presence of the probe molecule. An ideal probe molecule is one that can participate in the reactions occurring on the catalyst surface with minimal undesired effects, such as significant perturbation of the ongoing reaction or poisoning of surface sites. In previous work by our group (21–23), CH_3NO_2 was successfully used as a probe molecule to provide dynamic evidence of the active intermediates and reaction pathways for the formation of hydrocarbons in Fischer–Tropsch synthesis over supported Ru catalysts (24).

In the present work, CH_3NO_2 was selected again as a probe molecule to investigate the more complex reaction system of C_{2+} alcohol formation from CO/H_2 over a Co–Cu catalyst at high pressure and high temperature. The Co–Cu catalyst was prepared by impregnation of a commercial $Cu/ZnO/Al_2O_3$ catalyst with cobalt in an attempt to draw ideas from the knowledge obtained separately from the two different well-studied catalyst systems: Cu/ZnO based catalysts for methanol synthesis and Co as a Group VIII metal catalyst for hydrocarbon synthesis. BET surface area, X-ray diffraction (XRD), and temperature-programmed reduction (TPR) were applied to characterize the catalysts and to assist in understanding the role of Co and Cu in the synthesis of higher alcohols.

METHODS

Catalyst Preparation and Pretreatment

A $Co(5\%)/Cu/ZnO/Al_2O_3$ catalyst, designated 05Co-IW, was prepared by incipient wetness impregnation of a commercial methanol-synthesis catalyst (United Catalysts, Inc.) with an aqueous solution of cobalt nitrate, $Co(NO_3)_2 \cdot 6H_2O$, using a nominal weight loading of 5%. The impregnated sample was dried at 90°C overnight in air. The dried sample was calcined in O_2 (2% O_2 in He, 80 cc/min) at 400°C for 8 h after increasing the temperature

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TABLE 1

Catalyst Composition

	Composition (wt%)						
Catalyst	Co	Cu	Co_3O_4	CuO	ZnO	Al_2O_3	SiO_2
00Co-IW	—	43.9	—	55.0	36.0	8.0	1.0
05Co-IW	5.4	40.7	7.3	51.0	33.4	7.4	0.9
	Composition (at.%)						
	Co	Cu			Zn	Al	Si
00Co-IW	—	52.9			33.8	12.0	1.3
05Co-IW	7.1	49.2			31.4	11.1	1.2

from 25°C at 0.5°C/min. Prior to the CO hydrogenation reaction, the catalyst sample was reduced in dilute H_2 (5% H_2 in He, 80 cc/min) at 350°C for 8 h after increasing the temperature from 25°C at 0.5°C/min. A Co(0%)/Cu/ZnO/Al_2O_3 catalyst, designated 00Co-IW, was prepared as a base catalyst by performing an incipient wetness impregnation using HNO_3 instead of $Co(NO_3)_2 \cdot 6H_2O$ to obtain an aqueous solution with a pH value equivalent to that of the cobalt-containing sample. Subsequent treatments for 00Co-IW were the same as those for 05Co-IW. The composition of these two catalysts is given in Table 1.

Catalyst Characterization

BET surface area measurements were carried out on a standard static system using N_2 as the adsorption gas with the reduced samples of 00Co-IW and 05Co-IW. XRD experiments were performed on a Philips X'Pert system using a Cu$K\alpha$ source with both the calcined and the reduced samples of 00Co-IW and 05Co-IW. The reduced samples were passivated with O_2 (2% in He, 80 cc/min) at room temprature. TPR experiments were performed on a fixed-bed flow system (Altamira Instruments, Inc. AMI-1) using TCD detection for H_2 uptake measurements. Prior to TPR, the sample (about 60 mg/bed) was heated under flowing O_2 (5% O_2 in He, 30 cc/min) from 30 to 350°C at 5°C/min, held at 350°C for 8 h, and then cooled to 50°C. After the system was flushed with Ar (30 cc/min) at 50°C for 30 min, the flow was switched to 5% H_2 in Ar at 20 cc/min, and the temperature was increased at 1°C/min at 500°C. H_2 uptake by the catalyst during the reduction process was calculated based on the peak area of the TCD response vs time. The TCD response was calibrated with controlled pulse(s) of Ar into a stream of 5% H_2 in Ar (20 cc/min).

Reaction and Analysis

The reaction system has the capability of adding a controlled amount of probe molecule to the steady state reaction and analyzing the products on-line by both GC and MS. Detailed descriptions of the system and experimental conditions are given below.

Gas handling. H_2 (UHP, Liquid Carbonic Specialty Gas Co.) and CO (CP grade, Liquid Carbonic Specialty Gas Co.) were used as reaction gases. He (UHP, Liquid Carbonic Specialty Gas Co.) was used for pretreatments and blank tests. 4A molecular sieve traps (Linde) were installed on each gas introduction line to remove traces of H_2O. An activated carbon purifier (Scott) was used on the CO line to remove traces of hydrocarbons and metal carbonyls. Gas flow rates were controlled by mass flow controllers and measured with a bubble flow meter at the outlet. Compressed air (Ultra Zero, THC < 0.1 ppm, Liquid Carbonic Specialty Gas Co.), H_2, and He (the same as above) were used for GC analysis, with an oxygen trap (Scott Specialty Gases) on the H_2 line.

Reactor system and reaction conditions. The catalyst sample (50 ~ 500 mg) was placed in the center section of a fixed bed reactor (14" long, $\frac{3}{8}$" o.d. stainless steel tube) filled with glass wool. The reactant gas mixture was introduced from the top of the reactor and the reaction products exited from the bottom. The reactor was heated by an external shell furnace with a temperature-programmed controller. The temperature inside the reactor was measured by a thermocouple positioned directly beneath the catalyst bed. The system pressure was controlled by a back pressure regulator downstream from the reactor and measured by a pressure gauge upstream from the reactor. CO hydrogenation reactions were carried out at 500 psig, 290°C, $H_2/CO = 2$, total flow rate = 120 ± 2 cc/min, GHSV = 6000 ~ 60,000 h^{-1}. The total carbon conversion was maintained below 5% by varying the catalyst loading. Reaction products were typically analyzed after reaching steady-state operation, about 24 h after the start of the reaction as is typical in alcohol synthesis reactions (25).

Probe molecule introduction. The probe molecule, CH_3NO_2 (Aldrich, 99+%) was stored in a saturator immersed in a temperature-controlled bath. CH_3NO_2 was introduced to the steady-state reaction by diverting the flow of reactant mixture through the saturator. After a new steady state was achieved in the presence of CH_3NO_2, the probe molecule addition was stopped and the CO hydrogenation reaction was then continuously monitored to observe if the original steady state could be reestablished, as an indication of any poisoning effects introduced by the presence of the probe molecule.

Product sampling and analysis. A high-pressure, high-temperature, and chemical-resistant metering valve was installed on a line diverted from the reactor outlet before the first trap to allow a small gas stream flow to a GC sampling valve and an on-line mass spectrometer (Dycor Electronics Inc., M 100M). The GC (Varian 3000) was equipped with both FID and TCD detectors and with a Porapak-R and a Porapak-Q column in series. For confirmation of product identification, products from the outlet stream were collected during the reaction by two traps in series, cooled with ice in water. The traps were placed downstream after the metering valve and before the back pressure regulator. The liquid sample collected in the traps was analyzed after the reaction on a GC-MS (Extrel Series 800) using a DB-5 capillary column. All the lines from the reactor outlet to the on-line sampling section and the first trap were heated to avoid product condensation.

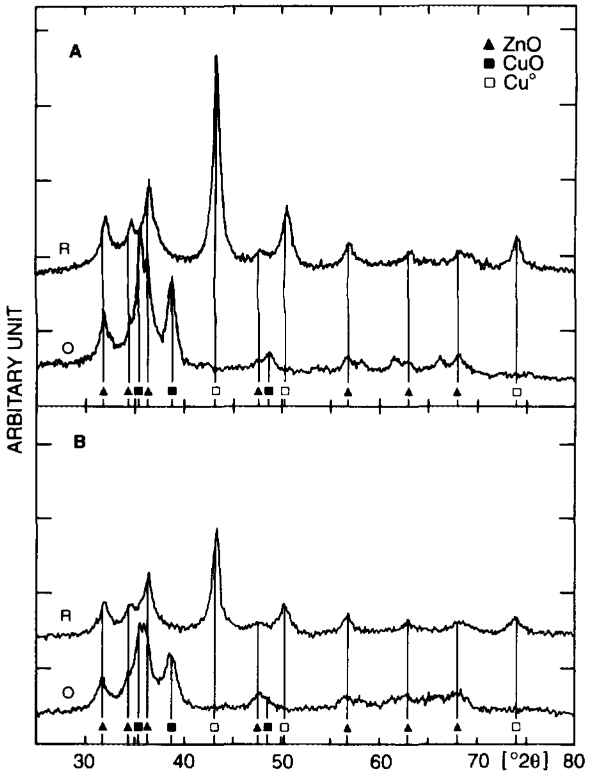

FIG. 1. XRD spectra of oxidized (O) and reduced (R) samples of (a) 00Co-IW and (b) 05Co-IW.

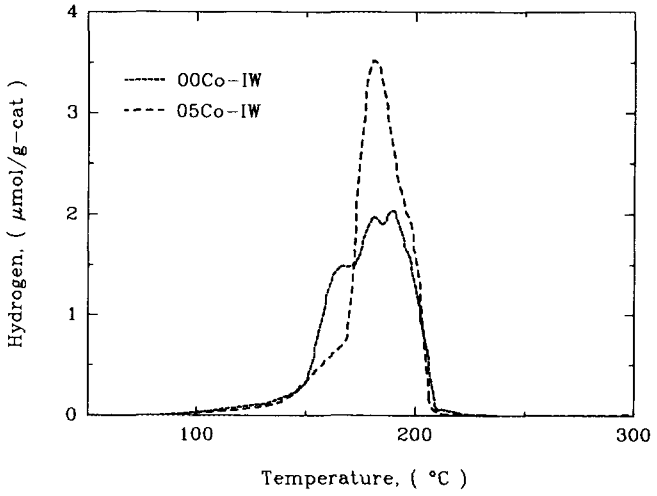

FIG. 2. Spectra of temperature programmed reduction of (a) 00Co-IW and (b) 05Co-IW.

RESULTS

Catalyst Characterization

BET and XRD measurements. The postreduction samples of both 00Co-IW and 05Co-IW exhibited similar BET surface areas of 60 ± 10 m^2/g. The XRD patterns of the calcined and reduced samples of 00Co-IW and 05Co-IW are shown in Fig. 1. No diffraction lines characteristic of cobalt-containing phases were detected in either the calcined or the reduced 05Co-IW. For both catalysts, the diffraction lines of the calcined samples were characteristic of CuO and ZnO phases, whereas those of the reduced samples were characteristic of Cu^0 and ZnO.

TPR measurements. Figure 2 shows the TPR profiles of 00Co-IW and 05Co-IW samples. The 05Co-IW sample exhibited a sharper TPR profile than did 00Co-IW, with a major peak at 180°C. A broader profile, centered at about the same temperature, was observed for 00Co-IW, with a low-temperature shoulder near 165°C. The integrated peak areas giving total H_2 uptakes from the TPR profiles confirmed total reduction of CuO for 00Co-IW. The extent of reduction of cobalt in 05Co-IW (assuming 100%

TABLE 2

Steady State Data of CO Hydrogenation Reaction without and with CH_3NO_2 Addition[a]

Catalysts:	00Co-IW			05Co-IW		
g-cat/bed:	0.075			0.536		
Steady states[b]	I	II	I′	I	II	I′
	(μmol/g-cat/min)			(μmol/g-cat/min)		
Products						
Methanol	214.36	457.90	232.40	23.88	14.72	25.39
Dimethyl ether	5.75	5.20	5.89	0.80	0.10	0.90
Ethanol	4.14	5.44	2.71	1.47	0.93	1.38
n-Propanol	0.17	0.14	0.17	0.40	0.23	0.41
Methane	6.43	5.63	5.88	5.32	6.63	5.24
C_2 HCs	0.64	0.65	0.87	1.87	1.82	1.84
C_{3+} HCs	3.03	4.03	2.73	1.01	1.05	0.98
CO_2	16.49	127.86	23.27	16.34	31.03	16.21
	Nitromethane addition					
CH_3NO_2 in feed	—	20.0	—	—	3.1	—
N-Containing products						
$(CH_3)_3N$	—	16.6	—	—	2.9	—
$(CH_3)_2NH$	—	1.0	—	—	0.1	—
CH_3NH_2	—	2.6	—	—	0.1	—
NH_3	—	0.4	—	—	0.0	—

Note. (—) Not applicable.

[a] 500 psig, 290°C, H_2: CO = 2, GHSV = 6000 ~ 60,000 h^{-1}.

[b] I, prior to CH_3NO_2 addition; I′, post to CH_3NO_2 addition, II, during CH_3NO_2 addition.

reduction of the copper phase) indicated close to complete reduction of the cobalt phase (Co_3O_4).

CO Hydrogenation Reaction

Standard conditions. The formation rates of the CO hydrogenation products at steady state over both catalysts under reaction condition I (without CH_3NO_2 in the feed) are given in Table 2. The major effect of Co addition was a drastic suppression of the formation rates of methanol and dimethyl ether (by almost an order of magnitude). C_{2+} alcohols, hydrocarbons, and CO_2 production were not strongly affected by the addition of Co to the catalyst. Because of the significantly higher activity for methanol synthesis (and hence higher overall activity) for 00Co-IW, a much smaller catalyst charge was used (ca. 50 vs 500 mg) in order to maintain low conversion for 00Co-IW under these conditions.

Addition of nitromethane. The steady-state rates of formation of CO hydrogenation products in the presence of CH_3NO_2 over both catalysts under reaction condition II (with CH_3NO_2 in the feed) are presented in Table 2. With the same concentration of CH_3NO_2 in the reactant mixture, the CH_3NO_2 added per gram of catalyst to 05Co-IW was much lower than that added to 00Co-IW because of the difference in catalyst loading as explained above.

A comparison of the rates without CH_3NO_2 addition is shown in Table 3. The most striking result observed upon the addition of CH_3NO_2 over the Co-promoted 05Co-IW was that the formation rates of C_1–C_3 alcohols were both suppressed to about 40%. Over 00Co-IW, the rate of methanol formation doubled, while the rates of dimethyl ether, ethanol, propanol, and hydrocarbons were not significantly affected.

The formation rates of the hydrocarbon products were not significantly affected by CH_3NO_2 addition. For both the Cu and the Co-promoted Cu catalysts, the CO_2 production rate was enhanced during nitromethane addition to a similar absolute extent based on the amount of nitromethane reacted, giving roughly five times as much CO_2 formed as nitromethane reacted. Consistent with the difference in the amount of nitromethane added to the unpromoted and Co-promoted catalysts, this increase in CO_2 was nearly eight-fold over 00Co-IW and twofold over 05Co-IW.

As shown in Table 2, products other than those of CO hydrogenation detected during the addition of CH_3NO_2 were methylamines and ammonia, with trimethylamine

TABLE 3

Ratio of CO Hydrogenation Rates with and without CH_3NO_2 Addition[a]

	Catalysts	
	00Co-IW (II/I)[b]	05Co-IW (II/I)[b]
Products		
Methanol	2.14	0.62
Ethanol	1.31	0.63
n-Propanol	0.82	0.58
Methane	0.88	1.25
C_2 HCs	1.02	0.97
C_{3+} HCs	1.33	1.04
CO_2	7.75	1.90

[a] 500 psig, 290°C, H_2: CO = 2, GHSV = 6000 ~ 60,000 h^{-1}.

[b] I, prior to CH_3NO_2 addition; II, during CH_3NO_2 addition.

being the dominant product. Over 00Co-IW, there was nearly 80% nitrogen conversion to trimethylamine. No NH_3 was formed over 05Co-IW, and methylamines were formed with about 90% nitrogen conversion to trimethylamine.

The rates of the formation of CO hydrogenation products after the addition of CH_3NO_2 are listed under I′ in Table 2, which showed reestablishment of close to the original steady state CO hydrogenation activity.

DISCUSSION

Effect of Cobalt-Inclusion in Cu/ZnO/Al_2O_3

The similar BET surface area of the reduced samples of 00Co-IW and 05Co-IW suggested that the change in catalytic behavior upon addition of cobalt could not be attributed to any gross structural changes. This was supported by XRD results indicating that no significant changes in particle sizes of Cu, CuO, or ZnO were caused by the addition of cobalt. Any significant differences in either adsorptive or catalytic properties between 00Co-IW and 05Co-IW should therefore be due to more subtle changes in surface properties.

The loss of the lower temperature feature in the TPR profile upon inclusion of cobalt is consistent with the fact that the reduction of cobalt oxides is more difficult than that of copper oxides, suggesting that the presence of cobalt inhibited the reduction of copper at low temperatures. On the other hand, the TPR studies of supported cobalt catalysts (7, 26) have shown that the major TPR peak for cobalt on SiO_2 or Al_2O_3 appears between 250 ~ 500°C, but no H_2 uptake was detected in this range of temperatures for 05Co-IW. This suggests that the reduction temperature of cobalt was in turn lowered by the presence of copper. Observations of cobalt reduction aided by copper have been repeatedly reported in the literature (1, 2, 8, 10). These opposing effects of cobalt and copper on their respective reduction temperatures suggest the presence of Co–Cu contact or interaction. The fact that XRD pattern of both calcined and reduced 05Co-IW did not show lines characteristic of cobalt species implies that the cobalt on Cu/ZnO/Al_2O_3 was very finely dispersed.

These characterization studies suggest that the significant effects on reactivity that the addition of Co caused cannot be explained by major structural changes in the catalyst. Since both TPR and XRD results suggested that the state of Cu remained the same upon addition of Co, the significant changes in activity and selectivity might be attributed to deactivation of active Cu sites by the finely dispersed Co particles via geometric blockage or electronic interaction. The drastic suppression of methanol formation that we observed upon cobalt addition to Cu/ZnO/Al_2O_3 and the concomitant significant drop in the overall activity of the catalyst was consistent with results for Co–Cu type catalysts reported in the patent and open literature (1, 2, 4, 6, 27–29) for the synthesis of C_{2+} alcohols from syngas. The cited rates are on the order of 10 times lower than for methanol synthesis over analogous Cu-only catalysts. Lin and Pennella (2) observed a similar phenomenon where even very small amounts of Co resulted in significant suppression of methanol formation and caused little change in the bulk properties of the catalyst.

Co acted as a selective poison for methanol synthesis and not as a true promoter of higher alcohol synthesis, suggesting that the type of Co–Cu interaction thought to be required (1–10) for such promotion was not achieved in the simple impregnation procedure used in preparing this catalyst. We are currently exploring the CO/H_2 activity of Co–Cu prepared by other methods, such as coprecipitation, which promise to produce a more intimate Co–Cu interaction.

Effect of Probe Molecule (CH_3NO_2) Addition to the CO Hydrogenation

The addition of nitromethane over Cu and Co–Cu catalysts gave results very different from those of our previous studies using CH_3NO_2 addition to CO hydrogenation over supported Ru catalysts (21–23). In those cases, the probe molecule was found to generate CH_x ($x \leq 3$) surface species via C–N bond cleavage, and these CH_x ($x \leq 3$) surface species acted as chain growth intermediates in the formation of C_{2+} hydrocarbons. The fact that the addition of CH_3NO_2 to the CO hydrogenation over Cu and Co–Cu catalysts resulted in nearly complete conversion of nitrogen into methylamines over both catalysts without promoting the formation of hydrocarbons indicates that CH_x ($x \leq 3$) surface species were not formed from CH_3NO_2 over Cu. Further, the addition of Co in 05Co-IW did not help to generate CH_x species. This unexpected result reveals how different the behavior of Co is in this catalyst system compared to its behavior in conventional Co Fischer–Tropsch catalysts or compared to other transition metals such as Ni or Ru.

The formation of methylamines suggests a route through reduction of CH_3NO_2 to CH_3NH_2:

$$CH_3NO_2 + 3\ H_2 \rightarrow CH_3NH_2 + 2\ H_2O. \qquad [1]$$

This is also supported by studies of the reaction of CH_3NO_2 with H_2 in the absence of CO over these catalysts, which resulted in the formation of methylamines (30). The reduction of CH_3NO_2 to CH_3NH_2 over Cu-based catalyst appears to be highly competitive with the C–N cleavage pathway even in the presence of Co.

The formation of predominantly trimethylamine suggests that hydrogenation of the probe molecule was followed by alkylation of the primary amine. This observation is consistent with the mechanism of methanol synthesis from CO/H_2 over a similar Cu/ZnO catalyst as revealed by a chemical trapping study (14) in which amines were used as trapping agents. In that study, it was concluded that the lower substituted amines, $R(R')NH$, trapped the aldehydic methanol intermediate, CH_xO (x = 1, 2), to form higher substituted amines, $R(R')NCH_3$:

$$R(R')NH + \{[CH_xO]\} \xrightarrow{[H]} R(R')NCH_3 + H_2O. \qquad [2]$$

The high conversion of N from CH_3NO_2 into $(CH_3)_3N$ indicates that some carbon in $(CH_3)_3N$ originated from CO. In addition, the low conversion of nitrogen from CH_3NO_2 to NH_3 suggests that disproportionation of methylamines was not the dominant pathway for the formation of $(CH_3)_3N$ as well as $(CH_3)_2NH$. Our current understanding of the mechanism of amine alkylation from alcohol and amine or ammonia over Cu catalysts (31) suggests that the N-containing species react with the surface aldehydic species formed from decomposition of the alcohol to give the alkylation products. Therefore, the involvement of carbon from CO in the formation of $(CH_3)_3N$ during CH_3NO_2 addition to CO/H_2 over these catalysts suggests that the CH_3NH_2 formed from CH_3NO_2 reduction diverted the methanol intermediate to form higher substituted methylamines

$$CO + H_2 \rightarrow [CH_xO] \xrightarrow{[H]} CH_3OH \qquad [3]$$

$$CH_3NH_2 + [CH_xO] \xrightarrow{[H]} (CH_3)_2NH + H_2O \qquad [4\text{-}1]$$

$$(CH_3)_2NH + [CH_xO] \xrightarrow{[H]} (CH_3)_3N + H_2O. \qquad [4\text{-}2]$$

An intriguing point raised from the results over 05Co-IW is that methanol, ethanol, and propanol were each suppressed to a similar extent upon CH_3NO_2 addition. This leads to the suggestion that the methanol intermediate formed from CO/H_2 is also involved in the pathway of C_{2+} alcohol formation:

$$(n-1)CO + (2n-1)H_2 + [CH_xO] \xrightarrow{[H]} C_nH_{2n+1}OH + (n-1)H_2O, \quad n = 2,3 \qquad [5]$$

This mechanism is consistent with the conclusion reached from reaction in the absence of the probe molecule that Co does not act as a true promoter of higher alcohols and that its major function of suppressing methanol formation merely magnifies the minor production of C_{2+} alcohols that was already occurring on the Cu catalyst in the absence of Co. Any modification of copper metal surface by the finely dispersed cobalt metal did not appear to form new active sites for C_{2+} alcohol synthesis and hence did not change the pathway of C_{2+} alcohol formation over 05Co-IW from that followed over 00Co-IW.

Role of CO_2 in Alcohol Synthesis

The significant increase in CO_2 upon the addition of CH_3NO_2 can be rationalized by considering that the water formed from the production of methylamines may be used to drive the water–gas shift (WGS) reaction:

$$H_2O + CO \rightarrow CO_2 + H_2. \qquad [6]$$

Equations [2], [4-1], and [4-2] show that for each mole of $(CH_3)_3N$ formed from the probe molecule, four moles of H_2O are produced which may lead to four moles of CO_2 through the WGS reaction in [6]. The increase in CO_2 with CH_3NO_2 addition over 00Co-IW and 05Co-IW were both about five times the amount of CH_3NO_2 converted (on a per-gram-catalyst basis), which is fairly close to the amounts predicted.

This increase in CO_2 production in the presence of nitromethane may also help to explain the doubling of the methanol rate observed during addition of the probe molecule over the unpromoted Cu catalyst, due to the promotional effect of CO_2 on methanol formation over Cu-based catalysts (32–34). The fact that the increase in CO_2 did not promote C_{2+} alcohol formation over the Cu catalyst suggests that the promotion of methanol formation by CO_2 on Cu/ZnO occurred via a different intermediate, such as surface formate [HCOO] (33–36), rather than the aldehydic intermediate suggested above (Eq. [3]) from the direct hydrogenation of CO.

Our results imply the coexistence of two different pathways to methanol formation from CO/H_2, a point which has been argued in the literature, one concerning CO hydrogenation involving an aldehydic intermediate and one relying on the presence of CO_2. Earlier work by our group has confirmed both the promotional effect of CO_2 on methanol formation over 00Co-IW and the role of Co (in loading from 1 to 10%) in suppressing this effect (37). Indeed, this idea can help explain the results of nitromethane addition over the two types of catalysts. It was suggested that the same intermediate was involved in the formation of methanol and higher alcohols for the Co-promoted catalyst and that the same mechanism should hold for higher alcohols on the pure Cu catalyst as well. That mechanism, however, does not explain the high activity for methanol formation over the Cu catalyst nor its suppression upon addition of Co. If two routes to methanol formation operate simultaneously, and if addition of Co to the Cu-based catalyst effectively inhibited the CO_2-promoted pathway to methanol, all of the present results may be reconciled.

The high methanol activity of the Cu-based catalyst is driven by the CO_2-promoted pathway. The much lower activity for C_1–C_3 alcohols following the secondary route involving an aldehydic intermediate outlined in this paper occurs over both Cu and Co–Cu catalysts. Addition of Co to this catalyst effectively suppressed the CO_2-promoted route to methanol but did not significantly alter the secondary aldehydic intermediate route.

CONCLUSIONS

The addition of cobalt to a commercial $Cu/ZnO/Al_2O_3$ catalyst by incipient wetness impregnation of cobalt selectively and significantly suppressed the rate of methanol formation without significantly altering the formation rates of C_{2+} alcohols and hydrocarbons. The results of both catalyst characterization and CO hydrogenation reaction suggested that the added cobalt was nearly completely reduced and finely dispersed on Cu, which selectively blocked the active sites of Cu for methanol synthesis without forming new active sites for the synthesis of C_{2+} alcohols.

Over Co-promoted catalyst, the addition of CH_3NO_2 as a probe molecule resulted in an identical suppression of the rates of C_1–C_3 alcohol formation. The interaction of CH_3NO_2 with the reaction network of CO hydrogenation over both catalysts suggested that an aldehydic methanol intermediate formed from CO and H_2 was also involved in the formation of C_{2+} alcohols. It was further suggested that a second route to methanol formation involving CO_2 operates over the Cu-based catalyst and is in fact the pathway that was suppressed upon addition of Co.

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