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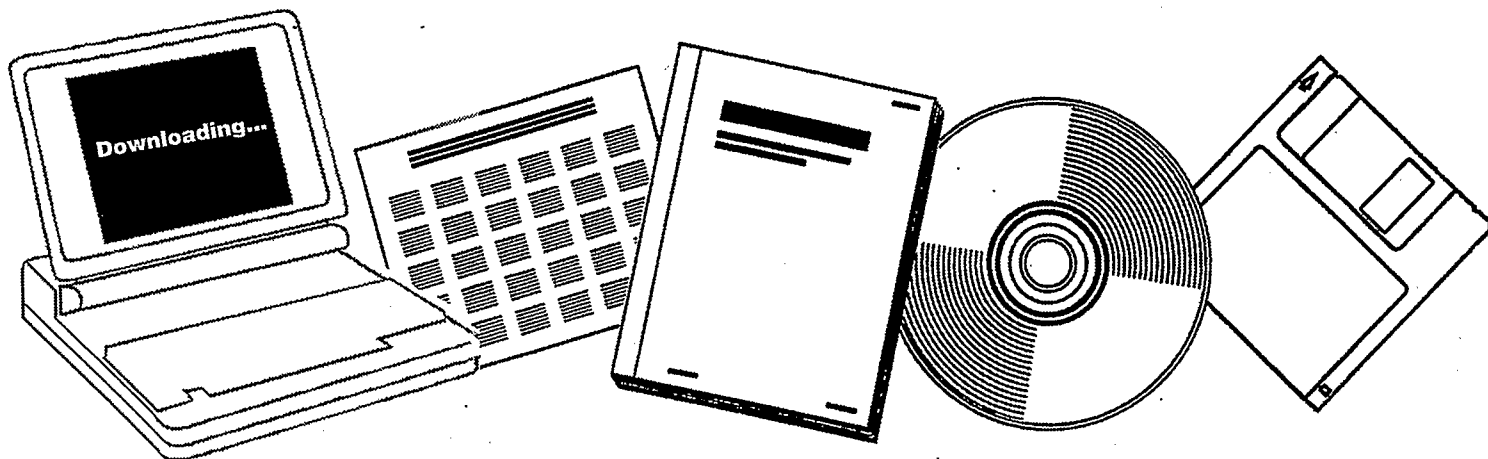
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**PROBE MOLECULE STUDIES: ACTIVE SPECIES IN
ALCOHOL SYNTHESIS. FIFTH QUARTERLY REPORT,
OCTOBER 1991--DECEMBER 1991**

**PITTSBURGH UNIV., PA. DEPT. OF CHEMICAL
AND PETROLEUM ENGINEERING**

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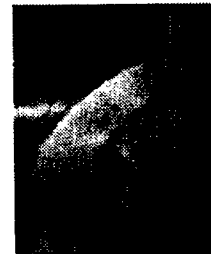
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DOE QUARTERLY REPORT, No.5, October 1991 - December 1991

**PROBE MOLECULE STUDIES:
ACTIVE SPECIES IN ALCOHOL SYNTHESIS**

5th Quarterly Report
October 1991 - December 1991

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Received by OSTI
APR 13 1992

December 1991

Prepared for the U.S. Department of Energy
under Grant No. DE-FG22-90PC-90305

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1. INTRODUCTION

The goal of this research is to develop a better understanding of the mechanism of alcohol synthesis from CO/H₂ by adding probe molecules (principally, CH₃NO₂) to the dynamic reaction mixture and following how the added probe molecule is incorporated into the products to distinguish the dominant pathways from the possibilities proposed in the literature. Cu/ZnO/Al₂O₃ and Co/Cu/ZnO/Al₂O₃ catalyst systems have been chosen for this study. It is well known that Cu/ZnO methanol synthesis catalysts can be made into higher alcohol synthesis catalysts by adding alkali metal (Cs, K, Na). The inclusion of Group VIII metals (Co, Fe) for the same purpose has been studied to a much lesser extent^[1-4]. Few mechanistic studies of the Co/Cu/ZnO/Al₂O₃ have been reported in the literature^[1]. Study of a catalyst system consisting of both Group VIII metal and well-known methanol synthesis catalyst may bridge the knowledge of supported metals and traditional alcohol synthesis catalysts.

2. SUMMARY OF PROGRESS

During this period, the effect of CH₃NO₂ addition to MeOH synthesis from H₂/CO/CO₂ over Cu/ZnO/Al₂O₃ has been further investigated. Analysis of the experimental results has raised many interesting questions about the nature of the interaction of CH₃NO₂ with Cu/Zn-based system. The Co/Cu/ZnO/Al₂O₃

system has been chosen for future studies of higher alcohol synthesis in the attempt to bridge the knowledge of supported metals and traditional alcohol synthesis catalysts as well as probing the similarities and differences between alcohol synthesis over this system and hydrocarbon chain growth over supported metals.

3. DETAILED DESCRIPTION OF TECHNICAL PROGRESS

In order to understand the behavior of CH_3NO_2 over Cu/ZnO under CO/H_2 conditions, experiments were carried out with CH_3NO_2 addition to a commercial methanol synthesis catalyst, $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$, under selected reaction conditions.

Blank runs with He , H_2 and CH_3NO_2 were carried out at 400 psi, 503 K, with $\text{GHSV} = 4190 \text{ hr}^{-1}$ over both the reactor filled with only glass wool and the reactor loaded with ~1 g $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$. Reaction of $\text{CO}/\text{H}_2/\text{CO}_2$ (40:80:6) over $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ (0.5-1 g) was studied at both 400 and 150 psi, 503 K, with $\text{GHSV} = 4190 \text{ hr}^{-1}$. The results are summarized below and in Table 1.

(a) $\text{He}/\text{CH}_3\text{NO}_2$ flow through the empty reactor showed no interaction with the reactor and demonstrated satisfactory performance of the system in plug flow.

(b) When CH_3NO_2 was added at about $2 \mu\text{mol}/\text{min}$ in He over $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$, steady-state production of about $1.2 \mu\text{mol}/\text{min}$ CO_2 was estimated by MS. No CH_3NO_2 or other C- or N-containing compounds were detected by FID (with capillary column) and MS (N_2 is always present in MS spectra due to contamination from

air in the syringe and hence it is difficult to quantify its presence in a sample). The fact that roughly 60% of the C from CH_3NO_2 introduced was converted to CO_2 shows that, in the absence of other reactants, a significant fraction of the CH_3NO_2 decomposed by breaking the C-N bond over $\text{Cu/ZnO/Al}_2\text{O}_3$.

(c) When 2.1 $\mu\text{mol/min}$ CH_3NO_2 was added to the catalyst surface in the presence of H_2 in He under the same conditions, mono-, di- and tri-methylamines were formed with trimethylamine in abundance, whereas no CO_2 was detected. A very small amount of CH_4 (~0.5% C from CH_3NO_2 was detected. When steady state was reached (after ~3 hr addition of CH_3NO_2), trimethylamine was the only product detectable (at a rate of about 0.7 $\mu\text{mol/min}$). Considering that three CH_3NO_2 molecules are required to produce one molecule of $(\text{CH}_3)_3\text{N}$, this shows a 100% conversion of CH_3NO_2 to $(\text{CH}_3)_3\text{N}$.

(d) As shown in Figure 1, when 2 $\mu\text{mol/min}$ CH_3NO_2 was added to CH_3OH synthesis at steady state (~3% conversion of CO to CH_3OH) under 400 psi, no perturbation to CH_3OH formation was observed, and no amines or other organic products were detected.

(e) When a large amount (6.7 $\mu\text{mol/min}$) of CH_3NO_2 was added to CH_3OH synthesis at steady state (2.7% conversion of CO to CH_3OH) under 400 psi, as shown in Figure 2, CH_3OH formation was suppressed (conversion dropped to ~0% within ~1 hr) but could be recovered easily (within 2 hours) by stopping CH_3NO_2 addition. No amines or other products were detected.

(f) When a large amount (6.3 $\mu\text{mol/min}$) of CH_3NO_2 was added

Table 1. Reaction Conditions and Results

(CH₃NO₂ Addition to CH₃OH Synthesis from CO/H₂ over Cu/ZnO/Al₂O₃)

Order		Reactants and Conditions					Products (upon CH ₃ NO ₂ Addition)				
		T = 230 °C, Wcat = 1 g									
	in	P	H ₂	CO	CO ₂	He	CH ₃ NO ₂	CH ₃ OH	CO ₂	(CH ₃) ₃ N	Other
	Text	(psi)	(cc/min)			(μmol/min)	(μmol/min)				
(b)		400	0	0	0	126	2.0	No	1.2	No	No
(c)		400	80	0	0	46	2.1	No	No	0.7	CH ₄ (CH ₃) ₂ NH CH ₃ NH ₂ trace only until ss.
(d)	Fig.1	400	80	40	6	0	2.1 Added after ss conversion to 3% CH ₃ OH (45 μmol/min) attained	45	No in addition to that added	No	No
(e)	Fig.2	400	80	40	6	0	6.7 Added after ss conversion to 2.7% CH ₃ OH (44 μmol/min) attained	Drop to zero	No in addition to that added	No	No
(f)	Fig.3	150	80	40	6	0	6.3 Added after ss conversion to ~ 4% CH ₃ OH (59 μmol/min) attained	Drop to 10 μmol/min after 250 min	No in addition to that added	~2	No
(g)	Fig.4	400	80	40	6	0	2.4 Added together with H ₂ /CO/CO ₂ to freshly reduced catalyst	34 (2.1% conversion) Reached s.s.	No in addition to that added	1.0	No

to CH₃OH synthesis at steady state. (~4% conversion of CO to CH₃OH) under 150 psi, a similar suppression of MeOH formation to that observed in case (e) occurred (see Figure 3). However, in this case the suppression was not as complete, and both this suppression under CH₃NO₂ and the recovery of CH₃OH synthesis activity after removal of CH₃NO₂ were slower. The amount of carbon in the (CH₃)₃N (~2.0 * 3 μmol/min) was about the same as that in the added CH₃NO₂. The catalyst in this experiment had undergone re-reduction after reaction under the conditions given in (g).

(g) When 2.4 μmol/min CH₃NO₂ was added to a fresh catalyst surface together with CO/CO₂/H₂ mixture at 400 psi, without first letting the alcohol synthesis mixture reach the catalyst prior to addition of the probe molecule, (CH₃)₃N was formed along with CH₃OH and they both reached steady state (2.1% CO conversion to CH₃OH, e.g. 34 μmol/min CH₃OH, 1.0 μmol/min (CH₃)₃N) within an hour (see Figure 4). The mole number of C in the (CH₃)₃N produced at steady state was 25% higher than the C mole number in the CH₃NO₂ stream, indicating that some of the carbon in the amine must have originated from CO. The steady-state CO conversion to CH₃OH in this case (2.1%) was slightly lower than that in case (d) (3%) and (e) (2.7%).

These results suggest some very interesting surface information about this CH₃OH synthesis catalyst:

(1) These results differ from those of the supported Ru case in a number of ways:

- No CO₂ was formed from CH₃NO₂ in either He or H₂ blanks

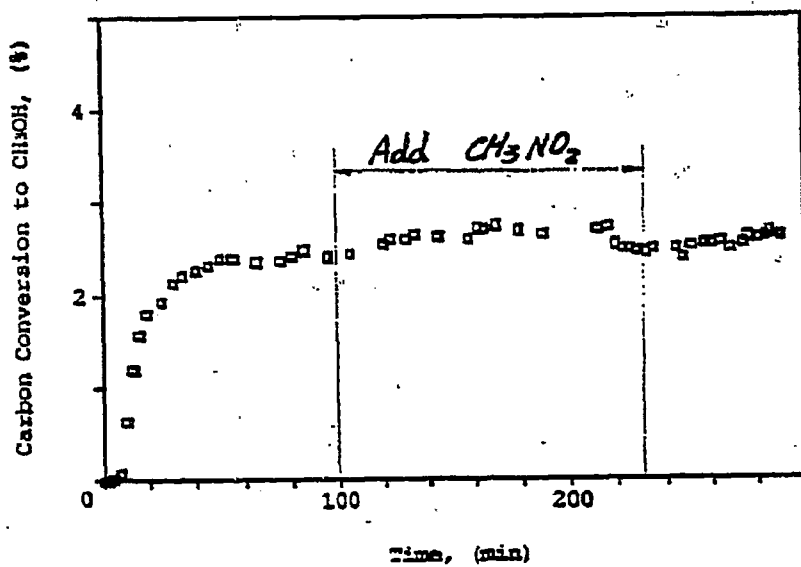


Figure 1. CH₃NO₂ addition (2.0 μmol/min) to CH₃OH synthesis from H₂/CO/CO₂ (80:40:6) at steady state. P=400 psi, T=230 °C, GHSV=4190 hr⁻¹.

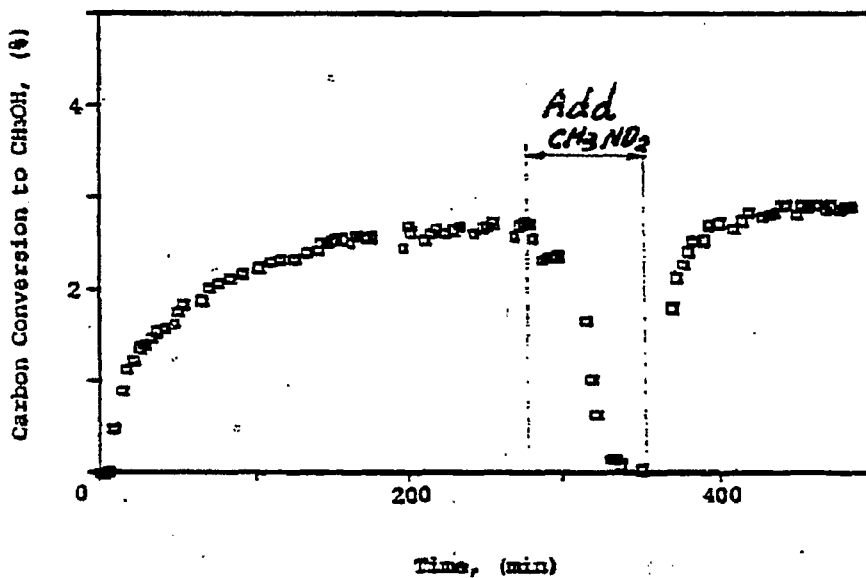


Figure 2. CH₃NO₂ addition (6.7 μmol/min) to CH₃OH synthesis from H₂/CO/CO₂ (80:40:6) at steady state. P=400 psi, T=230 °C, GHSV=4190 hr⁻¹.

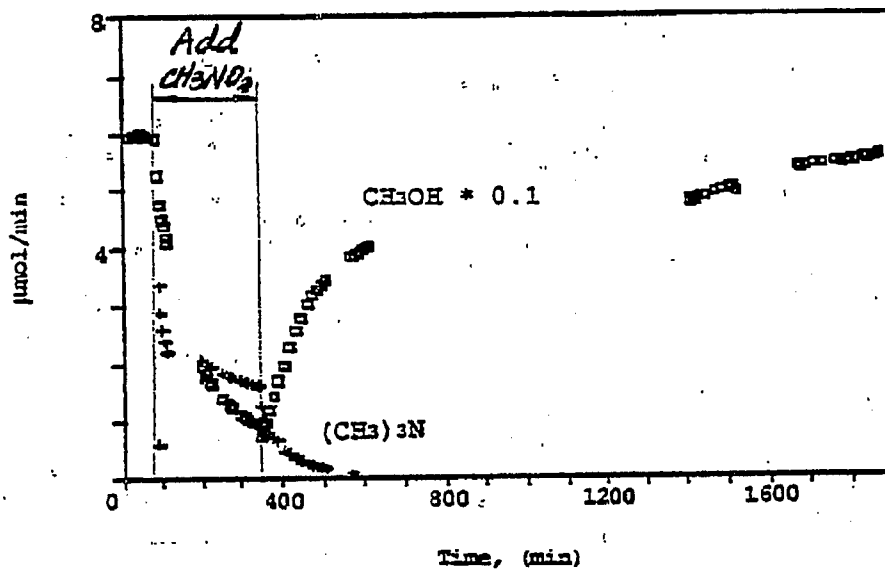


Figure 3. CH_3NO_2 addition ($6.3 \mu\text{mol}/\text{min}$) to CH_3OH synthesis from $\text{H}_2/\text{CO}/\text{CO}_2$ (80:40:6) at steady state. $P=150 \text{ psi}$, $T=230 \text{ }^\circ\text{C}$, $\text{GHSV}=4190 \text{ hr}^{-1}$.

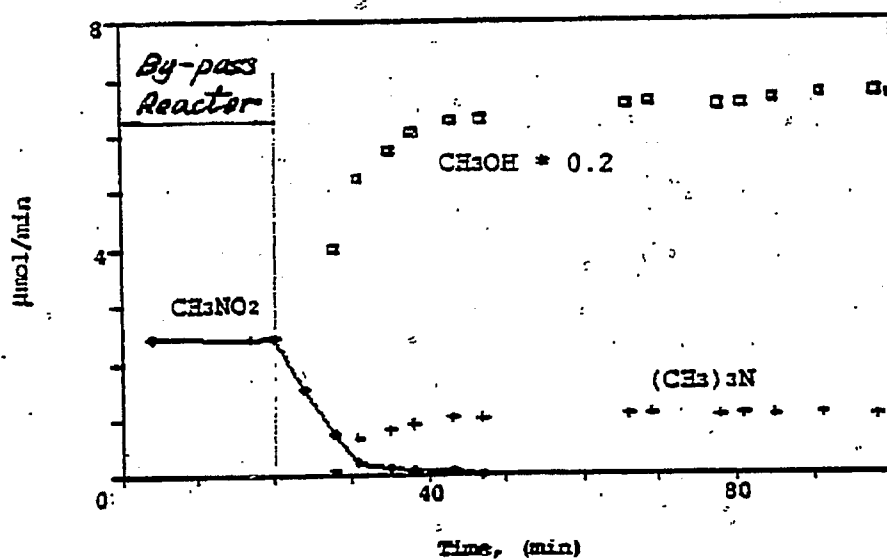


Figure 4. CH_3NO_2 addition ($2.4 \mu\text{mol}/\text{min}$) to CH_3OH synthesis from $\text{H}_2/\text{CO}/\text{CO}_2$ (80:40:6) at initial state. $P=400 \text{ psi}$, $T=230 \text{ }^\circ\text{C}$, $\text{GHSV}=4190 \text{ hr}^{-1}$.

on supported Ru;

- No compounds were detected in which the carbon-nitrogen bond of CH_3NO_2 was retained in any reactions over supported Ru.

- Large amount of CH_4 were found in H_2 and He blanks over Ru catalysts.

This clearly shows that the interaction of CH_3NO_2 with $\text{Cu/ZnO/Al}_2\text{O}_3$ is different from its interaction with Ru. Over $\text{Cu/ZnO/Al}_2\text{O}_3$, CH_3NO_2 behaves in a more complex manner than that was observed over supported Ru. It appears that in the presence of H_2 the C-N bond of CH_3NO_2 is not selectively cleaved and that CH_x species are not readily formed over $\text{Cu/ZnO/Al}_2\text{O}_3$.

(2) CH_3NO_2 was never detected in the product stream in any of those experiments in which CH_3NO_2 was added over $\text{Cu/ZnO/Al}_2\text{O}_3$. The same phenomenon was observed over supported Ru.

(3) CH_3NO_2 can be reduced to CH_3NH_2 in the presence of H_2 over $\text{Cu/ZnO/Al}_2\text{O}_3$. This opens the path for CH_3NH_2 to be converted to $(\text{CH}_3)_3\text{N}$ by disproportionation over Cu/ZnO as has been observed previously^[7].

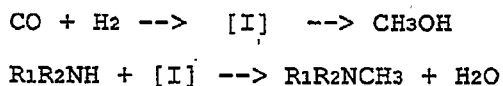
(4) CH_3NO_2 contacting the freshly reduced catalyst surface provides (or permits the surface to retain) sites for CH_3NO_2 reduction to CH_3NH_2 . When the reduced catalyst was first contacted with only syngas and reached steady state activity to CH_3OH formation, these sites were no longer present or were unavailable. Initial contact of the clean surface with $\text{CH}_3\text{NO}_2/\text{CO/H}_2/\text{CO}_2$ gave a steady state CO conversion to CH_3OH which was

lower by about 1/3 than that achieved when the probe was added at steady state. The parallel formation of $(\text{CH}_3)_3\text{N}$ and CH_3OH under these conditions suggests that the probe molecule may compete for sites with CH_3OH intermediates. It appears that this competition is only significant if contact occurs between the probe molecule and the surface before it achieves steady state CH_3OH activity. Probing this sites further may help to understand the surface processes occurring during the initial stages of CH_3OH synthesis which change the way CH_3NO_2 interacts with the catalyst.

(5) The fact that CH_3OH formation at steady state was not perturbed by a small amount (2 $\mu\text{mol}/\text{min}$) of CH_3NO_2 addition but was significantly suppressed with a higher amount (6-7 $\mu\text{mol}/\text{min}$) also suggests that the probe molecule can perturb CH_3OH synthesis even in the absence of activity for amine formation. This shows that further investigation of the interaction between CH_3NO_2 and the surface at steady state of CH_3OH synthesis may provide important information for better understanding of CH_3OH synthesis mechanism.

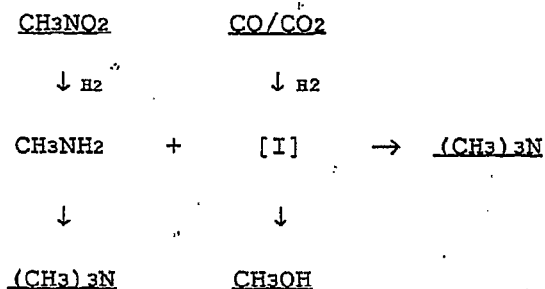
(5) The fact that the amount of C in the $(\text{CH}_3)_3\text{N}$ formed along with CH_3OH (after both processes reached steady state) was higher than the amount of C in the added CH_3NO_2 suggests that there is a second pathway for $(\text{CH}_3)_3\text{N}$ formation during CH_3OH synthesis over Cu/ZnO which involves CO . Chemical trapping studies of surface intermediate(s) in CH_3OH synthesis over Cu/ZnO in the presence of amines^[6] concluded that the C1 methanol precursor, an aldehydic type intermediate [I], under-

goes amination, e.g.

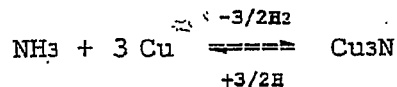


Our results are consistent with this scheme if we assume that CH_3NO_2 is hydrogenated to the monoamine before disproportionation to give $(\text{CH}_3)_3\text{N}$. It can also explain why CH_3OH yield at steady state with $(\text{CH}_3)_3\text{N}$ formation (~2% CO conversion) is lower than the yield without $(\text{CH}_3)_3\text{N}$ formation (~3% CO conversion).

Based on the available information, the following scheme is proposed:



NH_3 is a possible by-product of the amine disproportionation reaction, but it was not detected in our experiments. This could perhaps be due to separation or adsorption problems in the GC column or because any NH_3 formed could react with surface Cu to form a nitride:



which would only be removed under H_2 at 247°C [5,8] (the reaction temperature used was 230°C).

These results demonstrate that CH_3NO_2 can interact with CH_3OH synthesis catalysts in different ways under different conditions and that some of our observations may provide information about mechanisms for CH_3OH synthesis over Cu/ZnO -based catalysts. The possibility to observe C-N bond cleavage over Co as seen over Ru promises a more challenging study on alcohol synthesis from CO/H_2 over a $\text{Co}/\text{Cu}/\text{ZnO}$ catalyst using CH_3NO_2 as the probe molecule.

4. PLANS FOR THE NEXT REPORTING PERIOD

In the next reporting period, the focus will be on the following topics:

(1) The effect of nitromethane addition to CH_3OH over $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3$ will be further studied assisted by catalyst characterization by XRD before and after reactions under different conditions in order to understand better:

- What is the nature of the interaction of CH_3NO_2 with Cu/ZnO on the freshly reduced catalyst in the presence and absence of H_2 ? What is the nature of the sites with which that CH_3NO_2 interacts? Does CH_3NO_2 introduced in absence of $\text{CO}/\text{CO}_2/\text{H}_2$ irreversibly change the surface?

- How does the surface of the catalyst change during the induction period in CH₃OH synthesis? How does this change affect the sites for adsorption and hydrogenation of CH₃NO₂?

- Why is the suppression of CH₃OH formation sensitive to the amount of CH₃NO₂ introduced? Under what conditions can amines be formed during the CH₃OH synthesis reaction?

(2) Preparation of Co/Cu/ZnO/Al₂O₃ catalysts by incipient wetness impregnation will be attempted and the reactivity of the catalysts for higher alcohol synthesis will be tested to answer questions including:

- Can catalyst preparation and CO/H₂ reaction conditions be devised so that a Co/Cu/ZnO/Al₂O₃ catalyst system produces a significant amount of higher alcohols?

- What is the effect of addition of the probe molecule (CH₃NO₂) to this higher alcohol synthesis catalyst? What can we learn about the pathways of alcohol synthesis using this approach?

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