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Methanol Synthesis over a Cu/ThO_2 Catalyst

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A Cu/ThO_2 catalyst prepared from the binary alloy $ThCu_6$ was found active for the synthesis of methanol from carbon monoxide and hydrogen. X-Ray diffraction revealed the presence of a Cu^+ species, suggested as the active species for methanol synthesis. The effects of P_{CO}, P_{H_2} and temperature on the kinetics of methanol synthesis, suggest a Langmuir–Hinselwood mechanism for dual site adsorption in which CO is strongly adsorbed and H_2 weakly adsorbed. Studies of the effect of H_2/CO ratio revealed that the use of low hydrogen content synthesis gas, i.e., H_2/CO = 0.8/1.0, results in rapid catalyst deactivation. X-Ray diffraction and thermal gravimetric studies attributed catalyst deactivation to carbon formation, a probable consequence of the Boudouard reaction. Differential scanning calorimetry studies suggested that the carbon exists as both atomic carbon, readily reactive with hydrogen to yield methane, and amorphous or polymeric carbon, less reactive and the primary agent of catalyst deactivation.

INTRODUCTION

Recently, it was reported (*1*) that a $ThCu_6$ alloy derived catalyst was more active for methanol synthesis than a commercial $Cu/ZnO/Al_2O_3$ catalyst. Utilizing a CO_2 free syngas mixture with a H_2/CO ratio of 16/1 at 60 atm, 280°C, and a GHSV of 31,000 hr^{-1}, the amount of methanol in the product stream was reported to be seven times greater for the $ThCu_6$ derived catalyst, 44 mol% (excluding hydrogen) vs 6.5 mol%.

Herman *et al.* (*2*) have reported that commercial Cu/ZnO catalysts require CO_2 in the feed gas mixture to maintain catalyst activity. A $Cu/ZnO/Al_2O_3$ catalyst tested with a $H_2/CO/CO_2$ mixture of 70/24/6 mol% at 75 atm, 250°C, and a GHSV of 5000 hr^{-1} exhibited a methanol synthesis activity of 0.95 kg/hr/liter catalyst. However, upon testing the catalyst with a CO_2-free H_2/CO (76/24) mixture, after treating it with the mixture for 8 hr at ambient temperature, catalyst activity had decreased to 0.02 kg/hr/liter catalyst. Since carbon fouling was not detected, they suggested that CO_2 maintains catalyst activity by keeping the copper in the active Cu^+ state.

Gardner and Bartholomew (*3*) have reported carbon deposition on nickel catalysts during methanation at high CO partial pressures. They suggest that carbon deposition is a consequence of the Boudouard reaction and that both reactant hydrogen and product water reduce the steady-state concentration of carbon forming precursors, i.e., atomic carbon (*4*).

The purpose of this study was to develop a better understanding of methanol synthesis over the $ThCu_6$ alloy derived catalyst. Particular emphasis was directed toward explaining the unusual stability of this catalyst in CO_2-free synthesis gas.

EXPERIMENTAL

Materials. Premixed bottle synthesis gas containing 3 vol% nitrogen as an internal standard and H_2/CO molar ratios in the range of 0.5/1.0 to 4.4/1.0 and for some experiments 5–10 vol% CO_2 were obtained from Air Products and Chemicals. The $ThCu_6$ alloy, received from the Bureau of Mines' Reno Metallurgical Center, was prepared by arc-melting.

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Apparatus and experimental technique. Catalyst performance was evaluated in a Chemical Data System 810 microreactor system. Approximately 1.5–2.0 g of the $ThCu_6$ alloy (<100 mesh size) were used for all experiments. The catalyst, supported on a wad of quartz wool, was contained in a 0.5″ × 9″ down flow, fixed bed, isothermal, tubular reactor inserted in a heated inconel block.

Prior to testing the catalyst had to be activated. The procedure consisted of increasing the temperature to 180°C over a 1-hr period and then to 240°C at a rate of 20°C/hr while maintaining a unit pressure of 62 atm and a synthesis gas ($H_2/CO = 2.4/1$) GHSV of 20,000 hr^{-1}. All measurements of catalyst performance were recorded after the catalyst had been at 240°C for approximately 24 hr.

Although the unit was run around-the-clock on many occasions, product analysis was performed daily during a 9-hr period. Reactor effluent was analyzed via gas chromatography. Nitrogen, carbon monoxide, methane, carbon dioxide, dimethyl ether, and methanol were analyzed on a 6′ × $\frac{1}{4}$″ o.d. × 0.20″ i.d. stainless-steel column packed with 100 mesh Spherocarb B. Quantitative analysis of the product stream was obtained by electronic integration of the chromatogram peaks using a Hewlett Packard 3380A. Response factors were obtained from known standards.

X-ray powder diffraction. XRD analyses were obtained with a Philips Electronic Instruments XRG 2500 X-ray diffractometer equipped with a 3000 W, full wave rectified generator, a wide range scanning goniometer, a 2θ compensating variable slit system, and a graphite crystal diffracted beam monochromator. Prior to analysis, samples were ground in a helium atmosphere to <200 mesh and packed as a thin layer into a shallow sample holder backed with a glass slide. Samples were scanned using a CuK_α radiation (1.5418 Å) at a rate of 1°/min, a time constant of 1 sec and a chart speed of 0.5 in./min.

Thermal analyses. Experiments were performed using a Dupont 990 Thermal Analyzer with a Dupont 951 TGA and a standard DSC cell. For the TGA experiments, 48 mg of sample was placed on the platinum sample pan, with 40 mg weight suppressed out, leaving 8 mg on the 1 mg/in. chart scale. A gas flow rate (either air or a blend of CO, H_2, and N_2) of 250 cm^3/min was established, and the temperature was programmed up at 10°C/min.

DSC experiments were performed by placing 10 mg sample in an open aluminum pan and programming the temperature up at 10°C/min under 250 cm^3/min airflow. Sensitivity was 0.5 mcal/sec/in. on the Y axis.

RESULTS AND DISCUSSION

Characterization of the $ThCu_6$ Alloy and Activated Catalyst

Samples of the intermetallic compound ($ThCu_6$) and the activated catalyst were analyzed by powder X-ray diffraction. Nitrogen BET surface areas for these materials were 3 and 27 m^2/g, respectively. The patterns for the alloy and activated catalyst are illustrated in Fig. 1. The XRD pattern for

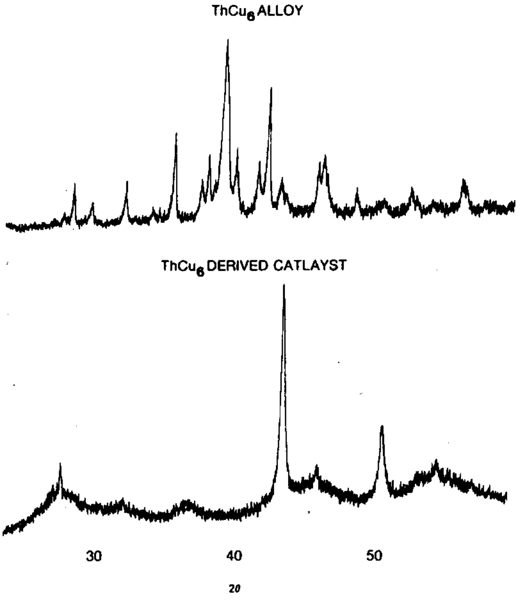

FIG. 1. X-Ray diffraction pattern of $ThCu_6$ alloy and $ThCu_6$ alloy derived catalyst.

the alloy is a very close match with that of $CeCu_6$ as reported in the literature (*5*). No pattern is reported for $ThCu_6$ in the JCPDS file of XRD powder patterns. The XRD pattern for the activated catalyst indicates the presence of elemental Cu as the major crystalline phase and ThO_2 as a minor crystalline phase. A weak peak at 36.45° 2θ is assigned to Cu_2O (*5*).

In an effort to further elucidate the $ThCu_6$ activation mechanism and chemical formulation of the activated catalyst, additional experiments were performed using thermal gravimetric analysis. In two separate experiments $ThCu_6$ was oxidized with air and synthesis gas (H/CO = 2.4/1). The TGA results, illustrated in Fig. 2 and summarized in Table 1, suggest that $ThCu_6$, in the presence of air, is oxidized to a mixture of Cu_2O, CuO, and ThO_2. These results are consistent with those reported by Imamura and Wallace (*6*) for the air oxidation of $ThNi_5$. However, in the presence of synthesis gas, $ThCu_6$ is selectively oxidized to Cu and ThO_2 in agreement with the XRD results for the activated catalyst.

Methanol Synthesis Reaction Kinetics over $ThCu_6$ Alloy Derived Catalyst

The simplest rate expression for methanol synthesis, ignoring the catalyst adsorption–surface reaction–desorption phenomena is

$$\text{Rate} = kp_{H_2}^{a}p_{CO}^{b}.$$

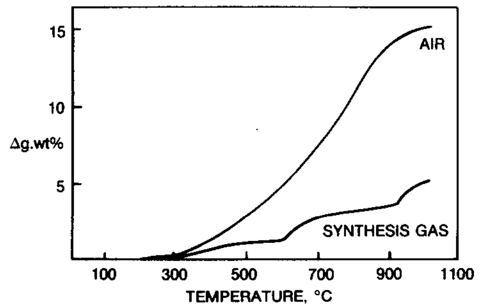

FIG. 2. Thermal gravimetric analyses of $ThCu_6$ alloy. Oxidation reactions conducted at feed rate of 250 cm³/min at 1.7 atm and temperature program rate of 10°C/min.

TABLE 1

Thermal Gravimetric Analysis[a] for $ThCu_6$ Oxidation

Experimental	
Oxidizing agent	Weight increase (%)
Air	15.4 ± 0.8
Synthesis gas (H_2 : CO = 2.4)	5.4 ± 0.3
Theoretical	
Reaction	Weight increase (%)
$ThCu_6 \rightarrow ThO_2(Cu_6O_3)$	13
$ThCu_6 \rightarrow ThO_2(CuO)_6$	20
$ThCu_6 \rightarrow ThO_2Cu_6$	5.2

[a] 23–1000°C at 10 psig, flow rate of 250 cm³/min, temperature program rate of 10°C/min.

Using the Arrhenius law this equation can be written as

$$\text{Rate} = Ae^{-E_a/RT}p_{H_2}^{a}p_{CO}^{b}$$

where A is a constant known as the frequency factor and E_a the energy of activation.

Prior to defining the order of the reaction in H_2 and CO the effect of temperature on initial CO conversion was defined as illustrated in Fig. 3. The results reveal a maximum level of CO conversion to methanol of 41% at 260°C. Above 260°C CO conversion to methanol decreases as the reaction becomes equilibrium limited, as previously reported (*1*). In addition, product selectiv-

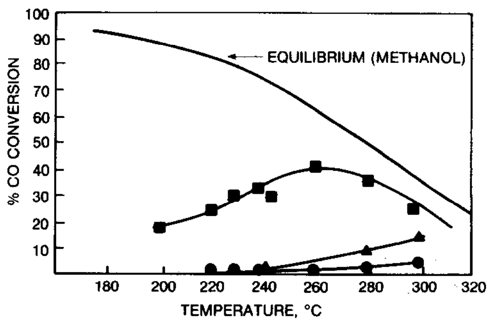

FIG. 3. The effect of temperature on product distribution at 62 atm, GHSV of 20,000 hr^{-1}, and H_2/CO of 2.4/1. (■) CH_3OH; (△) CO_2; (●) CH_4.

ity to methanol decreases as CH_4 and CO_2 selectivities increase.

Consequently, in an effort to define the order of the reaction in CO and H_2 experiments were done at 240°C. The results, illustrated in Fig. 4, suggest that methanol synthesis over a $ThCu_6$ alloy derived catalyst is first order in hydrogen and zero order in carbon monoxide.

An Arrhenius plot of the kinetic limited data of Fig. 3, illustrated in Fig. 5, for a first order reaction in hydrogen yields an apparent energy of activation of 9.7 kcal/mole and a frequency factor of 7.15×10^2 sec^{-1}. Although the energy of activation is low in comparison to previously reported values of 16.9 and 30.0 kcal/mole (*7*, *8*), experiments with smaller catalyst particle sizes and larger catalyst bed volumes suggest the reaction is not diffusion limited. Consequently, the rate expression can be written as

$$\text{Rate} = 7.15 \times 10^2 e^{-4.87\times 10^3/T} p_{H_2}.$$

The rate expression for the Langmuir–Hinselwood mechanism for dual site adsorption is (*9*)

$$\text{Rate} = \frac{k_2 K_{H_2} K_{CO} p_{H_2} P_{CO}}{(1 + K_{H_2} p_{H_2})(1 + K_{CO} p_{CO})}$$

where k_2 is the surface reaction rate constant and K_{H_2} and K_{CO} are the adsorption/desorption equilibrium constants for hydrogen and carbon monoxide, respectively. If it is assumed that CO is strongly adsorbed whereby $K_{CO}p_{CO} \gg 1$ and H_2 is weakly adsorbed whereby $K_{H_2}p_{H_2} \ll 1$ the above rate expression becomes

$$\text{Rate} = k_2 K_{H_2} p_{H_2}$$

equivalent to the experimentally derived equation.

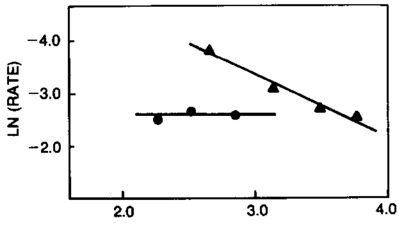

FIG. 4. The effect of hydrogen and carbon monoxide partial pressure on catalyst activity at 240°C. (▲) H_2; (●) CO.

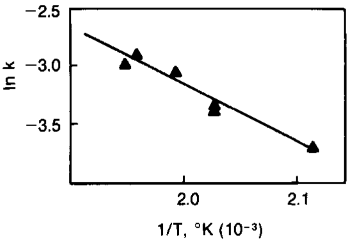

FIG. 5. Arrhenius plot for methanol synthesis over a $ThCu_6$ alloy derived catalyst at 62 atm, GHSV of 20,000 hr^{-1}, and H_2/CO of 2.4/1.

Catalyst Stability and the Effect of H_2/CO Ratio

As previously noted, Herman *et al.* have reported that the inclusion of CO_2 in the synthesis gas mixture is necessary to prevent catalyst deactivation. In agreement with the results of Baglin *et al.* (*1*), the $ThCu_6$ alloy derived catalyst did not exhibit any significant loss in catalyst activity over a 95-hr period when tested, with a CO_2-free synthesis gas mixture having a H_2/CO ratio of 2.4/1, at 900 psig, 245°C, and a GHSV of 20,000 hr^{-1}. However, when tested with a low hydrogen content synthesis gas mixture (H_2/CO = 0.8/1) at 900 psig, 245°C, and space velocities of 20,000 and 11,250 hr^{-1}

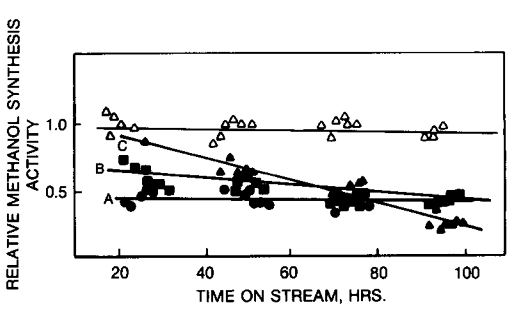

FIG. 6. $ThCu_6$ alloy derived catalyst stability studies at 62 atm, 245°C. (△) H_2/CO = 2.4/1, GHSV = 20,000 hr^{-1}; (▲) H_2/CO = 0.8/1, GHSV = 11,250 hr^{-1}; (■) $H_2/CO/CO_2$ = 42.2/52.8/5.0, GHSV = 8,660 hr^{-1}; (●) $H_2/CO/CO_2$ = 40/50/10, GHSV = 9,043 hr^{-1}.

TABLE 2

Experimental Results of Catalyst Stability Study[a]

$H_2:CO$ (molar)	GHSV (hr^{-1})	CO_2 (%)	CO conversion to methanol (%)	Catalyst deactivation		Coke (wt%)
				Rate[b] (Δ%/hr)	Correlation factor	
2.4	20,000	—	29.0	0.04	0.12	0.39
0.8	20,000	—	16.7	0.50	0.81	1.04
0.8	11,250	—	26.9	0.92	0.96	6.70
0.8	8,660	4.8	18.3	0.42	0.85	0.21
0.8	9,040	9.5	13.5	0.07	0.11	—

[a] Pressure = 900 psig; temperature = 245°C.

[b] Rate = (slope × 100)/(Y at 21 hr) (Fig. 6).

catalyst activity did decrease as presented in Table 2 and illustrated in Fig. 6.

Product selectivity, illustrated in Fig. 7, was also dependent on the H_2/CO ratio. With decreasing H_2/CO ratio, from 2.4/1 to 0.4/1, selectivity for methanol decreased from 98 mole% to 72 mole%; carbon dioxide selectivity increased from less than 1 mole% to 24 mole%; methane selectivity remained relatively constant at approximately 2 mole%.

TGA and DSC analyses using air, as presented in Table 2 and illustrated in Figs. 8a–d, suggest that catalyst deactivation in hydrogen deficient synthesis gas ($H_2/CO < 2.4/1$) is due to carbon deposition. The concurrent increase in CO_2 selectivity with decreasing H_2/CO ratio suggests that the mechanism for carbon deposition and resultant catalyst deactivation involves the Boudouard reaction (10).

$$2CO \rightarrow CO_2 + C$$

As illustrated in Figs. 8c, d, four exotherms are observed on the DSC curves for coked catalysts. The first exotherm commences at 140°C with a maximum at 190°C; the maximum of the second exo-

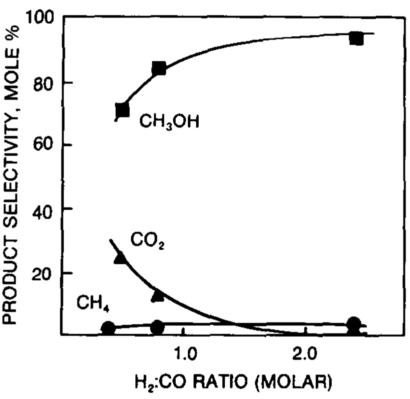

FIG. 7. The effect of H_2/CO ratio on product selectivity at 62 atm, 240°C, and GHSV of 20,000 hr^{-1}. (■) CH_3OH; (▲) CO_2; (●) CH_4.

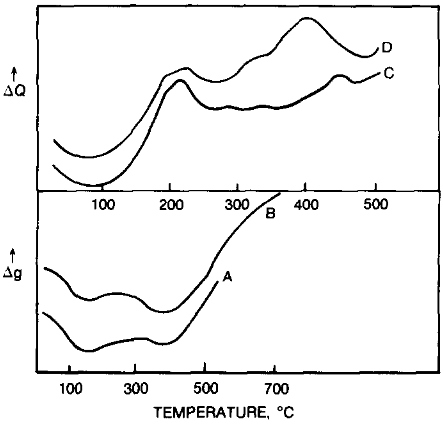

FIG. 8. Thermal gravimetric and differential scanning calorimetry analyses of partially deactivated $ThCu_6$ alloy derived catalysts tested at 62 atm, 245°C, GHSV of 20,000 hr^{-1} and H_2/CO ratio of (a) 2.4; (b) 0.8; (c) 2.4; (d) 0.8.

therm is at 215°C. The TGA results (Figs. 8a, b) show an increase in weight beginning simultaneously with the first exotherm. These results suggest that the first two exotherms are due to the surface oxidation of copper to cupric oxide.

The third exotherm commences at 270°C with a maximum at 330°C; the maximum of the fourth exotherm is at 400°C. The TGA results show a decrease in weight beginning at 270°C, the same temperature at which the exotherm commences. These results suggest that the last two exotherms are due to two different forms of coke, i.e., atomic carbon and polymeric carbon.

Recently, McCarty and Wise (*4*) reported similar results for temperature-programmed surface reaction studies of a Ni/Al_2O_3 catalyst exposed to CO at 277°C. Using hydrogen, two peaks with maxima at 197 and 407°C were observed. They attributed these results to two different carbon species, dispersed and polymerized carbon, respectively.

A comparison of the DSC and TGA curves in Figs. 8a–d reveals that as the level of coke increases the intensity of the fourth exotherm increases. This suggests that the coke species with the higher temperature exotherm is the cause of catalyst deactivation, possibly by blocking active sites for methanol synthesis.

The fact that catalyst deactivation is negligible for synthesis gas with a H_2/CO ratio of 2.4/1 is probably the result of a competing reaction, hydrogenation of atomic or polymeric carbon to methane, analogous to the results recently reported by Gardner and Bartholomew (*3*) during methanation of CO over a Ni/Al_2O_3 catalyst at high CO partial pressures. However, with decreasing H_2/CO ratio the rate of the Boudouard reaction increases, as evidenced by the increased CO_2 selectivity in the product stream, while the rate of methanation remains relatively constant. Consequently, the catalyst loses activity with time on stream as the level of coke increases.

Effect of CO_2 on Catalyst Stability

The results presented in Table 2 and illustrated in Fig. 6 demonstrate a significant reduction in the rate of catalyst deactivation and associated carbon deposition, during methanol synthesis with hydrogen deficient synthesis gas, upon addition of carbon dioxide to the reaction mixture. This reduction in the rate of deactivation is attributed to either an increase in the rate of the reverse Boudouard reaction, or the formation of H_2O resulting in direct gasification of carbon (*11*) or production of hydrogen via the water gas shift reaction which can also gasify carbon via methanation (*12*). With the addition of 5 and 10 vol% CO_2 to synthesis gas with a $H_2:CO$ ratio of 0.8 : 1, the rate of catalyst deactivation at 900 psig, 245°C, and a GHSV of approximately 9000 hr^{-1} decreased from a theoretically calculated value of 1.2 to 0.4 and 0.07%/hr, respectively. However, a poor correlation factor for the feed with 10 vol% CO_2 suggests that catalyst activity is constant.

CONCLUSION

The results presented suggest that the unusual stability of the $ThCu_6$ alloy derived catalyst is a consequence of its ability to establish a favorable steady-state condition between the ratio of coke deposition and subsequent methanation of the deposited coke. Furthermore, when using hydrogen deficient synthesis gas the catalyst suffers rapid deactivation due to coke formation which can be prevented by the addition of CO_2 to the feed gas.

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