sulfur prevents the hydrogenation of surface carbon, thereby increasing its rate of accumulation at high temperatures.

6. Metal promoters such as MoO_2 and Pt can significantly alter the activity of nickel for carbon deposition. Addition of MoO_2 to Ni/Al_2O_3 increases the rate by a factor of 10 while Pt lowers it by a factor of 2. These effects may be explained by the ability of the promoter to alter the hydrogenation activity or carbon solubility of the metal.

7. The results of this study are pertinent to commercial methanation processes since the range of partial pressures of CO and H_2 as well as the temperatures are representative of those actually encountered in a large portion of a fixed bed, recycle methanator after 85–90% of the feed has been converted. Carbon deposition is typically not a problem at the entrance to the bed since the temperature is too low for measurable rates of carbon formation. Most of the results obtained in this study for Ni/Al_2O_3 are at least qualitatively applicable to higher partial pressures of H_2 and CO.

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Methanol Synthesis Catalysts from Thorium–Copper Intermetallics. Preparation and Evaluation

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Bureau of Mines research into the use of intermetallic compounds as catalytic materials has shown catalysts prepared from binary alloys of copper and thorium to be active for the synthesis of methanol from carbon monoxide and hydrogen. Activation of the alloys resulted in oxidation of the thorium yielding high surface area catalysts containing copper interspersed on thoria. For example, catalysts prepared from $ThCu_x$ alloys by air oxidation at 400 °C had surface areas as high as 35 m^2/g and produced up to 6.7 times as much methanol as a traditional $Cu/ZnO/Al_2O_3$ catalyst from $16H_2$:CO synthesis gas in a continuous-flow microreactor at 280 °C and 60 atm pressure. Standard inlet space velocity was 31 000 h^{-1}.

Introduction

One aspect of the Bureau of Mines mission in recent years has been a concern with U.S. dependence upon foreign sources for certain economically important raw materials. Thus, for some time the Bureau of Mines has been investigating the substitution of domestic resources for expensive and domestically scarce catalytic materials such as platinum metals, nickel, cobalt, or chromium. Intermetallic compounds have been studied as hydrogenation catalysts because these materials easily break the hydrogen bond. Rare-earth transition metal intermetallics were found by VanVucht et al. (1970) to absorb hydrogen in interstitial sites. Kuijpers and Loopstra (1971) determined that the hydrogen was stored in atomic form, and a strong interest has since been developed by several researchers in utilizing these intermetallics in hydrogenation reactions.

Early studies involved the use of materials derived from binary alloys of iron, cobalt, or nickel, and rare-earth or actinide elements as methanation catalysts (Atkinson and Nicks, 1977, 1978). Other workers also studied the synthesis of methane (Coon et al., 1976), higher hydrocarbons (Elattar et al., 1977), and ammonia (Takeshita et al., 1976) over intermetallic derived catalysts. In the Bureau of Mines laboratory, the alloys were activated in gaseous atmospheres with the purpose of oxidizing the nontransition metal. When subsequently reduced, these catalysts consisted of the transition metal interspersed on an oxide of the nontransition metal. The activation procedure also resulted in the formation of catalysts with BET surface areas as high as 50 m^2/g. Thorium alloys were found to develop surface area more readily than most of the other alloys studied.

Modern industrial processes for the synthesis of methanol from carbon monoxide and hydrogen fall into two general categories: (1) high-pressure synthesis, where reactors are operated at 100 to 600 atm pressure and 250 to 400 °C over ZnO/Cr_2O_3 catalysts, and (2) low-pressure synthesis, where reactors are operated at 20 to 100 atm pressure and 230 to 300 °C over CuO/ZnO catalysts which generally also contain Cr_2O_3 or Al_2O_3. The CuO is reduced to elemental copper prior to use.

In this preliminary paper, catalysts prepared from thorium-copper alloys were found to be many times more active than a commercial $Cu/ZnO/Al_2O_3$ catalyst for methanol synthesis under low-pressure conditions (60 atm, 220 to 320 °C). A more complete examination of intermetallic compounds as methanol synthesis catalysts and as catalysts for a series of other hydrogenation reactions is being made in this laboratory, with future publication in mind.

Experimental Procedure

Catalyst Preparation. The binary phase diagram for the thorium-copper system indicates the existence of four intermetallic compounds—Th_2Cu, $ThCu_2$, $ThCu_{3.6}$, and $ThCu_6$. Materials of these compositions, as well as alloys of nominal composition $ThCu_5$, ThCuCr, and thorium containing 5 wt % Cu, were prepared by arc-melting the components on a water-cooled copper hearth in a helium atmosphere. (Caution should be observed in the handling and storage of thorium-copper alloys because of their radioactive nature and because they decrepitate with the evolution of heat when they are stored at ambient conditions. This pyrophoric nature was especially notable for Th_2Cu and $ThCu_2$.)

Th_2Cu and $ThCu_2$ were "self-grinding". The alloy buttons disintegrated as the thorium was oxidized to thoria in air at ambient laboratory conditions. $ThCu_{3.6}$ partially disintegrated under these conditions. The intact portion of the $ThCu_{3.6}$ button and the $ThCu_5$, $ThCu_6$, Th/5% Cu, and ThCuCr alloys were crushed and sieved to −25/+80 mesh. As an activation procedure, the resulting granules were reacted at 400 °C and atmospheric pressure with gas having sufficient oxidizing power to convert the thorium to thoria. Typical oxidizing media were air or air sparged through a water bubbler held at room temperature (~4% water). The air oxidation was followed by reduction with hydrogen or synthesis gas in the methanol synthesis reactor to convert to the elemental state any copper oxides formed during the air treatment. Other media utilized to oxidize the alloys were $3H_2$:CO synthesis gas, hydrogen containing ~4% water, or pure carbon dioxide.

For comparison, a $ThO_2/5Cu$ sample was prepared by coprecipitation of a solution of thorium and copper nitrates with Na_2CO_3 solution. The precipitate was filtered, washed with water, dried at 110 °C, and calcined at 350 °C. Reduction of the copper oxides occurred in the synthesis reactor.

A commercial $Cu/ZnO/Al_2O_3$ methanol synthesis catalyst (United Catalysis, Inc., C79-4) was also evaluated. (Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.)

Reactor Design. The catalysts were evaluated by supporting 0.2-cm^3 samples of −25/+80 mesh material between plugs of Pyrex wool in a $^1/_4$-in. inside diameter stainless steel continuous flow microreactor, part of a high-temperature/high-pressure reactor system. The reactor pressure was controlled at 60 atm with a heated back-pressure regulator. All gas lines and valves were contained in a 200 °C oven to prevent condensation of any reaction products. Helium was used to pressurize and flush the reactor. After outgassing, the helium was replaced with a $16H_2$:CO analyzed synthesis gas mixture, obtained commercially. Inlet standard space velocity was maintained at 31 000 h^{-1} by a fine metering valve. The temperature, measured by a thermocouple embedded in the reactor heat block at catalyst level, was generally raised to 220 or 240 °C and held until reproducible analyses of the exit gases were obtained. This generally took at least 2 h. The temperature was then raised in 10 to 20 °C increments until the amount of methanol produced started to decrease due to the effect of equilibrium. Maximum temperatures were 300 to 320 °C for the alloy-based catalysts and 340 and 360 °C, respectively, for the commercial and coprecipitated catalysts.

Extended tests of several days duration at constant temperature were performed on two active catalysts. Replicate tests produced results within approximately 10% of each other.

Analytical Procedure. Reactor off-gas analysis was performed chromatographically using matched heated gas sampling loops and Chromosorb 102 and 5A molecular sieve columns in a series bypass configuration. A thermal conductivity detector and integrating recorder completed the analytical system. The product gases were sometimes condensed and collected in a dry ice/acetone trap. The liquid product was analyzed by chromatographic separation on a Chromosorb 103 column, using a flame ionization detector.

Surface areas were measured by a standard gravimetric BET nitrogen adsorption method. X-ray diffraction patterns were recorded for powdered catalysts both before and after the methanol synthesis tests.

Results and Discussion

The formation of methanol from synthesis gas flowing over a catalyst in a fixed bed reactor proceeds exothermically according to the reaction

$$CO + 2H_2 \rightleftarrows CH_3OH$$

For this preliminary report a high ratio of hydrogen-to-carbon monoxide, $16H_2$:CO, was used to facilitate product analysis (to avoid overloading the gas chromatographic columns) and as a means of rapidly carrying away excess heat due to the exothermicity of the reaction. A more complete manuscript evaluating intermetallic based catalysts with a commercially feasible synthesis gas composition, $2.5H_2$:CO, is to be published.

Figure 1 shows the production of methanol as a function of temperature that resulted from the passage of $16H_2$:CO synthesis gas at 60 atm pressure over the $ThCu_x$ alloys which were "self-grinding", i.e., those in which the thorium was oxidized to thoria in air at ambient conditions. The temperature profiles for $ThO_2/5Cu$, prepared by coprecipitation, and United Catalysts, Inc., C79-4, $Cu/ZnO/Al_2O_3$, are included for comparison. Figure 2 depicts the temperature profiles for the higher copper-containing alloys that were preactivated in air at 400 °C. $ThCu_{3.6}$ was only partially degraded at ambient conditions and is therefore included on each graph. The ordinate of the temperature profiles represents mole percent methanol in the exit gas mixture, excluding the hydrogen that could not be measured with the gas chromatograph. The equilibrium curve was calculated after Ewell (1940). This curve, in effect, measures maximum conversion of carbon monoxide to methanol at 60 atm pressure from $16H_2$:CO synthesis gas. The experimental curves possess maxima

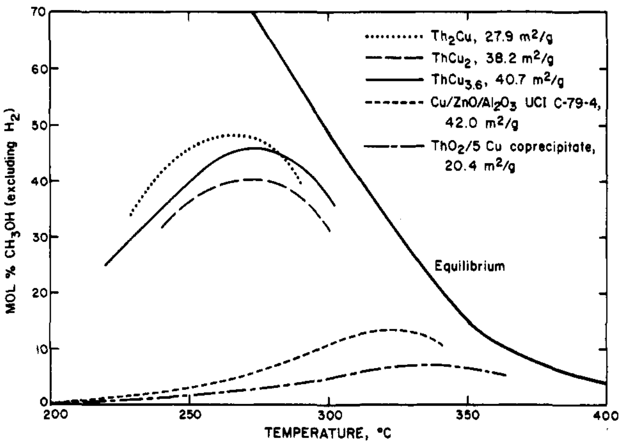

Figure 1. Methanol production as a function of temperature for "self-grinding" alloys, activated in air at ambient conditions: feed gas, 16 H_2:CO; 60 atm pressure; 31 000 GHSV.

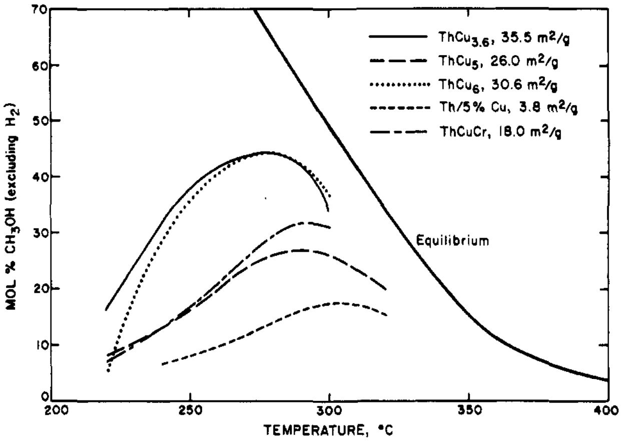

Figure 2. Methanol production as a function of temperature for alloys activated in air at 400 °C: feed gas, 16 H_2:CO; 60 atm pressure; 31 000 GHSV.

apparently owing to the inhibiting effects of equilibrium at higher temperatures. Thermal degradation of the catalysts and decreased methanol selectivity due to enhanced side product formation at higher temperatures may also contribute to the activity decrease, but the fact remains that the equilibrium line was never crossed in any experiment. As can be seen, under these conditions, the catalysts evolved from alloy precursors were many times more active than the commercial and coprecipitated materials. It should be pointed out that the commercial $Cu/ZnO/Al_2O_3$ catalyst was evaluated under conditions quite different from a typical industrial operation where carbon dioxide is often added to increase the carbon content of the gases and to maintain catalytic activity, and where synthesis gas of such high hydrogen content is unlikely to be used.

Some surface area, generally less than 10 m^2/g, was developed during the air activation. The surface areas increased considerably when the copper oxides were reduced in the reactor or when reduced by hydrogen in the surface area apparatus. The BET surface areas of the catalysts after removal from the methanol reactor are included in the graph legends. Areas as high as 40 m^2/g were attained. Conversion data could not be correlated with the total BET surface areas. It is feasible that the catalysts were thermally sintered by the high temperatures to which they were subjected resulting in the measurement of lower surface areas than were present at or below the maximum conversion temperatures. No standard method to measure active surface areas of copper catalysts is known to exist. Several procedures were investigated to see if meaningful active surface areas could be obtained for these intermetallic based catalysts. The N_2O adsorption/oxidation method of Scholten and Konvalinka (1969) did not produce reliable values. Carbon monoxide chemisorption was also investigated, again producing values which could not be correlated with BET total surface areas. Consequently, the activities could not be compared on the basis of turnover numbers.

Expansion of the materials was observed to take place during the air activation procedure; i.e., bulk density decreased. This would be expected as the thorium oxidized to thoria. The swelling ranged from a few percent to as much as 40% depending upon the sample. X-ray diffraction of the powdered air activated catalysts showed thoria, copper, and copper oxides before being loaded into the methanol reactor. After the methanol tests were completed, the catalysts invariably contained thoria and copper (and chromium in the case of the ThCuCr sample). The copper oxides were reduced to copper by the synthesis gas. Surface analysis of the catalysts could be very enlightening. Because of the difficulty of detecting small concentrations by X-ray diffraction, absence of diffraction lines for copper oxides does not preclude the presence of Cu^I or Cu^{II} in the reduced catalysts. Herman et al. (1978), on the basis of near infrared–visible–ultraviolet absorption spectra and other experimental evidence, proposed a Cu^I/ZnO solution to be the active catalytic phase in $Cu/ZnO/Al_2O_3$ or Cr_2O_3 methanol synthesis catalysts. Yet, they were able to identify only elemental copper, ZnO, and Al_2O_3, or Cr_2O_3 from their X-ray powder diffraction spectra.

Particle-size degradation generally occurred during the synthesis tests of air-activated samples. The granules were noticeably finer than the −25/+80 mesh starting material. The effect of this attrition was not investigated.

The $ThCu_x$ alloys, except for the Th_2Cu and $ThCu_2$ that oxidized in ambient air, were found to oxidize and activate directly in synthesis gas at 60 atm pressure in the methanol reactor. High methanol activity resulted, but owing to indeterminate expansion of the catalyst bed inside the reactor, the space velocities could not be controlled accurately enough for comparison with data from preactivated catalysts. To obtain a catalyst that could be compared, a 0.5-cm^3 sample of −25/+80 mesh $ThCu_6$ was pretreated for 24 h at 240 °C in 60 atm synthesis gas. The catalyst was removed from the reactor and rescreened to −25/+80 mesh. The bulk density was measured and a normal 0.2 cm^3 volume was reloaded into the reactor. A maximum of 38 mol % methanol was produced at 280 °C at a space velocity of 31 000 h^{-1}, which was somewhat less than the 44 mol % measured for air activated $ThCu_6$.

Other activation media, such as hydrogen–steam or pure carbon dioxide at 400 to 450 °C caused the development of surface area and the oxidation of the thorium, while leaving copper in the elemental state (according to X-ray diffraction analysis). Methanol activities for these catalysts were generally lower than those obtained with air or synthesis gas activation, yet were still higher than that of the commercial catalyst. For example, after carbon dioxide treatment, activities ranged from a low of 12.5 mol % methanol produced at 320 °C by $ThCu_6$ to a high of 37 mol % at 280 °C by $ThCu_2$. Likewise, hydrogen–steam pretreatment produced catalysts that yielded between 9 and 22 mol % methanol. Catalyst integrity was improved when these alternate activation media were used, with less particle size degradation observed than with air-oxidized materials.

Table I. Gaseous Product Analysis as a Function of Temperature from the Synthesis of Methanol over $ThCu_{3.6}$, Preactivated in Air at 400 °C; $16H_2$:CO; 60 atm Pressure; 31 000 GHSV

temp, °C	mol % excluding H_2						
	CO	CH_4	CO_2	C_2H_6	H_2O	CH_3OH	$(CH_3)_2O$
220	83.52	0.24	0.08			16.16	
240	67.22	0.60	0.28			31.89	
260	55.93	1.24	1.07	0.06		41.70	
270	52.26	1.99	1.58	0.08	0.56	43.54	
280	49.42	2.85	2.46	0.13	1.11	44.02	
300	54.44	5.49	3.65	0.17	1.91	34.04	0.31

Chromium was added to thorium and copper to make ThCuCr alloy. This was done to evaluate any stabilizing effect of chromium on the catalyst since Cr_2O_3 has often been added to catalysts to inhibit sintering and crystal growth. The conditions of the activation or synthesis procedures did not suffice to oxidize the chromium in the alloy. The methanol activity of the air-oxidized catalyst decreased approximately 9% in an overnight run at 260 °C, which is higher than the average overnight dropoff observed for other alloy compositions. Thus, no particular stabilization was apparent during the short time this catalyst was in the reactor. A longer aging test would be necessary to allow a more definitive statement concerning chromium stabilization.

Two samples were tested in the methanol reactor for extended periods of time. $ThCu_5$, activated in air at 400 °C, yielded 23 mol % methanol at 290 °C after 18 h on stream. The activity dropped to 18 mol % over 216 h. Th_2Cu, activated in air at ambient conditions, produced 48 mol % methanol at 270 °C. Methanol production decreased to 41 mol % after 161 h. Tests of even longer duration are currently being conducted to determine whether this decrease of 2 to 2.5% per day will continue or whether a leveling off of activity will occur. The results of such long-term experiments will be included in a subsequent paper.

Table I presents an analysis summary of the reactor off-gases for a typical catalyst, excluding unreacted hydrogen. The amount and number of side products formed increased with temperature. Small quantities of dimethyl ether often appeared at higher temperatures. At 280 °C where air-activated $ThCu_{3.6}$ produced 44 mol % methanol with methane, carbon dioxide, water, and ethane as side products yielding a methanol selectivity of 87%, the commercial catalyst formed only 6.5 mol % methanol with a few tenths of a percent carbon dioxide as the sole side product (methanol selectivity 97%). At 220 °C, however, the $ThCu_{3.6}$ catalyst yielded only small amounts of methane and carbon dioxide in addition to 16 mol % methanol (methanol selectivity 98%).

In some cases, the off-gases were condensed in a dry ice/acetone cold finger. Liquid product purity was greater than 99% methanol with ethanol as the principal impurity. Higher alcohols formed in lesser amounts. These alcohols did not appear on the chromatograms of the gaseous products because of their low concentrations and very long retention times.

Conclusions

Catalysts prepared from $ThCu_x$ intermetallic percursors have been found to be more active for methanol synthesis than a commercial $Cu/ZnO/Al_2O_3$ catalyst or a coprecipitated ThO_2/Cu catalyst of similar composition. Air or synthesis gas oxidation of the alloys to give a mixture of thoria and copper appears to be the best activation procedure. In summary, the amount of methanol detected in the off-gases of a methanol synthesis microreactor utilizing $16H_2$:CO synthesis gas at 60 atm pressure and an inlet standard space velocity of 31 000 h^{-1} was as much as 44 mol % (excluding hydrogen) at 280 °C over intermetallic based catalysts. A commercial catalyst yielded only 6.5 mol % methanol under identical conditions.

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