JOURNAL OF CATALYSIS 95, 385–395 (1985)

# Methanol Production from Carbon Monoxide and Hydrogen on Thorium Dioxide

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Received October 29, 1984; revised April 12, 1985

High-surface-area $ThO_2$ catalysts (~120 $m^2/g$) were prepared by a precipitation method and characterized by X-ray diffraction, BET surface area, transmission electron microscopy, and X-ray photoelectron and Auger electron spectroscopies (XPS and AES, respectively). Thoria precipitated from $Na_2CO_3$ (as Na-$ThO_2$) and $(NH_4)_2CO_3$ (as $NH_4$-$ThO_2$) were crystalline with particle size <5 nm and active for the production of mostly methanol and small amounts of isobutyl alcohol, isobutane, methane, and ethane/ethene. On the other hand, $ThO_2$ precipitated with $K_2CO_3$ formed large shards with a glassy appearance and a very small surface area (1.7 $m^2/g$); this catalyst was inactive for methanol production. Both X-ray diffraction and XPS measurements showed that Na-$ThO_2$ and $NH_4$-$ThO_2$ catalysts were $ThO_2$ after calcination in air at 520 K. XPS and AES measurements disclosed that the Na-$ThO_2$ catalyst contained ~10 at.% ionic sodium present as $Na_2O$. This catalyst showed a higher activity for isobutyl alcohol synthesis than the sodium-free thoria, while producing comparatively less isobutane. Synthesis experiments were carried out in a copper-lined tubular reactor as a function of gas-mixture composition ($H_2:CO = 2:1, 1:1$), pressure (2.0 to 6.5 MPa), and temperature (570 to 635 K) at an STP gas flow rate of 1.8 $m^3$/kg cat.-h, which corresponded to a space velocity of 5000 $h^{-1}$. Changing the flow rate between 5000 and 10,000 $h^{-1}$ had little effect on the synthesis reaction. Both Na-$ThO_2$ and $NH_4$-$ThO_2$ produced ~1 mole% methanol in the effluent gas under optimum conditions ($2H_2/CO$ at 5.4 MPa, 600 K, 5000 $h^{-1}$); this corresponds to ~3% carbon conversion (0.08 kg $CH_3OH$/l cat.-h). Both catalysts showed little tendency for gaseous hydrocarbon production and their selectivity varied between 85 and 95%. The effect of reactant pressure on the rate of methanol formation was tested by the Natta model for $ZnO/Cr_2O_3$ and $CuO/ZnO/Cr_2O_3$, and hydrogen was found to be more strongly adsorbed than carbon monoxide.

## INTRODUCTION

Most known catalysts for the hydrogenation of carbon monoxide to organic products are supported transition metals or oxide compounds of transition-metal ions. In the case of alcohol synthesis, most catalysts contain oxides of copper and zinc (*1*, *2*), though recently Group VIII metals, notably palladium supported on main group oxides, have been shown to be active and selective methanol synthesis catalysts (*3*).

Audibert and Raineau (*4*) reported that $ThO_2$ used as a single-component catalyst was inactive for methanol synthesis under conditions that were thermodynamically favorable for its formation. Later on, thorium dioxide was formulated into nickel (*5*) or cobalt-based catalysts for Fischer–Tropsch synthesis reactions, where its role was that of increasing the average chain length of the hydrocarbon products. Pichler and coworkers (*6–10*) successfully used $ThO_2$ catalysts to produce mostly isobutane and other liquid branched-chain hydrocarbons from 1:1 and 2:1 $H_2:CO$ mixtures in the process called "isosynthesis." They observed that optimum results were obtained at 60 MPa and 723 K. Their "standard thorium catalyst" was prepared by the precipitation of Th carbonate from a Th nitrate solution with sodium carbonate. The precipitate was washed to remove the excess sodium and air-dried at 573 K. The effect of additives and supports on $ThO_2$ affecting the yield of isobutane was thoroughly stud-

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ied by Pichler and Ziesecke (*7, 8*). Also investigated (*8*) was the production of methanol and isobutyl alcohol (along with lesser quantities of ethyl and propyl alcohols, and traces of isopropyl and tertiary butyl alcohols) over $ThO_2$, $ThO_2$-$K_2CO_3$, $ThO_2$-ZnO, and $ThO_2$-$Al_2O_3$ from $H_2$ + CO mixtures at 30 MPa and 673–723 K. Recently, the thorium–copper intermetallic compounds $Th_2Cu$, $ThCu_2$, $ThCu_{3.6}$, and $ThCu_6$ and alloys of nominal composition $ThCu_5$, ThCuCr, and Th–5 wt% Cu have been studied as methanol synthesis catalysts after decomposition into Cu + $ThO_2$ or CuCr + $ThO_2$ by oxidation in air, $3H_2$:CO synthesis gas, $H_2$ + 4%$H_2O$, or pure carbon dioxide (*11, 12*). The intermetallics that produced the best results were $ThCu_6$ and $ThCu_{3.6}$.

As part of our studies of the intrinsic catalytic properties of the actinide elements and their compounds, we have produced thorium dioxide catalysts (free of transition-metal components) that show significant activity for carbon monoxide hydrogenation to methanol under reaction conditions comparable to those used in modern, low-pressure, methanol-synthesis plants (reaction temperature ~550 K, pressure ~5 MPa). A brief report of this work has already been published (*13*), and we are presenting in this paper a detailed description of the preparation of thorium oxide catalysts, their characterization, and their catalytic behavior for carbon monoxide hydrogenation.

## METHODS

### *I. Catalyst Preparation*

The reagents used in catalyst preparation were Fisher Certified ACS $Th(NO_3)_4 \cdot 4H_2O$ containing 0.2% rare earths, 0.01% Ti, 0.002% Fe, and 0.002% heavy metals; Mallinkrodt AR $Na_2CO_3 \cdot H_2O$; Allied Chemical $NH_4CO_3$; and Fisher Certified ACS anhydrous $K_2CO_3$. Each one of the carbonates contained 5 ppm of iron.

(*A*) *Preparation of thoria using* $Na_2CO_3$ (*Na-*$ThO_2$ *catalyst*). In a typical experiment, 80.0 g of $Th(NO_3)_4 \cdot 4H_2O$ was dissolved in 220 ml $H_2O$, and 37.0 g $Na_2CO_3 \cdot H_2O$ was dissolved in 220 ml $H_2O$. Both solutions were brought to boiling, and the $Na_2CO_3$ solution was then rapidly added to the vigorously stirred thorium nitrate solution. The resulting precipitate was collected by suction filtration and then dispersed with cold water (500 ml) and filtered four times. The washed precipitate was allowed to dry in air for 16 h and then calcined in air at 520 K for 48 h.

(*B*) *Preparation of thoria using* $(NH_4)_2CO_3$ ($NH_4$-$ThO_2$ *catalyst*). Thorium oxide was prepared by dissolving 20 g $Th(NO_3)_4 \cdot 4H_2O$ in 200 ml $H_2O$, and the solution warmed to 313 K. A stoichiometric amount (7.0 g) of $(NH_4)_2CO_3$ was dissolved in 100 ml cold water, and this solution, which was at room temperature, was rapidly added to the stirred thorium nitrate solution. A precipitate formed and in a few minutes redissolved. A lasting precipitate was formed by subsequently adding 2.0 g $(NH_4)_2CO_3$ directly to the previous solution. The gelatinous precipitate was washed with several 200-ml portions of cold $H_2O$. The final precipitate was air-dried for 24 h and calcined in air at 500 K for 48 h.

(*C*) *Preparation of thoria using* $K_2CO_3$ (*K-*$ThO_2$ *catalyst*). Thorium oxide was prepared by dissolving 20 g $Th(NO_3)_4 \cdot 4H_2O$ in 200 ml $H_2O$ and 10.0 g $K_2CO_3$ in 50 ml $H_2O$. The $K_2CO_3$ solution was added rapidly to the stirred, boiling, $Th(NO_3)_4$ solution. Evolution of gas from this solution was observed to be much slower than in the case of $Na_2CO_3$-induced precipitation. The precipitate was suction filtered and washed several times with 200 ml $H_2O$. The precipitate was then air-dried and calcined in air at 513 K for 18 h.

### *II. Catalyst Characterization*

Surface areas, pore diameters, and pore volumes reported in this paper were determined by the BET method using nitrogen, and the crystal structures of the various catalysts were determined by X-ray diffraction techniques as a function of temperature. X-Ray photoelectron and Auger electron spectra were obtained on catalyst samples electrodeposited on copper foils. The ultrahigh-vacuum system (base pressure = $10^{-8}$ Pa) used for these studies was equipped with a double-pass electron spectrometer, which was operated with ~1 eV resolution. Photoelectron energies were calibrated using the Cu 2*p* and 4*s* lines.

Transmission electron micrographs (TEM) were obtained on a microscope with primary-beam energies up to 200 kV and operational magnification of up to 150,000×.

### *III. Methanol Synthesis Experiments and Analytical Techniques*

Synthesis gas reactions were carried out in a copper-lined, stainless-steel, tubular reactor (1.25 cm i.d. × 60 cm long) equipped with a coaxial thermocouple that projected into the catalyst bed. All experiments were run using a single pass of the gas stream through the catalyst, which consisted of particles 8–20 mesh in size. Copper was chosen as the liner for the reactor to prevent methane formation from CO + $H_2$, which is normally observed in iron-containing alloys. Pichler and Ziesecke (*6–10*) thoroughly evaluated and successfully used copper-lined reactors in their "isosynthesis" work, which employed temperatures as high as 873 K. X-Ray photoelectron spectra of used catalysts did not reveal the presence of copper as shown in Fig. 1. Furthermore, experiments using an empty reactor and a $2H_2:CO$ gas mixture at 600 K did not produce either hydrocarbons or alcohols.

Both gas chromatography and time-of-flight mass spectroscopy were used to analyze the effluent gas from the reactor. Routine analysis of the reaction products was carried out with a gas chromatograph equipped with a flame ionization detector and a Chromosorb 102 column. The main products detected by this technique were methane, ethane, methanol, isobutane, and isobutyl alcohol. $C_3$ hydrocarbons (~0.01 vol% detection limit) and $C_2$ + $C_3$ alcohols (~0.01 vol% detection limit) were not detected.

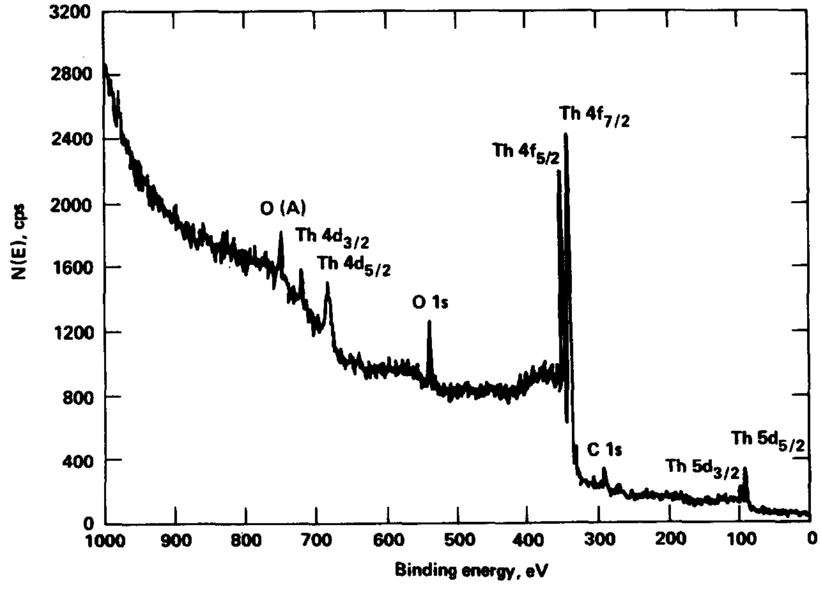


FIG. 1. X-Ray photoelectron spectrum of a used sodium carbonate-precipitated catalyst. The copper 2*p* lines at 932.4 and 952.2 eV are absent.

Premixed synthesis gases were found to contain methane and carbon dioxide (0.01 vol% total), as determined by mass spectroscopy. Any metal carbonyls present in the gas mixtures were removed with a trap filled with coconut charcoal and maintained at 195 K.

## RESULTS

### *I. X-Ray Diffraction, Surface-Area Analysis, and TEM Studies*

Na-$ThO_2$ and $NH_4$-$ThO_2$ catalysts were active for the production of methanol, but K-$ThO_2$ was not. Consequently, in this paper we present results for the first two and not for the latter.

Powder diffraction patterns of the Na-$ThO_2$ catalyst, taken after calcination in air at several temperatures between 523 and 750 K, and of both the Na-$ThO_2$ and $NH_4$-$ThO_2$ catalysts, after removal from the synthesis gas reactor, showed that these catalysts were $ThO_2$. The calculated lattice parameter $a_0$ along with the corresponding surface areas measured are presented in Table 1. As the calcination temperature was raised above 550 K, thoria became more crystalline, and the surface area decreased. Between 725 and 750 K, there was rapid sintering and a large loss in surface area. The used catalysts also showed surface areas which were significantly lower than the fresh material; in fact, they corresponded closely to those of thorias calcined in air at temperatures near 573 K. This is the temperature to which the catalysts were exposed in the synthesis gas reactions. The $a_0$ for the thoria catalyst calcined at 723 K was found to be very close to that reported in the literature for stoichiometric $ThO_2$ ($a_0$ = 5.5997 Å, Ref. (*14*)).

TABLE 1

Surface Area of Thoria Catalysts

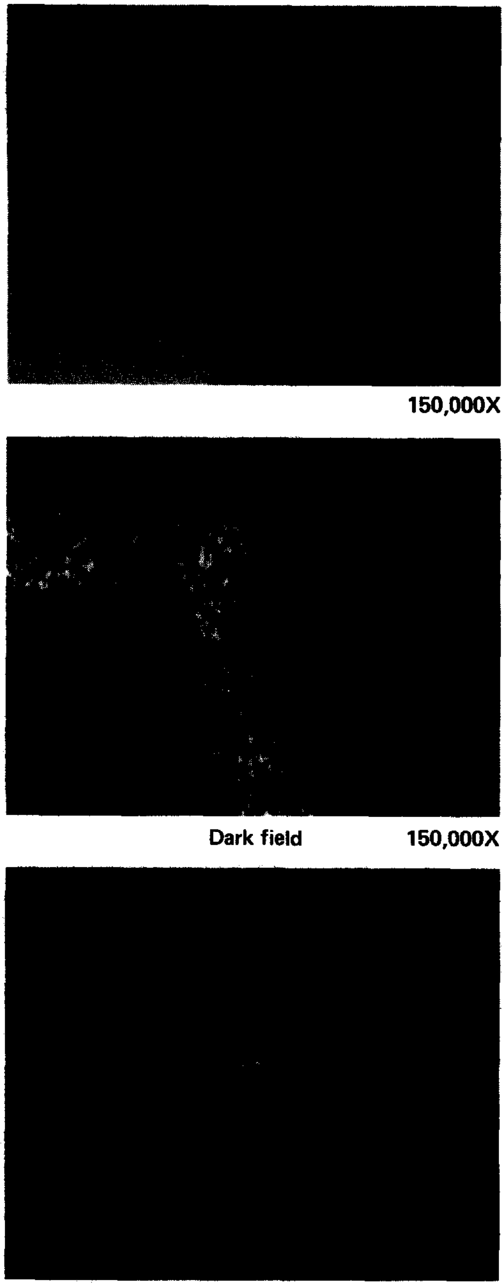
| Catalyst | Treatment | Area ($m^2/g$) | Lattice parameter $a_0$ (Å) |
|---|---|---|---|
| Na-$ThO_2$ | 520 K in air | 120 | 5.571 ± 0.014 |
| Na-$ThO_2$ | Used catalyst | 50 | 5.591 ± 0.019 |
| Na-$ThO_2$ | 723 K in air | 50 | 5.599 ± 0.004 |
| $NH_4$-$ThO_2$ | 520 K in air | 130 | 5.562 ± 0.021 |
| $NH_4$-$ThO_2$ | Used catalyst | 36 | 5.593 ± 0.011 |
| K-$ThO_2$ | 513 K in air | 1.7 | Amorphous |

TEM micrographs of an $NH_4$-$ThO_2$ catalyst that was calcined at 525 K confirmed that the compound was crystalline in nature; hence the weak and broad X-ray powder patterns observed were due to the extremely small crystallite sizes of $ThO_2$ (<5.0 nm) rather than to an amorphous structure. A dark-field micrograph of an $NH_4$-$ThO_2$ particle (Fig. 2) shows the very small $ThO_2$ crystallites as bright spots. Also, the (111) reflections of a catalyst crystallite are shown in Fig. 2.

The pore volume of thoria catalysts as a function of pore diameter is shown in Fig. 3. Sixty percent of the pores have diameters less than 20 nm and the rest lie between 20 and 120 nm.

Thorias which were calcined in air at temperatures higher than 523 K subsequently showed much lower catalytic activity. An induction period was always noticed for the onset of methanol production; a fresh catalyst exposed to 5 MPa of $2H_2:CO$ mixture at 540 K typically required 4–6 h to reach its highest activity. The Na-$ThO_2$ catalyst calcined in air at 725 K showed peak methanol-production rates less than half those of Na-$ThO_2$ calcined at 525 K. Thus, it appears that it is essential to contact the catalyst with the synthesis gas atmosphere to form and maintain catalytically active sites while sintering of the thoria particles takes place.

The fresh thoria catalysts were white (with a slight amber tint) after calcination. The color changed to shiny coal-black after use in the synthesis reaction. The color change, which was not caused by coke formation, clearly indicates that there is a change in the nature of the defects in the solid. A similar behavior has been observed in the oxidation of thorium metal in dry oxygen and in water vapor (or water vapor/oxygen). In the former case, white thoria rich in divalent oxygen vacancies was produced; in the latter case, black thoria was formed containing monovalent and divalent oxygen vacancies as well as $OH^-$ (*15*).


150,000X

Dark field 150,000X

Spot area diffraction

FIG. 2. Transmission electron microscope micrographs of the $NH_4$-$ThO_2$ catalysts calcined at 520 K, and (111) reflections from a $NH_4$-$ThO_2$ particle.

### *II. Photoelectron Spectroscopy (XPS) Studies*

Binding energies and surface compositions for the Na-$ThO_2$ and $NH_4$-$ThO_2$ catalysts (not exposed to synthesis gas) are presented in Table 2. Two trends were noted for the Na-$ThO_2$ catalyst: (1) at temperatures between 333 and 470 K, a large amount of carbon migrated to the surface; and (2) at 550 K, corresponding closely to the minimum temperature for which methanol activity was observed, additional Na migrated to the surface (~10 at.%). The value of the sodium Auger (*16*) parameter indicates that this element was present in the form of $Na_2O$.

The carbon content of the $NH_4$-$ThO_2$ catalyst was about half that of the Na-$ThO_2$ catalyst (Table 2). Analysis of a sample of $NH_4$-$ThO_2$ exposed to synthesis gas showed that the carbon content of the catalyst was approximately the same as for the unused material.

The O 1*s* photoelectron spectrum for the Na-$ThO_2$ catalyst calcined in vacuum at 550, 673, and 740 K is shown in Fig. 4. The decrease in the intensity of the photoelectron peak at a binding energy of 532.8 eV relative to the peak at 531.0 eV is probably due to conversion of hydroxyl and carbonate groups to oxide (lower O 1*s* binding energy) and significant dehydration of the sur-

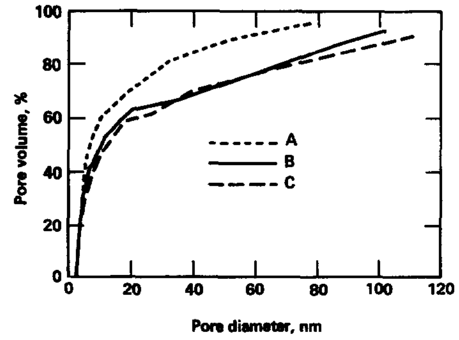


FIG. 3. Pore volume as a function of pore diameter for $ThO_2$ catalyst: (A) unused Na-$ThO_2$ calcined in air at 523 K for 48 h, (B) Na-$ThO_2$ exposed to synthesis gas, and (C) unused Na-$ThO_2$ calcined at 723 K for 16 h.

TABLE 2

Photoelectron Spectroscopy of Thoria Catalysts

| Catalyst | T (K) | Binding energy (eV) | | | | | Na Auger parameter (eV) |
|---|---|---|---|---|---|---|---|
| | | Th $4f_{7/2}$ | C 1s | O 1s | Na 1s | Na KLL | |
| Na-$ThO_2$ | 333 | 335.7(13) | 285.9(13) | 533.1(66) | 1074.7 | 265.0(8) | 2062.3 |
| | 550 | 335.0(8) | 285.9(32) | 531.2(42) | 1073.6 | 264.9(15) | 2062.6 |
| | 673 | 335.0(11) | 285.9(32) | 529.0<br>532.8 (45) | 1073.6 | 265.0(12) | 2062.6<br>2062.6 |
| | 740 | 335.0(12) | 286.0(34) | 531.0<br>533.0 (40) | 1073.9 | 265.0(14) | 2062.9 |
| $NH_4$-$ThO_2$ | 550 | 335.6(15) | 285.9(18) | 532.1<br>533.8 (67) | — | — | |

*Note.* Numbers in parentheses indicate the atomic percentage.

face. The large decrease in surface area that was observed at temperatures around 740 K may be associated with surface dehydration, which facilitates sintering of the thoria particles.

Changes in the Th 4*f* lines for the Na-$ThO_2$ catalyst as a function of temperature are presented in Fig. 5. At 333 K, the 4*f* levels were split into two lines each, showing the presence of thorium carbonate (~339 and ~347 eV) and oxide (~335.7 and ~344 eV). As the oxide–carbonate decomposed, the lines of pure $ThO_2$ emerged at 673 and 740 K.

### *III. Catalyst Activity as a Function of Temperature*

Figure 6 presents the product distribution for a reaction carried out at 577, 600, and 630 K, using 2 $H_2$:CO synthesis gas at a pressure of 5.4 MPa and an STP gas flow rate through the reactor of 1.8 $m^3$/kg cat.-h (space velocity = 5000 $h^{-1}$). At this flow rate, which was used for all reported experiments, the 1 mole% methanol in the reactor effluent corresponds to a methanol production rate of 26 g $CH_3OH$/kg cat.-h. On a mole basis, methanol is the predominant product for both the $NH_4$-$ThO_2$ and Na-$ThO_2$ catalysts throughout the temperature

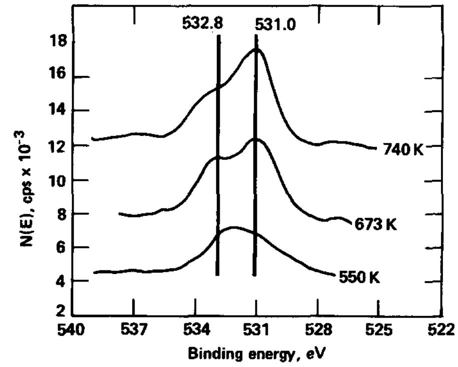


FIG. 4. The O 1*s* photoelectron spectra of the Na-$ThO_2$ catalyst calcined under vacuum at 550, 673, and 740 K.

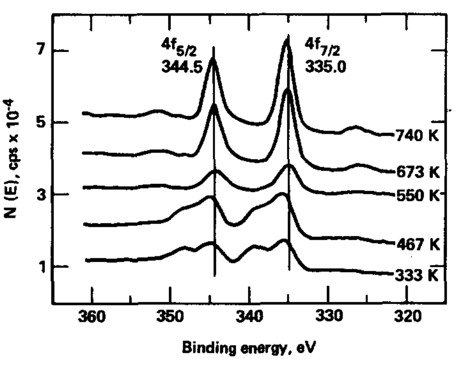


FIG. 5. The 4*f* photoelectron spectra of Na-$ThO_2$ as a function of calcination temperature under vacuum.

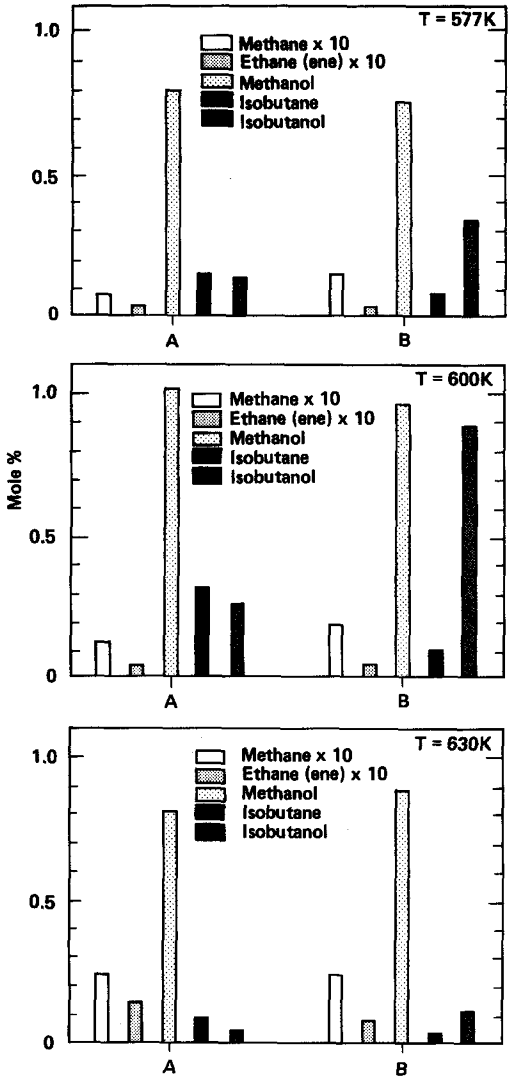


FIG. 6. Temperature dependence of the products produced on (A) $NH_4$-$ThO_2$ and (B) Na-$ThO_2$ using a $2H_2:CO$ gas mixture at 5.4 MPa and STP flow rate of 1.8 $m^3$/kg cat.-h.

range studied. These catalysts differed mainly in the yield of the $C_4$ products, which were isobutane and isobutyl alcohol and their respective proportions. The Na-$ThO_2$ catalyst showed increased activity for synthesis of isobutyl alcohol, while the $NH_4$-$ThO_2$ catalyst had a higher activity for isobutane synthesis. At temperatures above 570 K, $NH_4$-$ThO_2$ catalysts began to show significant production of ethane. The ethene/ethane ratio increased from 0.5 at 580 K to 1 at 630 K. Trace amounts of propane and $C_5$ hydrocarbons were produced by both catalysts throughout the temperature range studied.

The concentrations of methanol in the reactor effluent for both Na-$ThO_2$ and $NH_4$-$ThO_2$, as a function of temperature at a constant pressure of 5.45 MPa, are shown in Fig. 7. The activation energy ($E_A$) for methanol synthesis, determined from a log–log plot of catalyst activity vs $1/T$, is 45 kJ/mole for both catalysts. The $E_A$ for methane synthesis for the $NH_4$-$ThO_2$ catalyst is 64 ± 5 kJ/mole (565–620 K), and for the Na-$ThO_2$ catalyst, 27 ± 1 kJ/mole (577–630 K).

### *IV. Dependence of Catalytic Activity on Pressure and Hydrogen to Carbon Monoxide Ratio*

Figure 8 presents the mole% methanol in the reactor effluent for a $NH_4$-$ThO_2$ catalyst (STP flow rate = 1.8 $m^3$/kg cat.-h; space velocity = 5000 $h^{-1}$) and a $2H_2:CO$ gas mixture at 3.77 and 5.62 MPa and 605 K. The relatively low temperature of 605 K was chosen to minimize the effect of side reactions; at this temperature the mole percentage of methanol in the product varies between 85 at the lowest pressure to 95 at the highest. The enhanced yield of methanol with the higher pressure of synthesis gas indicates that the pressure dependence

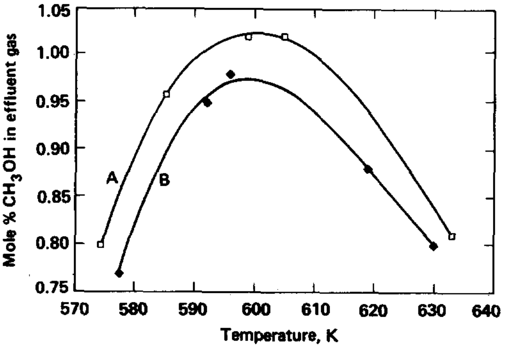


FIG. 7. Mole% conversion of a $2H_2:CO$ mixture (5.45 MPa) into methanol as a function of temperature (STP flow rate = 1.8 $m^3$/kg cat.-h): (A) Na-$ThO_2$ and (B) $NH_4$-$ThO_2$.

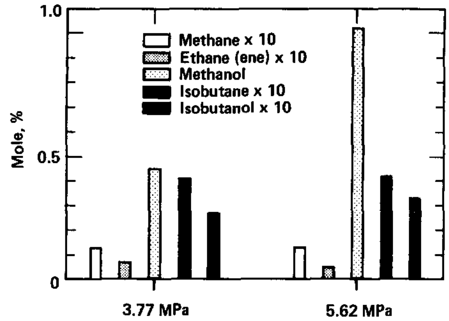


FIG. 8. Pressure dependence of the production of methanol on $NH_4$-$ThO_2$ using a $2H_2 : CO$ gas mixture at 605 K and an STP flow rate of 1.8 $m^3$/kg cat.-h.

for the reaction on $H_2$ must be greater than that for CO.

A satisfactory kinetic model was obtained using the rate equation given by Natta (2) for the $ZnO/Cr_2O_3$ and $CuO/ZnO/Cr_2O_3$ methanol synthesis catalysts:

$$A + BP(\mathrm{CO}) + CP(\mathrm{H_2}) = [P(\mathrm{CO}) \times P(\mathrm{H_2})^2/r_0]^{1/3}, \quad (1)$$

where

$A$ = constant,

$B$, $C$ = equilibrium constants for the adsorption of carbon monoxide and hydrogen, respectively,

$P$(CO) = partial pressure of CO,

$P(H_2)$ = partial pressure of $H_2$, and

$r_0$ = initial rate of methanol formation (the tangent to the reaction isotherm at the origin).

Equation (1) assumes a termolecular surface reaction and low conversion so that terms dependent on methanol partial pressures are negligible. The values of $A$, $B$, and $C$, obtained from a least-squares fit of our data from Fig. 9 to Eq. (1) were 46.44, 2.97, and 3.23, respectively. The agreement between calculated rates from the least-squares fit and experimental ones is clearly shown in Fig. 10. A value of $B/C = 0.9$ predicts that hydrogen is more strongly adsorbed than carbon monoxide at a temperature of 562 K. In contrast, Natta found that $B/C = 5$ for the $CuO/ZnO/Cr_2O_3$ catalyst at 573 K, indicating that carbon monoxide is much more strongly adsorbed than hydrogen.

## DISCUSSION

In our studies of carbon monoxide hydrogenation on $ThO_2$, we chose conditions which were thermodynamically favorable for the formation of oxygenated products. The thorium oxide catalysts, easily produced with readily available starting materials, gave product distributions which consisted mostly of methanol, with small

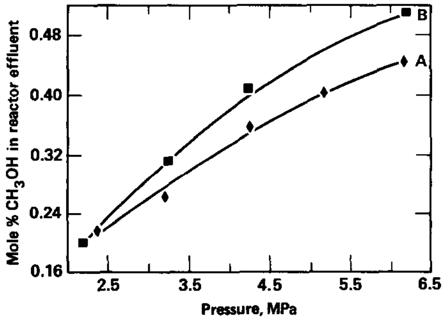


FIG. 9. Mole% conversion of a CO + $H_2$ mixture to methanol on a $NH_4$-$ThO_2$ catalyst at 562 K (STP flow rate = 1.8 $m^3$/kg cat.-h): (A) $H_2$:CO = 1:1 and (B) $H_2$:CO = 2:1.

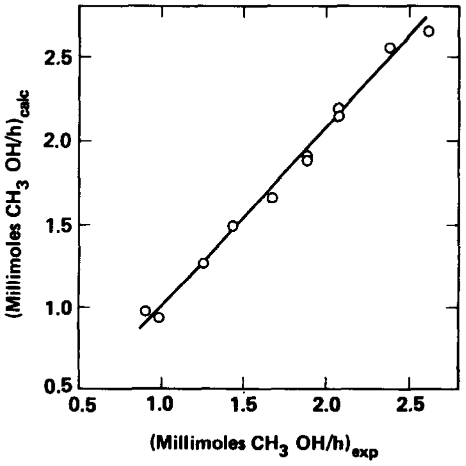


FIG. 10. Comparison of calculated (Natta's model) and experimental methanol formation rates (moles $CH_4OH$/h).

amounts of isobutyl alcohol and gaseous hydrocarbons. The catalysts showed constant activity and long life; furthermore, full activity was retained even after exposures to reaction temperatures of 630 K for over a week. No addition of carbon dioxide to the synthesis gas was required to maintain catalytic activity, and coking was not observed.

The initial surface areas (120–130 $m^2/g$) of the Na-$ThO_2$ and $NH_4$-$ThO_2$ catalysts prepared for this study are some of the largest reported in the literature; typical published values range between 20 and 60 $m^2/g$ (*17*). The large surface areas in our work are the direct result of the specific preparative procedures used. Large surface areas are significantly influenced by the preparation and calcination methods, as has been shown in many published studies (*17–20*). The Na-$ThO_2$ and $NH_4$-$ThO_2$ catalysts are crystalline after calcination (Fig. 2), in contrast to the K-$ThO_2$, which has the consistency and appearance of glass, as well as very low surface area (Table 1). The X-ray lattice parameters (Table 1) obtained for the Na-$ThO_2$ catalyst indicate that it is $ThO_2$; however, broadening of the diffraction lines by small particles prevents the determination of its exact stoichiometry.

The K-$ThO_2$ prepared for this study is inactive for the production of methanol/isobutyl alcohol, in contrast to a mixed catalyst of $ThO_2$ + 3% $K_2CO_3$ (*8*), which was found to be very good for the production of methanol and other alcohols from a 1 : 1 CO : $H_2$ mixture at 40.4 MPa and 673 K. Data at lower pressure and temperature, equivalent to the conditions for this study, were not explored in Ref. (*8*).

XPS data (Table 2, Figs. 4 and 5) show that Na-$ThO_2$ and $NH_4$-$ThO_2$ catalysts before calcination are a hydroxy-carbonate. The Th 4*f* lines (Fig. 5) are split, indicating the presence of two distinct compounds, presumably hydroxide and carbonate; this is also reflected on the oxygen 1*s* line (Fig. 4). As the temperature is raised, the thorium 4*f* levels (335.0 and 344.5 eV) show the presence of single lines and a satellite at ~7 eV from the $4f_{5/2}$ line corresponding to $ThO_2$ (*21–23*). The presence of a shoulder at ~533 eV in the oxygen 1*s* spectrum has been shown by McLean *et al.* (*22*) to be due to the chemisorption of $CO_2$ on $ThO_2$ as a monodentate carbonate, which is stable under vacuum up to 773 K. This finding is to be expected because the decomposition of thorium oxycarbonate produces $CO_2$ and $H_2O$. The OH from water would be detectable around 532 eV (*16*); however, its presence cannot be ruled out due to the broadness of the 0 1*s* peak (Fig. 5).

By XPS, the Na-$ThO_2$ catalyst was found to contain ~10 at.% ionic sodium, which is consistent with the behavior of $ThO_2$ as an inorganic ion exchanger with a strong affinity for alkali metal cations (*24, 25*). The role of sodium ions in the synthesis reaction is probably to control the surface acid–base chemistry. The Na-$ThO_2$ catalyst, which is expected to have a more basic surface than $NH_4$-$ThO_2$, produces comparatively more isobutyl alcohol than isobutane and does not show a significant tendency to produce ethane. Thus, the sodium ions presumably suppress acid-catalyzed dehydration reactions, which are part of the step forming hydrocarbon by-products after methanol is produced in the primary synthesis step on the catalyst surface.

To produce an active catalyst, it is essential to expose both Na-$ThO_2$ and $NH_4$-$ThO_2$ to synthesis gas at ~525–540 K. This phenomenon may be related to the removal of the strongly chemisorbed oxygen that these materials pick up on exposure to air during calcination. We found that this oxygen can be removed in the form of $H_2O$ by treatment with either $H_2$ or CO. This is in agreement with the results of Breysse (*26*), who determined that oxygen is strongly chemisorbed on $ThO_2$ and that it is not possible to remove it by heating under vacuum at 773 K. This chemisorbed oxygen was removed by treatment with hydrogen at 773 K for 5 h; the product was either stoichiometric or slightly substoichiometric $ThO_2$.

Our results with the Na-$ThO_2$ catalyst are compared in Table 3 to those obtained with $CuO/ZnO/Al_2O_3$ and Th/Cu intermetallics under optimal conditions. Thorium–copper intermetallic compounds ($Th_2Cu$, $ThCu_2$, $ThCu_{3.6}$, and $ThCu_6$), as well as alloys of nominal composition ($ThCu_5$, ThCuCr, and thorium with 5 wt% Cu), have been used as methanol catalysts after decomposition into Cu + $ThO_2$ or CuCr + $ThO_2$ by oxidation in air, $3H_2$:CO synthesis gas, $H_2$ + ~4% $H_2O$, or pure carbon dioxide (*11, 12*). The intermetallics producing the best results were $ThCu_6$ and $ThCu_{3.6}$. The performance of a $CuO/ZnO/Al_2O_3$ catalyst with and without $CO_2$ in the synthesis gas mixture is also included for comparison.

The energies of activation for methanol synthesis for ZnO, $Cr_2O_3$, and $ThO_2$ catalysts are ~126 (*2*), ~84 (*2*), and 45 kJ/mole (11 kcal/mole), respectively. The $E_A$ of 45 kJ/mole is quite close to that measured for the most active methanol synthesis catalyst (combinations of CuO, ZnO, and chromia or alumina) which fall in the range of 35–40 kJ/mole (*2*).

The kinetic model proposed by Natta was successfully tested with our data, and it indicates that the synthesis rate is a stronger function on hydrogen than on carbon monoxide, which is in agreement with the findings of Klier (*1*). Determination of the actual mechanisms involved will be studied in the future using XPS and other techniques.

## ACKNOWLEDGMENTS

We are very grateful to R. L. Smith for his help with all experimental aspects of this work. Work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48. Partial support was also obtained from the director of Basic Energy Sciences, Chemical Sciences Division of the U.S. Department of Energy under Contract DEACO-376SS-00098.

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TABLE 3

Comparison of Methanol Catalysts under Optimum Conditions

| Catalyst | Surface area after reaction ($m^2/g$) | Synthesis gas | *T* (K) | *P* (atm) | Space velocity ($h^{-1}$) | CO conversion to $CH_3OH$ | | Ref. |
|---|---|---|---|---|---|---|---|---|
| | | | | | | mole% | kg $CH_3OH$/liter cat.-h | |
| $N_a$-$ThO_2$ | 50.0 | CO : $2H_2$ | 600 | 53.5 | 5,000 | 3.0 | 0.08 | This work |
| $Cu/ZnO/Al_2O_3$[b] | 42.0 | CO : $16H_2$ | 598[a] | 60 | 31,000 | 13.0[a] | 0.34 | (*11*) |
| $Cu/ZnO/Al_2O_3$[b] | — | CO : $2.4H_2$ | 298[a] | 60 | 22,000 | 7.0[a] | 0.65 | (*12*) |
| $CuO/ZnO/Al_2O_3$ (66 : 17 : 17) | — | CO + $H_2$ + $CO_2$[d] | 523 | 70 | 200[c] | — | 4.75 | (*1*) |
| $ThCu_{3.6}$ | 35.5 | CO : $16H_2$ | 553 | 60 | 31,000 | 44.02 | 1.15 | (*11*) |
| $ThCu_6$ | | CO : $2.4H_2$ | 523 | 60 | 22,000 | 54.40 | 5.03 | (*12*) |
| $ThO_2$/5% Cu precipitate | 20.4 | CO : $16H_2$ | 613[a] | 60 | 31,000 | 8.0[a] | 0.21 | (*11*) |

[a] Temperature and percentage conversions were read from published plots in the reference.

[b] United Catalysts Lot C79-4.

[c] Moles per hour.

[d] Unspecified proportions.

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