Characterization of Catalysts Derived from Oxidation of Ru_xTh_y Intermetallics

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Ru methanation catalysts derived from oxidation of Ru, Th, intermetallics were characterized by X-ray photoelectron spectroscopy (ESCA), ion scattering spectroscopy (ISS), X-ray diffraction (XRD), BET surface area measurements, chemisorption, and gravimetric analysis. XRD measurements and gravimetric analysis indicated that all intermetallics were extensively decomposed by oxidation in air at 350 °C. ESCA and ISS Ru/Th intensity ratio measurements showed that surface segregation of ThO₂ occurred for all catalysts. The structure of the intermetallic-derived (IM) catalysts can best be described as Ru particles embedded in a ThO₂-rich overlayer. Comparison of hydrogen and CO uptake with N₂ BET surface area suggests that CO more accurately titrates surface Ru than does hydrogen. Extensive spillover of hydrogen from Ru to ThO₂ was also observed for all IM catalysts. The catalysts were tested for CO hydrogenation; exceptionally high methane selectivity was observed for all catalysts. On the basis of CO chemisorption, the CO hydrogenation turnover frequency was comparable for all the IM catalysts. The CO hydrogenation activities and selectivities are discussed on the basis of the structure sensitivity of CO hydrogenation on Ru catalysts and the special morphology of the IM catalysts.

Introduction

The use of intermetallic compounds $A_x B_y$, where A is a transition metal and B a rare earth or an actinide, as starting materials for catalyst preparation has been the subject of several investigations.¹⁻⁸ On oxidation, $A_x B_y$ is transformed into a material presumably similar to supported catalysts prepared by impregnation. After reduction, the intermetallic-derived (IM) catalysts are active for CO hydrogenation and show high selectivity for methane production. Recently, we have compared the catalyst derived from Ru₃Th₇ with the corresponding supported Ru/ThO₂ catalyst.⁹ The CO hydrogenation activity for the Ru₃Th₇-derived catalyst was 2 orders of magnitude higher than that of the corresponding supported catalyst. Exceptionally high methane selectivity was also observed for the IM catalyst.

The purpose of the present study was to investigate the change in surface structure of Ru_xTh_y intermetallics caused by oxidation and subsequent reactions (e.g., reduction, syngas reaction) as a function of Ru content. The materials were characterized by X-ray photoelectron spectroscopy (XPS, ESCA), ion scattering spectroscopy (ISS), hydrogen and CO chemisorption, BET surface area measurements, X-ray diffraction (XRD), and gravimetric analysis. The information obtained was used to explain performance of the IM catalysts.

Experimental Section

Four Ru_xTh_v intermetallic compounds (Ru₃Th₇, Ru₂Th₃, RuTh, and Ru_2Th^{10}) were prepared by induction melting of stoichiometric amounts of Ru (Alfa, 99.95%) and Th (Alfa, 99.9%) metals in a water cooled copper boat under an atmosphere of purified argon. Formation of the intermetallic compound was verified by comparing the X-ray diffraction pattern of the ground intermetallic with the ASTM diffraction file. The intermetallics were ground to 120 mesh before use. Four types of material were examined in this study: untreated, designated as $(Ru_xTh_y)_U$, referring to the intermetallics ground in air and sieved to 120 mesh immediately before use; oxidized, designated as $(Ru_xTh_y)_{Ox}$, referring to $(Ru_xTh_y)_U$ oxidized at 350 °C for 24 h in a muffle furnace that had been preheated to the oxidation temperature; reduced, designated as $(Ru_xTh_y)_R$, referring to $(Ru_xTh_y)_{Ox}$ reduced in a flow of hydrogen (Matheson, 99.999%) at 275 °C for 12 h; and reacted, designated as $(Ru_xTh_y)_s$, referring to the reduced series reacted with syngas $(H_2/CO = 3)$ at 185 °C for 12 h.

X-ray diffraction powder patterns were obtained with a Diano 700 X-ray diffractometer, which utilizes Ni filtered Cu K α radiation. The X-ray gun was operated at 50 kV and 25 mA and a scan rate of $0.4^{\circ}/\min(2\theta)$. Samples were mounted on glass slides using silicone grease as an adhesive. Compound identification was accomplished by comparison of the measured spectra with ASTM powder diffraction file data.

ESCA spectra were obtained with an AEI ES-200A X-ray photoelectron spectrometer. The spectrometer was equipped with an aluminum anode (Al K $\alpha_{1,2}$ = 1486.6 eV) and was operated at 12 kV and 22 mA. The base pressure of the sample chamber was below 10⁻⁸ Torr. The spectrometer was interfaced with an Apple II plus microcomputer for data collection and storage. Data analysis was carried out on the Apple or on a DEC-10 main frame computer after direct transfer from the Apple via a communication program.

Untreated intermetallics, $(Ru_xTh_y)_U$, were examined as powders. The $(Ru_xTh_y)_{Ox}$ series was examined both in powdered form and as pellets pressed under a pressure of 5000 kg/cm². No significant difference in the I_{Ru}/I_{Th} intensity ratio between the powdered and pellet forms was found. This indicates that pressing the pellet has no effect on ESCA measurements for the samples. Pellet samples of oxidized intermetallics were mounted on a sealable probe, described elsewhere,11 for reactions and ESCA measurements. The probe permits transfer of reacted samples from an external reactor to the spectrometer without exposure to air. Reduction was carried out under a flow of H₂ (99.999%) at 275 °C for 12 h. Hydrogenation of CO was carried out at 205 °C under a flow of syngas having the H_2/CO_2 ratio = 3. In all cases, a flow rate of 50 cm³/min was used.

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Because the ESCA Ru $3d_{3/2}$ peak overlaps the C 1s line, binding energy measurements for the $(Ru_xTh_y)_U$ series were referenced to Au $4f_{7/2} = 83.5$ eV. The gold was vacuum deposited on the samples before measurement. It should be noted that the Au 4f peaks overlap the Th $5d_{5/2}$ peak. However, the interference does not significantly affect the binding energy measurements of the Au 4f peaks since the latter are much more intense than the former. Also, the Au $4d_{5/2}$ peak overlaps the Th $4f_{7/2}$ peak but not the Th $4f_{5/2}$ peak. Therefore, the binding energy of the Th $4f_{7/2}$ peak can be obtained from the Th $4f_{5/2}$ peak, using the binding energy difference between the two peaks. The binding energy difference between the two Th 4f peaks is 9.2 ± 0.15 eV for both ThO₂ (determined experimentally using ThO₂) and Th metal.12

Since ThO_2 is not reduced under reaction conditions, the Th $4f_{7/2}$ line of ThO₂ (BE = 333.6 eV) was used as a reference for binding energy measurements of the treated series.² ESCA intensity ratios, $I_{\rm Ru}/I_{\rm Th}$, were calculated from the normalized areas of the Ru $3p_{3/2}$ and Th 4f lines. Overlap of the O 1s line from Al K β radiation with the Ru $3p_{3/2}$ line was accounted for by a method described elsewhere.9

For a homogeneous alloy, the ESCA intensity ratio of peaks associated with Ru and Th (I_{Ru}/I_{Th}) can be related to the surface atomic ratio $n_{\rm Ru}/n_{\rm Th}$ as shown below:¹³

$$\frac{I_{\rm Ru}}{I_{\rm Th}} = \frac{n_{\rm Ru}}{n_{\rm Th}} \frac{\sigma_{\rm Ru}}{\sigma_{\rm Th}} \frac{\lambda_{\rm Ru}}{\lambda_{\rm Th}} \frac{D_{\rm Ru}}{D_{\rm Th}} \tag{1}$$

where σ represents the modified Scofield photoionization cross section, $^{14,15}\,\lambda$ is the escape depth of the Ru $3p_{3/2}$ or Th 4f photoelectron, and D(Ru or Th) is the instrument transmission function for Ru or Th photoelectrons, which varies linearly with kinetic energy for the AEI instrument.²

ISS studies were carried out on an LHS-10 ESCA-ISS spectrometer equipped with a hemispherical analyzer to measure the energies of backscattered ions. A base pressure below 1×10^{-8} Torr was typical before filling the chamber with ²⁰Ne, which was used as the scattering gas. The incident ions had an energy of 1.5 keV. The samples were examined at a current density of 2 $\times 10^{-7}$ A/cm². The sputtering rate at this current density was estimated to be 1 monolayer per 5-10 min assuming 1015 atoms/cm² per monolayer and a sputtering yield of 0.5 atom/²⁰Ne⁺ ion.¹⁶ The average of spectra obtained in the first 10 min of measurement was used to obtain the surface Ru/Th atomic ratio. The relative scattering cross sections of Th (S_{Th}) and Ru (S_{Ru}) in ThO₂ and RuO₂ were determined experimentally according to the method of Wheeler:¹⁷ $S_{Th}/S_{Ru} = 4.4$.

Gravimetric Analysis. The oxidation/reduction behavior of the intermetallics was studied by use of a Cahn 113 microbalance. The freshly ground intermetallics were oxidized under a flow of air (Matheson, zero grade, 10 cm³/min) using a temperature ramp, increasing from room temperature to 350 °C in 20 min; the temperature was then held at 350 °C for 24 h. The weight change measured was used to calculate the amount of oxygen uptake during oxidation. After oxidation, the sample was reduced in a flow of hydrogen (Matheson, 99.999%, 50 cm³/min) at 350 °C until constant weight was obtained. The weight change measured was used to calculate the amount of oxygen removed during reduction.

 H_2/CO Chemisorption and N_2 BET Adsorption. Hydrogen chemisorption was determined by using a volumetric BET system. A catalyst weighing 300 mg was reduced at 275 °C for 16 h in circulating hydrogen with a liquid nitrogen trap. After reduction, the catalyst was evacuated at 275 °C for 30 min and cooled to





Figure 1. XRD patterns of the oxidized intermetallics.

room temperature. The hydrogen chemisorption isotherm was then measured at room temperature according to a method described previously.⁹ The zero-pressure intercept of the isotherm was taken as the total amount of hydrogen adsorbed. After the first isotherm was obtained, the catalyst was evacuated at room temperature for 30 min and a second isotherm was measured. The difference between the zero-pressure intercepts of the two isotherms was taken as a measure of the irreversibly adsorbed hydrogen. After the hydrogen chemisorption measurement, the temperature was raised to 275 °C at a rate of 5 °C/min and the catalyst was evacuated at 275 °C for 1 h. After cooling to room temperature, CO chemisorption was measured using the same method as for hydrogen chemisorption. Since no significant reversibly adsorbed CO was observed for the Ru₃Th₇-derived catalyst,9 only the total CO adsorbed was measured. After the CO chemisorption measurement, the catalyst was evacuated and reduced in hydrogen at 275 °C for 1 h followed by 30 min evacuation at 275 °C. After evacuation the catalyst was cooled in a liquid N_2 trap and the N_2 BET adsorption was measured. The ruthenium dispersion was estimated from hydrogen or CO chemisorption assuming a stoichiometry of H (or CO)/Ru = $1.^{18}$ The BET surface areas of the intermetallic-derived catalysts were calculated assuming the N₂ cross section to be 16.2 $Å^{2,19}$

CO hydrogenation activity was measured in a microreactor that permits monitoring up to four samples simultaneously. A 50mg-catalyst sample diluted with 450 mg of quartz powder was reduced at 275 °C in a flow of hydrogen (Matheson, 99.999%, 50 cm³/min) for 16 h before reaction. A synthesis gas mixture with $H_2/CO = 3$ was used for the reaction at 205 °C. In all cases, the flow rate was 25 cm³/min. Conversion rates were determined from the composition of the exit gas measured on stream by gas chromatography. Steady-state activities which normally were obtained after 4-8 h of reaction are reported.

Results

X-ray Diffraction (XRD). Figure 1 shows the XRD patterns of the four oxidized intermetallics. The intense lines observed

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TABLE I: XRD Results for Untreated and Treated Intermetallics

| inter- metallic | untreated | XRD phase oxidized | reduced | particle size of ThO ₂ , ^a nm |
|-----------------------------------|---|---|--|---|
| Ru3Th7 Ru2Th3 RuTh Ru2Th | $\begin{array}{c} Ru_3Th_7, ThO_2\\ b, ThO_2\\ RuTh, ThO_2\\ Ru_2Th, ThO_2\\ \end{array}$ | $\begin{array}{c} ThO_2, Ru\\ ThO_2, Ru, RuO_2\\ ThO_2\\ ThO_2\\ ThO_2 \end{array}$ | ThO ₂ , Ru ThO ₂ , Ru ThO ₂ , Ru ^c ThO ₂ , Ru ^c | 16 11 10 7 |

^aOxidized intermetallics, based on the ThO₂(200) line. ^bNo crystal structure can be assigned from the XRD pattern. ^cThe XRD lines of Ru metal were diffuse.

TABLE II: Gravimetric Analysis Results for Ru_xTh_y Intermetallics

| | oxid | ation | | | | |
|---------------------------------|-------------------------------------|------------------|----------------------------|---|------------|--|
| | | RuO ₂ | | reduction | | |
| | O ₂ uptake, ^a | forn % tot | ned, ^ø al Ru | weight reduced loss. ^a RuO ₂ , | | |
| | mg/g | A | В | mg/g | % total Ru | |
| Ru ₃ Th ₇ | 135 (166) ^c | 81 | 38 | 18.4 | 37 | |
| Ru_2Th_3 | 169 (178) ^c | 95 | 87 | 62.4 | 88 | |
| RuTh | 126 (192) ^c | 66 | 31 | 28.4 | 30 | |
| Ru_2Th | 101 (221) ^c | 46 | 18 | 27.5 | 19 | |

^a Measurements were reproducible to $\pm 0.5 \text{ mg/g}$. ^b(A) Assuming simultaneous oxidation, i.e., $\text{Ru}_3\text{Th}_7 + 10\text{O}_2 \rightarrow 3\text{RuO}_2 + 7\text{ThO}_2$. (B) Assuming sequential oxidation; see text. ^cTheoretical values for complete oxidation of intermetallics.

at $2\theta = 27.6^{\circ}$, 32.2° , and 46° are characteristic of ThO₂. The weak lines, at $2\theta = 38.5^{\circ}$, 42.2° , and 44° , detected in all samples except (Ru₂Th)_{Ox}, are ascribed to metallic Ru. Furthermore, a weak peak characteristic of RuO₂ at $2\theta = 35^{\circ}$ is detected in the XRD pattern of oxidized Ru₂Th₃. Compared to the XRD pattern of a corresponding physical mixture of Ru (or RuO₂) and ThO₂, the amount of metallic Ru and RuO₂ observed by XRD represents less than 10% of the Ru content in the oxidized intermetallics. Thus, the major part of the Ru phase must be present in an amorphous or highly dispersed state. No XRD lines characteristic of intermetallics were observed for any oxidized catalyst. This indicates that the intermetallics were extensively decomposed.

No significant change in the XRD patterns was observed on reduction, relative to the oxidic catalysts, except for $(Ru_2Th)_R$, where an additional diffuse XRD peak characteristic of Ru metal at $2\theta = 44^\circ$ was detected. A summary of the phases identified by XRD for the four intermetallics before and after treatment is given in Table I. Also shown in Table I are the particle sizes of ThO₂ in the oxidized intermetallics estimated from the XRD ThO₂(200) lines using the Scherrer equation.²⁰ The ThO₂ particle sizes decreased from 16 to 7 nm with increasing Ru content.

Gravimetric Analysis. Results of the gravimetric measurements are listed in Table II. The oxygen uptake ranged from 101 mg/g for Ru₂Th to 169 mg/g for Ru₂Th₃. By comparing the measured oxygen uptake to the theoretical value for complete oxidation to RuO₂ and ThO₂, one can readily note that Ru and Th in the intermetallics were not completely oxidized.

To estimate the extent of oxidation for the intermetallics, two possible mechanisms were considered:

A. The first mechanism was simultaneous oxidation of Ru and Th in the intermetallics (i.e., the amount of oxygen consumed is proportioned between Ru and Th according to the stoichiometry of the alloy). The following equation illustrates the appropriate stoichiometry:

$$Ru_{x}Th_{y} + (x + y)O_{2} \rightarrow xRuO_{2} + yThO_{2}$$
(2)

On the basis of the above equation, the percentage transformations of the intermetallics to RuO_2 and ThO_2 by oxidation are shown in Table II; they ranged from 95% for Ru_2Th_3 to 46% for Ru_2Th .

B. The second mechanism was preferential oxidation of the element having the higher heat of formation of the metal oxide

TABLE III: Results of Hydrogen and CO Chemisorption

| | total H,ª mmol/ | | total CO, ^a mmol/ | dispersion | |
|---|--------------------|-----------------------------|---------------------------------|------------|-------|
| | (g of Ru) | $H_{\rm i}/H_{\rm t}^{\ b}$ | (g of Ru) | Н | CO |
| (Ru ₃ Th ₇) _R | 2.09 | 0.53 | 0.49 | 0.21 | 0.05 |
| (Ru ₂ Th ₃) _R | 1.98 | 0.59 | 0.48 | 0.20 | 0.05 |
| (RuTh) _R | 1.63 | 0.53 | 0.02 | 0.16 | 0.002 |
| $(Ru_2Th)_R$ | 1.75 | 0.54 | 0.01 | 0.18 | 0.001 |

^a Measurements were reproducible to $\pm 0.02 \text{ mmol/g}$. ^b Fraction of irreversibly adsorbed hydrogen.

TABLE IV: Results of Surface Area Measurements for Catalysts Derived from Ru, Th, Intermetallics

| | surface area, $m^2/(g \text{ of catal})$ | | | | | | |
|---------------------|--|---------|-------|--------------------|---------------------|--|--|
| | S _{BET} ^a | | STEO. | | | | |
| catalyst | (oxidic) | reduced | only | $(S_{Ru})_{H}^{c}$ | $(S_{Ru})_{CO}^{c}$ | | |
| $(Ru_3Th_7)_R$ | (5.0) | 10.1 | 18.9 | 10.8 | 2.3 | | |
| $(Ru_2Th_3)_R$ | (4.7) | 11.4 | 27.5 | 14.6 | 3.5 | | |
| (RuTh) _R | (1.2) | 2.0 | 30.2 | 16.2 | 0.2 | | |
| $(Ru_2Th)_R$ | (<0.5) | 0.7 | 43.2 | 25.8 | 0.1 | | |

^a The measurements were reproducible to $\pm 0.5 \text{ m}^2/\text{g}$. ^b From particle size determined by XRD line broadening; assuming spherical particles. ^cAssuming H/Ru and CO/Ru = 1 and $1.63 \times 10^{19} \text{ Ru/m}^2$ (ref 33).

(i.e., Th). In other words, the oxidation of Ru can occur only after Th is completely oxidized. This is illustrated by the following equations:

$$Ru_{x}Th_{y} + yO_{2} \rightarrow xRu + yThO_{2}$$
 (3)

$$Ru + O_2 \rightarrow RuO_2 \tag{4}$$

On the basis of eqs 3 and 4, all Th in the intermetallics is completely oxidized to ThO₂. The percentages of Ru in the form of RuO₂ after oxidation are also shown in Table II; they ranged from 87% for Ru₂Th₃ to 18% for Ru₂Th.

Considering that RuO_2 is the only species reducible at 350 °C, the weight losses during reduction of the oxidized samples should correspond to the reduction of RuO_2 and therefore can be used to obtain an independent estimate of the degree of oxidation for the intermetallics. The weight losses along with the estimated percentages of RuO_2 present in the oxidized intermetallics obtained by reduction are shown in Table II. Compared to the results calculated from oxygen uptake, it is clear that the results obtained by reduction measurements agree well with calculations based on mechanism B. This indicates that preferential oxidation of Th in Ru_xTh_y intermetallics has occurred.

Hydrogen and CO Chemisorption. Table III shows the hydrogen and CO chemisorption results for the four reduced IM catalysts. The hydrogen uptakes ranged from 1.63 mmol of H/(g of Ru) for (RuTh)_R to 2.09 mmol of H/(g of Ru) for (Ru₃Th₇)_R. The fraction of irreversibly adsorbed hydrogen (H_i/H_t) was similar for all catalysts (0.55 ± 0.02). The CO uptakes ranged from 0.01 mmol/(g of Ru) for (Ru₂Th)_R to 0.49 mmol/(g of Ru) for (Ru₃Th₇)_R. It is evident from Table III that the amount of chemisorbed CO was lower than chemisorbed hydrogen for all four IM catalysts. It also can be seen that the two Th-rich samples adsorbed 25–50 times more CO than the two Th-poor catalysts. On the basis of the total hydrogen uptake, the Ru dispersion (16–21%) was similar for the four samples. However, on the basis of the amount of chemisorbed CO, a large difference in the Ru dispersion (0.001–0.05) was calculated for the catalysts.

Surface Area Measurements. The BET surface areas (S_{BET}) of the four oxidized intermetallic catalysts before and after reduction, measured by N₂ adsorption, are reported in Table IV. It can be seen that the surface areas of the Th-rich catalysts $((Ru_3Th_7)_{Ox} \text{ and } (Ru_2Th_3)_{Ox})$ were at least 4–10 times higher than those of the Th-poor catalysts $((RuTh)_{Ox} \text{ and } (Ru_2Th_3)_{Ox})$. The surface area of $(Ru_2Th_{Ox} \text{ was too low to be measured accurately}$ (<0.5 m²/g). On reduction, a ca. 2-fold increase in the BET surface area was observed for all samples.

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TABLE V: Results of ESCA and ISS Ru/Th Intensity Ratio Measurements^a

| | $I_{\rm Ru}/I_{\rm Th}$ | | Ru/ atomic | Th ratio | Ru/(Ru + Th) atomic ratio | |
|---|-------------------------|-------|---------------|-------------|------------------------------|-------|
| | ESCA | ISS | ESCA | ISS | ESCA | ISS |
| (Ru ₃ Th ₇) _U | 0.0082 | | 0.054 | | 0.051 | |
| $(Ru_2Th_3)_U$ | 0.0126 | | 0.083 | | 0.077 | |
| (RuTh) | 0.0466 | | 0.307 | | 0.235 | |
| (Ru ₂ Th) _U | 0.0824 | | 0.544 | | 0.352 | |
| $(Ru_3Th_7)_{Ox}$ | 0.0077 | 0.005 | 0.052 | 0.022 | 0.048 | 0.022 |
| $(Ru_2Th_3)_{Ox}$ | 0.0210 | 0.027 | 0.139 | 0.12 | 0.122 | 0.11 |
| (RuTh) _{Ox} | 0.0402 | 0.047 | 0.265 | 0.21 | 0.209 | 0.17 |
| $(Ru_2Th)_{Ox}$ | 0.0668 | 0.057 | 0.441 | 0.25 | 0.301 | 0.20 |
| $(Ru_3Th_7)_R$ | 0.0075 | 0.006 | 0.051 | 0.026 | 0.047 | 0.025 |
| $(Ru_2Th_3)_R$ | 0.0215 | 0.025 | 0.142 | 0.11 | 0.124 | 0.10 |
| (RuTh) _R | 0.0397 | 0.041 | 0.262 | 0.18 | 0.208 | 0.15 |
| $(Ru_2Th)_R$ | 0.0735 | 0.057 | 0.486 | 0.25 | 0.327 | 0.20 |
| $(Ru_3Th_7)_S$ | 0.0066 | | 0.044 | | 0.042 | |
| $(Ru_2Th_3)_S$ | 0.0194 | | 0.128 | | 0.113 | |
| (RuTh) _S | 0.0368 | | 0.243 | | 0.195 | |
| (Ru ₂ Th) _S | 0.0661 | | 0.436 | | 0.304 | |

^a The ESCA and ISS measurements were reproducible to $\pm 10\%$ and $\pm 15\%$, respectively.

On the basis of the assumption that all Th in the oxidized catalysts was transformed to spherical ThO₂ particles and detected by XRD, the surface area of ThO₂ per gram of oxidized intermetallic (S_{ThO_2}) can be calculated from the particle sizes estimated by XRD line broadening (XRDLB). The results are also shown in Table IV. The BET surface areas were significantly lower than the surface areas of ThO₂ in the oxidized intermetallics estimated by XRDLB.

Table IV also lists the Ru metal surface area calculated from hydrogen and CO chemisorption. Similar to the trend shown for S_{BET} , the Ru surface area based on CO chemisorption, $(S_{\text{Ru}})_{\text{CO}}$, sharply decreases for catalysts having high Ru contents. Furthermore, $(S_{\text{Ru}})_{\text{CO}}$ is always lower than S_{BET} . On the other hand, in contrast with the S_{BET} , the Ru surface area based on hydrogen uptake, $(S_{\text{Ru}})_{\text{H}}$, increases with increasing Ru content. The $(S_{\text{Ru}})_{\text{H}}$ values of the two Th-rich catalysts were comparable to S_{BET} whereas the $(S_{\text{Ru}})_{\text{H}}$ values of the two Th-poor catalysts were 8–40 times higher than the corresponding S_{BET} .

ESCA and ISS Measurements. The ESCA Ru $3p_{3/2}$ and $3d_{5/2}$ envelopes, in all cases, indicate the presence of a single oxidation state. The Ru $3p_{3/2}$ and Ru $3d_{5/2}$ binding energies for the untreated intermetallics (460.7 ± 0.3 and 279.3 ± 0.2 eV, respectively) are consistent with the presence of metallic Ru (461.0 and 279.5 eV, respectively). The Th $4f_{7/2}$ binding energy of 333.6 ± 0.2 eV for the untreated samples indicates that ThO₂ (333.6 eV) was present at the surface. In the oxidized intermetallics, the Ru $3p_{3/2}$ and $3d_{5/2}$ binding energies (462.7 ± 0.3 and 280.8 ± 0.1 eV, respectively) indicate the presence of RuO₂ (462.9 and 280.9 eV, respectively) at the surface. Following reduction or syngas treatment, the Ru $3p_{3/2}$ and $3d_{5/2}$ binding energies obtained (460.9 ± 0.2 and 279.5 ± 0.2 eV, respectively) are characteristic of Ru metal.

Table V shows the ESCA Ru $3p_{3/2}$ /Th 4f intensity ratios for the intermetallics before and after treatment. Also shown in Table V is the Ru surface content calculated from the ESCA Ru/Th intensity ratio. It can be seen that the surfaces of the untreated and oxidized intermetallics are deficient in Ru compared to the bulk. One can also note that, except for Ru₂Th₃, oxidation causes a slight decrease in the Ru/Th intensity ratio. Reduction of the oxidized sample, as shown in Table V, did not significantly affect the Ru/Th intensity ratio. This indicates that the surfaces of the reduced catalysts were similar to those of oxidic samples and deficient in Ru. ISS studies of the oxidic and reduced intermetallics were also carried out. The results of ISS studies are also shown in Table V. In agreement with ESCA results, the surface sampled by ISS (ca. a depth of 2 Å vs ca. 30 Å for ESCA) is deficient in Ru. No significant change in the surface Ru content on reduction was observed by ISS. Note that the Ru/Th intensity ratios measured by ISS are lower than those obtained by ESCA.

TABLE VI: CO Hydrogenation Activities, TOF's, and Methane Selectivities of Intermetallic-Derived catalysts

| | rate. ^{a,b} cm ³ / | % | TOF, (1000 s) ⁻¹ | | CH₄ selectivity. | |
|---------------------|---|------|--------------------------------|-----|---------------------|--|
| catalyst | [(g of Ru) h] | conv | H۴ | COd | wt % | |
| $(Ru_3Th_7)_R$ | 2420 | 4.5 | 16 | 66 | 99 | |
| $(Ru_2Th_3)_R$ | 2460 | 6.7 | 17 | 70 | 99 | |
| (RuTh) _R | 74 | 0.27 | 0.63 | 50 | 93 | |
| $(Ru_2Th)_R$ | 29 | 0.17 | 0.22 | 40 | 94 | |

^{*a*} Reaction conditions: $H_2/CO = 3$, 1 atm, 205 °C. ^{*b*} The measurements were reproducible to $\pm 20\%$. ^{*c*} Based on hydrogen uptake. ^{*d*} Based on CO chemisorption.

This may be attributed to the greater sampling depth of ESCA than ISS. Since the bulk of IM catalysts is Ru enriched, the greater the sampling depth, the higher the Ru/Th ratio that will be detected. After syngas reaction a decrease in the ESCA Ru/Th intensity ratio of ca. 10% is observed for all catalysts (Table V). This decrease may be due to the sintering of Ru particles during the syngas reaction.

CO Hydrogenation. CO hydrogenation results for the four catalysts, reduced at 275 °C, are shown in Table VI. The turnover frequencies (TOF, number of CO molecules converted to hydrocarbon per unit time per Ru) based on CO and hydrogen uptakes are included. The CO conversion rates exhibited by the two Th-rich catalysts are ca. 40 times higher than those for the other two catalysts. On the basis of hydrogen chemisorption results, the TOF's for the two Th-rich catalysts are also ca. 40 times higher than those for the two Th-poor catalysts. However, on the basis of CO chemisorption results, the TOF's of the four IM catalysts are comparable. All four catalysts are highly selective to methane formation (\geq 93%). The two Th-poor catalysts.

Discussion

Catalyst Structure. ESCA and ISS results for the untreated intermetallics clearly indicate preferential segregation of Th (Table V). This can be explained by the differences in the heats of sublimation and atomic radii between Th and Ru and the difference in the heat of formation between ThO₂ and RuO₂. It has been shown that, for a binary alloy, the constituent element with the lower heat of sublimation, larger atomic radius, and higher reactivity with the ambient gas (i.e., higher heat of formation of metal oxide) will segregate to the surface.^{1,21} For Th and Ru, all three factors (138 vs 156 kcal/mol for heat of sublimation,²² 1.80 vs 1.33 Å for atomic radii,²² and -292 vs -72.6 kcal/mol for heat of formation of ThO₂ and RuO₂²³) favor surface segregation of Th.

The intermetallics were extensively decomposed by oxidation at 350 °C, as indicated by XRD patterns (Figure 1) and gravimetric analysis (Table II). Moreover, agreement between the results of gravimetric analysis and the calculated data indicates that preferential oxidation of Th occurred during oxidation of intermetallics. The oxidized catalysts, as indicated by the XRD patterns in Figure 1, essentially consist of ThO₂, Ru metal, and RuO_2 . Since the Ru phase detected by XRD was less than 10% of total Ru content in the oxidized intermetallics, the major part of Ru must be present in an amorphous or highly dispersed state. The presence of metallic Ru in all oxidized intermetallics is also indicated by the incomplete oxidation of Ru to RuO₂ inferred from gravimetric analysis (Table II). However, ESCA shows that RuO₂ is the only Ru species at the surface of oxidized intermetallics. This suggests that metallic Ru must be coated by a layer of RuO₂ or encapsulated by ThO_2 and cannot be detected by ESCA.

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Both ESCA and ISS show surface enrichment of Th in the oxidized and reduced intermetallics (Table V). Therefore, the surface structure of the oxidized and reduced intermetallics can best be described as Ru particles embedded in a ThO2-rich overlayer. Similar structure has been proposed for catalysts derived from oxidation of Cu-rare earth alloys.⁷

Variation of BET Surface Area with Compositions of IM Catalysts. As shown in Table IV, the BET surface areas of the intermetallic-derived (IM) catalysts measured by N2 adsorption, (S_{BET}) , were much lower than the ThO₂ surface areas calculated from XRD line broadening (XRDLB). This indicates either that the ThO₂ observed by XRD is only a fraction of the total ThO₂ present or that the ThO₂ particles consist of aggregates of small crystallites. By comparison of the XRD patterns of IM catalysts with those of physical mixtures of RuO₂ and ThO₂ having the same composition as the oxidized intermetallics, we have verified that most ThO₂ (more than 70% for $(Ru_2Th)_{Ox}$ and more than 90% for the other three oxidized intermetallics) present in the oxidized intermetallics was detected by XRD. Therefore, the lower BET surface area of the oxidic catalysts must be due primarily to the agglomeration of ThO₂ crystallites.

Hydrogen and CO Chemisorption. The metal surface areas of reduced IM catalysts estimated by hydrogen uptake, $(S_{Ru})_{H}$, were comparable to S_{BET} for the two Th-rich catalysts and 8-40 times the S_{BET} for the two Th-poor catalysts (Table IV). This indicates that hydrogen uptake may overestimate surface Ru. Also note that the variation of $(S_{Ru})_H$ with Th loading is similar to that of ThO₂ surface area, S_{ThO_2} , determined from XRDLB. This may be an indication of extensive hydrogen spillover from the Ru surface to ThO_2 . It is also possible that some embedded Ru in intimate contact with ThO₂ can be accessed through diffusion of dissociated hydrogen. The occurrence of hydrogen spillover from Ru to ThO_2 may be the result of the special morphology of the IM catalysts. As stated previously, the Ru phase in the IM catalysts is embedded in a ThO2-rich overlayer. This may favor an intimate contact between Ru and ThO₂ phase that will facilitate hydrogen spillover. ThO₂ obtained by oxidation of Ru_xTh_y intermetallics may contain a high concentration of defect sites that can act as acceptors for spillover hydrogen. In contrast to the Ru surface areas measured by hydrogen chemisorption, the metal surface areas measured by CO uptake, $(S_{Ru})_{CO}$, in all cases were lower than S_{BET} (Table IV). Furthermore, the trend of $(S_{\text{Ru}})_{\text{CO}}$ is in accord with that of S_{BET} . This suggests that, in the case of IM catalysts, CO probes surface Ru more accurately than does hvdrogen.

In a previous study comparing catalysts derived from oxidation of Ru₃Th₇ with the corresponding Ru/ThO₂ supported catalysts,⁹ there was doubt about which TOF (based on hydrogen or CO uptake) should be used for the IM catalyst. The present study clearly indicates that the TOF based on CO chemisorption more accurately reflects the activity of the IM catalysts than that based on hydrogen uptake.

CO Hydrogenation Selectivity and Activity. All IM catalysts show high methane selectivity (Table VI). The methane selectivity is higher than that for most conventionally prepared supported Ru catalysts and unsupported Ru.²⁵⁻³¹ It is however, comparable to that reported for carbon-supported Ru catalysts.^{25,27,29} The high methane selectivity of Ru/C catalysts was attributed to the presence of a Ru morphology favorable to methane formation.²⁹ Similarly, an increase in methane selectivity following reduction-oxidation-reduction treatment of a Ru/Al₂O₃ catalyst was attributed to a change in Ru morphology resulting from the oxidation treatment.³⁰ It is thus possible that the preparation method of the IM catalysts leads to preferential formation of a Ru phase favorable to methane production.

The four intermetallic catalysts show large differences in the CO conversion rate. However, on the basis of CO chemisorption, the TOF's of the four IM catalysts are comparable. This indicates that the difference in the CO conversion rate of the IM catalysts is due mainly to the difference in the number of exposed Ru sites. On the basis of CO chemisorption, the TOF's of the IM catalysts are comparable to those of the most active Ru catalysts reported in literature.²⁵⁻²⁷ The catalytic activity of the IM catalysts, compared to supported Ru/ThO₂ catalysts having similar Ru contents, has been discussed in an earlier paper.9 The high TOF of the IM catalysts was mainly attributed to the structure sensitivity of Ru catalysts in CO hydrogenation,^{26,28} and the special morphology of the catalysts that may result in high concentration of active sites.9

Conclusions

1. XRD measurements and gravimetric analysis indicate that all Ru_xTh_y intermetallics are extensively decomposed on oxidation at 350 °Ć.

2. ESCA and ISS studies showed surface enrichment in Th for all intermetallic-derived catalysts. The structure of the intermetallic-derived catalysts can best be described as Ru particles embedded in a ThO_2 -rich overlayer.

3. Comparison of Ru surface areas calculated form hydrogen and CO uptakes with N₂ BET surface area suggests that CO more accurately titrates surface Ru than does hydrogen.

4. All intermetallic-derived catalysts show comparable CO hydrogenation turnover frequencies and high methane selectivity. The high methane selectivity is attributed to the special morphology of the intermetallic-derived catalysts.

Acknowledgment. We acknowledge financial support from the National Science Foundation under Grant No. Che-8401202.

Registry No. Ru₃Th₇, 52014-54-7; Ru₂Th₃, 52014-57-0; RuTh, 52014-55-8; Ru₂Th, 12039-02-0; Ru, 7440-18-8; ThO₂, 1314-20-1; H₂, 1333-74-0; CO, 630-08-0.

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