*Inorganica Chimica Acta*, *140* (1987) 39–40

# Production of Methanol and Light Hydrocarbons on $ThO_2$ and Doped-$ThO_2$ from $CO + H_2$ Mixtures[*]

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The use of pure $ThO_2$ and $ThO_2$ with 10 at% Na on its surface as catalysts for methanol and methanol–isobutyl alcohol, respectively, has been reported by Maj *et al.* [1]. As part of our studies of the intrinsic catalytic properties of the actinide elements and their compounds, we are extending the work of Maj *et al.* by studying the effect of small amounts of K, Rb and Pd on the activity and the selectivity of $ThO_2$ to produce methanol from a $2H_2$:1CO gas mixture.

## Experimental

The catalysts were prepared by precipitation of thorium oxycarbonate from boiling thorium nitrate solutions using an ammonium carbonate solution containing the dopant cation as a soluble nitrate or carbonate. The precipitate was washed with water several times and air-dried at room temperature for 16–24 h, followed by calcination in air at 520 K. Four doped $ThO_2$ catalysts were prepared for study: 100 ppm K, 1000 ppm K, 74 ppm Rb, and 100 ppm Pd. The preparation techniques have been described in detail elsewhere [1].

Synthesis gas reactions were carried out in a copper-lined, stainless-steel, tubular reactor (1.25 cm i.d. X 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 bed. 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 [2]. Experiments were carried out with a $2H_2$:1CO gas mixture at ~50 atm as a function of temperature (550–623 K) and flow-rate [40–150 $cm^3$ (STP)/min].

Analysis of the reaction products was carried out with a gas chromatograph equipped with a flame ionization detector and Chromosorb 102 column.

Surface areas of the freshly prepared and used catalysts were measured by the BET technique. Surface analyses of fresh and used catalysts were performed by X-ray photoelectron spectroscopy (XPS).

## Results and Discussion

The addition of dopants to $ThO_2$ resulted in an increase of the surface area of the fresh catalysts and in a less severe reduction in area after synthesis in comparison to pure $ThO_2$ and $ThO_2$ with 10 at% Na on the surface (Table I). The effect of K and Rb is not surprising considering that oxidized alkali metals are commonly used to increase and stabilize the surface area of catalysts [3].

TABLE I. Surface Areas of Doped $ThO_2$ Catalysts

| Catalyst | Surface area ($m^2$/g) | | % change in area |
|---|---|---|---|
| | As prepared | Used | |
| $ThO_2$ [1] | 130 | 36 | 72 |
| Na–$ThO_2$ [1] | 120 | 50 | 58 |
| 100 ppm K–$ThO_2$ | 148 | 103 | 30 |
| 1000 ppm K–$ThO_2$ | 156 | 114 | 27 |
| 74 ppm Rb–$ThO_2$ | 140 | 85 | 39 |
| 100 ppm Pd–$ThO_2$ | 164 | 157 | 38 |

XPS surface analysis of the doped catalysts did not show any segregation of K, Rb or Pd to the surface, in contrast with the Na-doped catalyst studied by Maj *et al.* [1], which had 10 at% Na on the surface present as $Na_2O$. Thus we speculate that these dopants may be present as substitutional cations in the $ThO_2$ oxide lattice, most probably as oxides [3]; future X-ray diffraction studies may provide the data required to answer these questions. Because $K_2O$ is a strong base it should affect strongly the performance of $ThO_2$ as a catalyst, followed by Rb [3].

Three of the catalysts studied (100 ppm K–$ThO_2$, 74 ppm Rb–$ThO_2$ and 100 ppm Pd–$ThO_2$) were predominantly methanol catalysts, as shown in a plot of production rate *versus* temperature (Fig. 1). The 100 ppm K catalyst nearly doubled the yield of methanol over that of pure $ThO_2$, while increasing the selectivity for this alcohol from 85–95% for pure $ThO_2$ to 99% for the doped catalyst. Catalysts with 74 ppm Rb and 100 ppm Pd increased the methanol yield by 15 and 12%, respectively, over that for $ThO_2$, and their selectivities were about 98 and 90%,

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[*] Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48. Paper presented at the Second International Conference on the Basic and Applied Chemistry of f-Transition (Lanthanide and Actinide) and Related Elements (2nd ICLA), Lisbon, Portugal, April 6–10, 1987.

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0020-1693/87/$3.50

TABLE II. Comparison of Yields for Doped $ThO_2$ Catalysts under Optimum Conditions

| Catalyst | T (K) | mol/kg catalyst-hour[a] | | | |
|---|---|---|---|---|---|
| | | $CH_4$ | $CH_3OH$ | i-$C_4H_{10}$ | i-$C_4H_9OH$ |
| $ThO_2$ [1] | 600 | 0.009 | 0.74 | 0.22 | 0.18 |
| Na–$ThO_2$ [1] | 600 | 0.014 | 0.67 | 0.08 | 0.61 |
| 100 ppm K–$ThO_2$ | 585 | 0.007 | 1.22 | trace | |
| 74 ppm Rb–$ThO_2$ | 583 | 0.007 | 0.85 | | |
| 100 ppm Pd–$ThO_2$ | 586 | 0.007 | 0.83 | 0.08 | 0.004 |

[a] All values normalized to 45.4 atm $2H_2$:1CO.

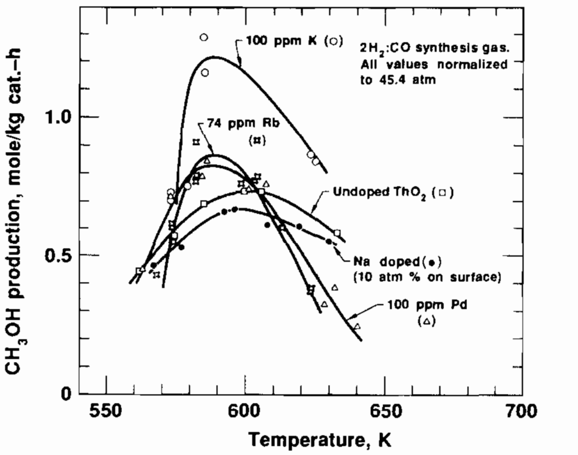

Fig. 1. Production of methanol on $ThO_2$ and doped-$ThO_2$ as a function of temperature.

TABLE III. Production of Methanol and Hydrocarbons on 1000 ppm K–$ThO_2$

| Component | mol/kg catalyst-hour | | |
|---|---|---|---|
| | 577 K | 739 K | 783 K |
| $CH_4$ | 0.0084 | 0.0270 | 0.3770 |
| $CH_3OH$ | 0.0180 | $<9 \times 10^{-5}$ | $<9 \times 10^{-5}$ |
| $C_2H_4$ | 0.0003 | 0.0026 | 0.0220 |
| $C_2H_6$ | 0.0012 | 0.0029 | 0.0750 |
| $C_3H_8$ | 0.0005 | 0.0090 | NM |
| i-$C_4H_{10}$ | 0.0005 | 0.0064 | 0.0450 |
| $C_4H_{10}$ | 0.0004 | 0.0012 | 0.0140 |
| i-$C_4H_8$ | 0.0006 | 0.0007 | 0.0160 |
| i-$C_5H_{12}$ | | 0.0013 | 0.0120 |
| $C_5H_{12}$ | | 0.0009 | 0.0040 |
| $C_6H_{14}$ | | | 0.0012 |
| $C_7H_{16}$ | 0.005 | | |

NM = not measured.

respectively. Other significant products produced by these catalysts were methane, isobutane and isobutyl alcohol (Table II). The very significant changes produced by K-doping may be due to (a) an increase in the basicity of the $ThO_2$ due to the strong basic character of $K_2O$; or (b) a change in the conduction mechanism of the $ThO_2$ caused by the introduction of singly charged oxygen vacancies if $K^+$ is in substitutional positions. This can in turn lead to significant work function changes in $ThO_2$ [4], which will affect its reactivity.

Increasing the potassium concentration to 1000 ppm changed drastically the properties of $ThO_2$. The methanol yield was reduced by a factor of 67 from that for the 100 ppm K-catalyst and small amounts of other hydrocarbons were produced as well (Table III). Methanol was still the main product (89%) at 577 K, but it was reduced to a trace at 739 K and higher temperatures.

The activation energy for the production of methanol over the 100 ppm K–$ThO_2$ catalyst was 42 kJ/mol, which is in good agreement with the values previously obtained for pure $ThO_2$ and Na-doped $ThO_2$, (45 kJ/mol) [1]. The values measured for the 74 ppm Rb and 100 ppm Pd catalysts were much lower (~25 kJ/mol) but we do not believe these values are very reliable.

## References

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