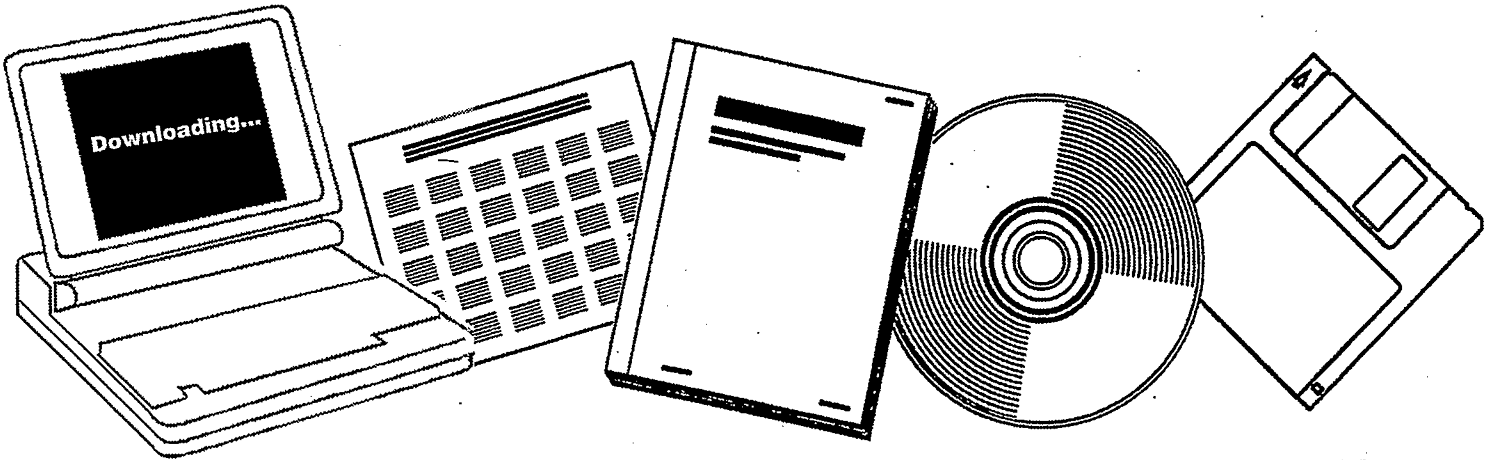
DE87010878

PRODUCTION OF METHANOL AND LIGHT HYDROCARBONS ON THO SUB 2 AND DOPED-THO SUB 2 FROM CO + H SUB 2 MIXTURES

LAWRENCE LIVERMORE NATIONAL LAB., CA

19 MAR 1987



CONF-870443--2

Received by OSTI

UCRL--95798

DE87 010878

PRODUCTION OF METHANOL AND LIGHT HYDROCARBONS ON ThO_2 AND DOPED-ThO_2 FROM $CO+H_2$ MIXTURES

C. A. Colmenares
T. McCreary
C. Evans

This paper was prepared for The 2nd International Conference on the Basic & Applied Chemistry of f-Transition (Lanthanide & Actinide) and Related Elements, Lisbon, Portugal, April 6-10, 1987

March 19, 1987

Lawrence Livermore National Laboratory

PRODUCTION OF METHANOL AND LIGHT HYDROCARBONS ON ThO_2 AND DOPED-ThO_2 FROM $CO+H_2$ MIXTURES

C. A. Colmenares*, T. McCreary, and C. Evans
University of California
Lawrence Livermore National Laboratory
Livermore, CA 94550

Abstract

High surface area ThO_2 catalysts (~120-150 m^2/g), pure and doped with 100 ppm K, 1000 ppm K, 74 ppm Rb, and 100 ppm Pd by weight, have been tested with a mixture of $2H_2$:1CO (~45 atm, 550-623 K) for their ability to produce methanol and other hydrocarbons in a differential high-pressure flow reactor. Pure ThO_2 was active for the production of mostly methanol (0.74 mole/kg cat.-h, 85-95% selectivity) and small amounts of isobutyl alcohol, isobutane, and ethane/ethene. Thoria doped with 100 ppm K nearly doubled the production rate of methanol over that for pure ThO_2 with a 99% selectivity for this product. Increasing the K to 1000 ppm decreased the methanol production by a factor of 67 from that for the 100 ppm K catalyst, but it was still the main product (89%) at 577 K. Other significant products were ethylene and methane. As the temperature was raised above 739 K the amount of methanol produced was negligible and the distribution of the main

---

* Correspondence should be addressed to this author.

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.

products was: 34.2% methane, 27.4% propane, 23.9% ethane, 5.6% 1-butene, and 4.4% n-butane. Catalysts with 74 ppm Rb and 100 ppm Pd increased the methanol yield by 15 and 12 percent, respectively, over that for ThO_2 and their selectivities for methanol were about 98 and 90%, respectively. X-ray photoelectron spectroscopy analyses of the doped catalyst did not show a preferential segregation of the dopants to the surface, indicating that they possibly are in substitutional lattice positions.

Introduction

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 Pb, 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 flowrate [40-150 cm^3(STP)/min].

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

Surface areas of the freshly prepared and used catalysts were measured by the BET technique. Surface analysis of fresh and used catalysts was 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 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)

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-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 percent, respectively, over that for ThO_2, and their selectivities were about 98 and 90% 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 effect 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/mole, which is in good agreement with the values previously obtained for pure ThO_2 and Na-doped ThO_2, (45-kJ/mole).(1) The values measured for the 74 ppm Rb and 100 ppm Pd catalysts were much lower (~25 kJ/mole) but we do not believe these values are very reliable.

References

1. J. Maj, C. A. Colmenares, and G. A. Somorjai, J. Catal., 95, 385 (1985).

2. H. Pichler, and K. H. Ziesecke, Brennst-Chem., 30, 13 (1949).

3. M. E. Dry in J. R. Anderson and M. Boudart (eds.) "Catalysis-Science and Technology," Vol. 1, Springer-Verlag, Berlin Heilderberg New York, 1981, Chap. 4, p. 159.

4. C. A. Colmenares, Prog. Solid State Chem. 15, 257 (1984).

1817J

Table I. Surface areas of doped -ThO$_2$ catalysts

Catalyst	Surface area, m^2/g		% change in area
	As prepared	used	
ThO$_2$ (ref. 1)	130	36	72
N_a-ThO$_2$ (ref. 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

Table II. Comparison of yields for doped-ThO_2 catalysts under optimum conditions

Catalyst	T (K)	moles/ kg cat.-h*			
		CH_4	CH_3OH	i-C_4H_{10}	i-C_4H_9OH
ThO_2 (ref. 1)	600	0.009	0.74	0.22	0.18
N_a-ThO_2 (ref. 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

*All values normalized to 45.4 atm $2H_2$:1CO.

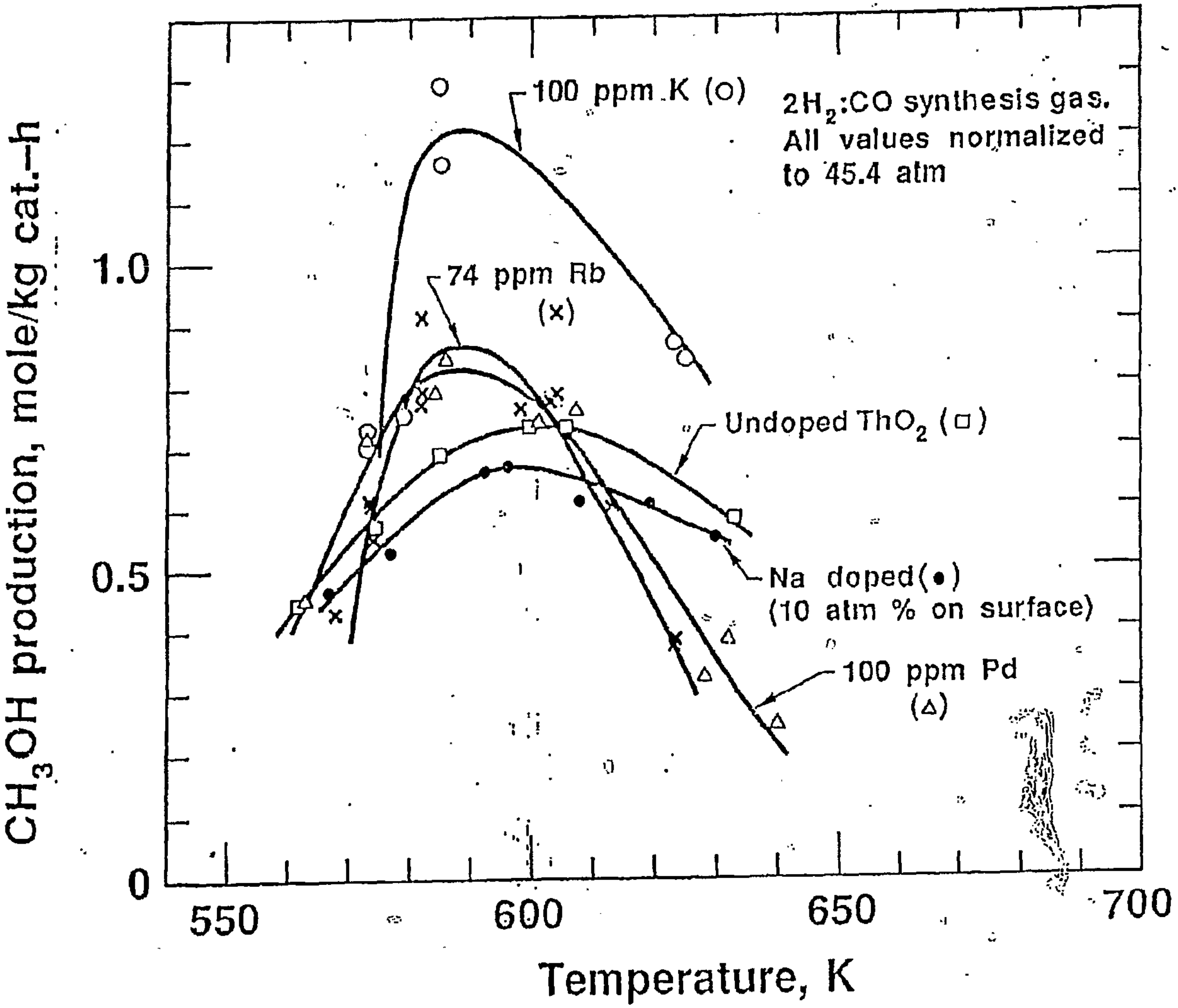
Table III. Production of methanol and hydrocarbons on 1000 ppm K-ThO_2

Component	moles/kg cat.-h		
	577K	739K	783K
CH_4	0.0084	0.0270	0.3770
CH_3OH	0.0180	$< 9x10^{-5}$	$< 9x10^{-5}$
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

Figure Captions

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


100 ppm K (○)
2H_2:CO synthesis gas. All values normalized to 45.4 atm
74 ppm Rb (×)
Undoped ThO_2 (□)
Na doped (●) (10 atm % on surface)
100 ppm Pd (△)
CH_3OH production, mole/kg cat.–h
0
0.5
1.0
550
600
650
700
Temperature, K