NOTES

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3473—3474 (1972)

A Study of Catalysis by Uranium Oxide and Its Mixed Catalysts. III.[1] A Comparison of the Uranium Oxide Catalyst with Vanadium Oxide, Molybdenum Oxide and Tungsten Oxide Catalysts for the Catalytic Oxidation of Carbon Monoxide

Fumio Nozaki and Keiichi Ohki

Department of Industrial Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba

(Received March 17, 1972)

The catalytic oxidation of carbon monoxide over various metal oxides has been studied by several workers discussing the order of oxidation activity.[2] However, there have been very few reports about the uranium oxide catalyst. The present authors have reported previously about the supported uranium oxide catalysts.[3] The purpose of this paper is to make a survey of the oxidation activity of U_3O_8, V_2O_5, MoO_3, and WO_3 catalysts, and to discuss the causative relationship between the catalytic activity and the thermodynamic properties of the oxides, such as the heat of formation or the heat of oxide-interconversion.

Experimental

Catalyst Samples. All of the catalysts were obtained by the usual method of preparation. U_3O_8 was prepared by the thermal decomposition of ammonium diuranate, $(NH_4)_2U_2O_7$, obtained from uranyl nitrate by precipitation with NH_4OH. The sample calcined at 450°C for 3 hr in an air stream was green-black in color and 20.8 m^2/g in B.E.T. surface area. The V_2O_5 catalyst was prepared from NH_4VO_3 by calcination. The sample calcined at 500°C for 3 hr in an air stream was tan-orange and 5.2 m^2/g in surface area. The MoO_3 catalyst was obtained by the calcination of the precipitate prepared from $(NH_4)_6Mo_7O_{24}$ and HNO_3. The sample calcined at 500°C for 2 hr in an air stream was white and 3.0 m^2/g in surface area. The WO_3 catalyst was obtained by the calcination of the precipitate prepared from $(NH_4)_{10}W_{12}O_{41}$ and HNO_3. After it had been calcined at 500°C for 2 hr, the sample was yellow and 12.1 m^2/g in surface area.

Catalytic Oxidation of Carbon Monoxide. The flow-type apparatus and the procedure for the rate measurements were the same as those previously reported.[3] All of the experiments were carried out under the following identical conditions: total flow rate of feed gas=100 m*l* (20°C)/min, feed ratio of $CO:O_2:N_2=3:3:4$, total pressure=1 atm. The amount of catalyst packed in the reactor was controlled in the range from 0.2 to 1.2 g according to the catalyst specimen in order to prevent the conversion of carbon monoxide from exceeding 20%. Under these experimental conditions, the observed conversion of carbon monoxide was proportional to the amount of catalyst used. The equation used in the calculation of the reaction rate was:

$$r = \frac{1}{S}\,\frac{y_0 x}{(W/F)} \tag{1}$$

where r: reaction rate per unit of surface area of the catalyst (mol/m^2 hr), y_0: CO mol fraction at the inlet of the catalyst bed (=0.3), S: surface area of the catalyst (m^2/g), W: amount of catalyst (g), F: total flow rate of feed gas (=0.268 mol/hr).

Results and Discussion

The conversion data as a function of the reaction temperature are shown in Fig. 1. We calculated the reaction rates by using Eq. (1) and plotted log (r) as a function of $1/T$ in Fig. 2. From Figs. 1 and 2, it is found that U_3O_8 is exceedingly high in oxidative activity and that the order of catalytic activity is as follows: $U_3O_8 > V_2O_5 > MoO_3 > WO_3$. We estimated the reaction rates from Fig. 2 at a reaction temperature of 500°C and have illustrated the rate data as a function of the heat of formation, $(-\Delta H^\circ_f)$[4] or of the heat of oxide-interconversion, $(\Delta H^\circ_{MO_{x-1}} - \Delta H^\circ_{MO_x})$[5]

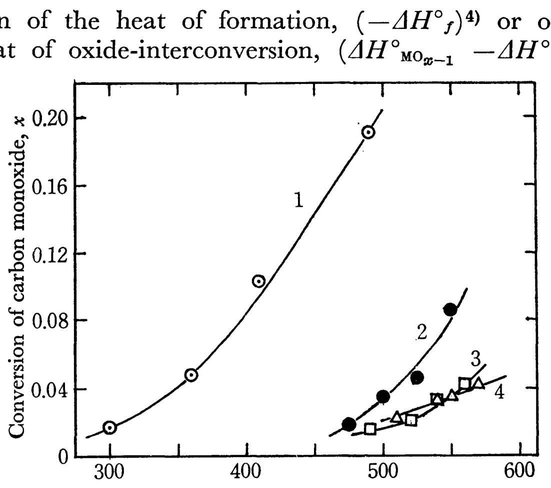

Fig. 1. Conversion of carbon monoxide as a function of reaction temperature.

1: —⊙— U_3O_8 (W=0.252 g)
2: —●— V_2O_5 (W=0.804 g)
3: —□— MoO_3 (W=1.202 g)
4: —△— WO_3 (W=0.623 g)

---

[1] Part II of this series; F. Nozaki and H. Okada, *Nippon Kagaku Kaishi*, **1972**, 842.

[2] a) S. Makishima, Y. Yoneda, and Y. Saito, *Shokubai (Catalyst)*, **2**, 168 (1960). b) M. Tarama, S. Teranishi, and A. Yasui, *Nippon Kagaku Zasshi*, **81**, 1034 (1960). c) T. Seiyama, A. Suematsu, and W. Sakai, *ibid.*, **82**, 292 (1961).

[3] F. Nozaki, M. Kobayashi, and S. Yoshida, *Nippon Kagaku Kaishi*, **1972**, 26.

[4] This is the heat of formation per metal atom (kcal/metal atom). The data of $-\Delta H^\circ_f$ are quoted from "Shokubai Kogaku Koza", Vol. 2 (ed. by Catalysis Soc. of Japan), p. 141 and "Chemistry of Uranium" (by Katz and Rabinowitch), p. 295.

[5] The value of $(\Delta H^\circ_{MO_{x-1}} - \Delta H^\circ_{MO_x})$ corresponds to the heat of reaction of the following deoxygenation: $MO_x \rightarrow MO_{x-1} + 1/2\ O_2$, where MO_{x-1} means the next lower oxidized state of metal oxide, MO_x. In the present case, the chemical formulas of MO_{x-1} are U_3O_7, V_2O_4, MoO_2, and WO_2 respectively. The data of the heat of reaction are quoted from the books noted in Ref. 4).

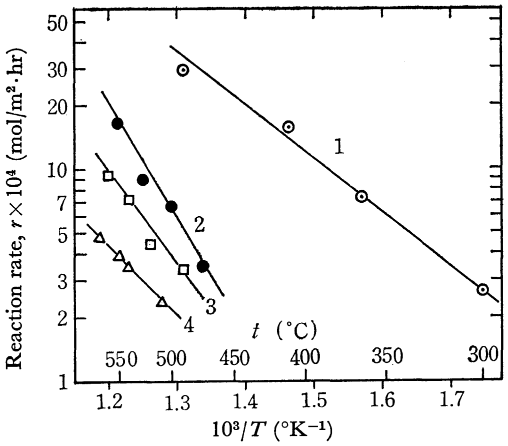

Fig. 2. Arrhenius plot.
1: U_3O_8 (apparent activation energy, $E_a=14$ kcal/mol)
2: V_2O_5 ($E_a=25$ kcal/mol) 3: MoO_3 ($E_a=22$ kcal/mol)
4: WO_3 ($E_a=16$ kcal/mol)

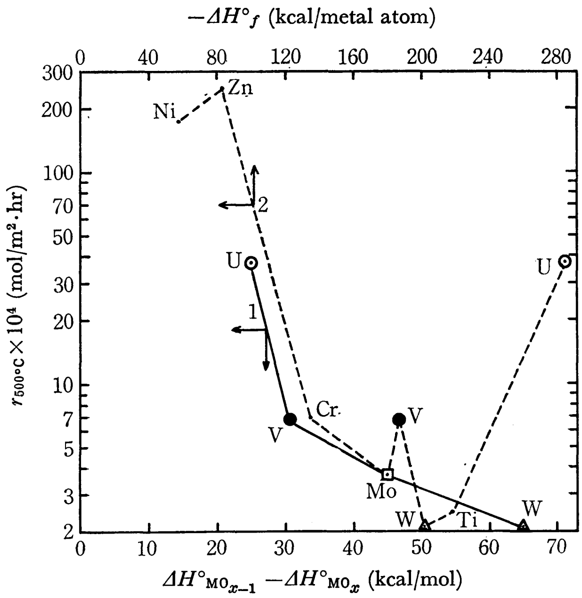

Fig. 3. Correlation between catalytic activity and thermodynamic property of catalyst oxides.
1: (solid line) reaction rate at 500°C *vs.* $(\Delta H^\circ_{MO_{x-1}} - \Delta H^\circ_{MO_x})$
2: (dotted line) reaction rate at 500°C *vs.* $-\Delta H^\circ_f$

in Fig. 3. In order to characterize the U_3O_8 catalyst, the available data or estimated values[6] of $r_{500^\circ C}$ in the cases of NiO, ZnO, Cr_2O_3, and TiO_2 are also illustrated in Fig. 3 by quoting data from published papers.[7-9]

As is shown in Fig. 3, the correlation between $r_{500^\circ C}$ and $-\Delta H^\circ_f$ has a tendency to move towards a low activity with the increase in $-\Delta H^\circ_f$; however, the activity of U_3O_8 is much higher, as would be expected from $-\Delta H^\circ_f$, and is situated between the ZnO (or NiO) and Cr_2O_3 (or V_2O_5) catalysts. It should be emphasized in this study that U_3O_8 is considerably high in oxidative activity for an *n*-type semiconducting oxide catalyst. Within the limits of the catalyst species investigated in this study, the correlation between $r_{500^\circ C}$ and $(\Delta H^\circ_{MO_{x-1}} - \Delta H^\circ_{MO_x})$ is regular and shows a predictable variation with a change in $(\Delta H^\circ_{MO_{x-1}} - \Delta H^\circ_{MO_x})$. A probable explanation of why U_3O_8 is active in spite of the large heat of formation can be given on the basis of the fact that U_3O_8 is readily reduced with CO and reoxidized with O_2 because of the small heat of oxide-interconversion.[3] This finding suggests that all of the oxygen atoms in U_3O_8 are not on an equal footing and that some of the specified oxygen atoms showing a high reactivity are involved, as Tarama *et al.*[10] have already pointed out with regard to the V_2O_5 catalyst. We will attempt to obtain more detailed information on this aspect after we have investigated the physico-chemical structure of the uranium oxide catalyst.

---

6) The values of $r_{500^\circ C}$ were computed or estimated from the rate equations or from the Arrhenius plots of the rate data for identical experimental conditions with this work.

7) I. Matsuura, Y. Kubokawa, and O. Toyama, *Nippon Kagaku Zasshi*, **81**, 997, 1003 (1960).

8) M. Tarama, S. Teranishi, and K. Hattori, *ibid.*, **63**, 714 (1960).

9) Y. Onishi, This Bulletin, **44**, 1460 (1971).

10) M. Tarama, S. Teranishi, S. Yoshida, and N. Tamura, "The Proc. 3rd Inter. Congress on Catalysis", North-Holland Pub. Co. (1965), p. 282.