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Effect of Hydrogen Reduction on Activity and Selectivity of Methanol Decomposition over Titanium Oxide

Both anatase and rutile, treated by oxygen or by air in the temperature range 700 to 1200 K, selectively dehydrate alcohols (*1–3*), although the oxides evacuated at 673 K show dehydrogenation selectivity (*4*). In their study of methanol decomposition, Taylor and Griffin (*5*) reported recently that the product selectivity during temperature-programmed decomposition was a strong function of the initial methanol coverage.

In the present paper, we have studied the effect of hydrogen reduction on the decomposition of methanol to find that both the activity and the selectivity depend greatly on the temperature of reduction.

EXPERIMENTAL

The titanium oxide was prepared by a precipitation method. A titanium(III) chloride solution was treated with an ammonia solution. The precipitate was filtered, washed, and dried overnight at 380 K. Then, the sample was crushed, sized (32–60 mesh), and treated at 623 K for 16 h in a stream of air.

Catalytic activity was measured by an atmospheric flow method with a quartz reactor, after reduction with hydrogen at a given temperature for 90 min. The reaction was carried out in the temperature range 573 to 773 K in a stream of helium (20 ml/min) containing 30.1 Torr of methanol vapor. The products were analyzed by gas chromatography with 4-m APS201/Flusin T and 0.5-m Molecular Sieve 5A columns.

The reaction of dimethyl ether was carried out with a pulsed reaction system under the following reaction conditions: helium flow rate = 20 ml/min, pulse size = 0.2 ml, reaction temperature = 673 K. The amount of oxygen removed was measured by a gravimetric method with a Cahn RG electrobalance. Specific surface area was measured by the BET method with adsorption of nitrogen at liquid nitrogen temperature. The XRD spectrum was recorded on a Rigaku Denki powder X-ray diffractometer with nickel-filtered Cu$K\alpha$ radiation.

Titanium(III) chloride (>98%) and methanol (spectroscopic grade) were obtained from Wako Pure Chemical, while dimethyl ether (>99%) was obtained from Tokyo Kasei Kogyo. Methanol was dried with Molecular Sieve 4A before use in the reaction. Helium, obtained from the Japan Helium Center, was purified through a Molecular Sieve 5A column and a rare gas purifier (Model RT-3, Japan Pure Hydrogen Co.), successively.

RESULTS AND DISCUSSION

Specific surface area and percentage of oxygen removed were measured after reduction treatment by hydrogen for 90 min at various temperatures. The specific surface area decreased greatly with increasing reduction temperature; the surface area of 93.3 m^2/g after treatment at 723 K decreased to 0.64 m^2/g after treatment at 1273 K. This suggests that intensive sintering occurred during reduction at higher temperatures. The color change of the sample after the treatment suggested that the sample was reduced. However, the percentage of oxygen removed was less than 1% even at a reduc-

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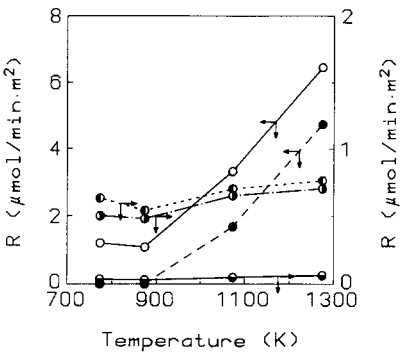

FIG. 1. Catalytic activity versus reduction temperature. Reaction temperature = 673 K. ○, Total rate; ●, formaldehyde; ◑, CO; ◐, methane; ◒, dimethyl ether.

tion temperature of 1273 K. This indicates that the reduction proceeded only at surface layers or at special sites.

The original sample was almost amorphous. After oxygen treatment at 1073 K for 90 min, a polycrystalline material of rutile structure was obtained. On the other hand, less crystalline materials were obtained in the treatment of hydrogen. Comparison with standard XRD specra (JCPDS powder X-ray diffraction data) indicated that after hydrogen treatment at 1273 K for 90 min, the sample was composed of rutile and possibly oxygen-deficient titanium oxide.

Figure 1 shows the catalytic activities at 673 K after reduction treatment for 90 min at various temperatures. At reduction temperatures less than 873 K, the total rate of reaction per unit surface area remained almost constant, and no formaldehyde was formed. At higher reduction temperatures, both the total rate and the rate of formation of formaldehyde per unit surface area increased almost in parallel with increasing reduction temperature, indicating that the selectivity of formaldehyde formation increases with increasing reduction temperature.

High-temperature treatment cannot be responsible for formation of the dehydrogenation sites, because both anatase and rutile, which were treated with oxygen-containing gas in the temperature range 700 to 1200 K, showed dehydration selectivity (*1–3*). This suggests that dehydration of the surface as well as sintering does not produce the active sites of dehydrogenation. Our activity measurement with the samle treated with oxygen at 1073 K for 90 min confirms the results in the literature, and indicates that the active sites of dehydrogenation are produced by reduction of the surface.

As the selectivity changed at the reduction temperature of 873 K, catalytic properties were studied in more detail for the catalysts reduced at 773 and 1273 K. Table 1 shows the results of activity measurements at 623 and 673 K on the catalyst reduced at 773 K for 90 min. Dimethyl ether, methane, and carbon monoxide were formed on this catalyst. Water and hydrogen were also found in the products. However, formaldehyde, methyl formate, and carbon dioxide were not detected. At the lower reaction temperature, the main product was dimethyl ether, indicating the dehydration selectivity of the catalyst. At the higher reaction temperature, the rates of formation of methane and carbon monoxide increased with a simultaneous decrease in the rate of formation of dimethyl ether. This fact suggests that dimethyl ether decomposes by the following reaction to form methane and carbon monoxide, at higher temperatures.

TABLE 1

Methanol Decomposition over TiO_2 Reduced at 773 K

	Reaction temperature	
	623 K	673 K
	Rate (μmol/min · m²)	
Dimethyl ether	0.42	0.04
Methane	0.08	0.71
Carbon monoxide	0.06	0.56
Formaldehyde	0	0
Methylformate	0	0

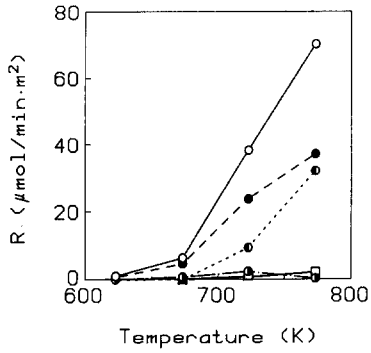

FIG. 2. Effect of reaction temperature. Reduction temperature = 1273 K. ○, Total rate; ●, formaldehyde; ◐, CO; ◑, dimethyl ether; □, methane.

$$CH_3OCH_3 \rightarrow CH_4 + CO + H_2$$

A pulsed reaction of dimethyl ether was studied at 673 K with the catalyst reduced at 773 K for 90 min, to confirm this fact. The reaction products were found to be methane, carbon monoxide, and hydrogen. The material balance indicated that this reaction proceeded on this catalyst. Catalytic activity decreased slightly after the first pulse, but remained almost constant at about 38% conversion after the fourth pulse.

Figure 2 shows the effect of temperature on the activity of the catalyst reduced at 1273 K. Formaldehyde, carbon monoxide, dimethyl ether, and a small amount of methane were formed on this catalyst. Hydrogen and water were also found in the products. The rate of formation of dimethyl ether was small, indicating a high dehydrogenation selectivity of this catalyst. The selectivity of formaldehyde formation increased with increasing reaction temperature, but it decreased with a further increase in the reaction temperature because of the decomposition of formaldehyde at higher temperatures. The selectivity showed a maximum value of 73% at 673 K.

The results of this study are summarized as follows.

The effect of hydrogen reduction on the catalytic activity of titanium oxide for decomposition of methanol was studied. Both the activity and the selectivity were greatly dependent on the temperature of reduction. The rate of reaction of methanol per unit surface area increased with increasing reduction temperature. On the catalysts reduced at the lower temperature (<873 K), the main product was dimethyl ether, which further decomposed by the reaction $CH_3OCH_3 \rightarrow CH_4 + CO + H_2$. At the higher reduction temperature, the dehydrogenation selectivity increased with increasing reduction temperature.

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