Isomerization and Disproportionation of Olefins over Tungsten Oxides Supported on Various Oxides

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The isomerizations of 1-butene and cyclopropane and the disproportionations of 1-butene, propylene, and ethylene were investigated over tungsten oxides supported on MgO, Al_2O_3, SiO_2, TiO_2, and ZrO_2. A combination of tungsten oxide with TiO_2, in which the amount of tungsten oxide was varied from 1 to 20 mol%, resulted in a generation of acid sites. The acid properties were well correlated with the catalytic activity in the isomerization of 1-butene. The production of acid sites also caused a marked decrease in the *cis/trans* ratio in 2-butene formed. The order of the activity of various supported catalysts for the isomerization of cyclopropane was $WO_3–Al_2O_3 > WO_3–ZrO_2 > WO_3–TiO_2 > WO_3 \gg WO_3–SiO_2 = WO_3–MgO = 0$, whereas that for the disproportionation of propylene was $WO_3–TiO_2 \gtrsim WO_3–ZrO_2 > WO_3–Al_2O_3 > WO_3–SiO_2 > WO_3–MgO = WO_3 = 0$. An optimum activity was obtained for 5 mol% tungstem oxide on $WO_3–TiO_2$.

During the disproportionation reaction of propylene over $WO_3–TiO_2$, the formation of *i*-butene was found. Production of propylene was also found in the reaction of ethylene over $WO_3–TiO_2$. The formation of *i*-butene from propylene and propylene from ethylene suggests that the reaction takes place via carbene intermediates.

INTRODUCTION

From the extensive works on various binary oxides, it was found that a combination of two oxides generates new acid sites (*1*). Most of the binary oxides, however, were the combination of relatively stable oxides such as $SiO_2–Al_2O_3$, $SiO_2–ZrO_2$, $Al_2O_3–B_2O_3$, etc. No work has been done on the acidic property of binary oxides including an easily reducible tungsten oxide. Thus, in the present work, we have investigated the acidic and catalytic properties of the supported tungsten oxides, in which tungsten ion may change its oxidation states by evacuation or reduction with hydrogen.

The supports tested here were Al_2O_3, TiO_2, ZrO_2, SiO_2, and MgO. Among them, TiO_2 will be an interesting support, since it showed a basic property when it was prepared from titanic acid by evacuation at high temperatures, e.g., 500°C, and such basic sites were attributed to the formation of Ti^{3+} by the reduction of Ti^{4+} during the evacuation (*2*). Zirconium oxide was re-

cently reported to show a reducing property, besides an oxidizing property (*3*). It might be interesting to examine how the acid–base properties or catalytic activities change by the combination of WO_3 with TiO_2 or ZrO_2 whose cations can alter their oxidation states. For this purpose, we have studied the isomerization of 1-butene and the rearrangement of cyclopropane on those catalysts from the viewpoint of the acid–base properties. Disproportionation reactions of ethylene, propylene, and butene have also been studied to see the effect of the supports on the catalytic activity, since it is known that some supported tungsten oxides catalyze the reaction.

EXPERIMENTAL

Catalysts and Reagents

Supported tungsten oxides were prepared by impregnating MgO, Al_2O_3, SiO_2, TiO_2, or ZrO_2 with an aqueous solution of $(NH_4)_{10}W_{12}O_{41} \cdot 5H_2O$. After evaporation of water, the catalysts were dried in air at 110°C and calcined at 500°C for 3 hr.
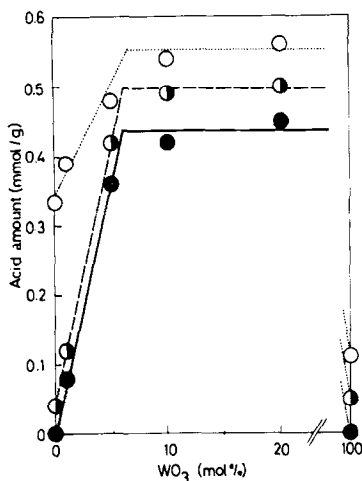
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FIG. 1. Acid amounts at various acid strengths of WO$_3$–TiO$_2$: O, pK_a = 4.8; ◑, pK_a = +3.3; ●, pK_a = 1.5.

Magnesium oxide was obtained by calcining the hydroxide at 500°C. Aluminum oxide and SiO$_2$ were obtained by calcining their hydroxides at 500°C which were prepared by the hydrolysis of Al(NO$_3$)$_3$ with aqueous ammonia and by the hydrolysis of ethyl orthosilicate, respectively. Titanium oxide and ZrO$_2$ were prepared by the hydrolysis of TiOSO$_4$ and ZrOCl$_2$ with aqueous ammonia, followed by calcining them at 500°C.
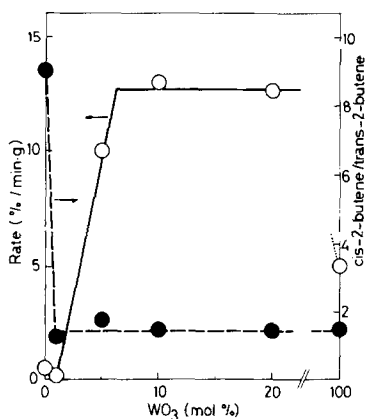
The content of WO$_3$ was 5 mol% except

FIG. 2. Isomerization of 1-butene over WO$_3$-TiO$_2$ at 100°C: O, activity; ●, ratio of cis-2-butene to trans-2-butene.

for WO$_3$–TiO$_2$ catalyst, where the amounts of WO$_3$ were 1, 5, 10, and 20 mol%.

Surface Area and Acidity Measurement

Surface area was measured by a BET method by using N$_2$ as an adsorbent. The acid amounts at different acid strengths on catalyst surfaces were determined by titrating the powders suspended in benzene with 0.1 N n-butylamine benzene solution, using methyl red (pK_a = 4.8), p-dimethylaminoazobenzene (3.3), and benzeneazodiphenylamine (1.5) as indicators (4).

Reaction

The reactions were carried out by using a closed recirculation system with a vacuum manifold and a Töpler pump for the purpose of sampling. The catalysts of 0.1 g were evacuated at 500°C for 3 hr prior to use. Most of the reactions were carried out at 100°C and under 100 Torr of hydrocarbons. Products were analyzed by a gas chromatograph which was equipped with a 5 m column of propylene carbonate.

RESULTS AND DISCUSSION

i. Acidic Properties and Catalytic Activities

The acidic properties and the catalytic activities and selectivities of WO$_3$ supported on TiO$_2$ are shown in Figs. 1 and 2, respectively. Table 1 shows the change of the surface area of WO$_3$/TiO$_2$. Though both TiO$_2$ and WO$_3$ have only a small amount of acid sites, a generation of acid sites by a combination of two oxides is clear (Fig. 1). An increase of acid amount was observed for each acid strength. The production of acid sites by mixing is well explained by the hypothesis of Tanabe et al. (5). According

TABLE 1

Surface Area of WO$_3$–TiO$_2$Catalysts

WO$_3$ (mol%)	0	1	5	10	20
Surface area (m^2/g)	90	95	103	105	106

TABLE 2

Isomerization and Disproportionation of Cyclopropane[a]

Rate	Catalyst					
	WO_3–Al_2O_3	WO_3–ZrO_2	WO_3–TiO_2	WO_3	WO_3–SiO_2	WO_3–MgO
r_0[b]	4.05	3.04	2.08	0.58	0	0
r_1[b]	3.71	2.26	1.30	0.58	0	0
r_2[b]	0.34	0.78	0.78	0	0	0

[a] Reaction temperature, 180°C.

[b] $r_0 = r_1 + r_2 (\times 10^{-4}\,mol/g \cdot min)$, r_0, rate of disappearance of cyclopropane: r_1, rate of formation of propylene; r_2, (rate of formation of ethylene) $\times 2$.

to the hypothesis, the model structure of WO_3–TiO_2 is pictured as shown below.

$$\begin{array}{c}
-O-Ti-O-W-O- \\
\end{array}$$
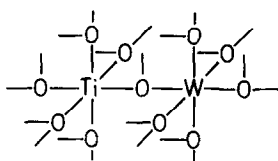
In this structure, the six positive charges of the tungsten atom are distributed to six bonds, i.e., a positive charge is distributed to each bond, while the two negative charges of oxygen atom are distributed to three bonds, i.e., $-\frac{2}{3}$ of a valence unit is distributed to each bond. The difference in charge for each bond is $+1 - \frac{2}{3} = +\frac{1}{3}$, and for all bonds the valence unit of $+\frac{1}{3} \times 6 = +2$ is excess. The excess of the positive charge is considered to cause the generation of Lewis acidity. If a small amount of water molecule exist on the surface, the Lewis acid sites would convert into Brönsted acid sites.

As seen in Fig. 2, the catalytic activity, which was obtained from the initial rate of the disappearance of 1-butene, increases with the increase of the amount of WO_3 mounted, and this increase is in good accordance with the changes in the acid amount shown in Fig. 1. Since the change of the surface area of the catalyst was small (Table 1), the activity increase can be attributed to the increase of acidic sites. An addition of a small amount of WO_3 (1 mol%) brings a drastic decrease in a cis-2-butene/trans-2-butene ratio from 9 to 1.5, which clearly shows that the surface property changes by the combination of two oxides. The ratio was kept constant over 1 mol% of WO_3. The marked decrease in the ratio of cis to trans-2-butene reveals that the dominant property of the catalyst in the isomerization reaction changes from basic to acidic, because high values of the ratio are known to be observed over basic catalysts (6–11), while low values are observed over acidic catalysts (10–14).

Since the ring opening isomerization of cyclopropane is known to be catalyzed by Brönsted acids (15), the reaction was examined at 180°C over WO_3 supported on MgO, Al_2O_3, SiO_2, TiO_2, and ZrO_2. The results are summarized in Table 2. The surface areas and the acidic properties of these catalysts are listed in Tables 3 and 4, respectively. The order of the activity was WO_3–Al_2O_3 > WO_3–ZrO_2 > WO_3–TiO_2 > $WO_3 \gg WO_3$–SiO_2 = WO_3–MgO = 0. An increase of the catalytic activity was observed over the catalysts where Al_2O_3,[1] TiO_2, and ZrO_2 were used as supports, while the activity disappeared by using SiO_2 and MgO as supports. Increase of the rates on Al_2O_3, ZrO_2, and TiO_2 is explained by the generation of the acid sites especially at $pK_a = +1.5 \sim 3.3$ by the combination of those oxides with WO_3. The acidity

[1] The editor kindly suggested the alumina is a catalyst for the isomerization reaction. So, our results on WO_3–Al_2O_3 may involve the contribution of Al_2O_3 itself. TiO_2 and ZrO_2 were inactive.

TABLE 3

Surface Area of WO$_3$ Supported by Various Oxides

Support	None	Al$_2$O$_3$	TiO$_2$	ZrO$_2$	SiO$_2$	MgO
Surface area (m^2/g)	3	196	103	41	200	178

increase by mixing WO$_3$ with Al$_2$O$_3$ or ZrO$_2$ is explained similarly as in the case of WO$_3$–TiO$_2$ by the hypothesis of Tanabe *et al.* (5). A slight increase in acidity was obtained on WO$_3$–SiO$_2$, though the hypothesis predicted no acidity increase. In the case of WO$_3$–MgO, it is expected from the examples of binary oxides including a strongly basic MgO such as MgO–Al$_2$O$_3$ (16) and MgO–TiO$_2$ (17) that acidity will not generate, which is in good accordance with the experimental results (Table 4), but basicity will increase. Though there is a qualitative agreement between the isomerization rate of cyclopropane and the acidity, it is not quantitative. This is considered due to the fact that the acidity measured by the amine titration method gives the sum of the Brönsted and Lewis acidities.

ii. Disproportionation of Ethylene, Propylene, and 1-Butene

Disproportionation of 1-butene was found to take place over WO$_3$–TiO$_2$ cata-

TABLE 4

Acid Properties of the Catalyst Used

Catalyst	Acidity (mmol/g)			
	−3.0	pk_a +1.5	+3.3	+4.8
WO$_3$–Al$_2$O$_3$	0.034	0.23	0.27	0.21
WO$_3$–ZrO$_2$	0.052	0.14	0.14	0.15
WO$_3$–TiO$_2$	+	0.36	0.42	0.48
WO$_3$	—	0.025	0.050	0.11
WO$_3$–SiO$_2$	0.030	0.082	0.088	0.18
WO$_3$–MgO	—	—	—	0.009
TiO$_2$	—	—	0.042	0.33
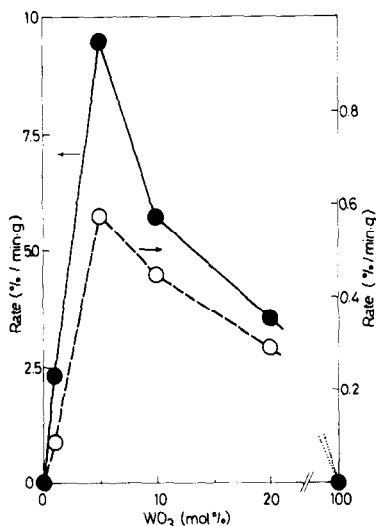
FIG. 3. Disproportionation of 1-butene over WO$_3$–TiO$_2$ and of propylene over H$_2$-treated WO$_3$–TiO$_2$ at 100°C: O, 1-butene over WO$_3$–TiO$_2$; ●, propylene over H$_2$-treated WO$_3$–TiO$_2$.

lyst, though the reaction rate was smaller than that of the isomerization. Figure 3 shows the changes of the rate, which was obtained from the initial rate of the formation of ethylene, of disproportionation vs the amount of WO$_3$ supported on TiO$_2$. In contrast with the activity variation in the isomerization, an optimum activity was obtained over the 5 mol% WO$_3$ catalyst. This suggests that the acidic property does not directly govern the activity of the metathesis reaction.

A hydrogen treatment enhanced the reaction. When the WO$_3$–TiO$_2$ catalyst was reduced partially by 100 Torr of H$_2$ at 500°C for 1 hr after the standard pretreatment, the catalytic activity for the disproportionation of 1-butene was increased about one order of magnitude. The reaction of propylene was also examined on the hydrogen-treated catalysts to see the disproportionation reaction itself. An optimum was again observed at 5 mol% (Fig. 3). Pure TiO$_2$ and WO$_3$ were completely inactive.

Disproportionation of cyclopropane during the ring opening isomerization was also observed on WO$_3$–Al$_2$O$_3$, WO$_3$–TiO$_2$, and WO$_3$–ZrO$_2$ catalysts (Table 1). The unsup-

ported, SiO_2- or MgO-supported WO_3 catalysts were inactive. Compared with the activity sequence of the disproportionation of propylene during the cyclopropane isomerization over hydrogen-treated catalysts (WO_3-TiO_2 $\gtrsim$ WO_3-ZrO_2 > WO_3-Al_2O_3 > WO_3-SiO_2 > WO_3-MgO = WO_3 = 0), it is considered that cyclopropane does not directly yield metathesis products, but isomerizes first and then forms ethylene, butenes, etc. It is interesting that the activity of WO_3 supported on TiO_2 or ZrO_2 is much higher than that of WO_3-Al_2O_3, which is a popular catalyst for disproportionation reactions.

We found the formation of the branched products such as isobutene or isopentene in the disproportionation reaction of propylene or 1-butene. It is unusual to obtain isoproducts from n-olefins in the disproportionation, especially when the lower olefins were used as reactants.

To elucidate the origin of the branched products, the reaction of ethylene was examined at 200°C by using a partially reduced WO_3 (5 mol%)-TiO_2 catalyst. The reaction time course is shown in Fig. 4, which obviously shows the formations of propylene and isobutene. The amount of n-butene formed was negligible. The formation of isobutene from propylene was plot-
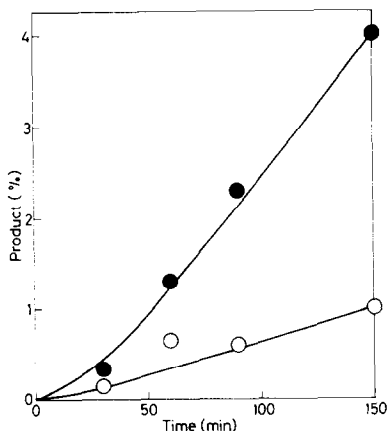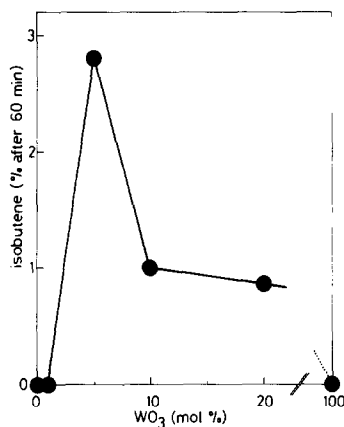

FIG. 5. Formation and isobutene from propylene at 100°C over WO_3-TiO_2 treated with H_2.

ted against the catalyst composition of WO_3-TiO_2 in Fig. 5. The variation in the formation of isobutene is quite similar to the variation in ethylene formation from propylene or 1-butene. Those observations lead us to the conclusion that isobutene from propylene and propylene from ethylene were obtained by the metathesis reaction, as propylene yielded ethylene and n-butenes by the same reaction. The formation of propylene and butene from ethylene was also reported on $Mo(CO)_6/Al_2O_3$ catalyst by O'Neil and Rooney (18). However, they did not mention the formation of branched products.

Our observations suggest the formation of metallocarbene (19) as the active intermediates of the metathesis reaction and probably of the propagation reaction of olefins, such as ethylene to propylene and propylene to isobutene.

FIG. 4. Formation of propylene and isobutene from ethylene at 200°C over WO_3-TiO_2 treated with H_2: $\bigcirc$, isobutene; $\bullet$, propylene.

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