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The Activity of WO_3-based Mixed-Oxide Catalysts

I. Acidic Properties of WO_3-based Catalysts and Correlation with Catalytic Activity

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The numbers of acidic sites in the WO_3–P_2O_5 binary system with different P/W ratios and in the WO_3–P_2O_5–X_nO_m ternary system (X_nO_m consists of different kinds of oxides) were determined by three methods, namely, a static method, a gas chromatographic-pulse technique, and a titration method. The values for acidity, obtained by studying the adsorption of NH_3 or pyridine from the gas phase, are consistent with those obtained by the titration method. Pure WO_3 is fairly low in acidity, but the introduction of P_2O_5 increases the acidity and a maximum occurs at P = 10–20 atom%. The addition of a third component to WO_3–P_2O_5 (P/W = 2/8), in small amounts, decreases the acidity, except in the case of Cr_2O_3, where it increases the acidity. The relationship between the acidity and the catalytic activities for the dehydration of isopropyl alcohol, the isomerization of 1-butene, and the decomposition of cumene was investigated. It was found that the acidic function of the catalysts is the factor deciding the catalytic activities for these reactions.

INTRODUCTION

WO_3 is a typical acidic oxide, much like MoO_3 and V_2O_5. It is generally known that WO_3-based mixed-oxide catalysts are effective for such acid-catalyzed reactions as the hydration, isomerization, and polymerization of olefins, the dehydration and esterification of alcohols, and the decomposition of various kinds of compounds. Therefore, a considerable amount of study has been directed to these reactions. However, there have been very few reports dealing with the directly measured acid–base properties of WO_3 or WO_3-based mixed-oxide catalysts (*1*).

In previous papers (*2–4*), we reported that the acid–base properties of mixed transition-metal oxides can be measured by studying the adsorption of basic and acidic molecules from the gas phase. Since pure WO_3 is light yellow, it also seems to be possible, for certain WO_3-based mixed oxides, to measure the acid–base properties by means of the titration method which is extensively employed for use with white or light-colored catalysts (*5–7*). Therefore, it is interesting and important to compare the values of acidity obtained from the titration method with those obtained from the adsorption methods and to confirm whether or not these methods of measurement are valid.

The present paper is first part of an investigation concerning the catalytic activity of WO_3-based mixed metal oxides. We attempted first to determine the acidic properties of WO_3–P_2O_5 binary and WO_3–P_2O_5–X_nO_m (where X_nO_m consists of different kinds of oxides) ternary systems by three different methods, to find how the

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introduction of other oxides into WO_3 modifies the acidic properties of the catalyst, and then to investigate how this modification in turn induces a change in the catalytic behavior.

EXPERIMENTAL METHODS

Catalysts

Two series of WO_3-based catalysts were used in this study: (i) the WO_3–P_2O_5 system with 10 different P/W ratios (P/W = 0–7/3), and (ii) the WO_3–P_2O_5–X_nO_m (W:P:X = 72:18:10 atomic ratio) system, where X_nO_m refers to 16 different metal oxides. The catalysts were prepared as follows. The required quantities of ammonium tungstate [$(NH_4)_{10}W_{12}O_{41} \cdot H_2O$] and 85 wt% H_3PO_4 were dissolved in hot water by using oxalic acid, and to this was added an aqueous solution or slurry of the third metallic component; thereafter, 10- to 20-mesh pumice was mixed with the solution, and the mixture was evaporated with vigorous stirring. The amount of pumice was 500 ml (about 150 g)/g-atom of W + P + X. The catalysts were calcined in a stream of air at 500°C for 4–5 hr. As the starting materials of the third components, X_nO_m, we used nitrates for Bi, Fe, Ni, Co, Cr, Cu, Zn, and Mn, ammonium salts of oxy acids for V and Mo, chlorides (converted to hydroxides by dilute ammonia) for Sn and Ti, hydrates for Al, Mg, and K, and acetate for U. The pumice used was a natural one originating from volcanic rocks in Kagoshima (a southwestern prefecture in Japan), which consists of macropores (the density is about 0.7 g/ml, and the surface area is less than 0.3 m^2/g) and is chemically inert. It was used in our studies merely in order to enhance the mechanical strength of the catalysts.

Acidity Measurements

The acidity of the WO_3-based catalysts, in their oxidized state, was measured by the following three methods.

Static method. The amount of NH_3 irreversibly adsorbed at a pressure of 300 mm Hg at 25 and 200°C was measured volumetrically. The details of the procedures were the same as those described in previous papers (*2*, *4*).

Gas chromatographic-pulse technique. The amount of pyridine required to inhibit completely the isomerization of 1-butene at 160°C was measured. The details of these procedures were also described in previous papers (*3*, *4*).

Titration method. The catalyst (1.0 g) was ground and calcined in air at 500°C for 3 hr and then was put in *n*-heptane (about 30 ml). The sample was titrated with an *n*-heptane solution of 0.024 *N* *n*-butylamine, using *p*-dimethylaminoazobenzene (pK = + 3.3), dicinnamalacetone (pK = − 3.0), and benzalacetophenone (pK = − 5.6) as indicators (*8*).

Catalytic Activity Measurements

The dehydration of isopropyl alcohol (IPA) and the isomerization of 1-butene were carried out in an ordinary continuous-flow reaction system. The concentrations of the IPA and butene were 1.65 and 0.67 mole%, respectively. The total flow rate (at 25°C) was kept constant at 1.5 liter/min, and the amount of catalyst used was 1.0–20 g. The reactor and the experimental procedures were the same as those employed in previous work (*2–4*, *9–11*).

The decomposition of cumene was carried out in a microreactor using the gas chromatographic-pulse technique. The reactor was a U tube (40 cm in length with a 4-mm i.d.), the catalyst weighed 1.0 g, and the carrier gas was He (about 50 ml of NTP/min). A sequence of the pulses of cumene was injected into the reactor (350°C) with a pulse size of 2 μl. The amount of propylene produced from cumene was evaluated by using a separation column (alumina: 2 m, 100°C).

RESULTS

The WO_3–P_2O_5 System

Surface area. The surface areas of the WO_3–P_2O_5 catalysts were checked by the BET method using nitrogen at −196°C. The results are shown in Table 1. The surface area increases a little with the addition of 1 atom% of P to W, but it gradually decreases with further increases in the P_2O_5 content.

Acidity. The acidity of the WO_3–P_2O_5 catalysts, as determined by the amount of NH_3 irreversibly adsorbed at 25 and 200°C and by the amount of pyridine required to poison completely the activity for the isomerization of 1-butene at 160°C, is plotted in Fig. 1 as a function of P_2O_5 content. The acidity measured by the titration method, using *p*-dimethylaminoazobenzene as an indicator, is also plotted in Fig. 1. In the cases of the two other indicators, the equivalence point in the titration was not clear.

Parallels were found among the values of acidity obtained by means of the different methods. In addition, the values of acidity obtained by the adsorption of NH_3 agreed fairly well with those obtained by the titration method. It was also found that, in the case of the WO_3–P_2O_5 catalysts, the amount of NH_3 irreversibly adsorbed at 200°C is almost the same as that adsorbed at room temperature.

The results indicate that the acidity of pure WO_3 is very low and that, with an increase in the P_2O_5 content of the catalyst, the acidity rapidly increases at first, passes through a maximum at the phosphorus content of 10–20 atom%, and then decreases again to a very low value.

TABLE 1

Surface Areas of the WO_3–P_2O_5 Catalysts

Composition P/(W + P)	Surface area (m^2/g)	Composition P/(W + P)	Surface area (m^2/g)
0	6.1	0.15	2.1
0.01	7.7	0.20	2.2
0.02	6.9	0.30	2.2
0.05	5.8	0.50	0.4
0.10	3.4	0.7	0.4

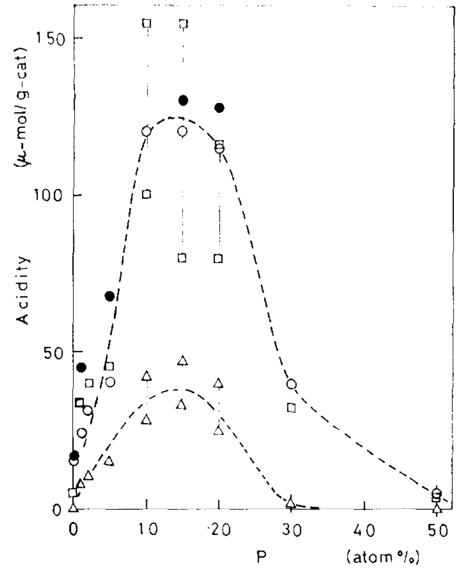

FIG. 1. Acidity of the WO_3–P_2O_5 catalysts as a function of phosphorus content. NH_3 adsorbed at (○) 200°C, (●) at 25°C (static method); (△) pyridine required to poison the isomerization activity (pulse method); (□) titration with *n*-butylamine (pK_a = + 3.3).

Dehydration activity for IPA. In previous studies (*2–4*), we pointed out that the catalytic activity for the dehydration of IPA to propylene is effective as a measure of acidity. This point was confirmed in the present study.

A gaseous mixture of IPA and air was passed through a bed of the catalyst under the above-mentioned conditions. It was found that the WO_3–P_2O_5 catalysts were active, even at a very low temperature (130–150°C), that the main product was propylene, and that the amounts of the other products, including acetone, were very small. The rate of dehydration at 140°C, r_P (moles per hour·grams of catalyst), was measured for each catalyst. Following the principle of the differential reactor, the conversion was held at a low

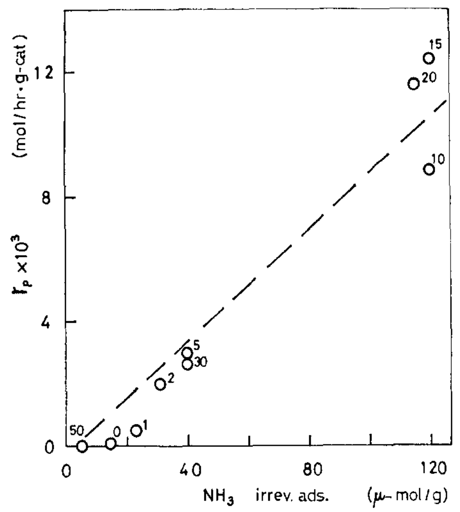

FIG. 2. Relation between the dehydration activity for IPA and the acidity. Activity = amount of NH_3 adsorbed at 200°C; r_p = dehydration rate; T = 140°C, IPA = 1.65 mole% in air. Numbers correspond to the concentration (atom percent) of phosphorus in the WO_3–P_2O_5.

level, i.e., usually below 10%. The results are plotted in Fig. 2 as a function of the acidity obtained by the adsorption of NH_3. A roughly proportional relationship is observed between activity and acidity. It should be noted that the WO_3–P_2O_5 catalysts are inactive for the dehydrogenation of IPA.

Isomerization activity for butene. The relationship between the acidity of the catalysts and the activity for isomerization was investigated. The reaction was carried out in air. As the activity decreases markedly with reaction time, especially at the beginning of the reaction, the rate of isomerization of 1-butene to 2-butenes, r_I (moles per hour·grams of catalyst), was measured after a 30-min reaction for every catalyst, from the data at low conversion of 1-butene. It is plotted in Fig. 3 as a function of the acidity of the catalysts. A proportional

TABLE 2

Surface Area and Acidity of the WO_3–P_2O_5–X_nO_m (Atomic Ratio: W–P–X = 72–18–10) Catalysts

X	Surface area (m^2/g)	Acidity (μmole/g of catalyst)			
		Pyridine	NH_3		Titration (pK_a = +3.3)
			25°C	200°C	
V	4.7	21	48	39	35
Mo	2.2	Trace	10	10	8–10
U	7.0	8.4	49	48	20–36
Ti	9.3	8.8	47	47	50–65
Sn	2.3	2.9	36	17	19–29
Fe	4.0	25	18	18	17–20
Al	7.0	29	92	90	23–29
Bi	2.5	7.5	72	40	35–44
Zn	14.7	11	240	64	70–160
Cr	8.7	113	230	180	180–250
Co	7.3	29	520	98	60–90
Mn	3.4	1.5	149	60	12–13
Ni	5.8	18	210	60	9–20
Cu	4.2	—	100	—	7–8
Mg	10.7	8.4	177	89	30–40
K	16.1	4.2	82	40	120–170
Cr–Co	10.2	83	190	190	31–34
None	2.2	25–40	132	120	77–120

relationship is obtained between activity and acidity.

The WO_3–P_2O_5–X_nO_m System

Various kinds of third metal oxides, X_nO_m, were added in small amounts (10 atom%) to the WO_3–P_2O_5 (P/W = 2/8) system, which has a dramatically high acidity, and the effect of the third component on the properties and catalytic activities of the catalyst was studied.

Acidity. The acidity of the WO_3–P_2O_5–X_nO_m catalysts, as determined by the amount of NH_3 irreversibly adsorbed at both 25 and 200°C, by the amount of pyridine required to poison completely the isomerization activity for 1-butene at 160°C, and by the titration using *p*-dimethylaminoazobenzene ($pK_a = +3.3$) as and indicator, are listed, together with the surface areas in Table 2. The relationships among the acidities obtained by the three different methods are shown in Figs. 4 and 5.

The values for acidity obtained by different methods are relatively consistent,

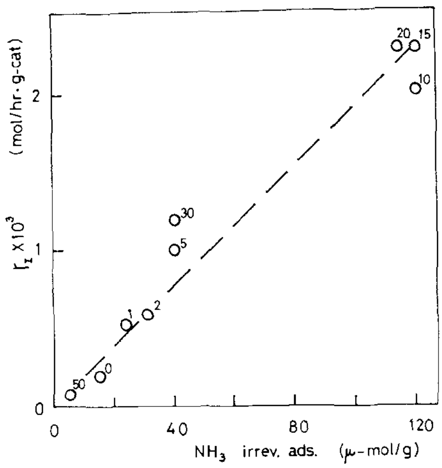

FIG. 3. Relation between the isomerization activity for 1-butene and the acidity. Acidity = amount of NH_3 adsorbed at 200°C; r_I = isomerization rate; T = 160°C; 1 − C_4H_8 = 0.67 mole% in air. Numbers correspond to the concentration (atom percent) of phosphorus in the WO_3–P_2O_5.

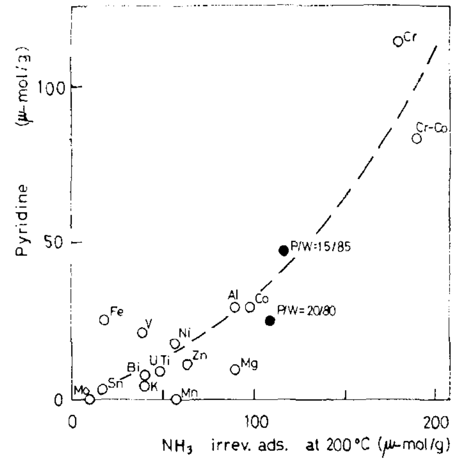

FIG. 4. Relation between the acidity of the WO_3–P_2O_5–X_nO_m (W–P–X = 72–18–10) catalysts obtained by the pyridine-pulse method and that obtained by the adsorption of NH_3 at 200°C.

though there is some disparity and uncertainty in these values. The addition of the third component to the WO_3–P_2O_5, in small amounts, decreases the acidity, except in the case of Cr_2O_3, in which it markedly increases the acidity.

Dehydration activity for IPA. The rate of the dehydration at 130°C, r_P, was measured for each catalyst, and its correlation

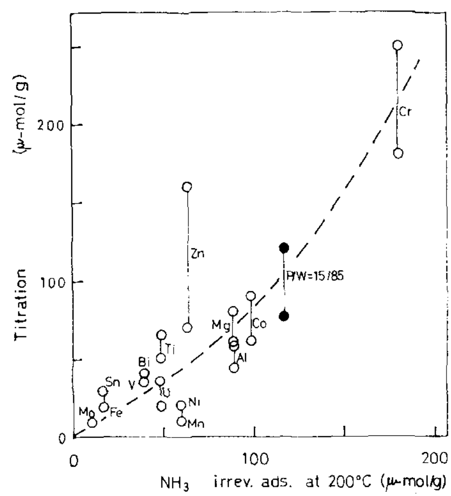

FIG. 5. Relation between the acidity of the WO_3–P_2O_5–X_nO_m (W–P–X = 72–18–10) catalysts obtained by the titration method and that obtained by the adsorption of NH_3 at 200°C.

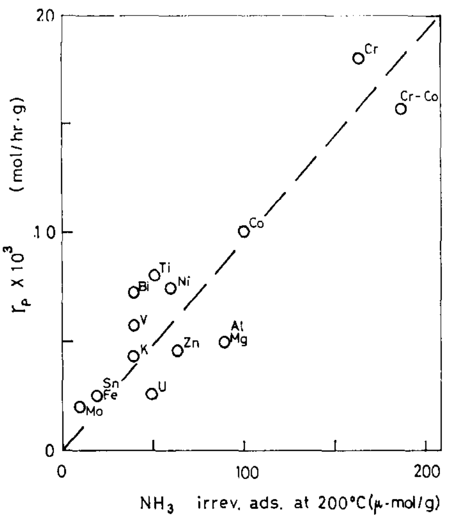

FIG. 6. Relation between the activity for the dehydration of IPA (r_p) and the acidity. Acidity = amount of NH_3 adsorbed at 200°C; r_p = dehydration rate; T = 130°C; IPA = 1.65 mole% in air.

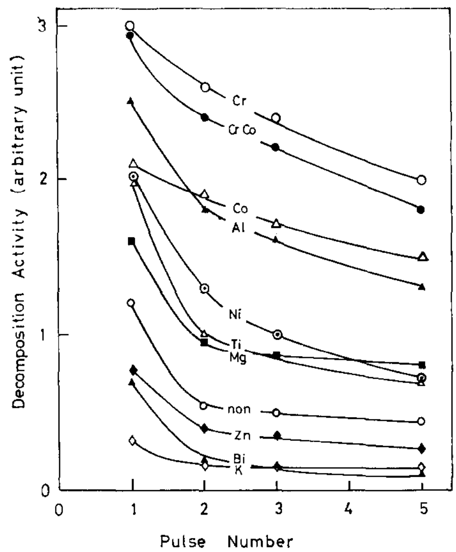

FIG. 8. Variation of the activity for the decomposition of cumene with the pulse number. Catalyst WO_3–P_2O_5–X_nO_m, with X indicated in the figure.

with the acidity of the catalyst was studied. Figure 6 shows that the activity is roughly proportional to the acidity, though the values of acidity contain some uncertainty.

Isomerization activity for butene. The relationship between the activity for the isomerization of 1-butene obtained in the same manner as before and the acidity of the WO_3–P_2O_5–X_nO_m catalysts is shown in Fig. 7. A roughly proportional relationship is obtained in this case, too.

Decomposition activity for cumene. The relationship between the activity for the decomposition of cumene to propylene and

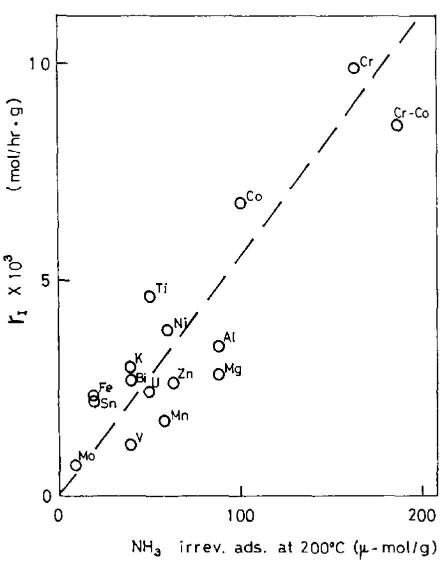

FIG. 7. Relation between the activity for the isomerization of 1-butene (r_I) and the acidity. Acidity = amount of NH_3 adsorbed at 200°C; r_I = isomerization rate; T = 160°C; 1-butene = 0.67 mole% in air.

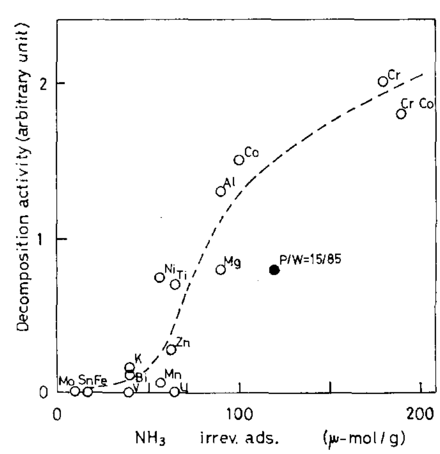

FIG. 9. Relation between the activity for the decomposition of cumene and the acidity. Acidity = amount of NH_3 adsorbed at 200°C.

the acidity of the catalysts was also investigated. The reaction was carried out in a He atmosphere with a microreactor using the gas chromatographic-pulse technique. A relatively high temperature, about 350°C, was required for this reaction, and the catalytic activity decreased gradually with pulse number (pulse size: 2 μl). Some representative results are shown in Fig. 8. Therefore, the activity at 350°C obtained at the fifth pulse was measured for each catalyst; it is plotted in Fig. 9 as a function of the acidity of the catalyst. A relatively good correlation is obtained between activity and acidity. The catalysts used were markedly reduced and were really black.

TABLE 3

Comparison of the Acidity (r_p) of Various Kinds of Mixed-Oxide Catalysts

Composition (atomic ratio)	$r_p \times 10^3$ [a] at 175°C	Composition (atomic ratio)	$r_p \times 10^3$ [a] at 140°C
W	2.0	W–P (8–2)	12
W–Mo (8–2)	2.5	W–P–Cr (72–18–10)	30
W–Mo (2–8)	0.08		
W–V (8–2)	0.5	Sn–Mo (7–3)	5
W–V (2–8)	4.7	Ti–Mo (5–5)	0.8
V	2.2	Fe–Mo (5–5)	1
W–Ti (4–6)	0.05	V–Mo (9–1)	1
W–Sn (4–6)	0.4		

[a] r_p is expressed at moles per hour·grams of catalyst. IPA = 1.65 mole% in air.

DISCUSSION

First, these experiments show that the values of acidity obtained by studying the irreversible adsorption of basic molecules in the gas phase are consistent with those obtained by the titration method.

Next, pure WO_3 is fairly low in acidity, but introduction of P_2O_5 to WO_3 induces a large increase in acidity, and a maximum occurs at P = 10–20 atom%, much as in the case of the MoO_3–P_2O_5 system (10). However, the acidity of WO_3–P_2O_5 at P = 10–20 atom% is much higher than that of MoO_3–P_2O_5 at P = 10–20 atom%; moreover, it is higher than that of SnO_2–MoO_3 (Mo/Sn = 3/7 atomic ratio), which is the highest of the MoO_3- and V_2O_5-based binary oxides (*3*).

The effects of the third components introduced into WO_3–P_2O_5 are not the same as those observed in the case of the MoO_3–P_2O_5–X_nO_m systems (Mo:P:X = 1:0.2:0.1 atomic ratio) (*11*); Cr_2O_3 is the sole component which can enhance the acidity of the WO_3–P_2O_5, while the introduction of many metal oxides enhances the acidity of MoO_3–P_2O_5. It seems difficult to obtain a clear correlation between the acidity of the WO_3–P_2O_5–X_nO_m ternary systems and the properties of the pure metal oxides corresponding to the third components. This may imply complexity of the acidity generation caused by the combination of several oxides.

In the cases of WO_3–P_2O_5 and certain WO_3–P_2O_5–X_nO_m catalysts, the amount of NH_3 irreversibly adsorbed at 200°C is the same as that adsorbed at room temperature. From this evidence, it is believed that the acidic sites of these catalysts are all characterized by great acid strength.

The absence of dehydrogenation activity for IPA suggests that the WO_3–P_2O_5 and WO_3–P_2O_5–X_nO_m catalysts are very low in basicity (*2–4, 11*).

The comparisons of catalytic activity for the dehydration of IPA to propylene with acidity data reveal that activity is proportional to acidity; this evidence proves that activity is valid as a measure of the acidity of the WO_3-based mixed-oxide catalysts.

The dehydration activities of the WO_3–P_2O_5 and WO_3–P_2O_5–Cr_2O_3 catalysts, which are adopted as measures of the acidity of the catalysts, are compared with those of the various kinds of mixed-oxide catalysts in Table 3. These results also indicate that the acidities of the WO_3–P_2O_5 and WO_3–P_2O_5–Cr_2O_3 catalysts are high, compared with those of any other mixed metal oxides, and that the introduction of no other oxides into WO_3 can enhance the acidity as strongly as introduction of P_2O_5. The introduction of about 50 atom% each of TiO_2 and SnO_2 into MoO_3 induces a sharp increase in the acidity (*3, 4*), but the introduction of these oxides into WO_3 decreases acidity.

Comparison of the isomerization activity for 1-butene with acidity data reveal that the activity is also proportional to the acidity. This evidence proves that, in the case of a continuous-flow experiment in an atmosphere of air, like this, the isomerization is catalyzed only by the acidic sites, much as in the cases of many MoO_3- and V_2O_5-based mixed-oxide catalysts (*2–4, 9–11*).

The WO_3–P_2O_5 and WO_3–P_2O_5–X_nO_m catalysts are susceptible to reduction by butene, even in the presence of excess air. The reduced catalysts cannot be returned to their initial color easily, even by heat treatment at 500°C in flowing air. This allows us to infer that the degradation of the activity is caused in part by the reduction of oxides.

A relatively good proportional relationship is observed between the decomposition activity for cumene and acidity, though the catalysts are reduced and the activity decreases much more markedly than in the case of the butene isomerization.

In any event, this study demonstrates that the acidic function of the catalysts is the factor deciding the catalytic activities for the dehydration of IPA, the isomerization of butene, and the decomposition of cumene.

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