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Catalytic Oxidation of Olefins over Oxide Catalysts Containing Molybdenum

V. Relation Between the Surface Concentration of Acidic Sites and the Catalytic Activity to Form Acetone

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The amount of acidic sites of a series of SnO_2–MoO_3 binary oxides was determined by *n*-butylamine titration and correlated to the catalytic activity to form acetone in the oxidation of propylene. It was found that the catalytic activity increases linearly with the surface concentration of acidic sites which are formed by the combination of stannic oxide and molybdenum trioxide. The same relation holds for other transition metal oxides combined with molybdenum trioxide which are also active for acetone formation. The role of the acidic sites is to promote the hydration of the olefin which is the first step of acetone formation.

INTRODUCTION

In the earlier papers of this series, we have reported that saturated ketones are mainly produced in the oxidation of olefins in the presence of water vapor over such binary oxides as Co_3O_4–, SnO_2–, TiO_2–, Cr_2O_3–, and Fe_2O_3–MoO_3 (*1–5*). Propylene, *n*-butenes, and 1-pentene are oxidized to acetone, methyl ethyl ketone, and methyl propyl ketone, respectively (*4*). The ketone formation is quite selective in the oxidation of propylene. A mechanism that ketone is produced via hydration of olefin to form alcohol or alcohoxy group as intermediate, followed by oxydehydrogenation, has been suggested (*4, 6*). This mechanism has been supported by evidence using $H_2{}^{18}O$ tracer that the oxygen atom found in the produced ketone is incorporated from the water molecule and not from molecular oxygen (*7, 8*).

Buiten has reported that a rapid hydrogen exchange reaction between propylene and water was observed on the SnO_2–MoO_3 catalyst (*6*) at the condition where propylene is oxidized to acetone, acrolein and acetic acid (*9*). We also observed that the reactant *n*-butene isomerized rapidly during the oxidation to methyl ethyl ketone over both SnO_2–MoO_3 and Co_3O_4–MoO_3 catalysts (*4*). Since it has been generally accepted that hydration, isomerization and hydrogen exchange reactions of olefins are promoted by acidic catalysts, it is expected that acidic sites of the binary oxide catalysts are active centers for the ketone formation. In the present work, the amount of acidic sites was determined by the normal butylamine titration (*10*). It was found that the amount of acidic sites is increased remarkably by the combination of two component oxides. The amount of acidic sites has been successfully correlated with the catalytic activity to form acetone in propylene oxidation.

EXPERIMENTAL SECTION

All runs were carried out using a conventional flow reactor at 1 atm pressure. The apparatus, the preparative method of catalysts and the analysis of reactants and products were the same as described previously (*1–5*).

The concentration of the surface acidic sites was determined by the titration of *n*-butylamine according to the method of

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Benesi (*10*). The indicator used in the amine titration was dimethyl yellow ($pK_a = 3.3$). Each catalyst sample was crushed to a powder smaller than 80 mesh and calcined at 550°C for 5 hr. After cooling the sample was dried at 100°C for 3 hr. Roughly 0.3 g of sample was transferred to each of five previously weighed glass stoppered conical flasks and reweighed precisely to obtain the exact sample weight. Ten milliliters of dry cyclohexane and then a known amount of 0.0145 or 0.0139 *M* *n*-butylamine in cyclohexane were added to each of five samples so as to bracket the expected titer by the appropriate amount of *n*-butylamine per 0.3 g of sample. The tightly stoppered samples were then equilibrated with *n*-butylamine while stirring for 2 hr at 60°C (*15*). After cooling to room temperature, the equilibrated catalyst suspensions were tested with dimethyl yellow. The above operation was repeated several times using smaller stepwise increases in *n*-butylamine content between the limits established in the previous trial. In some cases, especially in the case of deep colored samples, it was difficult to distinguish the color of the indicator where a small amount of the white powder of Al_2O_3 was added to the samples before the addition of *n*-butylamine. The color of the indicator was distinguished on the added Al_2O_3 particles after the adsorption of *n*-butylamine had attained equilibrium.

RESULTS AND DISCUSSION

As reported previously, SnO_2–MoO_3 is the most active catalyst for acetone formation from propylene, whereas pure stannic oxide or molybdenum trioxide has no catalytic activity for this oxidation (*4*). The effect of the addition of molybdenum trioxide to stannic oxide on this catalytic activity has been reexamined. The oxidation of propylene was carried out under constant reaction conditions over SnO_2–MoO_3 catalysts having different compositions. The yield of acetone was determined at two different reaction temperatures, 150 and 170°C, and is plotted against the concentration of molybdenum in the binary oxide catalysts in Fig. 1. The yield of acetone increases remarkably with the increase in molybdenum concentration at both reaction temperatures. Although the yield of acetone is not exactly proportional to the rate of oxidation of propylene to acetone because of the reoxidation of the produced acetone, the effect of the addition of molybdenum trioxide to stannic oxide on the catalytic activity to form acetone is quite apparent. Thus, it is clear that the active site for acetone formation is formed by the combination of the two different oxides.

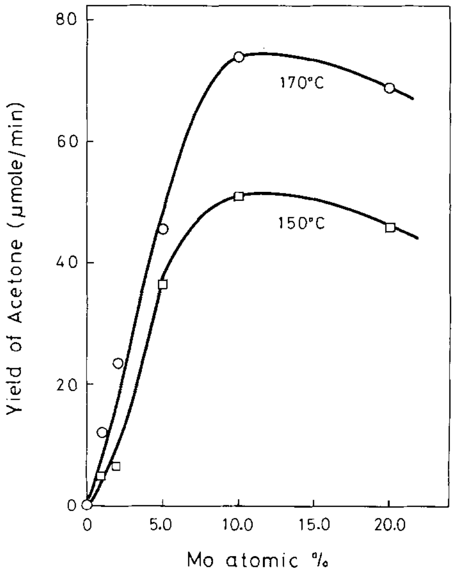
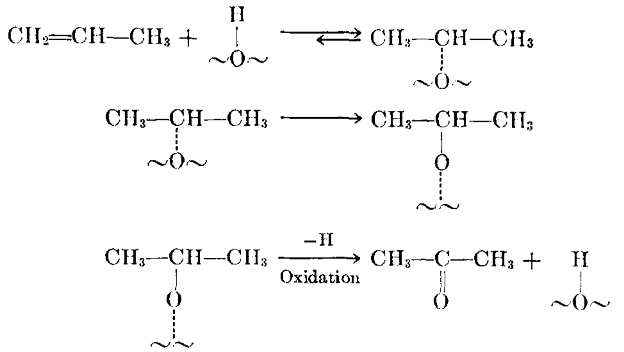


FIG. 1. Effect of the addition of molybdenum trioxide to stannic oxide catalyst on the yield of acetone in the oxidation of propylene. Catalyst used, 16.5 g; GHSV, 660 ml STP/ml cat hr; flow rate of reactant gas: propylene, 22.5 ml/min; oxygen, 29.7 ml/min; water, 33.3 ml/min; nitrogen, 22.8 ml/min.

The nature and the role of this active site in the oxidation of propylene were further investigated in connection with the mechanism for acetone formation. Since the oxygen atom in the produced acetone comes from a water molecule, not from molecular oxygen, the mechanism that acetone is formed by a direct interaction between propylene and an active species derived from molecular oxygen, can be ruled out (*7*, *8*). Two mechanisms which have been proposed for acetone formation seem to not be in conflict with the reported results. Buiten assumed that both the oxidation of propylene to acetone and the hydrogen exchange reaction of propylene with D_2O proceed via a common intermediate as CH_3CHCH_3 over SnO_2–MoO_3 catalyst and suggested the following pathway for acetone formation (*6*):

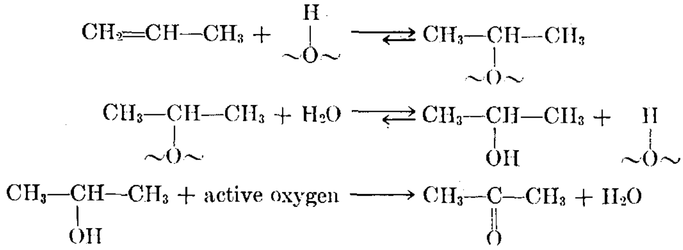


$$CH_2{=}CH{-}CH_3 + \underset{\sim O\sim}{\overset{H}{|}} \rightleftarrows CH_3{-}\underset{\substack{\vdots\\ \sim O\sim}}{CH}{-}CH_3 \qquad (1)$$

$$CH_3{-}\underset{\substack{\vdots\\ \sim O\sim}}{CH}{-}CH_3 \longrightarrow CH_3{-}\underset{\substack{|\\ O\\ \vdots\\ \sim\sim}}{CH}{-}CH_3 \qquad (2)$$

$$CH_3{-}\underset{\substack{|\\ O\\ \vdots\\ \sim\sim}}{CH}{-}CH_3 \xrightarrow[\text{Oxidation}]{-H} CH_3{-}\underset{\substack{\|\\ O}}{C}{-}CH_3 + \underset{\substack{|\\ \sim O\sim}}{H} \qquad (3)$$

where the surface hydroxyl group is probably in rapid equilibrium with water. A mechanism that alcohol may furnish an oxidation pathway has also been suggested (*4*, *8*), i.e.,



$$CH_2{=}CH{-}CH_3 + \underset{\sim O\sim}{\overset{H}{|}} \rightleftarrows CH_3{-}\underset{\substack{|\\ \sim O\sim}}{CH}{-}CH_3 \qquad (4)$$

$$CH_3{-}\underset{\substack{|\\ \sim O\sim}}{CH}{-}CH_3 + H_2O \rightleftarrows CH_3{-}\underset{\substack{|\\ OH}}{CH}{-}CH_3 + \underset{\substack{|\\ \sim O\sim}}{H} \qquad (5)$$

$$CH_3{-}\underset{\substack{|\\ OH}}{CH}{-}CH_3 + \text{active oxygen} \longrightarrow CH_3{-}\underset{\substack{\|\\ O}}{C}{-}CH_3 + H_2O \qquad (6)$$

Both mechanisms consist of two different steps. The first step is the reaction to form an isopropoxy group or isopropyl alcohol via the intermediate as CH_3CHCH_3 which has probably a partial positive charge and may be a carbonium ion. The back reaction from this intermediate to give the olefin results in the hydrogen exchange reaction and the isomerization as reported by Buiten (*6*) and by the authors (*4*). The second step is the oxidative dehydrogenation of the alcoholic intermediate to form acetone. This step will involve active species derived from molecular oxygen on the catalyst surface. Therefore, the active site which is formed by the combination of stannic oxide and molybdenum trioxide must promote at least one of these two steps.

In order to see which step is more promoted by the active site formed by the combination of the two different oxides, we chose two simple reactions corresponding to the two steps of the acetone formation and examined the activity changes of binary oxides for these two test reactions varying the catalyst composition. The double bond isomerization of 1-butene was chosen as the test reaction for the first step of the acetone formation. Of course, the carbonium ion is not the sole intermediate which has been reported for the isomerization of olefin; the alkyl radical has often been considered as the intermediate of the double bond isomerization which accompanies hydrogenation. An allylic species has also been suggested as an intermediate on chromia (*11*) and been proved spectroscopically over zinc oxide (*12*). However, alkyl and allylic intermediates seem to be possible only on metallic or highly evacuated oxide surfaces. The double bond isomerization observed in the presence of sufficient water vapor seems to proceed mainly via the carbonium ion intermediate. Thus, we assume that the catalytic activity for the first step of acetone formation is associated with that for the double bond isomerization of 1-butene.

Oxidation of propane to carbon dioxide was chosen as the test reaction for the second step of the acetone formation. It has been reported that the catalytic activity for propane oxidation depends only on the strength of the metal–oxygen bond of the catalyst oxide (*13*). Moreover, since propane has no functional group, its oxidation seems to be suitable to examine the reactivity of the active species of oxygen which would be involved in the second step of acetone formation.

Seventeen catalysts including pure stannic oxide and molybdenum trioxide were selected. Their compositions and surface areas are shown in the first and second columns in Table 1. At first, variation of the catalytic activity for propylene oxidation with the catalyst composition was examined quantitatively. The rates of propylene oxidation were measured under constant reaction conditions at various temperatures and Arrhenius graphs were plotted for each catalyst. Since the rates of the propylene oxidation differed considerably for each catalyst, a comparison of the reaction rates at a constant temperature was difficult without large extrapolations of Arrhenius graphs. Therefore, following Sachtler and De Boer (*14*), the catalytic activity of each sample is compared in terms of the temperatures, $T_{\text{propylene}}$ (°K), at which the specific rates reach a fixed value,

$$r_{\text{propylene}} = 5 \times 10^{-3}\ \mu\text{mole/sec m}^2\text{-cat.}$$

The catalytic activity for each sample is defined as

$$\text{Activity for } C'_3 \text{ oxidation} = \frac{10^3}{T_{\text{propylene}}}$$

TABLE 1

CATALYTIC ACTIVITY AND SURFACE CONCENTRATION OF ACIDIC SITES FOR THE SnO_2–MoO_3 BINARY SYSTEM

		Catalytic activity[a] (°K^{-1})				
Catalyst Sn:Mo atomic ratio in SnO_2–MoO_3	Surface area of catalyst (m^2/g)	C_3H_6 oxidation $10^3/T_{\text{propylene}}$	1-C_4H_8 isomer. $10^3/T_{\text{1-C'}_4}$	C_3H_8 oxidation $10^3/T_{\text{propane}}$	Selectivity to acetone at $T_{\text{propylene}}$ (%)	Concn of acidic sites (μeq/m^2-cat)
100:0	16.9	1.70	1.81	1.44	Tr	0.04
99:1	40.1	1.77	1.80	1.43	44.8	0.76
98:2	58.3	1.89	2.29	1.53	60.5	0.80
95:5	41.5	1.93	2.12	1.53	50.0	1.04
90:10	32.7	2.14	2.55	1.63	72.8	4.15
80:20	30.2	2.22	2.55	1.61	77.1	2.53
70:30	38.1	2.15	2.53	1.59	61.2	4.06
60:40	33.9	2.18	2.62	1.64	57.7	3.77
50:50	26.2	2.19	2.57	1.64	43.7	4.88
40:60	23.3	2.20	2.42	1.62	60.4	3.73
30:70	20.8	2.16	2.49	1.55	64.0	4.42
20:80	33.5	2.20	2.44	1.57	58.9	3.79
10:90	16.2	2.15	2.33	1.59	58.6	3.70
5:95	14.8	2.06	2.28	1.50	68.0	1.98
2:98	7.6	1.68	2.14	1.53	41.0	2.67
1:99	6.9	1.44	2.08	1.53	12.2	2.42
0:100	0.5$_4$	1.56	1.96	1.38	Tr	1.46

[a] Reciprocal temperature at which the specific reaction rate reaches 5×10^{-3} μmoles/m^2-cat sec. Reaction conditions: catalyst used, 16.0 g; flow rate of each reactant: propylene, 1-butene or propane, 22.6 ml/min; oxygen, 33.4 ml/min; water, 33.3 ml/min; nitrogen, 22.6 ml/min.

the values of which are listed in the third column in Table 1. The selectivity to acetone at the temperature $T_{\text{propylene}}$ is also listed in the sixth column. The rates of the isomerization of 1-butene and the oxidation of propane were also measured at various temperatures and activities for each sample were expressed in the same way.

$$\text{Activity for 1-C}'_4\text{ isomerization} = \frac{10^3}{T_{1\text{-C}'_4}}$$

$$\text{Activity for C}_3\text{ oxidation} = \frac{10^3}{T_{\text{propane}}}.$$

$T_{1\text{-C}'_4}$ and T_{propane} are the temperatures at which the specific rates of the 1-butene isomerization and the oxidation of propane, i.e., $r_{1\text{-butene}}$ and r_{propane}, reach a value,

$$r_{1\text{-butene}} \text{ or } r_{\text{propane}} = 5 \times 10^{-3}\ \mu\text{mole/sec m}^2\text{-cat.}$$

The obtained values for $10^3/T_{1\text{-C}'_4}$ and $10^3/T_{\text{propane}}$ are summarized in the fourth and fifth columns in Table 1.

The values obtained for the catalytic activities for the oxidation of propylene, the isomerization of 1-butene and the oxidation of propane are plotted against the concentration of molybdenum in the binary oxide catalysts in Figs. 2–4. As shown in Fig. 2, the catalytic activity for the oxidation of propylene is increased remarkably by the combination of stannic oxide and molybdenum trioxide. Increase in the specific activity for the isomerization of 1-butene is also increased very much by the combination of two different oxides. This variation of the specific activity for the isomerization of 1-butene seems to correspond to that for the propylene oxidation. On the other

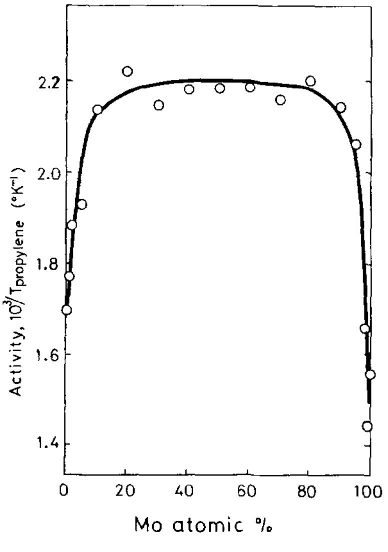


FIG. 2. Variation of the catalytic activity for the oxidation of propylene with the composition of SnO_2–MoO_3 binary oxide.

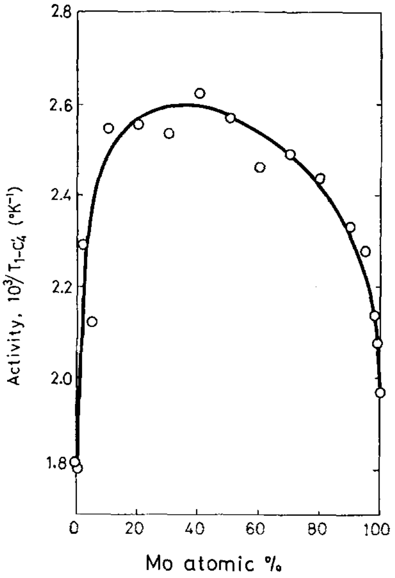


FIG. 3. Variation of the catalytic activity for the double bond isomerization of 1-butene with the composition of SnO_2–MoO_3 binary oxide.

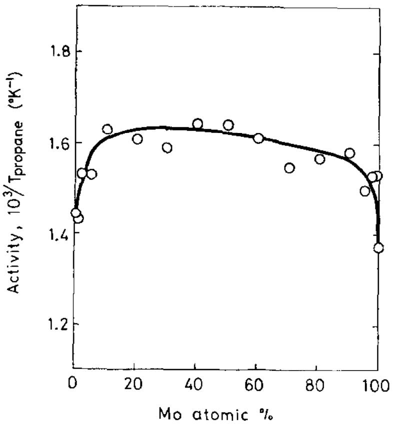


FIG. 4. Variation of the catalytic activity for the oxidation of propane with the composition of SnO_2–MoO_3 binary oxide.

hand, the specific activity for the propane oxidation does not change appreciably with the composition of the binary oxide catalysts. Although some increase of activity is observed by the addition of the second oxide, it is too small to be attributable to the activity change of the propylene oxidation. It is not clear that all sites active for the double bond isomerization are also active for the propylene oxidation via alcoholic intermediate and vice versa. However, the dramatic increases of the catalytic activity by the combination of two oxides in Figs. 2 and 3 suggest that both catalytic activities of the mixed oxides are associated with each other. Thus, it may be estimated that the active sites formed by the combination of stannic oxide and molybdenum trioxide mainly promote the first step of the acetone formation.

It has been generally accepted that hydration of olefins is accelerated by an acidic catalyst. Hence it is expected that the active sites formed by the combination of two different oxides may have acidic nature. The surface concentration of the acidic sites for 17 binary oxides used in this work was determined by *n*-butylamine adsorption using dimethyl yellow ($pK_a = 3.3$) as indicator and values are listed in the last column in Table 1. It was found that pure stannic oxide has virtually no acidic sites on its surface. When stannic oxide is combined with molybdenum trioxide, the concentration of acidic sites is increased remarkably with the amount of added molybdenum trioxide up to 10 atom % molybdenum. The effect of addition of stannic oxide to molybdenum trioxide is also observed from 90% molybdenum binary oxide to pure molybdenum trioxide.

The rate of acetone formation observed at 140°C is plotted against the concentration of the acidic sites in Fig. 5 for the binary oxides effective for acetone formation having the composition of 1–95 atomic % molybdenum. The temperature of 140°C was chosen because the selectivity to acetone with isopropyl alcohol over each catalyst is higher than 85% of the converted propylene at this temperature. The open circle and the bar in Fig. 5 refer to the observed rate of acetone formation including isopropyl alcohol and the rate of consumption of propylene over each catalyst, respectively. The products different from acetone and isopropyl alcohol are acetaldehyde, acetic acid and carbon dioxide under these conditions (*5*). Since these by-products are formed by two different routes, i.e., the direct formation from propylene and the consecutive oxidation of acetone, the bar in Fig. 5 indicates an upper limit of the rate of oxidation via alcoholic intermediate. As shown in Fig. 5, the deviation of the observed rate of acetone formation (open circle) from the rate of oxidation via alcoholic intermediate is not large. A linear relationship between the rate of acetone formation and the surface concentration of acidic sites holds for each binary oxide from 1 to 95% molybdenum concentration. Thus, it is clear that the combination of stannic oxide and molybdenum trioxide forms acidic sites which promote mainly the first step of acetone formation.

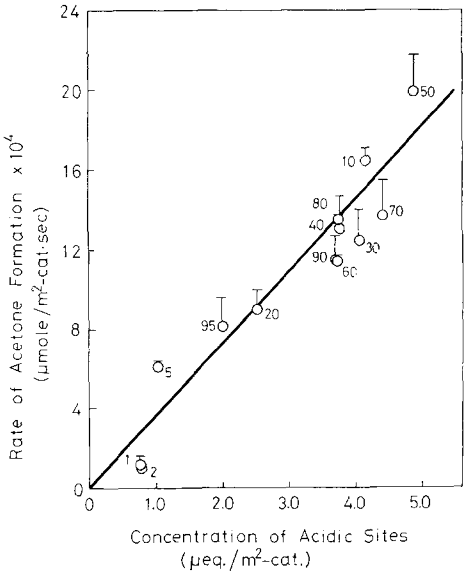


FIG. 5. Relation between the rate of acetone formation at 140°C and the surface concentration of acidic sites of SnO_2–MoO_3 catalysts. Numbers in the figure are the concentration of molybdenum in the SnO_2–MoO_3 binary oxides. Open circle and bar represent the rate of acetone formation and the rate of consumption of propylene over each catalyst, respectively.

Correlation between the catalytic activity to form acetone and the surface concentration of acidic sites was further examined for several transition metal oxides combined with molybdenum trioxide. TiO_2, SnO_2, Cr_2O_3, CuO, Mn_2O_3, ZnO and ThO_2 were selected for this examination. As reported previously (*5*), a considerable amount of isopropyl alcohol is formed in the oxidation of propylene over some of these catalysts. Since isopropyl alcohol seems to be an intermediate to acetone, catalytic activity to form acetone including isopropyl alcohol was correlated with the acid concentration of the catalysts. The results are summarized in Table 2, where catalytic activity is expressed in terms of $1/T_a$ because of large differences among the values for each catalyst. As shown in Table 2, TiO_2–MoO_3 and SnO_2–MoO_3 having a higher concentration of acidic sites show higher activity for acetone formation. On the other hand, ZnO–MoO_3 and ThO_2–MoO_3 having no surface acidic sites are almost inactive for acetone formation. The catalytic behavior of Mn_2O_3–MoO_3 is somewhat different. Although Mn_2O_3–MoO_3 has some acidic sites, carbon dioxide was the sole product in the oxidation of propylene. The reason is not clear but it may be because the activity of adsorbed oxygen on Mn_2O_3–MoO_3 is so large that all intermediate formed on the catalyst surface gets rapidly oxidized to carbon dioxide. The linear dependence of the catalytic activity to form acetone for the SnO_2–MoO_3 system on the surface concentration of the acidic sites holds substantially for other transition metal oxides combined with molybdenum trioxide except for Mn_2O_3–MoO_3.

Thus, it is clear that the catalytic activity to form acetone of binary oxides containing molybdenum trioxide depends upon the surface concentration of the acidic sites which are formed by the combination of the transition metal oxides with molybdenum trioxide. These acidic sites probably consist of the surface hydroxyl group of the oxide catalyst. They promote mainly the first step of acetone formation, i.e., the formation of isopropyl alcohol or the isopropoxy group. There is no definite evidence to clarify whether isopropyl alcohol or the isopropoxy group is the more reasonable as the intermediate of the acetone formation. However, we consider that acetone is formed via isopropyl alcohol as expressed by Eqs. (4)–(6) for the following reasons:

1. When the surface hydroxyl group acts as a Brønsted acid, the bond between the oxygen atom in the hydroxyl group and the metal ion attached to the hydroxyl group

TABLE 2

SURFACE CONCENTRATION OF ACIDIC SITES AND CATALYTIC ACTIVITY TO FORM ACETONE FOR VARIOUS TRANSITION METAL OXIDES COMBINED WITH MOLYBDENUM TRIOXIDE[a]

Catalyst[b]	Acidic site (μeq/g-cat)	Catalytic activity[c] $10^3/T_a$ (°K^{-1})	Selectivity at T_a[d] (%)	
			Acetone	IPA
TiO_2–MoO_3	177.0	2.54	30.0	67.5
SnO_2–MoO_3	135.8	2.66	85.0	15.0
Cr_2O_3–MoO_3	89.0	2.21	81.4	1.5
Mn_2O_3–MoO_3	21.0	—[e]	—	—
CuO–MoO_3	9.4	1.80	22.7	Tr
ZnO–MoO_3	0.0	1.17	2.5	0.0
ThO_2–MoO_3	0.0	Very low	—	—

[a] Reaction conditions for propylene oxidation are the same as described in Table 1.

[b] Catalyst composition is X(transition metal):Mo = 9:1 in metal atom ratio.

[c] Reciprocal temperature at which the reaction rate to form acetone and isopropyl alcohol reaches 5×10^{-3} μmole/sec g-cat.

[d] Percentage of reacted propylene which was converted to acetone or isopropyl alcohol. Other main products are acetaldehyde, acetic acid, acrolein, carbon monoxide and carbon dioxide.

[e] Carbon dioxide is the only product formed in the oxidation.

will be ionic and stable. Such an oxygen atom will not be reactive for CH_3CHCH_3 intermediate as expressed by Eqs. (2) and (3).

2. Some amount of isopropyl alcohol was detected in the products over several binary oxide catalysts, especially over TiO_2–MoO_3 (5).

3. Tertiary butyl alcohol was mainly produced from isobutene which has no corresponding ketone (*4*).

The oxidation of olefin to the corresponding saturated ketone is a different reaction from the allylic oxidation (*14*) which has been mainly reported on transition metal oxide catalysts. As mentioned above, the reaction requires both an oxidative and an acidic nature in the catalyst. We expect that further new reactions will be discovered by the combination of two different characteristics of the catalyst.

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