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^{18}O Tracer Studies of Catalytic Oxidations of Olefin over Transition Metal or Metal Oxide Catalysts

I. Oxidation of Propylene over SnO_2–MoO_3 Catalyst

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The route of oxygen incorporation into oxidized products has been studied in the heterogeneous oxidation of propylene by molecular oxygen over stannic oxide combined with molybdenum trioxide in the presence of $[^{18}O]H_2O$ tracer. ^{18}O tracer is incorporated into the acetone produced but is not incorporated into the acrolein produced simultaneously with acetone. Incorporation of ^{18}O tracer into the acetone does not depend on the exchange reaction between molecular oxygen and water or the exchange reaction between acetone and water. These results lead to the conclusion that there are two different active species of oxygen on the catalyst surface, one of which is derived from water and the other from molecular oxygen. Oxidation to acetone depends on the interaction with an active species derived from a water molecule, while oxidation to acrolein depends on a species derived from molecular oxygen. The mechanism of acetone formation seems to involve the surface reaction between a carbonium ion and the active species of water to form an alcoholic intermediate.

INTRODUCTION

It has generally been found in oxidation reactions that the oxygen atom is incorporated into the oxidized product in two different ways. One is the case where the oxygen atom is incorporated from molecular oxygen, and the other is where the atom is incorporated from a water molecule:

$$A + \tfrac{1}{2}O_2 \rightarrow AO, \qquad (1)$$

$$A + \tfrac{1}{2}O_2 + H_2O^* \rightarrow AO^* + H_2O, \qquad (2)$$

where A is the molecule to be oxidized. For example, in biochemical oxidation, Eq. (2) is commonly observed and is catalyzed by oxidase, while it has been proved that the oxidation catalyzed by oxygenase (*1*) or mixed function oxidase (*2*) follows Eq. (1).

In recent years, a number of catalytic oxidations of hydrocarbons have been developed on transition metal oxide catalysts (*3*). The mechanisms of these oxidations have been studied by the tracer technique with regard to the behavior of hydrocarbons (*4–8*). In particular, the adsorbed species of olefins formed on the oxide surface have been studied extensively by tracer techniques (*4–11*), kinetic methods (*12–14*), and spectroscopic methods (*15–17*). Adsorbed species of oxygen have also been studied and O_2^- and O^-, as distinct from O^{2-}, have been identified on several transition metal oxide surfaces (*18–21*). However, little work has been done on the mechanism of oxygen incorporation into the oxidized product. It has generally been considered that atomic species of adsorbed oxygen (such as O^- or O^{2-}) is active for the oxidation and no reaction represented by Eq. (2) has ever been reported in the heterogeneous oxidation over transition metal oxide catalysts.

The present investigation was started in an attempt to discriminate between Eqs. (1) and (2) in the heterogeneous oxidation of olefins. A clear discrimination of the route of oxygen incorporation into the oxidized product will undoubtedly be helpful for the understanding of the mechanism of heterogeneous oxidation and of the role of the active site on the catalyst surface. This paper deals with the oxidation of propylene over SnO_2–MoO_3 catalyst. We chose this reaction for the following reasons. First, it has been reported that saturated ketone is the main product in the oxidation of olefins on SnO_2–MoO_3 (*22–24*). This is quite different from the reaction products reported in the usual heterogeneous oxidation of olefins on transition metal oxide catalysts but identical to those reported in metal ion oxidations in aqueous solution (*25–27*). Thus, this oxidation may be the first example of the reaction represented by Eq. (2) in heterogeneous oxidation of olefins. Second, propylene is the simplest olefin which follows this type of oxidation. The work was carried out using $[^{18}O]H_2O$ tracer.

EXPERIMENTAL

Catalysts. Two types of SnO_2–MoO_3, (A) and (B), were used as the catalysts. The composition of both catalysts Sn/Mo = 9/1, in metal-atom ratio. SnO_2–MoO_3 (A) was prepared by the decomposition of stannous hydroxide mixed with ammonium molybdate solution. The oxide powder was pressed into cylindrical pellets and calcined in air at 550°C for 5 hr. The BET surface area was 45.6 m^2/g. SnO_2–MoO_3 (B) was prepared from ammonium molybdate and stannic oxide obtained by the calcination of stannous hydroxide in air at 800°C for 5 hr. The stannic oxide (24–35 mesh) was impregnated with the ammonium molybdate solution, dried on a water bath, and then calcined in air at 550°C for 5 hr. The BET surface area of the sample was 7.4 m^2/g.

Materials. Water enriched with ^{18}O was obtained from BIO.RAD Laboratories. The water was also enriched with deuterium (3% as atomic fraction). Deuterium was removed by an exchange reaction with H_2 over a platinum–asbestos catalyst at 250°C, until mass spectrometry showed a deuterium concentration in the $[^{18}O]$-enriched water lower than 0.1%.

Procedure. All the oxidation runs were carried out using a flow system at 1 atm pressure. A Pyrex tube reactor 8 mm in diameter was used, with the catalyst temperature controlled by a thermoelectric controller. The gaseous reactants were introduced from cylinders through needle valves. Water was introduced by evaporation in the gaseous reactant stream. The reaction products were cooled by water, separated into gaseous or liquid phase, and analyzed by gas chromatography (GC) and mass spectrometry. The GC columns used were Molecular Sieve 5A for oxygen and carbon monoxide, β,β'-oxidipropionitrile supported on 60–80 mesh Al_2O_3 for carbon dioxide and propylene, polyethylene glycol supported on 60–80 mesh Celite for acetone, acrolein, and acetaldehyde, and dioctyl sebacate with 5% sebacic acid supported on 60–80 mesh Celite for acetic acid, propionic acid, and acrylic acid.

Determination of the ^{18}O content of the reaction products. The ^{18}O content of the oxidized products was determined by mass spectrometry after the separation and purification by GC. The mass spectra obtained at 80 ionization voltages were corrected for natural isotopes, and ionization efficiency for the isomer containing ^{18}O was assumed equal to that containing ^{16}O. The ^{18}O content of the oxidized products was calculated from the peak height ratio in the corrected mass spectra. The peak height ratios adopted for the calculation are h_{45}/h_{43} for acetone, h_{58}/h_{56} for acrolein, h_{31}/h_{29} for acetaldehyde, and h_{46}/h_{44} for carbon dioxide. The ^{18}O content of the issuing water was also determined by mass spectrometry. The values are liable to be somewhat inaccurate because of the difficulty of the mass spectrometry of water.

The ^{18}O content of the unreacted oxygen was determined by mass spectrometry after conversion to carbon dioxide. The unreacted oxygen gas was separated by a Molecular Sieve 5A column and then introduced into a closed circulating reaction system where it was completely converted to carbon dioxide by reaction with the stoichiometric amount of carbon monoxide using Pt–asbestos catalyst at 250°C.

RESULTS

Oxidation to acetone. Propylene was oxidized to acetone in the presence of water vapor enriched with ^{18}O on the SnO_2–MoO_3 (A) catalyst under two different conditions. The oxidation to acetone was quite selective, as reported previously (*22–24*). The ^{18}O contents of acetone, unreacted oxygen, and water are summarized in Table 1. In every run, the ^{18}O contents of the products were determined, rejecting those obtained in the first hour. As can be seen in Table 1, ^{18}O tracer was detected in the acetone produced. It is clear that the oxygen atom from the water molecule is incorporated into the oxidized product. The first four runs in Table 1 were carried out under the same experimental conditions using water of 5.48% ^{18}O content. Although the ^{18}O content of the input water decreases during the course of the reaction, the values of the ^{18}O content for the acetone produced are smaller than those for the output water. The differences seem to be beyond experimental error. The situation is quite similar in Run 8. Thus, in spite of the apparent evidence that the oxygen atoms from the water molecules are incorporated into the acetone produced, the ^{18}O contents of the acetone are slightly lower than those of water in the reaction system.

Two oxygen exchange reactions were examined in connection with the oxygen incorporation. One is the oxygen exchange reaction between molecular oxygen and water:

$$^{16}O_2 + H_2{}^{18}O \rightleftharpoons {}^{16}O^{18}O + H_2{}^{16}O. \qquad (3)$$

The ^{18}O contents of the unreacted oxygen are listed in the last column in Table 1. The oxygen exchange reaction between molecular oxygen and water was scarcely observed at the conditions adopted in the runs. The result rejects a possibility that ^{18}O in the acetone was incorporated from the resulting $^{16}O^{18}O$ molecule from the exchange reaction as expressed in Eq. (3).

Another oxygen exchange reaction between acetone and water,

TABLE 1

^{18}O CONTENT OF REACTION PRODUCTS IN THE OXIDATION OF PROPYLENE TO ACETONE[a]

	^{18}O content (atomic %)			
Run	H_2O (input)	H_2O (output)	CH_3COCH_3	O_2 (output)
1[c]	5.48	4.62	4.11	0.02
2[c]	5.48	4.91	3.68	0.04
3	5.48	4.59	3.93	0.01
4	5.48	4.78	4.55	0.02
5	4.59	—	2.72	tr.
6	4.59	—	2.40	tr.
7	4.59	—	2.79	tr.
8[c]	8.60	8.47	6.73	0.01

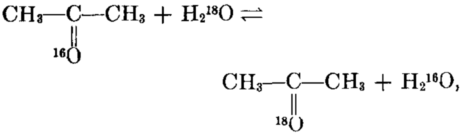
Reaction condition

Run	Temperature (°C)	Catalyst used[b] (g)	Flow rate (ml/min)	C'_3 conversion (%)	Selectivity to acetone (%)
1–7	125	3.6	21.8	4.0	93.7
8	225	2.0	34.3	1.7	68.1

[a] Reactant gas composition: Propylene, 20 vol %; Oxygen, 30%; Water, 30%; Nitrogen, 20%.

[b] SnO_2–MoO_3(A).

[c] Taken from the data in Reference 31, where the values for ^{18}O content of acetone were miscalculated.



$$CH_3\text{—}\underset{^{16}O}{\underset{\|}{C}}\text{—}CH_3 + H_2{}^{18}O \rightleftharpoons CH_3\text{—}\underset{^{18}O}{\underset{\|}{C}}\text{—}CH_3 + H_2{}^{16}O, \quad (4)$$

was also checked using water enriched with ^{18}O. The contact time of acetone and its concentration in the reactant gas were adjusted to be the same as in the oxidation runs (Runs 1–7 in Table 1). The reactant gas composition and other conditions were the same as adopted in the oxidation runs, except that propylene in the reactant gas was replaced by nitrogen. The results are shown in Table 2. Some exchange reaction was observed under these conditions, but the rate was slower than that of the oxidation. The ^{18}O contents observed in the produced acetone are not attributable to the exchange reaction as expressed in Eq. (4). Thus the possibility that the ^{18}O tracer found in the acetone is incorporated by the exchange reaction between water and the acetone which is formed by reaction between propylene and molecular oxygen (or some derivative from molecular oxygen) can be rejected.

Oxidation to acrolein and acetaldehyde as well as to acetone. Propylene is oxidized to acrolein and acetaldehyde as well as to acetone on SnO_2–MoO_3 at higher reaction temperatures (*28*). The product distribution obtained in the oxidation over the low surface area catalyst, SnO_2–MoO_3 (B), is shown in Table 3. This oxidation was also investigated using $H_2{}^{18}O$ in a similar manner. The results are summarized in Table 4.

In the oxidation at higher temperatures, ^{18}O was also incorporated into the produced acetone, but it was difficult to check the exchange reaction between the produced acetone and water at the same conditions because of the rapid oxidation of acetone to smaller fragments. Although an appreciable amount of ^{18}O was incorporated into the produced acetone, the ^{18}O content of acetone was much lower than that of the reactant water. It was about 40% of the value for the water in the reaction system.

In contrast to the oxidation to acetone, hardly any ^{18}O tracer was incorporated into the acrolein produced. A small amount of ^{18}O was found in the acetaldehyde. Since the oxygen exchange reaction between molecular oxygen and water was observed to some extent under the experimental conditions, a part of the ^{18}O found in the acetaldehyde may be incorporated from the $^{16}O^{18}O$ resulting from the exchange reaction. The ^{18}O content of the acetaldehyde is somewhat larger than that of the molecular oxygen in the reaction system. Since acetaldehyde is formed in the the oxidation of acetone as well as in the direct oxidation of propylene at these conditions, some part of the ^{18}O in the acetaldehyde seems to be due to the consecutive oxidation of the acetone produced. In any event, the ^{18}O

TABLE 2
OXYGEN EXCHANGE REACTION BETWEEN ACETONE AND WATER ON THE SnO_2–MoO_3(A) CATALYST[a]

Run	^{18}O content (%)	
	H_2O (input)	CH_3COCH_3
1	4.59	1.29
2	4.59	1.69
3	4.59	1.37
4	4.59	1.62
5	4.59	1.72
6	5.48	2.36
7	5.48	2.65

[a] Reaction temperature: 125°C. Reactant gas composition: Oxygen, 33.7 vol %; Nitrogen, 40.9%; Water, 24.6%; Acetone, 0.87%. Other experimental conditions are the same as described in Table 1.

TABLE 3
PRODUCTS IN THE OXIDATION OF PROPYLENE OVER SnO_2–MoO_3(B) CATALYST[a]

Temperature (°C)	355	370
C'_3 conversion (%)	3.09	3.44
Yield (μmole/min)		
CH_3COCH_3	2.25	1.93
$CH_2{=}CHCHO$	1.10	1.40
$2/3CH_3CHO$	0.45	0.54
$2/3CH_3COOH$	1.32	1.32
$CH_2{=}CHCOOH$	0.67	1.28
$1/3CO$	4.63	4.65
$1/3CO_2$	1.45	2.10

[a] Reactant gas composition is identical with that in Table 1. Flow rate of total reactant gas: 37.6 ml-STP/min. Catalyst: SnO_2–MoO_3(B), 2.0 g.

TABLE 4

^{18}O CONTENT OF THE REACTION PRODUCTS IN THE OXIDATION OF PROPYLENE TO ACETONE, ACROLEIN, AND ACETALDEHYDE[a]

Reaction temperature (°C)	^{18}O content (atomic %)[b]			
	CH_3COCH_3	$CH_2{=}CHCHO$	CH_3CHO	O_2 (output)
365	2.21	0.20	0.43	0.54
366	3.51	0.11	0.43	0.19
367	2.07	0.34	0.48	0.20
370	2.38	0.00	0.45	0.58
366	2.62	0.03	0.47	0.32
average	2.56	0.14	0.45	0.37

[a] Experimental conditions are the same as those described in Table 3.

[b] ^{18}O content of water: Input 6.70%, Output 5.5%.

contents found in the acrolein and acetaldehyde are far lower than those of the water in the reaction system. It can be reasonably concluded that propylene is oxidized to acrolein and acetaldehyde by active species derived from molecular oxygen or by oxygen ions in the bulk oxide as demonstrated by Keulks (*29*) and Wragg *et al.* (*30*) in the oxidation of propylene over MoO_3–Bi_2O_3 catalyst.

DISCUSSION

The labeled oxygen atoms in the water molecules are incorporated into the acetone produced. The incorporation does not depend on the exchange reaction between molecular oxygen and water or between the produced acetone and water at 125°C.* This suggests that there is some active species which is derived from a water molecule. The most reasonable mechanism to form acetone appears to involve the active species of water and may be sketched as shown in Fig. 1 (Mechanism I). However, there is some room for the alternative mechanism (Mechanism II), that acetone is produced by a reaction of propylene (or some derivative from propylene), with the active species derived from molecular oxygen which is in rapid equilibrium with the water on the oxide surface. When the oxygen exchange reaction between gaseous oxygen and adsorbed species is not so rapid, we cannot detect this rapid oxygen equilibration on the catalyst surface. It seems

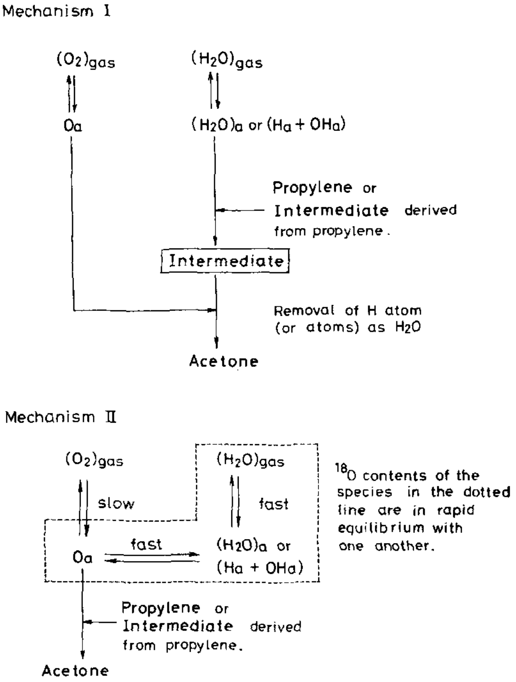


FIG. 1. Possible mechanisms of oxygen incorporation into acetone. The charge of each species is omitted in the figure. Ha, OHa, and Oa do not necessarily mean the adsorbed hydrogen, hydroxyl radical, and oxygen atom. Oa represents the active species derived from molecular oxygen. It includes also the active species via the bulk oxide.

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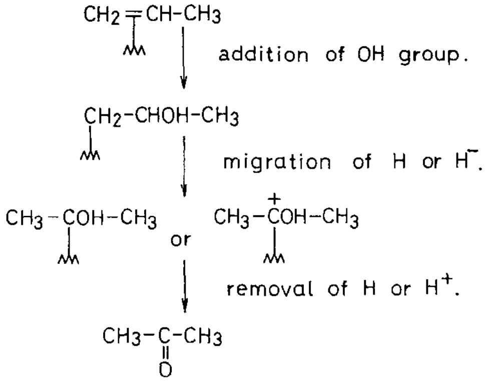
* There remains a possibility that ^{18}O tracer was incorporated into the produced acetone by exchange reaction between some precursor to form acetone and water on the catalyst surface. However, elucidation of this possibility seems to be beyond the ability of the tracer technique.

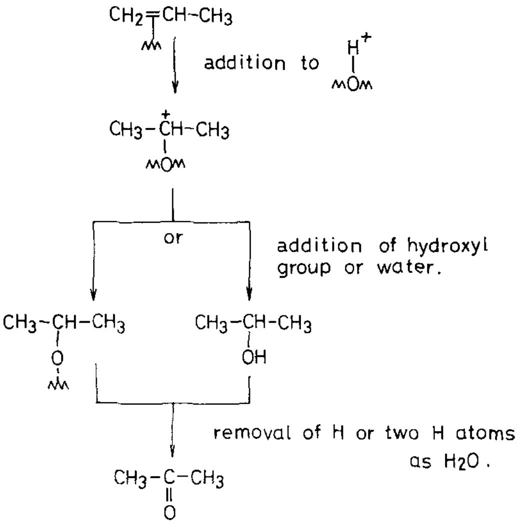
to be difficult to discriminate between Mechanisms I and II directly. However, when the oxidation proceeds according to Mechanism II, ${}^{18}O$ must be incorporated into all of the oxidation products which are formed simultaneously on the catalyst surface. In practice, as shown in Table 4, ${}^{18}O$ tracer was only found in acetone. It was scarcely incorporated at all into the acrolein which was formed simultaneously with acetone on the catalyst surface. Hence, assuming that the oxidation to form acetone obeys the same mechanism irrespective of the reaction temperature, it seems reasonable that the rapid oxygen exchange reaction depicted in Mechanism II does not occur on the catalyst surface. Of course, if the mechanism of acetone formation at 365°C is different from that at the lower reaction temperature and incorporation of ${}^{18}O$ into acetone at 365°C is entirely due to the exchange reaction between the water and the produced acetone, Mechanism II is still valid. In addition, some more complicated interpretations may be possible. One of them is that there exist two different active species derived from molecular oxygen and one of these, which is active for the acetone formation, is in the rapid oxygen exchange reaction with water vapor, whereas the other is not. The results obtained in this work cannot reject these alternative mechanisms. However, these alternatives are based upon too many assumptions. We think, at present, that Mechanism I is the most probable for acetone formation.

Although the incorporation of ${}^{18}O$ into acetone is considered to be due to the direct interaction between the active species of propylene and of water, ${}^{18}O$ contents found in the acetone were somewhat lower than those of water in the reaction system. The difference was prominent especially in the runs at the higher temperatures (Table 4). This indicates that the incorporation of oxygen into the acetone also involves some active species originating from molecular oxygen, as well as from water. One possible explanation may be that the oxidation to form acetone involves a hydroxyl group which is formed by a reaction between atomic oxygen and propylene or some intermediate derived from propylene. When this is the case, this hydroxyl group formed on the catalyst surface may be indistinguishable from the active species of water, and the oxidation to form acetone may be a chain reaction. Unfortunately, the ${}^{18}O$ content of the reactant water used in this work is too low to discriminate such fine details. It must await further investigation using water of higher ${}^{18}O$ content.

The fact that ${}^{18}O$ in the water was incorporated into the acetone produced and that the oxidation to form acetone seems to follow Eq. (2), suggests some possible mechanisms for this oxidation. One is analogous to the mechanism for metal ion oxidation in aqueous solution (*34*). Propylene is oxidized to acetone by Pd^{2+}, Hg^{2+}, and Tl^{3+} in aqueous solution and the mechanisms of these oxidations have been well established (*25–27*, *32*). A π-complex formation between the olefin and the metal ion is followed by insertion of a hydroxyl group into the π-bond to form a σ-complex. This σ-complex decomposes to a carbonyl compound with displacement of a hydrogen atom and reduction of the metal ion.



Another mechanism involves an intermediate such as CH_3CHCH_3, which is probably a carbonium ion (*23*, *33*, *34*). The attack of an OH group or water on this intermediate will form a secondary alcohol which is easily oxidized to a carbonyl compound (*23*). Buiten (*33*) has suggested that the CH_3CHCH_3 species changes into an isopropoxy group bonded to the catalyst surface rather than to isopropyl alcohol and that this isopropoxy group furnishes an oxidation pathway to acetone. When the surface hydroxyl group is in rapid oxygen equilibration with water vapor, incorporation of ^{18}O into the acetone will be also possible according to Buiten's mechanism. Since it is not definite whether the isopropoxy group or isopropyl alcohol is the more reasonable for the intermediate to acetone, the mechanism is depicted as follows:



Further information concerning the mechanism of the oxidation of propylene to acetone may be summarized as follows:

(1) Propylene is oxidized to acetone not only on the SnO_2–MoO_3 catalyst used in this work but also on TiO_2–, Co_3O_4–, Cr_2O_3–, and Fe_2O_3–MoO_3 catalysts. A small amount but about half of the equilibrium concentration of isopropyl alcohol was detected in the oxidation of propylene on the above catalysts (*24*).

(2) Tertiary butyl alcohol is mainly produced in the oxidation of isobutene which has no corresponding ketone (*23*).

(3) Isopropyl alcohol is easily oxidized to acetone on SnO_2–MoO_3 under the conditions adopted in this work (*23*).

(4) 1– or 2–butene is oxidized to methyl ethyl ketone on SnO_2–MoO_3, and reactant *n*-butene is isomerized rapidly during the oxidation reaction (*23*).

(5) A hydrogen exchange reaction between propylene and D_2O was also observed on SnO_2–MoO_3 but the hydrogen atom attached to the central carbon atom in propylene was not concerned in the exchange reaction (*33*).

(6) SnO_2 and MoO_3 are inactive for acetone formation when they are used separately. Metal oxides such as SnO_2 and Co_3O_4 are active only when they are combined with molybdenum trioxide (*23*, *24*, *34*).

(7) Although pure SnO_2 has no acidity, it displays marked acidity as determined by Benesi's method (*35*) when it is combined with molybdenum trioxide.

Although these facts do not rule out the possibility of the mechanism similar to the metal ion oxidation, they seem to be favorable for the mechanism via the carbonium ion and the alcoholic intermediate. The carbonium ion has commonly been reported as the intermediate for the isomerization of olefin on a number of mental oxides (*10*, *11*). If acetone formation follows the mechanism involving the carbonium ion, it is expected that the surface acidity will play an important role in the oxidation. This may be partly revealed in (6) and (7) which have been described above. The quantitative relation between the catalytic activity and the surface acidity will be examined in a subsequent investigation.

Oxygen-18 tracer was not found in the acrolein produced in the oxidation of propylene on the SnO_2–MoO_3 catalyst. It is not clear whether the oxygen atom is incorporated into acrolein from an active species derived directly from molecular oxygen or from an active species coming via bulk oxide. Anyhow, oxygen incorporation into acrolein is quite different from that into acetone. Acrolein is usually formed in the oxidation at reaction temperatures higher than 300°C on metal oxide catalysts (*3*). On the other hand, acetone is mainly produced below 300°C, especially from 100°C to 200°C (*24*). This effect of the reaction temperature on the selectivity of the oxidation may depend on the different modes of oxygen incorporation. Since the two independent oxygen incorporations are competitive, the selectivity of the oxidation is determined by their relative rates. The reactivity of adsorbed species derived from molecular oxygen or from oxygen ions in the catalyst oxide seems to increase monotonically with the reaction temperature. On the other hand, the formation of alcoholic intermediate seems to become unfavorable irrespective of derivation via carbonium ion or not at a higher reaction temperature, as can be seen from the equilibrium constant for isopropyl alcohol formation from propylene and water. This probably explains why oxidation to form acetone is predominant at lower temperatures, while oxidation to form acrolein is mainly observed at higher temperatures.

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