JOURNAL OF CATALYSIS 17, 132–142 (1970)

Catalytic Oxidation of Olefin over Oxide Catalysts Containing Molybdenum

III. Oxidation of Olefin to Ketone over Co_3O_4–MoO_3 and SnO_2–MoO_3 Catalysts

SYOJI TAN, YOSHIHIKO MORO-OKA, AND ATSUMU OZAKI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo, Japan

Received February 11, 1969; revised September 19, 1969

Oxidation of various olefins and some related hydrocarbons over Co_3O_4–MoO_3 and SnO_2–MoO_3 (Co or Sn:Mo = 9:1) are described. Both binary oxides are effective catalysts for the oxidation of olefins to corresponding ketones, while SnO_2–MoO_3 is the better one. Propylene is converted to acetone at 100–160°C with more than 90% selectivity over SnO_2–MoO_3. *n*-Butenes and 1-pentene are oxidized to methyl ethyl ketone and methyl propyl ketone (including diethyl ketone), respectively. However, ethylene is converted exclusively to carbon dioxide. Isobutene, which has no corresponding ketone, is converted to *t*-butyl alcohol and diisobutene over SnO_2–MoO_3 and to α-methyl acrolein over Co_3O_4–MoO_3. On the other hand, primary and secondary alcohols are easily oxidized to corresponding aldehyde and ketone, respectively, over both catalysts. The ketone formation is concluded to proceed via oxydehydrogenation of alcohol or alcoholic intermediate formed by hydration of olefin. The active site seems to involve an acidic point which is formed by the combination of tin or cobalt oxide with molybdenum trioxide.

INTRODUCTION

In the first paper of this series, the authors reported that the binary oxide containing molybdenum and cobalt oxides is an excellent catalyst for the oxidation of propylene to acetone (*1*). The selective formation of acetone was particularly prominent over the catalysts containing 10 to 20% molybdenum on a metal atom basis. Although a number of oxidations of olefins promoted by solid catalysts have been reported, most of them dealt with the allylic oxidation, e.g., propylene, *n*-butenes, and isobutene are oxidized to acrolein and/or acrylic acid, butadiene, or maleic anhydride, and α-methyl acrolein, respectively. The synthetic method for the selective formation of ketone by one-step oxidation of olefin had not been reported except the oxidation using $PdCl_2$–$CuCl_2$ catalyst in aqueous medium (*2*).

A further investigation was made examining the catalytic activity of various transition metal oxides mixed with 10 atomic % molybdenum for the oxidation of propylene to acetone (*3*). It was found that those systems containing SnO_2, Cr_2O_3, NiO, and Fe_2O_3 are also effective for this reaction. The SnO_2–MoO_3 system was most efficient and the selectively to acetone from propylene was above 80% at 130 to 180°C.

On the other hand the same catalyst system, SnO_2–MoO_3, was investigated by Buiten (*4*) for the oxidation of propylene in the presence of steam, whereas the method of catalyst preparation and the reaction temperature were different from those adopted in the work mentioned above. The main product found by Buiten was also different and consisted of acetic acid, acrolein, and acetone. No mechanism for the formation of acetone was given.

It was accordingly decided to investigate the mechanism of acetone formation over these catalysts. Two catalyst systems were selected for this study, one was Co_3O_4–MoO_3 which had been studied since initiation of this work, and the other was SnO_2–MoO_3 which gave the best result for the formation of acetone. The method adopted here is, in principle, chemical characterization of the reaction, which seems to be fruitful as the first step.

The present paper deals with the results obtained in the oxidation of various olefins to corresponding ketones. A possible mechanism of the oxidation of olefin over both catalyst systems is discussed on the basis of the results.

EXPERIMENTAL SECTION

1. Procedure

All the data were obtained by using a flow system described previously. A Pyrex glass reactor of 25-mm i.d. held about 20 g of catalyst. The length of the catalyst bed was about 30 mm. All the experimental runs were carried out under a constant gas hourly space velocity, i.e., 400 ml/ml-cat hr, and at atmospheric pressure. The reactant gas composition used in the oxidation of each reactant were as follows:

	Composition (vol %)			
Reactant	Hydrocarbon or alcohol	Oxygen	Nitrogen	Water
Olefin (except for 1-C_5) or paraffin	20	30	20	30
1-Pentene	3	30	37	30
Alcohol	1–3	30	37–39	30

All the analyses were carried out by gas chromatography. Mass spectrometry was used for the identification of organic products.

2. Catalyst Preparation

SnO_2–MoO_3. Stannous chloride and ammonium molybdate were used as the starting materials. The precipitation obtained by adding aqueous ammonia solution to stannous chloride solution was filtered and washed with water sufficiently. The stannous hydroxide thus obtained was mixed with ammonium molybdate solution to give a tin to molybdenum atomic ratio of Sn-90/Mo-10. The mixture was dried and decomposed to oxide by heating in air at 300°C for 2 hr. The obtained powder of the binary oxide was pressed into cylindrical shape (3 mm in diameter and 4 mm in length) and calcined at 550°C for 5 hr. The surface area measured by nitrogen adsorption was 45.6 m^2/g.

Co_3O_4–MoO_3 and Co_3O_4. Co_3O_4–MoO_3 having a cobalt to molybdenum atomic ratio of Co-90/Mo-10 was used for this experiment. Both Co_3O_4–MoO_3 and pure Co_3O_4 catalysts were obtained from the same batch used in the previous experiment (*1*).

SnO_2. Pure stannic oxide catalyst was obtained by the same procedure as for the SnO_2–MoO_3 catalyst except for the mixing with ammonium molybdate solution. The surface area was 40.6 m^2/g after the calcination in air.

RESULTS

1. Oxidation of Olefins

Propylene. The results obtained by the oxidation of propylene over SnO_2–MoO_3 are shown in Table 1. Acetone was produced with about 90% selectivity at lower conversion and at temperatures below 135°C.

A comparison of these data with those obtained over Co_3O_4–MoO_3 (*1*) shows that a higher activity as well as selectivity to acetone was obtained with SnO_2–MoO_3 at the same conversion. The higher activity is shown by the lower reaction temperature. The product distribution in this work is, in comparison with Buiten's (*4*), remarkable in the high selectivity to acetone. The formation of acetic acid was rather low, and acrolein and acrylic acid were not detected in the oxidation product.

***n*-Butenes.** Methyl ethyl ketone (MEK) was produced by the oxidations of 1-butene, *cis*-2-butene, and *trans*-2-butene over both

TABLE 1
OXIDATION OF PROPYLENE OVER SnO_2–MoO_3 AND Co_3O_4–MoO_3

Catalyst:	SnO_2–MoO_3				Co_3O_4–MoO_3[a]		
Reaction temp (°C):	115	124	135	175	195	210	280
Conversion (%):	2.9	3.9	9.0	22.0	2.0	4.0	18.0
CH_3COCH_3	90.0	90.0	85.3	65.0	80.9	75.3	20.0
$CH_2{=}CHCHO$	—	—	—	—	Trace	1.3	3.0
$CH_2{=}CHCOOH$	—	—	—	—	0.5	0.6	2.0
$\frac{2}{3}CH_3COOH$	Trace	Trace	2.6	2.0	9.9	11.4	6.0
$\frac{1}{3}CO$	—	—	Trace	3.0	—	0.8	9.0
$\frac{1}{3}CO_2$	10.0	10.0	12.1	30.0	8.7	10.6	60.0

[a] Taken from the data in Ref. (*1*).

SnO_2–MoO_3 and Co_3O_4–MoO_3. The results are summarized in Tables 2 and 3.

MEK was the main product in the 1-butene oxidation over both SnO_2–MoO_3 and Co_3O_4–MoO_3. This feature was somewhat different in the case of 2-butenes, particularly over Co_3O_4–MoO_3. That is, the amounts of acetaldehyde and acetic acid were increased, with the total selectivity to C_2 products exceeding that to MEK. Although MEK was the main product from *trans*-2-butene over SnO_2–MoO_3, considerable amounts of acetaldehyde and acetic acid were also formed. The selectivity to ketone from butene was generally lower than that in the propylene oxidation.

Butadiene, which is expected from allylic oxidation of *n*-butenes, was not detected in any case. As shown in the last columns of the Tables 2 and 3, rapid isomerizations of reactant *n*-butenes were observed at higher temperatures. Most of the reaction product obtained at higher temperatures seemed to result from the equilibrium mixture of *n*-butenes.

In summary, the selectivity to ketone from butene was generally lower than that in the propylene oxidation, and was more

TABLE 2
OXIDATION OF 1-BUTENE OVER SnO_2–MoO_3 AND Co_3O_4–MoO_3

Catalyst:	SnO_2–MoO_3				Co_3O_4–MoO_3		
Reaction temp (°C):	135	160	180	210	240	255	274
Conversion (%):[a]	4.8	6.1	8.4	17.5	2.2	3.0	5.2
Oxidation[a]							
$CH_3COC_2H_5$	85.3	60.3	38.7	24.7	60.8	44.3	27.8
$\frac{3}{4}CH_3COCH_3$	Trace	3.9	2.0	1.4	—	—	—
$\frac{3}{4}C_2H_5COOH$	Trace	2.3	2.9	1.5	—	—	—
$\frac{1}{2}CH_3CHO$	2.2	3.9	2.8	2.4	7.2	7.0	6.9
$\frac{1}{2}CH_3COOH$	2.6	5.2	8.7	4.9	7.2	13.6	24.8
$\frac{1}{4}CO$	Trace	3.6	10.6	12.5	—	5.5	8.7
$\frac{1}{4}CO_2$	9.9	20.8	34.3	52.6	24.8	29.6	31.8
Isomerization[b]							
cis-2-C_4H_8	16.4	28.0	31.4	37.0	16.5[c]	20.8[c]	29.2[c]
trans-2-C_4H_8	11.2	26.1	38.0	44.4			

[a] The value exclusive of the isomerization.

[b] The value is the percentage of the feeded 1-butene isomerized into a given product.

[c] Mixture of *cis*- and *trans*-2-C_4H_8.

TABLE 3

OXIDATION OF 2-BUTENES OVER SnO_2–MoO_3 AND Co_3O_4–MoO_3

2-Butene:	*trans*-2-C_4H_8			*cis*-2-C_4H_8		*trans*-2-C_4H_8		
Catalyst:	SnO_2–MoO_3			Co_3O_4–MoO_3		Co_3O_4–MoO_3		
Reaction temp (°C):	130	155	200	266	275	233	255	270
Conversion (%):	4.0	9.2	20.0	5.0	7.0	2.5	4.0	6.7
Oxidation								
$CH_3COC_2H_5$	60.6	58.8	32.8	14.5	12.9	26.7	17.4	14.3
$\frac{3}{4}CH_3COCH_3$	tr	3.1	2.1	—	—	tr	tr	3.0
$\frac{3}{4}C_2H_5COOH$	tr	tr	tr	—	—	—	—	—
$\frac{1}{2}CH_3CHO$	15.2	11.1	7.7	10.4	12.1	16.9	18.3	9.7
$\frac{1}{2}CH_3COOH$	18.0	12.9	6.8	38.0	35.4	18.2	22.3	30.4
$\frac{1}{4}CO$	tr	2.1	9.8	6.5	9.1	6.7	9.7	10.3
$\frac{1}{4}CO_2$	6.2	12.0	40.8	30.6	30.5	31.5	32.3	32.3
Isomerization								
1-C_4H_8	tr	3.6	9.7	9.7	9.6	tr	tr	2.0
cis- or *trans*-2-C_4H_8	tr	18.0	31.9	8.3	8.0	—	—	tr

favorable with 1-butene than with 2-butene. The catalyst SnO_2–MoO_3 gave a better performance over Co_3O_4–MoO_3.

1-Pentene. 1-Pentene was oxidized over SnO_2–MoO_3 at 158 and 185°C with the results shown in Table 4. The main product was methyl propyl ketone (MPK) including some amount of diethyl ketone. The selectivity was fairly high in spite of higher conversion, although this result seems to be due to the low concentration of 1-pentene in the reactant gas. All the products other than MPK were those formed by C–C bond rupture. A rapid isomerization of 1-pentene was also observed in this case.

TABLE 4

OXIDATION OF 1-PENTENE OVER SnO_2–MoO_3

Reaction temp (°C):	158	185
Conversion (%):	8.0	22.0
Oxidation		
$CH_3COC_3H_7$[a]	65.4	52.6
$4/5C_3H_7COOH$	1.0	1.4
$3/5CH_3COCH_3$	Trace	2.2
$3/5C_2H_5COOH$	Trace	2.1
$2/5CH_3CHO$	1.0	1.4
$2/5CH_3COOH$	2.0	3.0
$1/5CO$	2.0	9.9
$1/5CO_2$	25.6	27.4
Isomerization		
2-C_5H_{10}	57.4	70.4

[a] Including diethyl ketone.

Isobutene. Since isobutene has no corresponding ketone, it is expected that some information about the reaction mechanism to form ketone may be obtained from the oxidation of this olefin. The results are shown in Table 5.

Over Co_3O_4–MoO_3, there was no significant effect of reaction temperature on the selectivity. α-Methyl acrolein was obtained at about 50% selectivity. The selectivities to acetone and acetic acid were 11–16% and 5%, respectively, on the carbon atom basis. On the contrary, over SnO_2–MoO_3, the selectivity depended seriously on the reaction temperature. Below 105°C, *tert*-butyl alcohol was selectively obtained. From 136 to 195°C, diisobutene was the main product with small amounts of acetaldehyde, acetic acid, and acetone. Formation of carbon dioxide increased rapidly with increasing temperature and at 240°C, more than 60% of reacted isobutene was converted to carbon dioxide with small amounts of diisobutene, acetone, and α-methyl acrolein.

Butadiene, ethylene and *n*-butane. Butadiene was oxidized at three temperatures over Co_3O_4–MoO_3 (Table 6). The reactivity of butadiene was somewhat lower than

TABLE 5

REACTION OF ISOBUTENE OVER SnO_2–MoO_3 AND Co_3O_4–MoO_3

Catalyst:	SnO_2–MoO_3					Co_3O_4–MoO_3			
Reaction temp (°C):	90	105	136	178	195	232	254	264	280
Conversion (%):	2.7	4.8	7.2	7.5	10.0	1.9	3.8	5.0	8.5
$CH_3C(CH_3)_2OH$	100	82.6	19.3	7.1	Trace	Trace	Trace	—	—
$CH_2{=}C(CH_3)CHO$	—	—	—	—	—	51.6	47.9	49.8	50.5
2DIB[a]	Trace	17.4	71.9	65.4	47.2	—	—	—	—
$\frac{3}{4}CH_3COCH_3$	—	—	2.1	5.8	8.3	15.9	16.2	11.3	11.8
$\frac{1}{2}CH_3CHO$	—	—	3.5	2.6	2.0	—	—	—	—
$\frac{1}{2}CH_3COOH$	—	—	0.7	1.3	1.7	5.7	5.1	5.5	4.6
$\frac{1}{4}CO$	—	—	—	3.7	9.8	5.4	9.3	8.5	8.1
$\frac{1}{4}CO_2$	—	—	2.5	15.0	31.0	21.4	21.5	24.9	25.0

[a] Diisobutene (C_8H_{16}).

monoenes used in this work. Furan was obtained with 10% selectivity accompanied by equal amount of acrolein. This product distribution is similar to that reported by Adams in the oxidation of butadiene over MoO_3–Bi_2O_3 (5). Methyl vinyl ketone, croton aldehyde and diketone which are expected to form from butadiene by an analyogical reaction, were not detected.

TABLE 6

OXIDATION OF BUTADIENE OVER Co_3O_4–MoO_3

Reaction temp (°C):	250	270	290
Conversion (%):	2.0	4.0	8.0
Furan	11.6	10.8	9.3
$3/4CH_2{=}CHCHO$	11.6	13.9	10.7
$1/2CH_3COOH$	19.2	6.9	3.4
$1/4CO$	15.1	20.1	22.8
$1/4CO_2$	37.0	44.8	51.1
Carboxylic acids[a]	5.5	3.5	2.7

[a] Total carboxylic acids exclusive of acetic acid.

Ethylene was oxidized over both catalysts. Although a trace amount of acetaldehyde was detected over SnO_2–MoO_3 at temperatures lower than 140°C, the product was mainly carbon dioxide in all cases.

n-Butane was oxidized very slowly at 205–250°C but violently above 260°C over Co_3O_4–MoO_3. *n*-Butenes which are expected to form in the oxidative dehydrogenation of *n*-butane was not detected at any temperature and at any conversion. The only product was carbon dioxide.

Oxidation of propylene over SnO_2, Co_3O_4, and MoO_3. Some oxidations of propylene were carried out over the component oxides. The results obtained by pure SnO_2 are shown in Table 7. The activity of SnO_2 was much lower than that of SnO_2–MoO_3. Propylene was hardly oxidized below 300°C. Above 300°C, more than 90% of reacted propylene was converted to both carbon monoxide and dioxide.

TABLE 7

OXIDATION OF PROPYLENE OVER PURE SnO_2

Reaction temp (°C):	259	290	315	360	415
Conversion (%):	0.3	3.5	10.4	18.3	33.6
CH_3COCH_3	+[a]	Trace	2.2	1.0	0.6
$CH_2{=}CHCHO$		—	4.7	3.9	1.1
$CH_2{=}CHCOOH$		—	—	—	Trace
$\frac{2}{3}CH_3CHO$		—	Trace	Trace	Trace
$\frac{2}{3}CH_3COOH$		—	0.4	0.2	0.2
$\frac{1}{3}CO$	++[a]	40.8	46.6	37.5	13.0
$\frac{1}{3}CO_2$	++[a]	59.2	46.1	57.4	85.4

[a] The selectivity could not be determined precisely.

TABLE 8

REACTION OF IPA OVER SnO_2–MoO_3 AND Co_3O_4–MoO_3

Reactant gas composition: IPA, 2 vol %; O_2, 30%; N_2, 38%; H_2O, 30%.

Catalyst:	SnO_2–MoO_3							Co_3O_4–MoO_3			
Reaction temp (°C):	95	105	125	135	135	135	155	195	210	237	260
Conversion (%):	2.0	5.7	51.0	86.7	48.0[a]	33.0[b]	91.0	22.0	33.0	46.0	50.0
CH_3COCH_3	>90	52.6	45.1	34.9	29.6	25.4	35.3	99.2	86.6	51.5	27.9
$CH_2{=}CHCH_3$	Trace	47.4	52.7	61.7	65.0	63.6	58.9	Trace	Trace	24.0	25.5
$2(CH_3)_2CHOCH(CH_3)_2$	—	—	Trace	Trace	4.6	9.5	Trace	—	—	—	—
$\frac{2}{3}CH_3COOH$	—	—	Trace	0.3	Trace	Trace	0.4	Trace	2.9	4.9	10.4
$\frac{1}{4}CO_2$	Trace	Trace	2.3	3.1	0.8	1.5	5.4	0.8	10.5	19.6	36.2

[a,b] Reactant gas compositions are IPA, 4 vol %; O_2, 30%; N_2, 30%; H_2O, 30%; and IPA, 9%; O_2, 30%; N_2, 31%; H_2O, 30%, respectively.

The activity of pure MoO_3 was extremely low as reported previously (*1*). It was completely inactive at temperatures below 350°C. The selectivity at 485°C and at 15% conversion was as follows; acrolein, 44.4%; acrylic acid, 1.0%; $\frac{2}{3}$ acetic acid, 6.7%; $\frac{1}{3}$ carbon monoxide, 31.5%; $\frac{1}{3}$ carbon dioxide, 16.4%.

It has been reported that Co_3O_4 is the most active oxide for the oxidation of olefin and produces only carbon dioxide as oxidized product (*1, 6, 7*). Under the reaction condition used in this study, 15% of propylene was converted to carbon dioxide at 220°C. No other products were detected in the effluent gas from the reactor. These results show that the component oxides are completely inactive for the formation of ketone.

2. Oxidation of Alcohols

Alcohol is a possible intermediate to form ketone from olefin. Some alcohols corresponding to the olefins used in this study were oxidized over the both catalysts.

Isopropyl alcohol. The results over both catalysts are summarized in Table 8. Isopropyl alcohol (IPA) was converted to acetone and propylene over SnO_2–MoO_3 at a rate much faster than the oxidation of corresponding olefin. Formation of carbon dioxide was extremely small. The selectivity to ketone decreased with increasing temperature. Diisopropyl ether was formed in addition to acetone and propylene in the case of higher concentration of IPA in the reactant gas.

IPA was also selectivity oxidized to acetone over Co_3O_4–MoO_3 at 195 and 210°C as shown in Table 8. However considerable amounts of carbon dioxide and acetic acid were formed in addition to propylene and acetone at 237 and 260°C. The selectivity to the byproducts remarkably increased with increasing temperature over Co_3O_4–MoO_3 in contrast with SnO_2–MoO_3. This feature resembles that observed in the oxidation of propylene.

***sec*-Butyl alcohol.** *sec*-Butyl alcohol (SBA) was oxidized over both catalysts with the results summarized in Table 9. Over SnO_2–MoO_3 MEK was formed quite selectively at 100°C. The selectivity to ketone dropped rapidly with increasing temperature with concurrent increase of formation of *n*-butene isomers. Selectivities to carbon dioxide, actic acid, and acetaldehyde were at most a few percent.

On the other hand, over Co_3O_4–MoO_3, a large amount of acetic acid was formed in addition to MEK at 200°C. *n*-Butenes were also formed above 215°C. Substantial formation of carbon dioxide was observed particularly at higher temperatures.

***tert*-Butyl alcohol.** The results are given in Table 10. *tert*-Butyl alcohol (TBA) was selectively converted to isobutene over SnO_2–MoO_3. Co_3O_4–MoO_3 was also selective for this dehydration of TBA at 237°C, whereas the oxidation to carbon dioxide exceeded dehydration at higher temperature. No ketone was detected in any case.

Ethyl alcohol. Ethyl alcohol selectively gave acetaldehyde at 195 and 207°C over Co_3O_4–MoO_3 as shown in Table 11. Selectivity to acetaldehyde decreased with con-

TABLE 9
REACTION OF SBA OVER SnO_2–MoO_3 AND Co_3O_4–MoO_3

Catalyst:	SnO_2–MoO_3				Co_3O_4–MoO_3				
Reaction temp (°C):	100	117	130	155	200	215	225	240	265
Conversion (%):	5.6	38.4	58.0	75.0	24.7	45.5	52.7	59.5	67.5
$CH_3COC_2H_5$	>90	41.1	19.3	7.9	43.0	7.9	5.5	Trace	—
C_4H_8	Trace	56.4	75.9	78.8	5.0	43.6	47.7	51.2	40.1
$\frac{3}{4}C_2H_5COOH$	—	—	Trace	Trace	—	—	—	—	—
$\frac{1}{2}CH_3CHO$	—	—	Trace	1.6	7.5	5.1	5.1	2.5	Trace
$\frac{1}{2}CH_3COOH$	Trace	Trace	1.0	5.0	37.3	31.2	26.0	27.9	25.0
$\frac{1}{4}CO_2$	Trace	3.5	3.8	6.7	7.2	11.2	15.7	18.4	34.9

TABLE 10
REACTION OF TBA OVER SnO_2–MoO_3 AND Co_3O_4–MoO_3

Catalyst:	SnO_2–MoO_3				Co_3O_4–MoO_3			
Reaction temp (°C):	100	120	135	160	237	250	275	290
Conversion (%):	75.0	76.8	77.0	78.0	54.0	56.0	61.0	70.0
$CH_2{=}C(CH_3)_2$	100	96.9	96.4	89.9	87.4	77.1	44.3	16.8
2DIB	—	1.4	1.4	Trace	—	—	—	—
$\frac{3}{4}CH_3COCH_3$	—	—	—	2.9	—	—	—	—
$\frac{1}{2}CH_3COOH$	—	—	—	0.2	2.0	5.5	5.9	4.6
$\frac{1}{4}CO_2$	—	—	Trace	7.0	9.0	14.6	45.0	77.0
$\frac{1}{4}CO$	—	—	—	—	1.6	2.8	4.8	1.6

current increases of acetic acid and carbon dioxide at higher temperature. Ethylene was not detected in any case. The product distribution was quite different from that in ethylene oxidation mentioned before.

DISCUSSION

1. Reaction Path of the Ketone Formation

Tables 1 to 4 show that the two catalysts used in this study are effective for the selective formation of ketone from olefin. SnO_2–MoO_3 is the better system, both in the selectivity and the activity, the latter being shown by lower reaction temperature.

Three mechanisms were suggested for the acetone formation from propylene in Part I (*1*). Mechanism 1 assumes an anionic intermediate formed by nucleophilic attack of oxygen anion (O^- or O^{2-}). Mechanism 2 assumes an alcoholic intermediate formed by hydration of carbonium ion. Mechanism 3 assumes a σ-complex of alcoholic intermediate formed by nucleophilic attack of hydroxyl anion as accepted for oxypalladation of olefin in aqueous medium (*8, 9*).

TABLE 11
OXIDATION OF ETHYL ALCOHOL OVER Co_3O_4–MoO_3[a]

Reaction temp (°C):	195	207	240	260
Conversion (%):	8.8	17.3	31.0	40.0
CH_3CHO	86.5	80.6	47.0	28.3
CH_3COOH	Trace	5.9	24.9	26.4
$1/2CO_2$	13.5	13.5	28.1	45.3

[a] No ethylene was detected at any condition.

Mechanism 2 seems to be most favorable for the formation of ketone on the basis of following results:

1. Tertiary butyl alcohol was produced from isobutene which has no corresponding ketone. This means the catalysts have an ability to hydrate olefin.

2. No carbonyl compound was formed from ethylene which is known to be hard to hydrate. This result is reasonable with mechanism 2, while hardly explained by the nucleophilic addition to olefin (*10*).

3. Secondary alcohol was readily oxidized to the corresponding ketone under the same reaction condition as in the olefin oxidation. This means the alcoholic intermediate assumed in mechanism 2 can be converted to ketone.

4. Dehydration to form the corresponding olefin also took place in the oxidation of alcohol. This again shows that the catalysts are able to promote the hydration of olefin.

The results 2 and 3 also indicate that the oxidation of alcoholic intermediate is not rate-determining in mechanism 2. The slow step seems to be the hydration of olefin. In agreement with this view, no alcohol was detected in the effluent gas of the olefin oxidation except the oxidation of isobutene which can not be oxidized to the ketone.

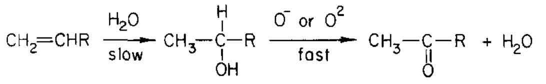
Since molecular hydrogen was not detected in the product gases obtained by the reactions of olefin and alcohol, it is obvious that the formation of ketone from alcohol occurred by oxydehydrogenation. Acetone was also produced from IPA in the absence of oxygen over the both catalysts. How

TABLE 12

Selectivities to Lower Carboxylic Acids and Aldehyde in the Oxidation of *n*-Olefin over SnO_2–MoO_3

n-Olefin	Temp (°C)	Conversion (%)	Selectivity			
			C_3H_7COOH	C_2H_5COOH	CH_3COOH	CH_3CHO
$CH_2{=}CH_2$	170	8.0	—	—	—	—
$CH_2{=}CHCH_3$	135	9.0	—	—	2.6	Trace
$CH_2{=}CHCH_2CH_3$	180	8.4	—	2.9	8.7	2.8
$CH_3CH{=}CHCH_3$	155	9.2	—	—	12.9	11.1
$CH_2{=}CHCH_2CH_2CH_3$	158	8.0	1.0	Trace	2.0	1.0

ever, the reaction rate of alcohol to ketone was much slower than that in the presence of oxygen. This demonstrates that O^- or O^{2-} takes part in the ketone formation. Thus the reaction path for the formation of ketone can be described as Eq. 1.

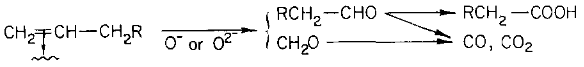


$$CH_2{=}CHR \xrightarrow[\text{slow}]{H_2O} CH_3-\underset{OH}{\overset{H}{C}}-R \xrightarrow[\text{fast}]{O^- \text{ or } O^2} CH_3-\underset{\overset{\|}{O}}{C}-R + H_2O \quad (1)$$

2. Mechanism for the Side Reaction

There were some other reaction products such as carbon oxides, aldehydes, and carboxylic acids which must be formed by the side reaction to cause the fission of the carbon–carbon bond of the reactant olefins. As shown in the results, these side reactions were increased with the reaction temperature. The lower aldehydes and acids obtained by the side reaction of each olefin over the SnO_2–MoO_3 catalysts are summarized in Table 12. It should be noted in Table 12 that the carboxylic acid of a carbon chain shorter than the reactant olefin by one carbon atom was obtained in the oxidation of α-olefin, whereas C_3-carboxylic acid was not detected in the product and instead, substantial amounts of acetaldehyde and acetic acid were formed in the oxidation of 2-butene. A fairly high yield of acetic acid from 1-butene seems to be formed after isomerization to 2-butenes. Similar results were obtained over Co_3O_4–MoO_3.

These results suggest that the side reactions producing lower acids and aldehydes were caused by the decomposition of olefins at the double bond. The adsorbed state of olefin on oxide may be conceived as a π complex with some electron donated to oxide surface as shown for nickel oxide (*11, 12*) and cobalt oxide (*13*). The π-adsorbed olefin would react with active oxygen on the catalyst surface to break the double bond, one fragment possessing one carbon atom being immediately oxidized to carbon oxides, and another fragment possessing longer carbon chain being oxidized to acid or aldehyde as expressed by Eq. (2).



$$CH_2{=}CH-CH_2R \xrightarrow[O^- \text{ or } O^{2-}]{} \begin{cases} RCH_2-CHO \rightleftarrows RCH_2-COOH \\ CH_2O \longrightarrow CO,\ CO_2 \end{cases} \quad (2)$$

According to the same mechanism acrolein would be formed by the oxidation of butadiene. In fact, this was the case shown in Table 6. It has been shown for the adsorption of olefin over oxide that β-olefin is adsorbed more strongly than corresponding α-olefin (*11–13*). Furthermore, when the double bond is attacked by the electrophilic reagent, the reaction rate of β-olefin is admittedly higher than that of α-olefin (*14*). In this connection, it seems reasonable that the side reaction to form lower aldehyde and acid was much more pronounced in the oxidation of 2-butenes than 1-butene over both catalysts as shown in Tables 2 and 3.

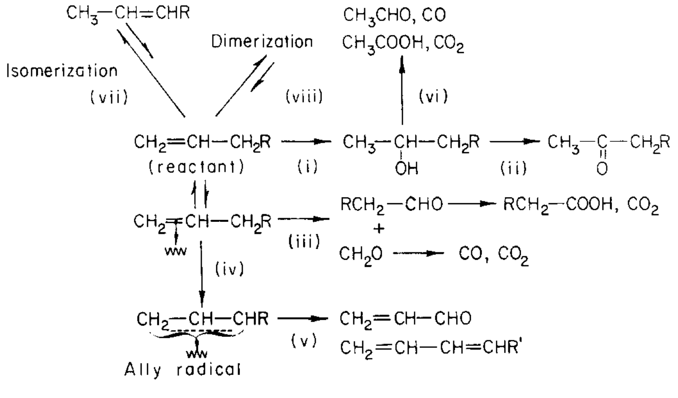
Isobutene was oxidized to α-methyl acrolein with about 50% selectivity over Co_3O_4–MoO_3. This reaction is well known over MoO_3–Bi_2O_3 and has been reported to proceed via an allylic intermediate formed by the abstraction of a hydrogen atom of α-position to the double bond (*15–19*). Since propylene is also oxidized to acrolein at higher temperature over Co_3O_4–MoO_3, it seems that some allylic oxidation occurs as a side reaction. On the other hand, any reaction product corresponding to the allylic oxidation was not observed in the oxidation of olefin over SnO_2–MoO_3.

The reaction rate of paraffin was quite low on both catalysts. This suggests that decomposition in the alkyl part of olefin far from the double bond occurs with difficulty under the reaction condition. The above discussion is summarized in the reaction scheme shown in Scheme I.

In Scheme I, the selectivity of the reaction is determined by the rate of ketone formation relative to that of direct oxidations of olefin (iii and iv). The former is, as described above, seemingly controlled by the hydration step at lower temperature, but it is expected at higher temperature that the hydration step reaches an equilibrium, because it is unfavorable for alcohol at higher temperature. If this is the case, the rate-determining step would be shifted to the step of alcohol oxidation. This circumstance seems to be demonstrated in the results of alcohol oxidation (Tables 8 and 9). The selectivity to ketone, relative to olefin from alcohol, decreases with increase in the reaction temperature. In this case, the heat effect for the rate of ketone formation is reduced by the heat of hydration. On the other hand, the rate of direct oxidation of olefin usually exhibits a higher heat effect over various oxide catalysts. Accordingly, the apparent heat effect for the ketone formation from olefin would be lower than that for the direct oxidation of olefin. It seems that the higher selectivity to ketone at lower temperature and the higher selectivity over SnO_2–MoO_3 than over Co_3O_4–MoO_3 are reasonably explained on the basis of the above discussion.

The above view also explains the difference in the product distributions between Buiten (*4*) and present authors. In Buiten's work, runs over SnO_2–MoO_3 were made at temperatures higher than 272°C, which is about 150°C higher than the present case. It seems obvious that this difference in the reaction temperature brought about the difference in product distribution, i.e., selective formation of ketone in the present case and formation of acetic acid accompanied with acetone and acrolein in Buiten's work.

As shown in Tables 8 and 9, the formation of carbon dioxide was usually low in the oxidation of alcohol over SnO_2–MoO_3. This means direct oxidation of alcohol to carbon dioxide and secondary oxidation of the produced ketone are low in this catalyst. On the other hand, considerable amounts of decomposed products were obtained in the oxidation of alcohols over Co_3O_4–MoO_3. This is another reason why



Scheme I

the selectivity to ketone was lower over Co_3O_4–MoO_3 than over SnO_2–MoO_3.

3. Active Site Effective for the Ketone Formation

As reported previously (*1*), olefin was not oxidized over MoO_3 at the temperatures below 400°C. Pure SnO_2 was also inactive for the oxidation of olefin at the temperature below 300°C. Above 300°C, most of the reacted propylene was converted to carbon oxides as shown in Table 7. On the other hand, pure Co_3O_4 was remarkably active for the oxidation of olefin. It was more active than any binary oxides between MoO_3 and Co_3O_4 (*20*), whereas, the product was only carbon dioxide. These results over the pure component oxides showed that the modifications of SnO_2 and Co_3O_4 by a small amount of MoO_3 are quite remarkable. The formation of carbon dioxide over Co_3O_4 was markedly suppressed by the addition of 10% MoO_3. In the case of SnO_2, both activity and selectivity were increased remarkably. These facts suggest that the nature of active sites formed on the surface of binary oxides are quite different from those of pure oxides.

As shown in Tables 2 to 4, both SnO_2–MoO_3 and Co_3O_4–MoO_3 are effective for the isomerization of olefins under the conditions adopted in this study. Furthermore, dimerization of isobutene occurred over SnO_2–MoO_3 (Table 5). These reactions, in addition to hydration of olefin, are common reactions observed on solid acid catalysts. In this connection, the activity of SnO_2–MoO_3 and Co_3O_4–MoO_3 for the formation of ketone seems to result from the acidic site which is formed by combination of two different oxides. Since the slow step of the ketone formation is considered to be the hydration of olefin, the different activity of catalysts would be attributable to the acidity of the catalysts.

It is well known that silica–alumina possesses acidic sites formed by the combination of two oxides. The situation looks similar in both cases, although the origin of the acidity in the present case should be investigated further.

REFERENCES

1. Moro-oka, Y., Tan, S., and Ozaki, A., *J. Catal.* **12**, 291 (1968).

2. Smidt, J., Hafner, W., Jira, R., Sedlmeier, J., Sieber, R., Ruttinger, R., and Kojer, H., *Angew. Chem.* **71**, 176 (1959); Smidt, J., Hafner, W., Jira, R., Sieber, R., Sedlmeier, J., and Sabel, A., *Angew. Chem.* **74**, 93 (1962).

3. Moro-oka, Y., Takita, Y., Tan, S., and Ozaki, A., *Bull. Chem. Soc. Jap.* **41**, 2820 (1968).

4. Buiten, J., *J. Catal.* **10**, 188 (1968).

5. Adams, C. R., Voge, H. H., Morgan, C. Z., and Armstrong, W. E., *J. Catal.* **3**, 379 (1964).

6. Moro-oka, Y., and Ozaki, A., *J. Catal.* **5**, 116 (1966).

7. Moro-oka, Y., Morikawa, Y., and Ozaki, A., *J. Catal.* **7**, 23 (1967).

8. Jira, R., Sedlmeier, J., and Smidt, J., *Justus Liebigs Ann. Chem.* **693**, 99 (1966).

9. Henry, P. M., *J. Amer. Chem. Soc.* **86**, 3246 (1964).

10. Henry, P. M., *J. Amer. Chem. Soc.* **88**, 1595 (1966).

11. Moro-oka, Y., and Ozaki, A., *J. Amer. Chem. Soc.* **89**, 5124 (1967).

12. Moro-oka, Y., and Ozaki, A., *Proc. Int. Congr. Catal. 4th, Moscow, 1968.* Symp. 1.

13. Moro-oka, Y., Otsuka, M., and Ozaki, A., to be published.

14. Sato, S., and Cvetanovic, R. J., *J. Amer. Chem. Soc.* **81**, 3223 (1959).

15. Voge, H. H., Wagner, C. D., and Stevenson, K. P., *J. Catal.* **2**, 58 (1963).

16. Adams, C. R., and Jennings, T. J., *J. Catal.* **2**,, 63 (1963).

17. Sachtler, W. M. H., *Rec. Trav. Chim. Pays-Bas* **82**, 243 (1963).

18. McCain, C. C., Gough, G., and Godin, G. W., *Nature (London)* **198**, 989 (1963).

19. Sixma, F. L. J., Duynstee, E. F. J., and Hennekens, J. L. J. P., *Rec. Trav. Chim. Pays-Bas* **82**, 243 (1963).

20. Moro-oka, Y., Tan, S., and Ozaki, A., *J. Catal.* **17**, 125 (1970).