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Catalytic Oxidation of Olefin over Oxide Catalysts Containing Molybdenum

I. Product Distribution in Propylene Oxidation over the Cobalt-Molybdenum System

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The oxidation of propylene has been investigated over a series of binary oxide catalysts of cobalt and molybdenum in the presence of water vapor. The catalytic activity of binary oxide increased with the ratio of cobalt to molybdenum. The major products were acetone, acrolein, and acrylic acid, whereas the selectivities to these products depended remarkably on the catalyst composition.

A selective formation of acetone was found with the cobalt-rich catalyst. Addition of only 10% of molybdenum oxide to cobalt oxide caused a remarkable suppression of the formation of carbon dioxide. On the molybdenum-rich catalyst allylic oxidation was predominant. As far as the allylic oxidation is concerned the variation of the product distribution with increase in the concentration of cobalt seems to correspond with the variation in the catalytic activity.

INTRODUCTION

In the recent study of catalytic oxidation reactions of hydrocarbons, the oxidation of propylene with molecular oxygen has been studied extensively by many workers. A number of catalysts which allow the formation of partially oxygenated products have been discovered; most of them contain molybdenum oxide as one of the components. These catalyst systems are usually composed of binary or ternary complex oxides of molybdenum with some other transition metal such as bismuth (*1*), cobalt, iron, tin, vanadium, etc. (*2*). On the other hand, it is well known that the complex oxides containing molybdenum are also active for the oxidation of methanol to formaldehyde, of benzene to maleic anhydride, and of naphthalene and *o*-xylene to phthalic anhydride.

The kinetics and mechanism of the oxidation of propylene to form acrolein are well understood (*3–11*). The π-allyl mechanism has been completely established by means of a method using isotopes (*5–10*). This mechanism was obtained with the well-known catalyst system, MoO_3-Bi_2O_3. The effect of catalyst composition on the selectivity of the oxidation on this catalyst system was also studied (*12*). However, little work has been reported on the catalytic actions of other systems containing molybdenum oxide, though the oxidation products obtained by these catalyst systems depend remarkably on the element combined with molybdenum oxide (*2*).

In this series of study, it has been attempted to investigate the catalytic properties of binary oxides of molybdenum–transition metal systems. This paper which is concerned with the oxidation of propylene by the binary oxides of cobalt and molybdenum, is the first report of this series, and deals with the effect of catalyst composition on the product distribution. This catalyst system has been claimed to be an efficient catalyst for the production of acrylic acid from propylene (*13*) and is known as a dehydrosulfurization catalyst.

EXPERIMENTAL SECTION

Preparation of the catalyst. Eleven mixtures were made (pure MoO_3 and Co_3O_4 included) varying molybdenum concentration with 10 atom % difference each. Aqueous solutions of ammonium molybdate and cobalt nitrate were used as starting materials. They were mixed at pH about 5. This was followed by evaporation of water and by decomposition of the deposit at 400°C. The obtained powder of the oxides was pressed to cylindrical pellets (3 mm in diameter and 4 mm in length) that were calcined at 550°C for 5 hr.

Procedure. All data were obtained using a flow system at atmospheric pressure. About 20 g of catalyst was placed in a Pyrex glass tube (25 mm ID) mounted vertically. The height of the catalyst bed was about 30 mm.

The gaseous reactants were fed from cylinders through needle valves. Steam was fed by evaporating water in the stream of the gaseous reactants. The reactant gas composition was fixed as follows: propylene, 20 vol %; oxygen, 30 vol %; steam, 30 vol %; nitrogen, 20 vol %. The exit gases from the reactor were cooled by a water-cooled condenser to separate water and liquid products from gases and vapors.

Analysis. All the analyses were performed by gas chromatography. Columns used for the analyses of the exit gas were as follows: for propylene and carbon dioxide, β,β'-oxidipropionitrile supported on Al_2O_3 (60–80 mesh); for oxygen and carbon monoxide, molecular sieve 13X; for acetaldehyde, acrolein, propionaldehyde, and acetone, polyethylene glycol 1500 supported on Al_2O_3 (60–80 mesh). The liquid products were analyzed by gas chromatography with a flame-ionization detector using a dioctyl sebacate column supported on Al_2O_3. In all runs, the total amount of products detected by gas chromatography reached to more than 95% and usually 98–99% of converted propylene.

RESULTS

1. Effect of Catalyst Composition on the Reaction Products

The products obtained by oxidation of propylene on the catalyst system of cobalt and molybdenum binary oxide are summarized in Table 1. All values were determined under a constant gas hourly space velocity (400 GHSV) and at a constant composition of the reactant gas (20 vol % propylene, 30% oxygen, 30% steam, and 20% nitrogen). In most cases the selectivity values were obtained at 15% conversion of propylene, while those given by the catalysts of higher concentration of cobalt (Co/Mo, g/1–7/3) were obtained at somewhat lower conversion because it was difficult to control the conversion level at 15% due to the high activity of the catalyst.

As can be seen in Table 1, major products other than carbon oxides were acrolein, acrylic acid, and acetone. However, selectivities to these products remarkably depended on the ratio of cobalt and molybdenum in the binary oxide catalysts.

Up to 20 atom % Co the main product was acrolein, as is known for pure MoO_3. Small amounts of acetic acid and acrylic acid were also obtained. The yields of carbon monoxide and carbon dioxide were nearly equal.

From 30 to 50 atom % Co, acrolein and acrylic acid were the main products accompanying some acetic acid. Carbon monoxide decreased and carbon dioxide increased with increase in the concentration of cobalt.

From 70 to 90 atom % Co, acetone was formed with high selectivity. The yields of acrolein and acrylic acid were negligible. Cobalt oxide gave only carbon dioxide at any temperature and at any GHSV. The drastic modification of the selectivity of cobalt oxide by addition of a small amount of molybdenum oxide is to be noted.

2. Effects of Temperature and GHSV on the Selectivity of the Reaction over Co-90/Mo-10 Catalyst

As described above acetone was the main product of the oxidation of propylene over

TABLE 1

DEPENDENCY OF THE SELECTIVITY OF PROPYLENE OXIDATION ON THE CATALYST COMPOSITION[a]

Catalyst comp. Co/Mo	Reaction temp. (°C)	Conversion (%)	Selectivity (%)[b]						
			CH_3COCH_3	$CH_2=CHCHO$	$CH_2=CHCOOH$	$\frac{2}{3}CH_3COOH$	$\frac{1}{3}CO$	$\frac{1}{3}CO_2$	Others (trace)
10/0	180–220°	1.0–13.7	—	—	—	—	—	100.0	
9/1	210°	4.0	75.3	1.3	0.6	11.4	0.8	10.6	AA[c]
8/2	260°	6.5	44.6	tr.	tr.	16.4	6.3	32.7	AA
7/3	280°	7.0	42.6	6.0	tr.	14.0	4.4	30.1	AA
6/4	370°	13.0	7.5	10.8	3.8	10.1	10.8	58.2	AA
5/5	370°	15.5	2.5	19.8	6.2	3.4	20.0	46.4	AA, PA[d]
4/6	387°	15.8	1.2	20.1	15.7	7.5	17.7	37.8	AA, PA
3/7	390°	14.8	tr.	30.6	14.5	9.6	18.6	25.4	AA, PA
2/8	430°	14.1	—	40.4	2.5	7.1	22.7	27.3	AA, PA
1/9	477°	16.0	—	37.5	2.0	5.0	28.0	27.5	AA, PA
0/10	485°	13.0	—	44.4	1.0	6.7	31.5	16.4	AA

[a] Catalyst 18 g, GHSV 400. Reactant gas composition: C_3H_6, 20 vol %, O_2, 30%, H_2O, 30%, N_2, 20%.

[b] The selectivity is defined as the percentage of the reacted propylene converted to a given product.

[c] Acetaldehyde.

[d] Propionic acid.

TABLE 2

EFFECT OF THE REACTION TEMPERATURE ON THE SELECTIVITY OF PROPYLENE OXIDATION OVER Co-90/Mo-10 CATALYST[a]

Reaction temp. (°C):	175°	195°	210°	280°
Conversion (%):	1.0	2.0	4.0	18.0
CH_3COCH_3	79.8	80.9	75.3	20.0
$CH_2{=}CHCHO$	Trace	Trace	1.3	3.0
$CH_2{=}CHCOOH$	0.8	0.5	0.6	2.0
$\frac{2}{3}CH_3COOH$	11.8	9.9	11.4	6.0
$\frac{1}{3}CO$	—	—	0.8	9.0
$\frac{1}{3}CO_2$	7.6	8.7	10.6	60.0

[a] Catalyst 18 g, GHSV 400.

the catalysts rich in cobalt. To obtain further information of this reaction, the effects of the reaction temperature and GHSV were examined with Co-90/Mo-10 catalyst in the range of lower conversion of propylene.

The results obtained by changing reaction temperature are shown in Table 2. Up to 210°C the reaction temperature had virtually no effect on the selectivity of the reaction. The selectivity to acetone exceeded 75% of converted propylene. The byproducts were acetic acid (about 10%), and traces of acrolein, acetaldehyde, and acrylic acid. The formation of carbon dioxide was less than 10%. On the other hand, at 280°C, the formation of acetone was only 20% of converted propylene. Most of the reacted propylene was converted to carbon dioxide.

The reaction was also carried out at varying GHSV and at a constant temperature (200°C). The results are summarized in Table 3. The selectivity to acetone decreased slightly and that to carbon dioxide increased gradually when GHSV was changed from 2400 to 400. It seems that the effect of contact time is not so serious and a further oxidation of acetone is relatively slow at this temperature.

TABLE 3

EFFECT OF THE CONTACT TIME ON THE SELECTIVITY OF PROPYLENE OXIDATION OVER Co-90/Mo-10 CATALYST[a]

GHSV:	2400	1300	600	400
Contact time (sec):	1.5	2.8	6.0	9.0
Conversion (%):	1.4	2.1	4.0	5.8
CH_3COCH_3	80.9	78.1	76.4	74.0
$CH_2{=}CHCHO$	Trace	Trace	Trace	Trace
$CH_2{=}CHCOOH$	0.3	0.5	0.4	0.4
$\frac{2}{3}CH_3COOH$	12.5	16.3	12.9	11.9
$\frac{1}{3}CO$	—	Trace	0.3	1.1
$\frac{1}{3}CO_2$	6.3	5.1	10.0	12.6

[a] Catalyst 18 g, temperature 200°C.

3. Effects of Temperature and GHSV on the Reaction over Co-40/Mo-60 Catalyst

The Co-40/Mo-60 catalyst was typical in converting propylene to both acrolein and acrylic acid. The effects of the reaction temperature and GHSV on the product distribution were also examined on this catalyst at lower conversion.

The effect of the reaction temperature is summarized in Table 4. At the lowest temperature (302°C), acrolein was the main product while a substantial amount of the reacted propylene was converted to acetone, acrylic acid, and acetic acid. Formations of carbon monoxide and carbon dioxide were both less than 10% of the reacted propylene. The increase of the temperature caused a decrease in the selectivity to acetone and also to acrolein, the formation of the former being negligible at higher temperature, with concurrent increases in both carbon monoxide and dioxide. The selectivity to acrylic acid reached a maximum at intermediate temperature.

The effect of contact time was examined by varying GHSV at 401°C and the results are summarized in Table 5. The selectivity to acrolein decreased and those to carbon oxides increased with contact time. The selectivities to acrylic acid and acetic acid were not seriously affected by contact time, while a slight increase in the former was

TABLE 4

EFFECT OF THE REACTION TEMPERATURE ON THE SELECTIVITY OF PROPYLENE OXIDATION OVER Co-40/Mo-60 CATALYST[a]

Reaction temp. (°C):	302	330	357	387
Conversion (%):	3.0	5.5	10.0	15.8
CH_3COCH_3	17.6	9.0	2.5	1.2
$CH_2{=}CHCHO$	37.0	32.5	25.4	20.1
$CH_2{=}CHCOOH$	13.5	21.7	24.5	15.7
$\frac{2}{3}CH_3COOH$	14.2	16.5	15.9	7.5
$\frac{1}{3}CO$	8.1	6.3	9.5	17.7
$\frac{1}{3}CO_2$	9.6	14.0	22.2	37.8

[a] Catalyst 18 g, GHSV 400.

TABLE 5

Effect of the Contact Time on the Selectivity of Propylene Oxidation over Co-40/Mo-60 Catalyst[a]

GHSV:	2000	1300	1000	840	510	350
Contact time (sec):	1.8	2.8	3.6	4.3	7.1	10.2
Conversion (%):	3.3	5.7	7.5	10.5	15.0	18.5
CH_3COCH_3	5.7	4.9	3.9	1.8	1.5	1.0
$CH_2{=}CHCHO$	33.1	31.0	28.8	25.1	18.0	16.2
$CH_2{=}CHCOOH$	23.0	26.2	27.3	25.4	22.0	20.1
$\frac{2}{3}CH_3COOH$	11.3	11.0	9.9	9.2	9.2	8.0
$\frac{1}{3}CO$	9.4	10.1	11.2	13.9	19.1	16.4
$\frac{1}{3}CO_2$	17.5	16.8	18.9	24.6	30.2	38.3

[a] Catalyst 18 g, temperature 401°C.

detectable at intermediate contact time. After all, the increase in contact time was in effect similar to that in temperature.

4. The Reaction over Co-60/Mo-40 Catalyst

The effect of the reaction temperature on the selectivity of the oxidation was also examined with the Co-60/Mo-40 catalyst. The results are shown in Table 6.

The distribution of the products obtained at relatively low temperatures was quite similar to that obtained with the Co-90/Mo-10 catalyst. Acetone was the main product and the formations of acrolein and acrylic acid were negligible. On the other hand, at higher temperatures, the reacted propylene was mostly converted to carbon dioxide, with about 10% each of acrolein and acetic acid and small amounts of acrylic acid and acetone. However, the selectivities to acrolein and acrylic acid were much lower than those obtained with the Co-40/Mo-60 catalyst. The increase in GHSV from 400 to 1250 at 345°C caused a decrease in the conversion from 10.8% to 3.9% but virtually no substantial change in the product distribution. It seems that the reaction mechanism at low temperatures is different from the mechanism at high temperatures

Discussion

Cobalt oxide has been known to be the most active catalyst among the transition metal oxides for the oxidation of hydrocarbons and to give only carbon dioxide as the reaction product (*14–16*). On the other hand molybdenum oxide is far less active than cobalt oxide, as can be seen from Table 1, whereas it gives acrolein as the main oxidation product. The activity of the binary oxide catalyst of these two oxides increases with the concentration of cobalt in the catalyst (Table 1, column 2). The major oxygenated products other than carbon oxides are acrolein, acrylic acid, and acetone, whereas the distribution of these products depends remarkably on the ratio of cobalt to molybdenum.

A selective formation of acetone was

TABLE 6

Effect of the Reaction Temperature on the Selectivity of the Propylene Oxidation over Co-60/Mo-40 Catalyst[a]

Reaction temp. (°C):	270°	285°	300°	315°	333°	345°		360°	370°
Conversion (%):	2.9	3.6	4.1	5.8	7.9	10.8	3.9[b]	13.0	17.5
CH_3COCH_3	72.3	63.8	46.0	29.8	21.2	12.6	14.4	7.5	4.2
$CH_2{=}CHCHO$	—	2.0	6.2	11.3	10.8	11.3	12.9	10.0	8.1
$CH_2{=}CHCOOH$	—	tr.	2.5	2.8	3.7	3.7	2.0	3.8	2.8
$\frac{2}{3}CH_3COOH$	10.5	13.5	15.8	19.2	17.0	15.5	9.7	10.1	7.1
$\frac{1}{3}CO$	1.7	2.4	4.1	5.9	8.4	8.7	13.0	10.4	9.7
$\frac{1}{3}CO_2$	15.5	18.1	25.4	31.0	38.9	48.2	48.0	58.2	68.1

[a] Catalyst 17.2 g, GHSV 400.

[b] Values at GHSV 1250.

found with the cobalt-rich catalysts. The results obtained by the Co-90/Mo-10 catalyst are particularly important. Addition of only 10% of molybdenum oxide to cobalt oxide caused a remarkable suppression of the formation of carbon dioxide. Acetone was virtually the sole product at suitable conditions. So far as we are aware, the selective formation of acetone by one-step oxidation of propylene on an oxide catalyst is a novel catalytic oxidation,* though it has been reported that palladium chloride combined with copper chloride is an effective catalyst to produce acetone by the oxidation of propylene in the presence of hydrogen chloride and water by either homogeneous and heterogeneous reactions (*17*).

Selective formation of acrolein was found with molybdenum-rich catalysts such as pure MoO_3, Co-10/Mo-90, and Co-20/Mo-80. Since the product distributions obtained by these catalysts are similar to the distribution with MoO_3-Bi_2O_3 or Cu_2O catalyst, the oxidation seems to proceed mostly via an allylic intermediate, as has already been established (*5–10*).

The formation of acrylic acid in concurrence with acrolein was observed with Co-30/Mo-70 and Co-40/Mo-60 catalyst. It is likely that acrylic acid was formed via acrolein or some adsorbed complex similar to acrolein. In agreement with this view, the selectivity to acrolein decreased and that to acrylic acid first increased with increase in the contact time (Table 5, columns 2–4).

The formation of acetic acid was observed with all the catalysts examined, giving no correlation between the catalyst composition and the selectivity to acetic acid. From this it appears that acetic acid was formed by the oxidative fission of the olefin double bond which was in competition with the oxidation to acrolein or acetone.

After all, concerning the oxidation by the allylic mechanism, the overall features of the variation in the product distribution seem to correspond to the variation in the catalytic activity due to the concentration of cobalt. That is, the more active cobalt-rich catalysts produce highly oxygenated products, via, acrylic acid and carbon dioxide, whereas the less active molybdenum-rich catalysts produce mainly a less oxygenated product, acrolein. The formation of acetone on the cobalt-rich catalysts is exceptional—the mechanism of its formation must be different from the allylic oxidation. This view is supported by the fact that acetone was formed mainly at low temperature but at high temperature the product distribution was quite different even on the same catalyst. It is unlikely that acetone arise from a peroxide intermediate. Oxidation of propylene via a peroxide intermediate was reported to be nonselective (*18*).

Three possible mechanisms may be considered for acetone formation. (See scheme on opposite page.) Mechanism 1 involves the attack of active oxygen on the doubly bonded carbon atom of π-adsorbed propylene. Mechanisms 2 and 3 are based on an alcoholic intermediate. In the latter cases oxygen is first introduced to propylene in the form of a hydroxyl group which is followed by the oxidative dehydrogenation to form a carbonyl group. It has been well known that molybdenum oxide combined with transition metal oxides forms heteropolyacids. If Mechanism 2 is true, the acidic nature required for the catalyst would be provided by this property of molybdenum. Mechanism 3 is analogous to that of oxypalladation (*19*). Discrimination among these mechanisms will be the subject of the subsequent papers.

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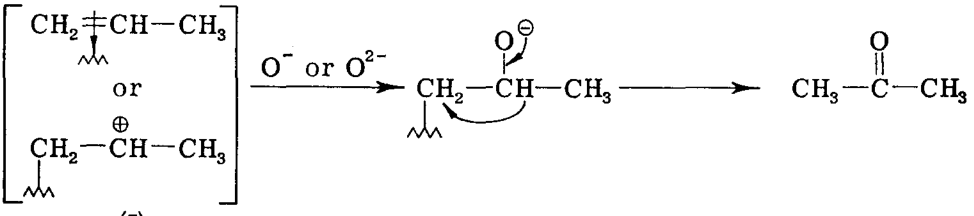
* After completion of the present paper, we came across a report by Buiten (*20*), who studied the propylene oxidation over SnO_2-MoO_3 catalysts. It was reported that acetone was formed as one of the oxidation products. The selectivity to acetone was at best 47% of the reacted propylene.

Mechanism 1.



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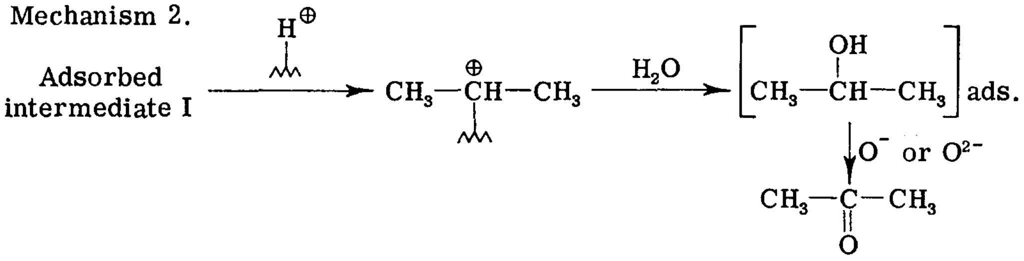
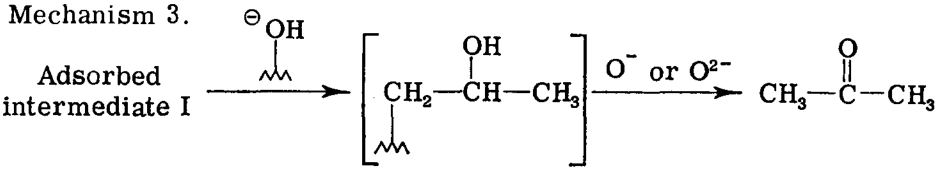
Mechanism 2.



Mechanism 3.



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