

Catalytic Oxidation of Olefin over Oxide Catalysts Containing Molybdenum

II. Variation of Kinetic Parameters of Propylene Oxidation with Composition of Cobalt-Molybdenum Binary Oxide Catalysts

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Variation of catalytic property of Co_3O_4 - MoO_3 binary oxide with its composition was investigated in the oxidation of propylene. Some kinetic data such as specific activity, apparent activation energy, and reaction orders in propylene and in oxygen were determined, varying molybdenum concentration with 10 atomic % difference each. Addition of a small amount of molybdenum trioxide to cobalt oxide caused remarkable changes in these kinetic parameters. On the contrary, addition of cobalt oxide did not seriously affect the catalytic property of molybdenum trioxide. These variations of kinetic parameters seem to correspond to the variation of the product distribution in the oxidation of propylene. Active species for the acetone formation was investigated by means of X-ray diffraction and infrared absorption.

INTRODUCTION

In the first paper of this series attention was paid to the variation of the product distribution with the composition of Co_3O_4 - MoO_3 binary oxide catalyst in the oxidation of propylene in the presence of water vapor (1). It was shown that two different types of oxidation occur in two different ranges of the catalyst composition.

One is the well-known allylic oxidation to form acrolein and acrylic acid, which was observed over the molybdenum-rich catalysts. The other is a new type reaction to form acetone, which was characteristic of the cobalt-rich catalysts. The result obtained by the Co-90/Mo-10 catalyst was particularly interesting. Addition of small amount of molybdenum oxide to cobalt oxide caused remarkable suppression of the oxidative decomposition of propylene and changed the product from carbon dioxide to acetone.

In order to investigate the cause of such

variation in the product distribution, a further work was done on the variation of kinetic parameters with the composition of the Co_3O_4 - MoO_3 catalysts in the oxidation of propylene. Structural studies of the binary oxide were also made by means of X-ray diffraction and infrared absorption. In the present paper those kinetic and structural data are discussed in relation to the product distribution in the propylene oxidation.

EXPERIMENTAL SECTION

Eleven binary oxide catalysts (including pure Co_3O_4 and MoO_3) were obtained from the same batch as used previously (1). Mechanical mixtures of component oxides were prepared from pure molybdenum trioxide and pure tricobalt tetroxide both baked separately and were pressed into cylindrical pellets. The apparatus and the analytical methods for reactants and products were the same as described previously (1).

Determination of Activation Energy and Specific Activity

The run for the determination of apparent activation energy and specific activity was carried out under a constant gas composition (propylene 1.8 vol %, oxygen, 29.7%, nitrogen 38.8%, steam 29.7%) and at a constant flow rate (118 ml STP/min) using 16 to 20 g of catalyst. Following the principle of the differential reactor, the conversion of propylene was held in low level, i.e., at most 15% and usually below 10%. Accordingly the apparent activation energy was obtained directly from Arrhenius plots of the propylene conversion.

Variation of the specific activity with the catalyst composition was so spread that a comparison of these specific activities at one constant temperature demands large extrapolations. Therefore, the specific activity was compared by the reaction temperature, T_r , at which the specific rate reached a prefixed value, i.e., $r = 2.00 \times 10^{-4}$ ml STP/m² cat sec. The values of apparent activation energy, specific activity, and BET surface area of the catalysts are summarized in Table 1.

Determination of Reaction Orders in Propylene and Oxygen

The reaction orders in both reactants were determined by varying the partial pressure of one reactant, with the other being kept constant under the same condition as adopted for the determination of the activation energy. The values were obtained from the log-log plots of the reaction rate against the partial pressures and are listed in the last two columns in Table 1.

X-Ray Diffraction and IR Absorption of the Catalysts

X-Ray diffraction diagrams of the catalysts were obtained by Geiger Flex D2-F using a cobalt target. Two kinds of samples, fresh and used, were submitted to the analysis. Another sample made by mechanical mixing of the component oxides was also examined. The infrared spectra of the binary oxides were measured with Perkin-

Elmer-125 in the range of 2000–400 cm⁻¹ using KBr disk technique.

RESULTS

1. Dependence of the specific activity and the activation energy on the catalyst composition. The specific activity of the binary oxide, Tr^{-1} , was plotted against atomic % of molybdenum as indicated by curve A in Fig. 1, where Tr^{-1} decreases monotonously with increase in the atomic fraction of molybdenum. Since there is a large difference between the activities of both component oxides ($Tr_{\text{Co}_3\text{O}_4} = 210^\circ\text{C}$, $Tr_{\text{MoO}_3} = 574^\circ\text{C}$), their mechanical mixture should behave like a mixture of Co_3O_4 with an inert material so that Tr^{-1} of the mechanical mixture is close to that of pure Co_3O_4 as shown by the curve B. The observed activity change of binary oxide, curve A, is quite different from curve B as shown in Fig. 1. Comparison of curves A and B shows that the addition of molybdenum trioxide exhibits a striking effect on the activity of the binary oxide. This effect can not be attributable to formation of CoMoO_4 , because the activity change of the mechanical mixture of Co_3O_4 and CoMoO_4 is estimated from the activities of Co_3O_4 and CoMoO_4 as represented by curve C in Fig. 1. The marked effect of molybdenum trioxide addition was also observed in the product distribution as reported in the previous paper. That is, the oxidation product was radically changed from carbon dioxide over the pure Co_3O_4 to acetone over the catalyst containing 10 atomic % of molybdenum.

On the other hand, those catalysts rich in molybdenum are similar to pure molybdenum trioxide both in the specific activity, as shown in Fig. 1, and in the reaction product, which was mainly acrolein (1). In other words, a small addition of cobalt oxide does not seriously affect the catalytic property of molybdenum trioxide.

It may be concluded from the above discussion that the catalytic property of the Co_3O_4 - MnO_3 binary oxide is mainly governed by the molybdenum component. This feature is further demonstrated by the variation of the activation energy with the

TABLE 1
VALUES FOR KINETIC PARAMETERS IN OXIDATION OF
PROPYLENE OVER THE Co_3O_4 - MoO_3 BINARY OXIDES

Catalyst comp. Co/Mo	Surface area (m^2/g)	Activation energy (kcal/mole)	Pre-expo. factor ($\text{ml}/\text{sec m}^2$)	T_r^a ($^\circ\text{K}$)	Specific activity ($1/T_r$)	Reaction order	
						Propylene	Oxygen
10/0	0.80 ^b	31.0	10.2 ₆	483	2.07	0	0.6 ₆
9/1	13.9	14.2	1.7 ₉	565	1.77	0.5 ₀	0.2 ₀
8/2	4.57	13.9	1.6 ₁	571	1.75	0.6 ₄	0.1 ₂
7/3	6.79	15.7	1.9 ₆	606	1.65	0.7 ₀	0.2 ₀
6/4	6.44	12.1	0.2 ₁	676	1.48	0.7 ₀	0.1 ₅
5/5	6.17	13.0	0.3 ₉	695	1.44	0.6 ₅	0.1 ₅
4/6	6.50	15.0	0.5 ₇	769	1.30	—	—
3/7	6.73	13.0	-0.1 ₃	794	1.26	0.8 ₀	0.0 ₃
2/8	2.66	12.6	-0.3 ₈	826	1.21	—	—
1/9	2.06	16.1	0.6 ₃	820	1.22	0.8 ₂	0.1 ₀
0/10	1.18	13.1	-0.3 ₂	847	1.18	0.9 ₁	0.0 ₂

^a A temperature at which the specific rate reached a value, $r = 2.00 \times 10^{-4}$ ml STP/ m^2 cat sec.

^b Calcined at higher temperature.

catalyst composition as shown in Fig. 2. The activation energy is 31 kcal/mole over pure cobalt oxide and 13.1 kcal/mole over pure molybdenum trioxide. The values over those catalysts from 10 to 90% of molybdenum were almost constant at 14 ± 2 kcal/mole, which is closer to that over molybdenum trioxide.

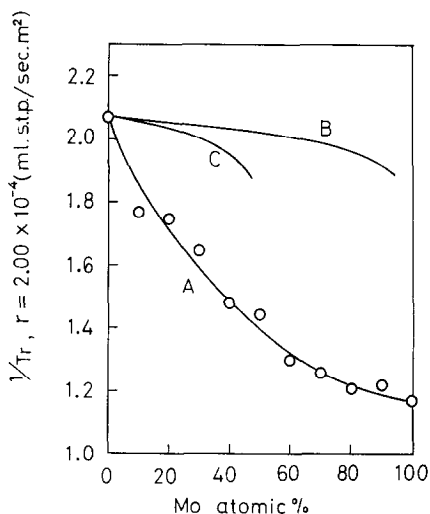


FIG. 1. Dependence of the specific activity on the catalyst composition: (A) observed; (B) calculated curve for mechanical mixture of Co_3O_4 and MoO_3 ; (C) calculated curve for mechanical mixture of Co_3O_4 and CoMoO_4 .

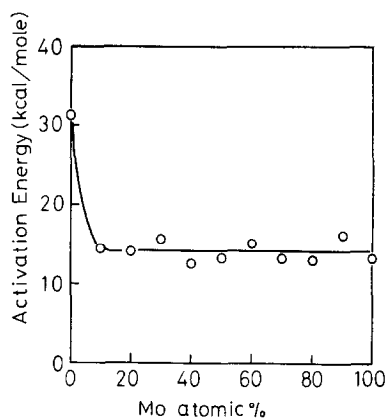


FIG. 2. Dependence of the apparent activation energy on the catalyst composition.

2. Variations of the reaction orders with the catalyst composition. The observed pressure dependence of the reaction rate over pure Co_3O_4 shows a striking contrast to that on pure MoO_3 . The kinetics over Co_3O_4 were 0.6₆ order in oxygen and independent of propylene, while the kinetics over MoO_3 were virtually first order in propylene and independent of oxygen. The latter is quite analogous to the kinetics for the allylic oxidation of olefins to form unsaturated aldehyde or diene over MoO_3 - Bi_2O_3 catalyst (2-4).

The reaction orders in propylene and oxy-

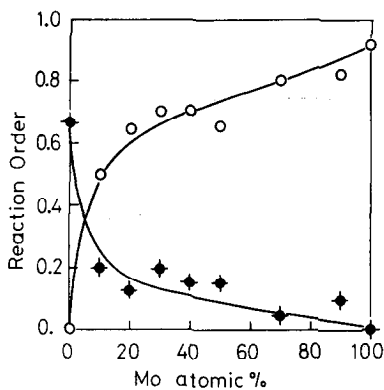


Fig. 3. Dependence of the reaction orders on the catalyst composition: ○, reaction order in propylene; ◆, reaction order in oxygen.

gen are plotted against the concentration of molybdenum in Fig. 3. The most remarkable change is observed again from 0 to 10% molybdenum. The order in propylene increases from zero to 0.5 and that in oxygen decreases from 0.66 to 0.2 in this region. The former increases to unity and the latter decreases to zero with further increase in

molybdenum concentration up to 100%. No remarkable change in both reaction orders is observed from 90 to 100% molybdenum concentration. These characteristic variations in reaction orders seem to be originated from the same effect of molybdenum addition which causes the variations in the catalytic activity, the apparent activation energy and the product distribution.

3. Structural study of the catalyst. In considering the remarkable effects of MoO_3 addition as shown above, the structural change in the catalyst solid would be important. Some qualitative characterizations of the catalyst were made by means of X-ray and IR absorption.

X-ray diffraction diagrams of the catalysts are shown in Fig. 4. These diffraction diagrams of the catalysts were not changed after the oxidation runs as exemplified for Co-60/Mo-40 catalyst (Fig. 4g,h). The diagrams of pure cobalt oxide and pure molybdenum oxide agreed with the patterns of Co_3O_4 and MoO_3 , respectively. The lines assigned to CoO , Co_2O_3 , and molybdenum

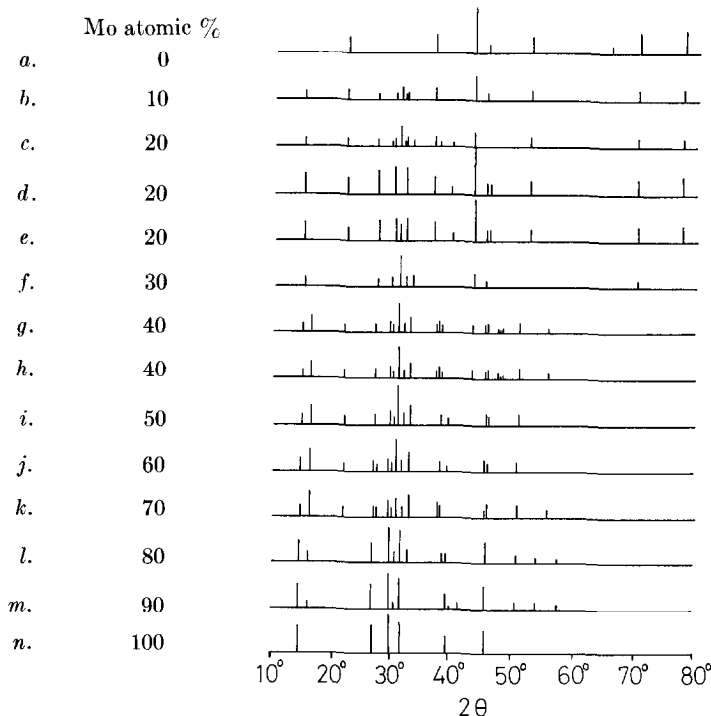


FIG. 4. X-ray diffraction patterns of the $\text{Co}_3\text{O}_4\text{MoO}_3$ binary system: a-c, f-n, binary oxides prepared by the method in Ref. (1); g,h, fresh and used, respectively; d,e, mechanical mixtures of component oxides; e, calcined at 550°C for 5 hr in air after mixing.

oxides of lower valences were not detected in any diagram of the catalysts.

As shown in Fig. 4, those peaks assigned to Co_3O_4 abruptly diminish with increase in the concentration of molybdenum, and mostly disappear from the diagram of Co-60/Mo-40 catalyst. On the other hand, those peaks of MoO_3 are observed even in the diagrams of cobalt-rich catalysts such as Co-80/Mo-20 and Co-90/Mo-10. This difference between Co_3O_4 and MoO_3 is probably due to readier crystallization of free MoO_3 .

Some peaks which can be assigned to CoMoO_4 (5) are found in the diagrams of binary systems. One of them at $2\theta = 30.6^\circ$ ($d = 3.38$) already exists in Co-90/Mo-10 catalyst, grows up with increase of molybdenum concentration till 50 atomic %, and then diminishes. The peaks at $2\theta = 21.6^\circ$ ($d = 4.75$), 33.0° (3.15), 37.6° (2.77) and 50.6° (2.085) show similar trend with the peak at 30.6° . On the other hand those peaks at $2\theta = 16.2^\circ$ ($d = 6.33$) and 29.2° (3.54) grow up until 70 atomic % molybdenum. The structure of CoMoO_4 was well defined by Smith and Ibers (7). It was shown that there exists only one compound, CoMoO_4 , but that this occurs in various modifications (6, 7). In addition, it

is known that various polycobalt molybdates are formed in the range of higher concentration of molybdenum. The observed variation of peaks with catalyst composition suggests that some modifications of CoMoO_4 occurs in the molybdenum-rich catalysts.

An interesting result is found in the X-ray diagram of a mechanical mixture of both component oxides and in its catalytic behavior. The simple mixture of both pure oxides (Co-80/Mo-20) naturally does not show any peak of cobalt molybdate (Fig. 4d). Although small amount of acetone was formed over this catalyst, the selectivity is low as shown in Table 2. However, after heating at 550°C for 5 hr, this mixture showed a remarkable activity for the acetone formation and simultaneously a diffraction line at $2\theta = 30.6^\circ$. The mechanical mixture of Co-90/Mo-10 showed similar catalytic behavior (Table 2).

The observed infrared spectra of each catalyst are given in Table 3. The absorption bands at about 940, 850, and 780 cm^{-1} are reported to belong to CoMoO_4 (8). The strongest band at 940 cm^{-1} is found in the molybdenum concentration from 10 to 90% and reaches maximum at Co-50/Mo-50 catalyst.

TABLE 2
OXIDATION OF PROPYLENE OVER THE PELLETED MECHANICAL MIXTURE OF PURE COMPONENT OXIDES^a

Catalyst	Heat treatment	Temp (°C)	Conversion (%)	Product distribution (%)						
				CH_3COCH_3	$\text{CH}_2=\text{CHCHO}$	$\frac{2}{3}\text{CH}_3\text{COOH}$	$\frac{1}{3}\text{CO}_2$	$\frac{1}{3}\text{CO}$		
Co-80/Mo-20	None	200	1.6	34.4	—	tr	65.6	—		
		217	3.4	25.6	tr	2.4	72.0	tr		
		240	9.2	14.0	4.6	1.7	74.6	5.1		
		260	18.0	6.5	2.0	1.2	87.4	2.9		
	550°C 5 hr in air	220	1.5	78.3	—	1.4	20.3	tr		
		245	2.5	73.5	tr	1.9	24.6	tr		
		260	4.3	65.5	tr	7.8	26.7	tr		
		275	6.5	53.0	1.8	5.4	37.4	2.4		
		Co-90/Mo-10	None	180	1.7	13.7	—	2.2	80.6	3.5
				195	1.2	87.3	—	1.8	10.9	tr
Co-90/Mo-10	550°C 5 hr in air	250	3.4	40.2	—	4.2	55.6	tr		

^a Gas composition: propylene, 20 vol %; oxygen, 30%; nitrogen, 20% steam, 30%. Catalyst: 16 g, GHSV, 400.

TABLE 3
 IR SPECTRA OF THE Co_3O_4 - MoO_3 BINARY OXIDES

Catalyst Co/Mo	Absorption band ^a (cm^{-1})							
10/0						667w,sh	656vs	565vs
9/1		930s	845w,b	780m	725w	667w,sh	656vs	565vs
8/2		932s	845w,b	780m	725w,sh	667w,sh	656vs	565vs
7/3	988vw	933vs	845m	780m	725w,sh		656vs	565s
6/4	988vw	938vs	855m,sh	780vw			656vs	565m,b
5/5	988w	940vs	ca850m,b	780vw			656vs,b	
3/7	988w	942s					650s	
2/8	988vs,sp	942s	858vs	816w,sh			ca600vs,b	
1/9	988vs,sp	949m	865vs	816w,sh			ca600vs,b	
0/10	988s,sp		860vs	816w,sh			580s,b	

^a s = strong, m = mean, w = weak, v = very, sp = sharp, sh = shoulder.

On the other hand absorption bands at 850 and 780 cm^{-1} are found only from 10 to 50% molybdenum catalysts and give maximum peaks at 30% molybdenum concentration.

A new band at about 725 cm^{-1} is found in the Co-90/Mo-10 catalyst with decreasing intensity as the molybdenum concentration increases and disappears from 40% molybdenum catalyst. The variation of the intensity of this band seems to be in accordance with the selectivity to acetone in the propylene oxidation.

DISCUSSION

Remarkable effects of molybdenum addition are shown in the kinetic parameters such as the activation energy, the specific activity and the reaction orders in propylene and oxygen as well as in the product distribution. These effects may be partially explained as follows. The catalyst composition is not uniform in a way that the added molybdenum is localized in the surface layers of the particles. However the drastic change in the product distribution from Co_3O_4 to the Co-90/Mo-10 catalyst must be due to some chemical effect of MoO_3 .

As shown in the results, the simple mechanical mixture of both component oxides showed low activity of acetone formation which was greatly intensified by baking at 550°C for 5 hr. This result suggests that the acetone formation is promoted by a composite oxide of both components. CoMoO_4

is the sole composite oxide identified by X-ray and IR absorption. However, the diffraction line at 30.6° already found in 10% molybdenum catalyst grows with the concentration of molybdenum and reaches maximum at 50% molybdenum. This line can be detected even in 90% molybdenum catalyst. On the other hand the optimum concentration of molybdenum for the acetone formation lies in 10–30% molybdenum. The selectivity to acetone was low over the Co-50/Mo-50 catalyst. Acetone was scarcely formed over the molybdenum-rich catalyst (1). Acrolein and acrylic acid, which were main products over the molyb-

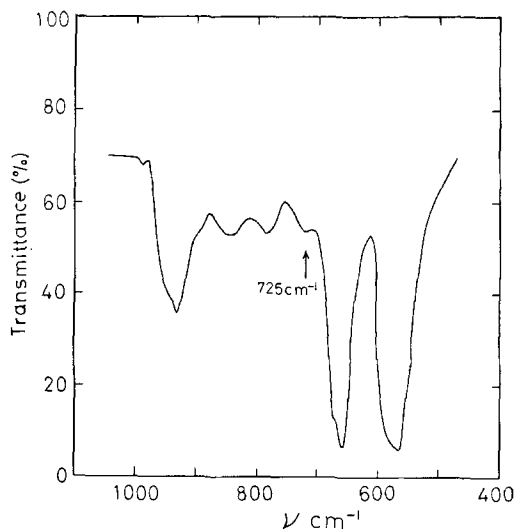


FIG. 5. IR spectra of the Co-90/Mo-10 catalyst.

denum-rich catalysts, seem to be formed independently of acetone. These facts suggest that CoMoO_4 itself is not the active species for the acetone formation.

The real active species is not yet clear, but possible cases may be mentioned. Some compound other than CoMoO_4 might be responsible for the acetone formation. IR absorption at 725 cm^{-1} might be related to this compound because it is only found in those catalyst which are effective in the acetone formation. However the role of Co_3O_4 which is found also in those effective catalysts may not be ignored. Cooperation of Co_3O_4 with the composite oxide such as CoMoO_4 might be the case. Anyway, some kind of composite oxide seems to be involved in the acetone formation.

It was previously reported that the reaction orders, in the oxidation of lower olefins over transition metal oxides, change regularly as the catalytic activity varies from one oxide to another (9, 10). That is, the reaction order in olefin increases and that in oxygen decreases as the activity of metal oxide decreases with increasing the heat of formation of metal oxide divided by the number of oxygen atoms in the oxide molecule. This general tendency has been interpreted in a way that the lower reaction order in oxygen and the lower activity of oxide are due to the stronger adsorption of oxygen. Although this interpretation is based on the complete oxidation of propylene, it seems to be applicable to

the present case of MoO_3 - Co_3O_4 system to explain the drastic reduction of carbon dioxide formation. The observed effect of a small addition of molybdenum would be caused by a strengthening of the adsorption bond of oxygen on the active sites of the catalyst. The accompanied reduction in the reactivity of adsorbed oxygen would suppress the splitting of the carbon-carbon bond by an adsorbed oxygen attack, thus changing the product distribution toward acetone or allylic oxidation products such as acrolein and acrylic acid.

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