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# Propane oxidation over various metal molybdate catalysts

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**Abstract**

Catalytic activities of various metal molybdates were tested for the gas-phase partial oxidation of propane with molecular oxygen under an atmospheric pressure in the temperature range 325–500°C. Metal molybdate catalysts were found to mostly promote the oxidative dehydrogenation of propane to propene. More than 80% selectivity to propene was attained on each catalyst but their catalytic activities differed greatly. Of the catalysts, cobalt molybdate showed the highest catalytic performance for the oxidative dehydrogenation and the catalytic property strongly depended on the catalyst composition. $Co_{0.95}MoO_x$ catalyst gave 60% selectivity to propene at 20% conversion of propane at 450°C. The catalytic activity and selectivity of each catalyst in the propane oxidation is discussed in terms of surface acidity and reactivity of lattice oxide ions.

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## 1. Introduction

The functionalization of propane by catalytic oxidation processes with molecular oxygen, such as oxidative dehydrogenation to olefin [1], oxygenation to form unsaturated aldehyde [2], ammoxidation to nitriles [3,4], hydroxylation to alcohols [5], etc. has recently been of great interest in solid-state catalysis chemistry. In this paper, we investigated the catalytic oxidative dehydrogenation of propane over various metal molybdates.

Several catalysts and processes have been reported so far for the oxidative dehydrogenation of propane to propene. Kung and coworkers [1] have recently reported $V_2O_5/MgO$ catalysts which showed high catalytic performance in the oxidation of propane, giving ca. 20% conversion with about 60% selectivity to propene. The selectivity, however, decreased with increasing conversion. $V_2O_5/Bi_2O_3$ catalysts also show considerable activities for the oxidative dehydrogenation [6]. It is suggested that the loading of $V_2O_5$ catalyst on metal oxides having solid–base properties or the formation of complex metal oxides between $V_2O_5$ and basic metal oxides, reduce the strong oxidation ability of $V_2O_5$ to attain higher selectivity to oxidative dehydrogenation. Quite recently, Ross and coworkers [7] reported that hydrated niobia calcined at temperatures above 500°C exhibits a high selectivity for propane oxidation to propene although the conversion of propane is extremely low. They also reported that vanadium oxide supported on niobia exhibited quite high activity and selectivity to form propene [8]. According to their characterization work on this catalyst, an oxygen anion bound both vanadium and niobium seems to be responsible for the selective formation of propene.

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There are other active catalysts reported, most of which are based on vanadium [9–11].

On the other hand, molybdenum-based oxides, which are very important catalysts for the selective oxidations of olefins, have received less attentions [12–15], probably because molybdenum-based oxide catalysts are believed to be ineffective for abstracting hydrogen which has a higher bond energy. Here, we summarized the catalytic performance of various metal molybdates in the oxidation of propane and discussed their catalytic activity and selectivity in terms of surface acidity and reactivity of lattice oxide ions.

## 2. Experimental

Various metal molybdates were prepared from aqueous solutions of corresponding metal nitrates and ammonium paramolybdate. After mixing each solution and adding ammonium hydroxide, precipitates were solidified by evaporation of water at 80°C. The resulting solid was calcined in air at 300°C for 3 h, and calcined again for 5–9 h at 450–600°C. Cobalt molybdate catalysts having various Co/Mo ratio were also prepared by the same method with the desired amounts of the starting cobalt nitrate and ammonium paramolybdate. The prepared catalysts except the cobalt molybdate with different Co/Mo ratio were confirmed to be monophasic by XRD patterns. All catalysts were used in the form of powder of 100–200 mesh after dilution by quartz chips.

The propane oxidation was carried out at atmospheric pressure in a conventional flow system equipped with a Pyrex tube reactor (18 mm I.D). A 6 mm O.D. Pyrex tube runs longitudinally through the center of the reactor to serve as a thermowell. The volume in the reactor except the catalyst zone was minimized to prevent gas-phase reactions. The standard conditions for the oxidation are as follows: the feed compositions were 18 mol-% of propane, 7 mol-% of oxygen, the remainder being nitrogen. The catalysts (4 g) were mounted in the middle of the reactor. The reaction temperature was varied in the range 325–500°C and the space velocity was 810 $cm^3$ g-$cat.^{-1}$ $h^{-1}$. No reaction took place without catalysts being under the above reaction conditions. The feed and products were analyzed by an on-line gas chromatograph operating with two sequential columns (Gaskuropak 54, 6 m and molecular sieve 13×, 1 m).

Temperature-programmed desorption of ammonia and catalyst reduction with propane were carried out by a conventional pulse micro reactor connected with a gas chromatograph having a TCD cell. The products from propane oxidation with lattice oxide ions in the catalyst reduction experiments were analyzed by GC with a column (Unibeads 1S, 1 m).

## 3. Results and discussion

### 3.1. Catalytic performance of metal molybdates

Catalytic performances of various molybdates of divalent and trivalent metal cations in the oxidation of propane were tested at the temperature range 325–500°C. The results were summarized in Table 1 along with the surface area determined by BET method (nitrogen adsorption at liquid nitrogen temperature). It can be seen that most of the catalysts predominantly promoted the oxidative dehydrogenation of propane to form propene. Products, in addition to propene, at higher conversions are carbon oxides, and the formation of oxidized products such as acrolein were extremely small. More than 80% selectivity to propene was achieved at lower conversions, irrespective of the kind of metal cation of the catalysts. However, as the conversion increased with the increase of either the reaction temperature or the contact time, the selectivity to propene decreased and those to carbon oxides increased in every catalyst.

The catalytic activity, on the other hand, strongly depends on the kind of metal cations. $CoMoO_4$ catalyst was found to be most active and selective for the oxidative dehydrogenation of propane of the molybdates tested in this work. $NiMoO_4$ showed the highest activity for the pro-

Table 1 Oxidative dehydrogenation of propane over various metal molybdate catalysts

| Catalyst ( /°C)[a] | Surface area ($m^2.g^{-1}$) | Reaction temp. (°C) | Conversion of propane(%) | Selectivity to propene(%) [ ][b] | Formation rate of propene (μmol.$min^{-1}.g^{-1}$)[c] |
|---|---|---|---|---|---|
| $MgMoO_4$(600) | 4.2 | 500 | 8.9 | 67[85] | 0.97 |
| $CaMoO_4$(600) | 1.6 | 500 | 5.3 | 83[92] | 0.77 |
| $SrMoO_4$(550) | 1.0 | 500 | 1.1 | 62[65] | 0 |
| $BaMoO_4$(550) | 0.7 | 500 | 1.5 | 78[77] | 0 |
| $ZnMoO_4$(600) | 0.3 | 500 | 0.2 | 100 | 0 |
| $CoMoO_4$(600) | 9.3 | 500 | 10.9 | 63[88] | 1.59 |
| $Co_{0.95}Na_{0.05}MoO_x$(600) | 1.9 | 490 | 0 | - | 0 |
| $NiMoO_4$(600) | 23.0 | 432 | 12.4 | 35[70] | 3.68 |
| $MnMoO_4$(600) | 1.2 | 500 | 1.4 | 49[45] | 0 |
| $CuMoO_4$(600) | 0.9 | 500 | 3.9 | 17[22] | 0 |
| $Fe_2Mo_3O_{12}$(600) | 1.2 | 500 | 1.3 | 83[80] | 0 |
| $Bi_2Mo_3O_{12}$(450) | 1.2 | 500 | 0.3 | 73[d] | 0 |
| $Ce_2Mo_3O_{12}$(600) | 1.0 | 500 | 1.7 | 57[53] | 0.22 |
| $La_2Mo_3O_{12}$(600) | 3.6 | 500 | 6.3 | 57[70] | 0.61 |
| $Sm_2Mo_3O_{12}$(600) | 2.2 | 500 | 5.9 | 73[88] | 0.80 |
| $Al_2Mo_3O_{12}$(550) | 6.1 | 500 | 10.5 | 26[57] | 0.92 |
| $Cr_2Mo_3O_{12}$(550) | 6.9 | 476 | 12.3 | 14[19] | 0.65 |

a) Calcination temperature.
b) Propene selectivity at 2% conversion of propane under different reaction temperature.
c) Formation rate of propene at 400 °C.
d) Selectivity to acrolein.

pane oxidation but was nonselective. $MnMoO_4$ catalyst revealed a very poor activity. All molybdates of metal oxides having solid–base properties such as MgO, CaO, SrO, BaO, $La_2O_3$, $Sm_2O_3$, and ZnO showed quite high selectivity to propene formation but the catalytic activities were much lower than that of $CoMoO_4$. $Al_2Mo_3O_{12}$ and $Cr_2Mo_3O_{12}$ catalysts were highly active but nonselective.

$Bi_2Mo_3O_{12}$, $Fe_2Mo_3O_{12}$, and $Ce_2Mo_3O_{12}$ are well-known as important molybdate phases in active multicomponent bismuth molybdate catalysts for selective propene oxidation to acrolein and it is also known that they have redox properties. $CuMoO_4$ catalyst is also known to be active for the propene oxidation and the lattice oxide ions are active oxygen species. Interestingly, all these catalysts are virtually inactive for propane oxidation.

The above-mentioned brief activity order of the metal molybdate catalysts was also clearly revealed in the rate of propene formation as shown in the last column of Table 1. The listed values were the formation rate of propene from propane at 400°C. Under this reaction temperature the obtained selectivity of each catalyst was more than 80% except for a few catalysts, $NiMoO_4$, $Al_2Mo_3O_{12}$, and $Cr_2Mo_3O_{12}$. Although the activity order is clear from Table 1, effects of surface area on the selectivity and activity should be taken into account more precisely, because the catalysts having a surface area lower than 1.5 $m^2$ $g^1$ tend to show lower activity for the propane oxidation. The effects of surface area will be discussed later.

### 3.2. *Effect of catalyst composition*

Since it has been reported that catalytic properties of metal molybdates in olefin oxidations are strongly influenced by the catalyst composition [14], we further tested the catalytic performance of the cobalt molybdate catalyst which revealed the highest catalytic property among the various metal molybdates. $MgMoO_4$ seems also to be a suitable catalyst for the experiments about catalyst composition. The results will be reported elsewhere. The results on Co–Mo–O catalyst system are shown in Fig. 1. Co/Mo ratio was widely varied in the range from 0 to 1.3. At Co/Mo = O, the catalyst phase is $MoO_3$. Between Co/Mo = 0 to 1, the catalyst was composed with $MoO_3$ and $CoMoO_4$ (β-$CoMoO_4$ structure) phases. At Co/Mo = 1, single $CoMoO_4$ phase existed. Above this ratio (Co/Mo = 1), a crystalline part of the cata-

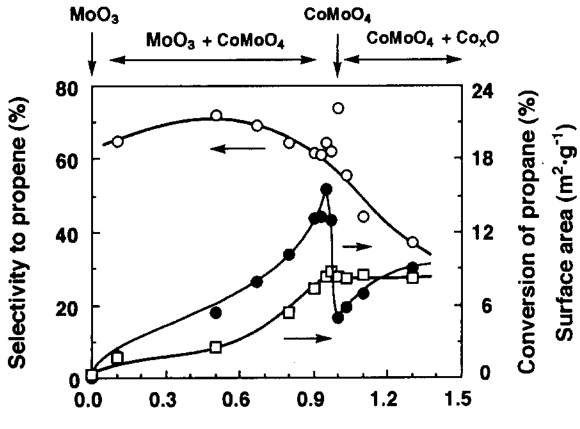

Fig. 1. Oxidative dehydrogenation of propane over cobalt molybdate catalysts having different compositions at 460°C. (●) Conversion, (○) selectivity, (□) surface area.

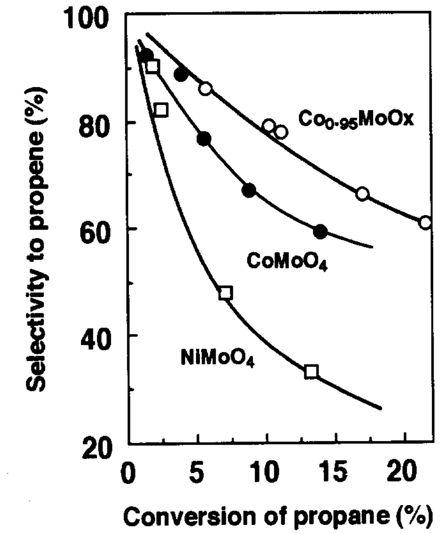

Fig. 2. Effect of conversion on propane selectivity in the propane oxidative dehydrogenation.

lyst is $CoMoO_4$ phase and no other clear phases based on cobalt oxide were detected by XRD measurements.

As can be seen in Fig. 1, the catalytic activity of the cobalt molybdates was highly sensitive to the catalyst composition. The propane conversion changes drastically in the range around Co/Mo = 1. $Co_{0.95}MoO_x$ catalyst showed the maximum conversion which is about 4 times higher than that of pure $CoMoO_4$ catalyst. The selectivity to propene also decreased by increasing the ratio from Co/Mo = 1 to the above. The effect of molybdenum concentration on the selectivity is more clearly demonstrated in Fig. 2 where the selectivities to propene were plotted against the propane conversion over $CoMoO_4$, $Co_{0.95}MoO_x$, and $NiMoO_4$ catalysts. Although each catalyst showed high selectivities, more than 90% at extremely low conversions, the selectivity decreased with increasing conversion. Obviously, the $Co_{0.95}MoO_x$ catalyst can sustain higher selectivity than the $CoMoO_4$ catalyst at higher conversions. The $NiMoO_4$ catalyst was worse. Since the surface area of the catalysts was almost the same in the region where the catalytic activity drastically changed, a small amount of excess molybdenum oxide on the surface seems to play an important role in the course of propane oxidation.

Typical catalytic performance data as a function of the reaction temperature are shown in Fig. 3 obtained with the $Co_{0.95}MoO_x$ catalyst calcined at 550°C (surface area, 12.6 $m^2$ $g^{-1}$). As a result, 60% selectivity to propene was achieved at 20% conversion over the $Co_{0.95}MoO_x$ catalyst under the presently optimized reaction conditions. This catalytic performance obtained in this work is comparable to that attained on $V_2O_5/MgO$ catalyst [1].

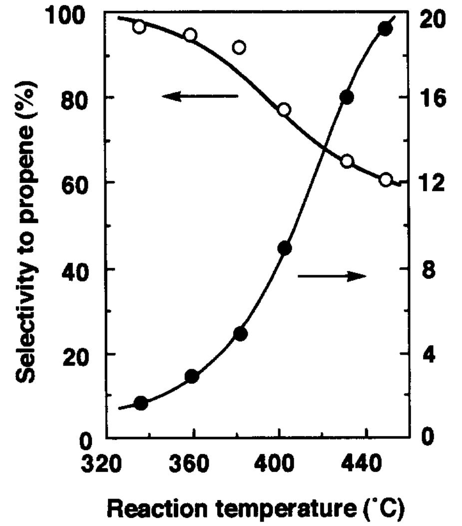

Fig. 3. Oxidative dehydrogenation of propane over $Co_{0.95}MoO_x$ catalyst calcined at 550°C.

### *3.3. Role of acidic site and involvement of lattice oxide ions in the reaction*

In the oxidative dehydrogenation, propane may first react by breaking a methylene C–H bond to form an adsorbed ispropyl radical, because a methylene C–H bond is weaker than a methyl C–H bond by 3.6 kcal $mol^{-1}$. Rapid breaking of a second C–H bond at terminal carbons of the isopropyl radical then takes place, forming propene. The rate determining step of the oxidative dehydrogenation of propane may be the breaking of methylene C–H bond of propane on the catalyst surface. On the other hand, it is known that the rate determining step in the catalytic oxidation of propene is abstraction of allyl hydrogen of propene on the catalyst surface. Both reactions thus need surface basic lattice oxide ions and/or surface acidic sites for the hydrogen abstractions.

In our previous paper [16,17], we compared the catalytic performance of some metal molybdates in the oxidations of propane and propene, and there observed no clear relationship between the conversions. However, as noted in Table 1, the catalysts, $CuMoO_4$, $Bi_2Mo_3O_{12}$, $Fe_2Mo_3O_{12}$, and $Ce_2Mo_3O_{12}$, all of which show redox behavior in propene oxidation, were commonly inactive for propane oxidation to propene. In other words, there is a reverse relationship between the propene yield in the propane oxidation and the acrolein yield in the propene oxidation over the metal molybdate catalyst. The result suggests either that the reactivity of lattice oxide ions for propane oxidation is largely different from that for propene oxidation, or that surface acidic sites promote hydrogen abstraction of propane in the rate determining step.

In order to investigate the role of the acidic property of the metal molybdates, we carried out temperature-programmed desorption (TPD) measurements of ammonia. TPD spectra of the typical metal molybdate catalysts are shown in Fig. 4. Ammonia was adsorbed at 50°C on each catalyst preheated at 500°C for 1 h in a He stream. TPD spectra were recorded at 10°C $min^{-1}$ in a He stream (20 ml $min^{-1}$) in the temperature range from 50 to 500°C. The TPD spectra were divided roughly into two main peaks; one is a narrow peak appeared around 150°C (weak acid sites) and another is a very broad peak appeared above 270°C (stronger acid sites). Both less selective catalysts, $CoMoO_4$ and $NiMoO_4$ (see Fig. 2), have these two peaks in their TPD spectra, although the peak areas are different in each case. On the other hand, the active and selective catalyst, $Co_{0.95}MoO_x$, has a single narrow peak and its peak maximum is slightly lower, below 150°C, than that of $CoMoO_4$. Very small desorption of ammonia with no appreciable peaks was observed in both inactive catalysts, $Bi_2Mo_3O_{12}$ and sodium-containing cobalt molybdate $Co_{0.95}Na_{0.05}MoO_x$ (see Table 1). These results strongly suggest that the surface acidic sites of metal molybdates play key roles in the course of the oxidative dehydrogenation of propane to propene and also influence the propene selectivity. Probably, the considerably weak surface acid site, which corresponds to the low temperature peak below 150°C, may effectively promote the oxidative dehydrogenation at

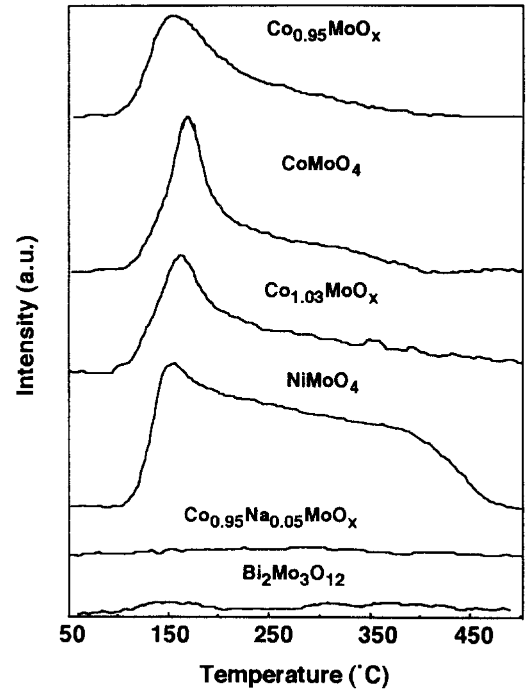

Fig. 4. TPD spectra of ammonia adsorbed on various metal molybdates.

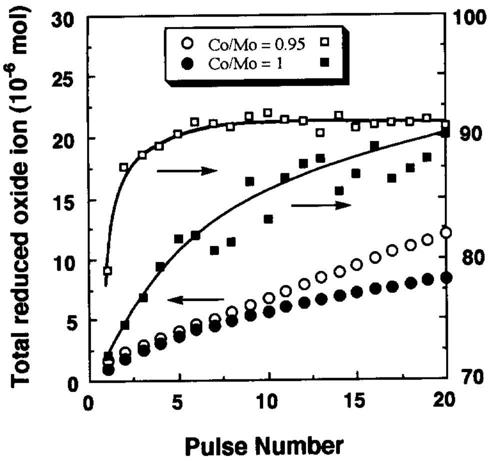

Fig. 5. Pulse reduction of the catalyst (0.1 g) with propane (7.5 μmol) at 550°C.

high reaction temperatures. The existence of stronger acid sites, which corresponds to the higher temperature broad peak, may relate the decrease in the propene selectivity; a strong acid site may provide an adsorption site for propene formed from propane and strongly adsorbed propene will be further oxidized to carbon oxides.

Active oxygen species seems to be also important in deciding the catalytic activity and selectivity in the oxidative dehydrogenation of propane. Here, the involvement of lattice oxide ions of the molybdate catalysts in the reaction was examined by pulse reduction of the catalyst with propane. The results for $CoMoO_4$ and $Co_{0.95}MoO_x$ catalysts are shown in Fig. 5. In each propane pulse, propene was selectively formed, indicating that lattice oxide ions are active for propene formation. Since the selectivity to propene increased with increasing the extent of reduction and then reached constant selectivities, a slightly reduced surface, in other words, lower surface concentration of lattice oxide ion is preferable for the selective formation of propene. Presumably, the lower selectivity to propene at the starting pulses is due to the higher probability for the reaction of lattice oxide ions with propene once formed from propane. This situation is more prominent for $CoMoO_4$ because of which the strong acidic sites for propene adsorption. The propene formation by the reduction still occurred at the 20th pulse which resulted in about 80% reduction of the surface lattice oxygen.

By summarizing the above TPD and pulse reduction experiments, it appears that molybdate catalysts possessing weak acid sites on the surface are active for the oxidative dehydrogenation of propane and their reduced surface is more selective for the formation of propene. Presumably, excess molybdenum oxo anions partially cover the surface of metal molybdates which have relatively stronger acid sites, and then provide the weak acid sites. Furthermore, its slightly reduced state may be an active site for propane oxidation. If molybdate catalysts are well sintered, in other words, have very low surface area, such molybdenum oxo anions may not exist on the surface to generate surface acid sites. This would partly explain why these catalysts are so inactive.

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