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CATALYTIC OXIDATION OF PROPANE OVER MOLYBDENUM-BASED MIXED OXIDES

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Abstract – Catalytic oxidation of propane to produce propene was investigated over molybdenum-based mixed oxide catalysts. Cobalt or magnesium oxide combined with molybdenum oxide exhibits the best catalytic performance for the oxidative dehydrogenation of propane. Catalytic activities of both Co-Mo-O and Mg-Mo-O vary drastically on the catalyst composition and $Co(Mg)_{0.95}Mo_{1.0}O_X$ having small amounts of free MoO_3 on the $Co(Mg)MoO_4$ surface shows the highest catalytic activity keeping a considerably high selectivity to propene. The catalytic activity also depends strongly on the acidic properties of catalysts and MoO_3 clusters formed on the surface of $Co(Mg)MoO_4$ are responsible for the activities for the oxidative dehydrogenation of propane.

Key words: *Propane, Oxidative Dehydrogenation, Cobalt Molybdate, Magnesium Molybdate, Acidic Property*

INTRODUCTION

Oxidative dehydrogenation of propane to produce propene is one of the prospective oxidation process to utilize cheaper feedstock and has been investigated mainly by employing vanadium-based mixed oxide catalysts [Moro-oka and Ueda, 1994; Kung, 1994]. We have recently investigated the reaction on molybdenum-based catalyst systems and found that cobalt-molybdenum and magnesium-molybdenum mixed oxides show fairly high activities for the oxidative dehydrogenation of propane [Yoon et al., 1994, 1995a, 1995b, 1996]. The selectivity to propane reaches to 65 % at 20 % conversion of propane and 60 % at 30 % conversion under the best conditions. These achievements are almost comparable or rather better than the best results ever reported [Chaar et al., 1988] but still insufficient for further development beyond laboratory scale. However, some useful information has been obtained for the reaction mechanism and catalyst system on the selective activation of lower alkane [Yoon et al., 1995b; Lee et al., 1997]. In this paper, we make a brief review of our recent works [Yoon et al., 1994, 1995a, b, 1996; Lee et al., 1997] on the oxidative dehydrogenation of propane to produce propene over molybdenum-based mixed oxide catalysts.

EXPERIMENTAL

1. Catalyst Preparation

Cobalt and magnesium molybdate catalysts having various Co(Mg)/Mo ratios were prepared with aqueous solutions of required amounts of metal nitrates with pH=2 and ammonium molybdate with pH=9. After mixing each solution, precipitates were solidified by the evaporation of water at 80 °C. The resulting sourry was dried at 110 °C for 20 h and calcined stepwise at 300 °C for 3 h in air. The calcined solid was ground into a fine powder and calcined again for 9 h at 600 °C. Chemical composition of the prepared catalysts were calculated on the basis of the amounts of the starting chemicals in the preparation.

Supported catalyst were prepared by the impregnation method. $Mg_{1.01}MoO_X$ was immersed in aquous solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and dried by the evaporation of water at 40 °C. Each sample of $MoO_3/Mg_{1.01}MoO_X$ was calcined in air at 500 °C for 2 h prior to the reaction.

Acid-base treated catalysts were prepared by the treatments of $Mg_{0.95}MoO_X$ and $Mg_{1.05}MoO_X$ catalysts in aqueous solution of ammonia or acetic acid (25 %) for 1 h at room temperature. The samples were filtrated after acid or base treatment, washed with acetone, and dried at 150 °C for 12 h.

2. Characterization and Catalytic Oxidation Procedure

Phases of the prepared catalysts were identified by XRD measurements. Surface area of each sample was determined by BET method of nitrogen absorption at liquid nitrogen temperature.

The oxidation of propane with molecular oxygen was carried out at atmospheric pressure in a conventional flow system equipped with a Pyrex tube reactor (18 mm I.D.). The standard conditions for the reaction are as follows: The feed composition was 18 mol % of propane, 7 mol % of oxygen, the remainder being nitrogen. 4 g of the catalyst diluted with 2 g of quartz chips was mounted in the middle of the reactor. The reaction temperature was varied in the range of 360-520 °C and the space velocity was fixed at 810 $cm^3g\text{-cat.}^{-1}hr^{-1}$ if not especially noted. The feed and product gas were analyzed by an on-line gas chromatograph operation with two sequential columns. A molecular sieves 13X (1 m) was used at 40 °C to separate O_2, N_2, and CO, and Gaskuropak 54 (6 m) was used with increasing temperature from 60 to 160 °C to sepa-

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rate the hydrocarbons, oxygen-containing products and CO_2.

To investigate the acidity and basicity of the catalysts, 2-propanol dehydration/dehydrogenation (IPA reaction) was carried out in a conventional pulse equipment with TCD cell of a gas chromatograph. A column of PEG 20M (3 m) was used for analysis and 6.5 μmol of 2-propanol was injected over 10 mg of the catalysts at 300 °C.

Catalyst reduction with propane in the absence of gaseous oxygen was carried out using a conventional pulse micro reactor connected with a gas chromatograph having a TCD cell. Propane (7.4 μmol) was injected several times into the pulse flow line (He carrier, 20 $ml \cdot min^{-1}$) and reaction with lattice oxide ions of the catalyst (20 mg) was carried out at 550 °C. The products were analyzed by on-line gas chromatograph with a column of Unibeads 1S (1 m) at 140 °C.

RESULTS AND DISCUSSION

1. Oxidative Dehydrogenation of Propane over Cobalt and Magnesium Molybdate Catalysts

We have already reported that $CoMoO_4$ and $MgMoO_4$ show the best catalytic performance for the oxidative dehydrogenation of propane to form propene among various metal molybdates [Yoon et al., 1994, 1996]. Figs. 1 and 2 show the catalytic properties of cobalt-molybdenum and magnesium-molybdenum mixed oxide catalyst systems for the oxidative dehydrogenation of propane, where Co/Mo and Mg/Mo ratios are varied in the range from 0 to 1.3. The catalytic activity depends strongly on the composition of the catalyst in both systems where $Co(Mg)_{0.95}MoO_X$ shows the highest activity keeping a considerably high selectivity to propene.

The products besides propene were CO_2, CO and small amounts of C_2H_4 and acrolein. As shown in Figs. 1 and 2, the catalytic activity changes drastically around Co/Mo and Mg/Mo=1. The catalytic activity decreases sharply above Co(Mg)/Mo=1 and the selectivity also does with increasing Co(Mg)/Mo ratio than unity. On the other hand, the selectivity to propene is sufficiently high on the molybdenum-rich catalysts but the activity also decreases with decreasing Co(Mg)/Mo ratio mainly by decreasing surface area.

The catalyst systems were composed of various complex oxides. $CoMoO_4$ is only binary oxide between cobalt and molybdenum oxide, whereas α- and β-$MgMoO_4$ and $Mg_2Mo_3O_{11}$ are known between magnesium and molybdenum oxides. The main phases of pure and binary oxides found by XRD are also shown in Figs. 1 and 2 for both catalytic systems. Around Co(Mg)/Mo=1, the phase formation was very critical, strongly depending on the preparation conditions. XRD and XPS analyses showed that small particles of MoO_3 were dispersed on the $Co(Mg)MoO_4$ crystals in the catalyst systems. These MoO_3 clusters seemed to play an important role in the course of propane oxidation and the role of them will be discussed in the latter part.

The conversion-selectivity relationships on cobalt-molybdenum mixed oxide catalysts are shown in Fig. 3. Since the selectivity of propene approaches to 100 % at lower conversions on every mixed oxide catalyst examined, it is clear that combustion to carbon oxides takes place mainly via the consecutive oxidation of propene. Typical catalytic performance data

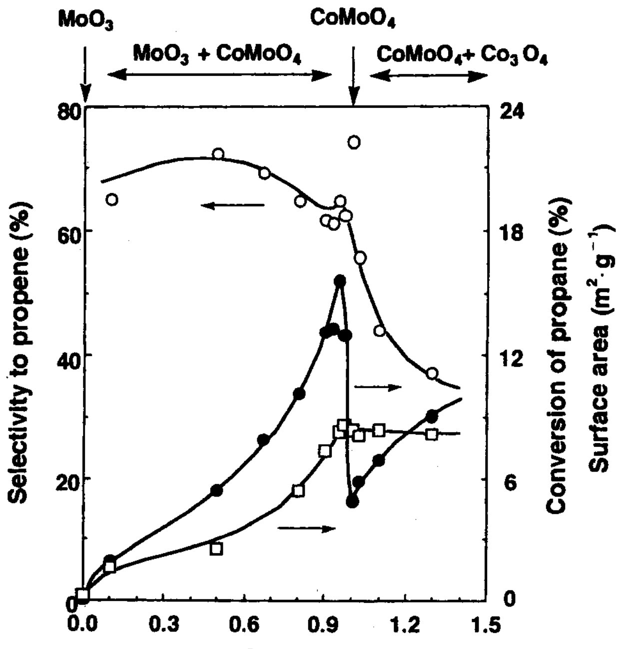

Fig. 1. Dependencies of the catalytic activity and selectivity of Co-Mo-O system for the oxidative dehydrogenation of propane at 460 °C on the composition of catalyst.
●: Conversion of propane, ○: Selectivity to propene, □: Surface area of catalyst.

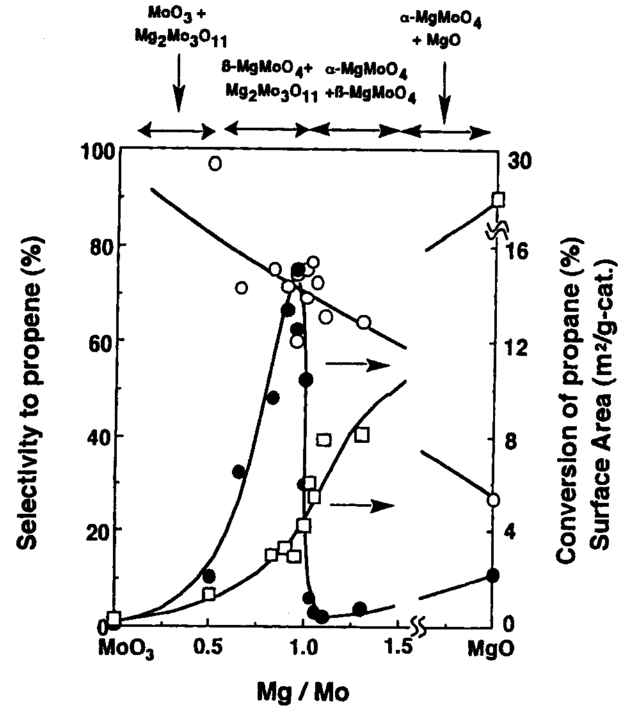

Fig. 2. Dependencies of the catalytic activity and selectivity of Mg-Mo-O system for the oxidative dehydrogenation of propane at 480 °C on the composition of catalyst.
●: Conversion of propane, ○: Selectivity to propene, □: Surface area of catalyst.

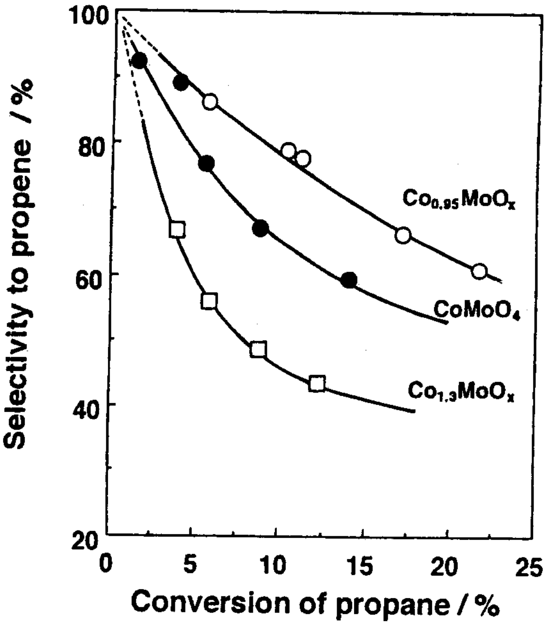

Fig. 3. Relationship between the conversion of propane and the selectivity to propene in the oxidative dehydrogenation of propane over Co-Mo-O catalysts at 480 °C.

obtained on the $Co_{0.95}MoO_X$ catalyst are shown in Fig. 4 as a function of the reaction temperature. The reaction of propane took place at about 330 °C and the conversion of propane increased with increasing reaction temperature. On the other hand, the selectivity to propene decreased with increasing reaction temperature. Under the presently optimized reaction conditions, the selectivity to propene of 60-63 % was achieved at the conversion of 20-23 % over both $Co_{0.95}MoO_X$ and $Mg_{0.95}MoO_X$ catalysts.

2. Role of Acidic Site and Involvement of Lattice Oxide Ion in the Reaction

In the oxidative dehydrogenation of propane, the first step may be the C-H bond cleavage of methylene to form adsorbed isopropyl group, because the bond strength of methylene C-H is weaker than methyl C-H by 3.6 kcal/mol. Rapid breaking of one terminal C-H bond of isopropyl group may follow it forming a propene molecule. It is generally accepted that the first step is rate-determining where acidic site and/or lattice oxide ion may be involved to assist the C-H bond cleavage. In order to examine the possibility that acidic site plays some role in the rate-determining C-H bond cleavage, acidic nature of the catalysts was measured by the reaction of 2-propanol. The main product of the pulse reaction of 2-propanol was propene and the formation of dehydrogenation product, acetone, was negligible. The results suggested that mixed oxide catalysts employed in the oxidative dehydrogenation of propane have acidic properties. The specific formation rate of propene in the oxidative dehydrogenation of propane on each catalyst was plotted against the specific reaction rate of 2-propanol in Fig. 5. It is clear that the rate of formation of propene from propane increases almost in parallel with the surface acidity of catalyst determined by the dehydration of 2-propanol. The $Mg_{0.95}MoO_X$ catalyst having the highest acidity shows the highest rate of propene formation in the oxidative dehydrogenation of propane. Thus, it is reasonably concluded that the rate-determining methylene C-H bond cleavage is not simple homolytic dissociation but surface acidic site is involved to accept species formed by the C-H bond cleavage.

The participation of lattice oxide ion of cabalt-molybdenum mixed oxide catalysts in the oxidative dehydrogenation of propane was examined by the pulse reduction of the catalyst with propane and the results are shown in Fig. 6. Propene was selectively formed in the pulse reduction. Since water

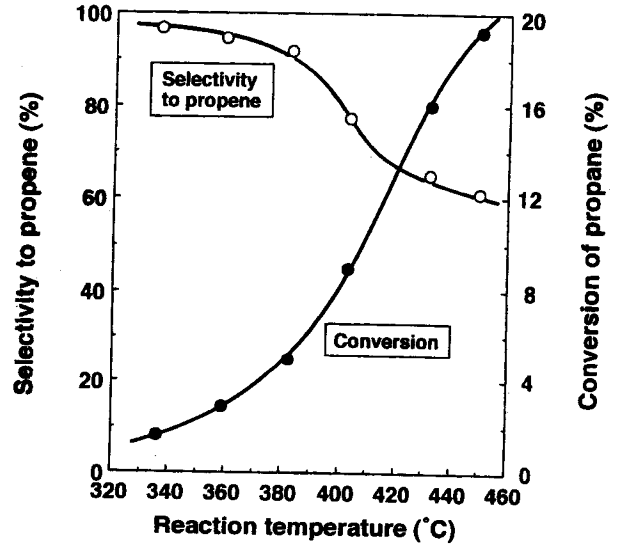

Fig. 4. Dependencies of catalytic activity and selectivity of the oxidative dehydrogenation of propane over $Co_{0.95}$-MoO_X catalyst on the reaction temperature.

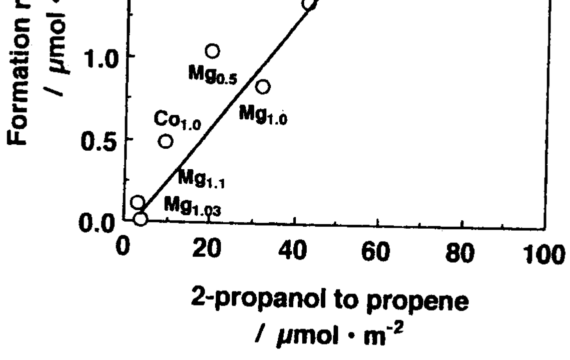

Fig. 5. Relationship between the catalytic activities of Co-Mo-O and Mg-Mo-O systems for the oxidative dehydrogenation of propane at 460 °C and those for the 2-propanol dehydration at 300 °C.

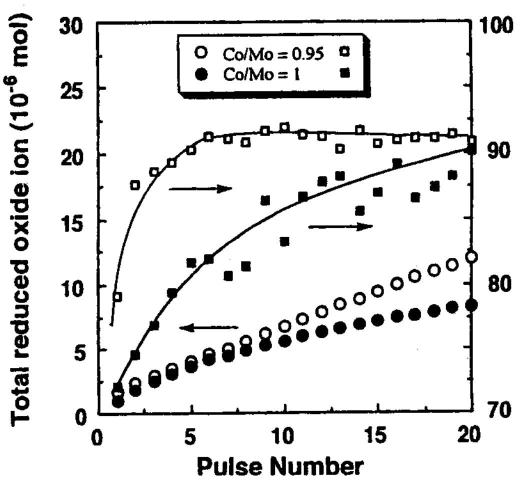

Fig. 6. Pulse reduction of Co-Mo-O catalysts with propane at 550 °C.

was detected in the effluent gas but no hydrogen, it is clear that lattice oxide ion is effective for the propene formation. Since the selectivity to propene increased with increasing number of propane pulse and then reached to the constant value, the reduced surface which means lower concentration of surface oxide ion is favorable for the selective formation of propene. The same results were obtained in the pulse reduction of magnesium-molybdenum mixed oxide catalysts [Yoon et al., 1995b]. This characteristic feature has been commonly observed in every catalytic oxidation of paraffinic hydrocarbons. In the oxidation of n-butane to maleic anhydride on $V_2P_2O_7$ catalyst, the reaction of n-butane without gaseous oxygen usually gives higher selectivity than the reaction in the presence of gaseous oxygen [Contractor et al., 1989].

3. The Role of MoO_3 Clusters Dispersed on the Catalyst Surface

As written earlier, the catalytic activity of cobalt- or magnesium-molybdenum mixed oxide catalyst depends strongly on the composition of the catalyst, especially around Co(Mg)/Mo=1 and several mixed oxide catalysts which include small amounts of excess molybdenum, e.g. $Co(Mg)_{0.95}MoO_X$, show higher catalytic activities. All these results suggest that small amounts of MoO_3 clusters dispersed on the stoichiometric binary oxides play some important role in the oxidative dehydrogenation of propane. In order to clarify the possibility, several supported catalysts, $MoO_3/Mg_{1.01}MoO_X$, and acid or base treated catalysts were prepared and their catalytic activities were examined in the reaction of propane. The results are shown in Figs. 7-9. As already written, the catalytic activity of $Mg_{1.01}MoO_X$ is not so high. As shown in Fig. 7, loading of small amounts of MoO_3 on the $Mg_{1.01}MoO_X$ increases its catalytic activity to some extent. The catalytic activity reaches maximum and further loading beyond 1.0 % is not so effective. The variation of the catalytic activity of $Mg_{0.95}MoO_X$ with the treatment time of aqueous NH_3 solution is shown in Fig. 8 and the effect of the treatment of aqueous acetic acid solution on $Mg_{1.05}MoO_X$ catalyst is also shown in Fig. 9. It was confirmed that a part of molybdenum in the surface layer of the catalyst was solved by the treatment of NH_3 solution and magnesium was done by acetic acid solution. The catalytic

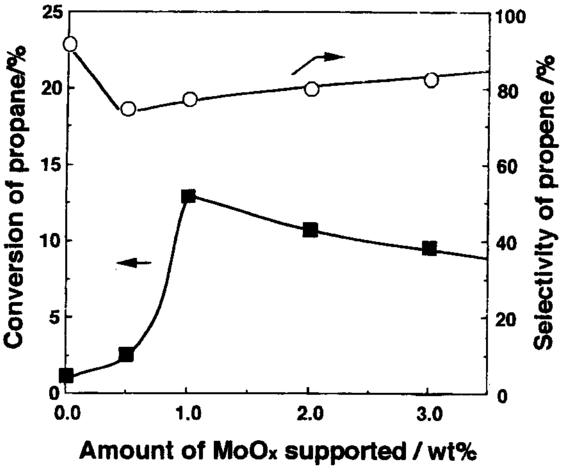

Fig. 7. Variation of the catalytic activity of $MoO_3/Mg_{1.01}MoO_X$ catalyst with loading amount of MoO_3 (Reaction temp.: 430 °C).

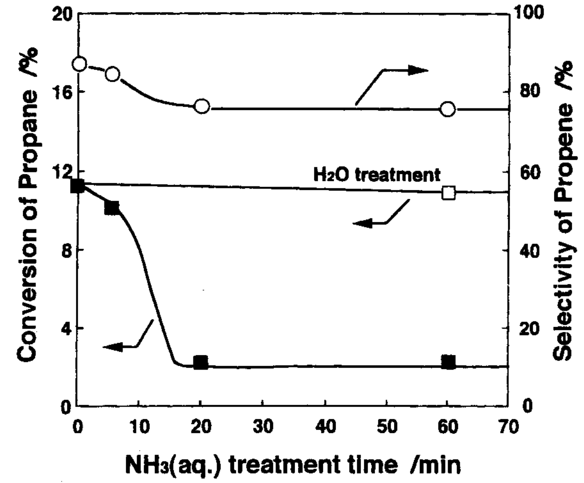

Fig. 8. Effect of the treatment of $Mg_{0.95}MoO_X$ catalyst with aqueous NH_3 solution on its catalytic activity (Reaction temp.: 480 °C).

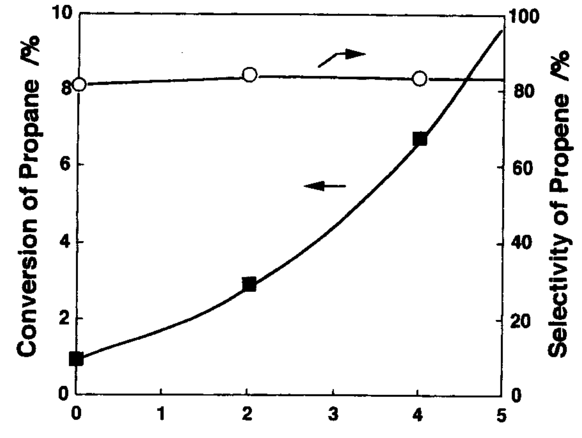

Fig. 9. Effect of the treatment of $Mg_{1.05}MoO_X$ catalyst with aqueous acetic acid solution on its catalytic activity (Reaction temp.: 480 °C).

activity of $Mg_{0.95}MoO_X$ clearly decreases by the removal of excess molybdenum and that of $Mg_{1.05}MoO_X$ increases with the removal of magnesium from the catalyst surface. All these facts suggest that the MoO_3 clusters dispersed on the catalyst surface play some important role in the catalysis. Further investigations on the detailed mechanism involving MoO_3 clusters are now in progress.

CONCLUSION

Cobalt- and magnesium-molybdenum mixed oxides show high catalytic activities for the oxidative dehydrogenation of propane to form propene. The catalytic activity depends strongly on the composition of the catalyst system and $Co(Mg)MoO_4$ having small amounts of free MoO_3 clusters dispersed on the catalyst surface shows the highest catalytic activity keeping higher selectivity to propene. It is suggested that the acidic site is involved in the rate-determining C-H bond cleavage. Lattice oxide ion is also involved into the reaction and more reduced surface is favorable for the selective formation of propene. MoO_3 clusters dispersed on the catalyst surface serve as a key active component for the reaction, though detailed mechanism involving them is still not clear.

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