An evidence of active surface MoO_x over $MgMoO_4$ for the catalytic oxidative dehydrogenation of propane

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In order to clarify whether $MgMo_xO_y$ catalysts with slight excess of molybdenum relative to the stoichiometric $MgMoO_4$ compound showed increased activities for propene formation in the propane oxidative dehydrogenation, we investigated the catalytic properties of MoO_3 supported on $MgMoO_4$ and of $MgMo_xO_y$ catalysts treated with acid or base. Supporting MoO_3 on magnesium-rich $MgMo_{0.99}O_y$ catalysts which are poorly active, or treating them with acetic acid to remove excess magnesium, resulted in drastic activity increases. On the other hand, the ammonia treatment of molybdenum-rich $MgMo_{1.05}O_y$ catalysts which are highly active turned out to give a remarkable decrease in activity, because surface MoO_x dissolved in ammonia water. A clear correlation was observed between the catalytic activities for propane oxidation and the dehydration of 2-propanol to propene over the supported catalyst and the treated catalysts. Since the bulk structures were unchanged by supporting or by the treatments, the existence of MoO_x clusters formed on the surface of $MgMoO_4$ are responsible for the activities in the oxidative dehydrogenation of propane.

Keywords: metal molybdate, MoO_x clusters, oxidative dehydrogenation, propane, acidic property

1. Introduction

The functionalization of alkanes by catalytic oxidation processes with molecular oxygen has recently been of great interest in solid-state catalysis chemistry [1]. Among them the catalytic oxidative dehydrogenation of propane has been extensively investigated and many catalysts and processes have been reported so far [2–6]. Mostly the catalysts are based on V_2O_5 [2]. We, on the other hand, have investigated a variety of metal molybdate catalysts for the oxidative dehydrogenation of propane and found that most of the molybdates tended to show higher selectivity to propene and among them cobalt and magnesium molybdate catalysts revealed pronounced activity [7–9]. Cadus et al. are also interested in magnesium molybdate catalysts and reported interesting results recently [10–12]. The most characteristic point in this magnesium molybdate catalyst system is that $MgMo_xO_y$ catalysts with slight excess of molybdenum relative to the stoichiometric $MgMoO_4$ compound showed pronounced activities for propene formation in the propane oxidative dehydrogenation, as reported in our previous paper [9]. The pure stoichiometric $MgMoO_4$ compound was intrinsically inactive, so that the results suggest the surface excess MoO_3 plays important roles in the catalytic activation of propane and molecular oxygen. In order to confirm the roles of the surface excess MoO_3, we prepared MoO_3 supported on the $MgMoO_4$ and $MgMo_xO_y$ catalysts treated with acid or base for removing either surface Mo or Mg. In this Letter, we will clearly demonstrate the importance of the surface excess MoO_3 for the oxidative dehydrogenation of propane.

2. Experimental

2.1. Catalyst preparation

$MgMo_xO_y$. Magnesium molybdates having various compositions were prepared from aqueous solutions containing desired amounts of magnesium nitrate and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$. After mixing each solution and adding ammonium hydroxide the precipitates were carefully solidified by evaporation of water with stirring at 80°C. The resulting solid was calcined in air at 300°C for 3 h. The calcined solid was ground into a fine powder and calcined again for 9 h at 600°C. Chemical compositions of the prepared catalysts were calculated on the basis of the amounts of the starting chemicals in the preparation.

Supported catalyst. Two methods were employed: (1) the prepared $MgMo_{0.99}O_y$ was immersed in a benzene solution of $Mo(CO)_5$ and dried by evaporation of benzene at 40°C, (2) the prepared $MgMo_{0.99}O_y$ was immersed in an aqueous solution of

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$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ and dried by evaporation of water at 40°C. The loading amount of MoO_3 was 1 wt% in both cases. The catalyst prepared by the former method is denoted by 1 wt% $MoO_3/MgMo_{0.99}O_y$[CO] and the latter by 1 wt% $MoO_3/MgMo_{0.99}O_y[Mo_7]$. Both samples were calcined in air at 500°C for 2 h prior to the reaction.

Acid-base treated catalysts. The prepared $MgMo_{1.05}O_y$ was immersed in a solution of ammonium in water (25%) for 1 h at room temperature and then filtered, washed with acetone, and dried at 150°C for 12 h. It was confirmed by XRF that molybdenum was dissolved in the ammonium solution. The same procedure was applied for the prepared $MgMo_{0.95}O_y$ with neat acetic acid instead of ammonia for removing surface magnesium. The catalyst prepared by the former method is denoted by $MgMo_{1.05}O_y[NH_3]$ and the latter by $MgMo_{0.95}O_y$[Acid].

2.2. *Catalytic oxidation procedure and characterization*

The procedure and reaction apparatus have been reported in our previous reports [7–9]. Briefly, the propane oxidation was carried out at an atmospheric pressure in a conventional flow system equipped with a tube reactor. 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 reaction temperature was 380–480°C and the space velocity was 810 cm^3 $g\text{-}cat^{-1}$ h^{-1}. The feed and products were analyzed by an on-line gas chromatograph operating with two sequential columns (a molecular sieve 13X 1 m, 40°C for the separation of O_2, N_2, and CO, and Gaskuropak 54 6 m, 60–160°C for hydrocarbons and CO_2).

Phases of the prepared catalysts were identified by XRD measurements. Surface area of the catalyst powder was measured by the BET method of nitrogen adsorption at liquid nitrogen temperature. In the experiment of 2-propanol reaction, 6 μmol of 2-propanol was reacted by the pulse reaction method over the catalyst (20 mg) at 300°C and the products were analyzed by an on-line gas chromatograph with a column of PEG 20M, 3 m at 70°C.

3. Results and discussion

Activity of the supported catalysts

The catalytic activity and selectivity to propene formation in the oxidation of propane over MoO_3 supported on $MgMo_{0.99}O_y$ are compared with that over the $MgMo_{0.99}O_y$ catalyst in figure 1. The results were summarized along with the surface area. Most of the catalysts predominantly promoted the oxidative dehydrogenation of propane to propene. Products besides propene at higher conversions are carbon oxides, and the formation of oxidized products such as acrolein was extremely small. About 80% selectivity to propene was achieved irrespective of the catalysts. However, the activity for the propane oxidation is largely different: The reaction rate of propane over the 1 wt% $MoO_3/MgMo_{0.99}O_y[Mo_7]$ catalyst was ten times higher than that over the $MgMo_{0.99}O_y$ catalyst. A similar activity increase was also observed on the 1 wt% $MoO_3/MgMo_{0.99}O_y$[CO] catalyst but was not so remarkable as observed on the 1 wt% $MoO_3/MgMo_{0.99}O_y[Mo_7]$ catalyst. This is simply due to the surface area difference as shown in figure 1; the reaction rates per unit surface area on both the supported catalysts were exactly the same. Again figure 1 apparently shows that the reaction rate per unit surface area on the supported catalysts is one and half times higher than that on the non-supported catalyst. Since neither the surface area nor the activity changed by processing the $MgMo_{0.99}O_y$ sample without any molybdenum sources in the supporting procedure, it is obvious that surface molybdenum oxide species intro-

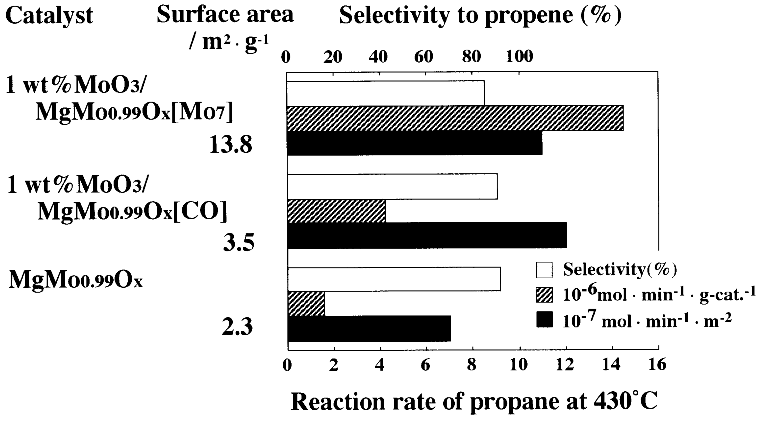

Figure 1. Comparison of the catalytic activity and selectivity of $MgMo_{0.99}O_y$ and $MoO_3/MgMo_{0.99}O_y$ for the oxidative dehydrogenation of propane at 430°C.

duced by the loading on the $MgMo_xO_y$ are responsible for the selective oxidative dehydrogenation of propane to propene.

We observed that the activity of the $MgMo_{0.99}O_y$ catalyst increased markedly with increasing the MoO_3 loading up to 1 wt%, but further loadings caused deceases in the activity. Since the 1 wt% loading corresponds to less than double monolayer coverage with MoO_3, the results suggest that a cluster type of the surface molybdenum oxide is necessary for the oxidation of propane and that a crystalline MoO_3 is ineffective. In addition, the observed dependency on the loading amount is consistent with the composition effect of the $MgMo_xO_y$ catalysts on the activity that was reported in our previous paper [9]. Therefore, such active surface molybdenum oxide species are formed on the active $MgMo_xO_y$ catalysts during the preparation by coprecipitation and even on the slightly magnesium-rich $MgMo_xO_y$ catalyst the formation of the surface species is considered to take place to some extent, because this $MgMo_xO_y$ catalyst showed activity.

In order to further demonstrate the importance of the surface molybdenum oxide cluster species, we conducted two experiments of surface treatments with acid or base; one is the removal of surface molybdenum on the active $MgMo_{1.05}O_y$ catalyst with ammonia water treatment to get a magnesium-rich surface, whereby an activity decrease can be expected, and the other is the removal of surface magnesium on the inactive $MgMo_{0.95}O_y$ catalyst with acetic acid treatment to get a molybdenum-rich surface, whereby an activity increase can be expected. The results are shown in figure 2. As reported earlier, the catalytic activity of the $MgMo_{1.05}O_y$ sample is high, but on the other hand the $MgMo_{0.95}O_y$ catalyst is almost inactive for the oxidative dehydrogenation of propane. When the active $MgMo_{1.05}O_y$ catalyst was treated with ammonia ($MgMo_{1.05}O_y[NH_3]$), the activity remarkably decreased as expected, although the surface area increased largely. It was confirmed that neither the surface area nor the activity changed by treating the $MgMo_{10.5}O_y$ with pure water. When the inactive $MgMo_{0.95}O_y$ catalyst was treated with acetic acid ($MgMo_{0.95}O_y$[Acid]), the activity prominently increased as expected too. The surface area decreased slightly. By comparing the activity per unit surface area, the activity changes by the treatments are very drastic, whereas the selectivity to propene was not affected much. All these results strongly support the substantial role of the surface molybdenum oxide cluster on selectively oxidizing propane, although it should be taken into consideration that such surface treatments are often accompanied with unknown surface modifications or changes which might cause activity changes.

One of the things that cause ambiguity in the discussion is a structural effect. As reported in our previous paper [9], two structural phases were observed in the catalysts prepared by coprecipitation; one is β-$MgMoO_4$ which belongs to the entire group of tetrahedral molybdates isotypic to α-$MnMoO_4$ and the other is α-$MgMoO_4$ which is isotypic to α-$ZnMoO_4$ having a distorted tetrahedral coordination around molybdenum. As shown in figure 3, where the propane conversions are plotted against the bulk phase composition, β-phase-rich $MgMoO_4$ catalysts tend to show higher activity than α-phase-rich $MgMoO_4$ catalysts. Therefore, one would assume that the supporting effect and the acid–base treatment effect described above are regarded as structural effects. However, fortunately the initial structural phases were kept completely after loading and treating in each case irrespective of the phase compositions, so that it is strictly concluded that the bulk structures have no influence on the catalytic properties of the surface molybdenum oxide cluster species.

It is now necessary to know whether the surface molybdenum oxide cluster species are the only major and common active sites for the propane oxidation in all the $MgMo_xO_y$ catalysts or not. To get an insight in this we have investigated surface properties of the catalysts using 2-propanol dehydration as a test reaction. The results are summarized in figure 4, where the formation

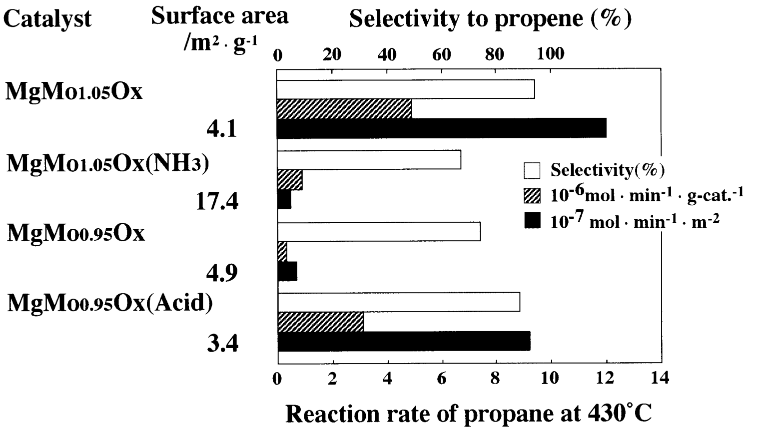

Figure 2. Changes of the catalytic activity and selectivity of $MgMo_xO_y$ by the treatments with ammonia or acetic acid.

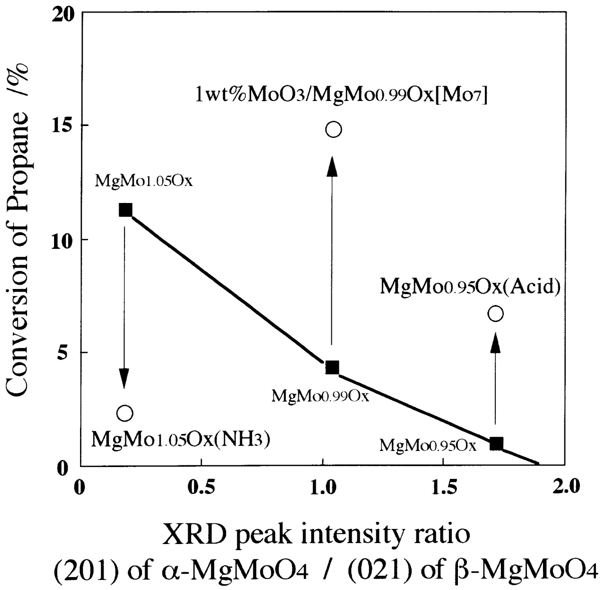

Figure 3. Comparison of the propane conversion (450°C) over $MgMo_xO_y$ catalysts having different bulk-phase compositions. The prepared catalysts by coprecipitation (■) and their treated catalysts by supporting or with acid and base (○).

rate of propene in the propane oxidation was plotted against the formation rate of propene in the 2-propanol dehydration. The main product in the 2-propanol reaction was propene over all the catalysts, and the formation of acetone was very little, indicating that the surface of the catalysts has mainly acidic property. As reported previously, a clear linear relationship was observed between the oxidation activity and the surface acidity for the catalyst prepared by the coprecipitation. It was found in the present study that all the supported catalysts and the treated catalysts obeyed exactly this linear relationship observed for the catalyst prepared by coprecipitation, indicating that the surface molybdenum oxide species are the common active sites for the propane oxidation in the $MgMo_xO_y$ catalyst system. Furthermore, it was observed by a separate NH_3 TPD experiment that all the $MgMo_xO_y$ catalysts showed a quite similar desorption profile irrespective of the preparations and the treatments. Therefore, the formation rate of propene in the 2-propanol dehydration is considered to be determined by the concentration of surface acidic sites. This means that the catalysts with different activities for the propane oxidation do not have different active sites but different numbers of active sites, and hence the surface molybdenum oxide cluster species are considered the only major active sites for the propane oxidation in the $MgMo_xO_y$ catalysts.

In the oxidative dehydrogenation, propane may first react by breaking a methylene C–H bond to form an adsorbed isopropyl 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, therefore, is the breaking of a methylene C–H bond of propane on the catalyst surface. The surface molybdenum oxide cluster species seems to be involved in this step. Presumably, an oxygen-deficient molybdenum oxide cluster formed by dehydra-

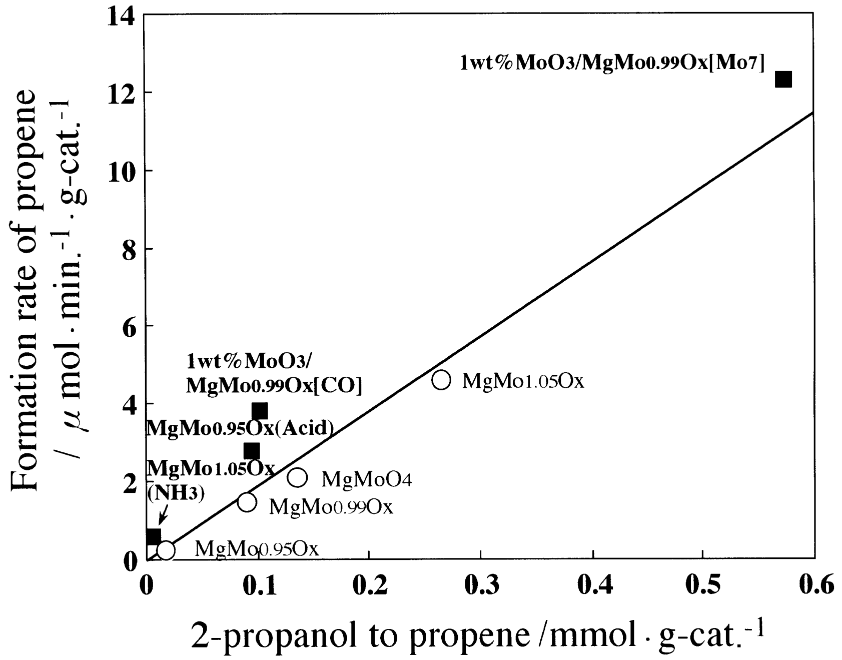

Figure 4. Linear relationship between the catalytic activities of various $MgMo_xO_y$ for the oxidative dehydrogenation of propane (430°C) and for the 2-propanol dehydration (300°C).

tion under the catalytic oxidation conditions provides a Lewis acid site abstracting hydride from propane.

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