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Selective oxidative dehydrogenation of propane over surface molybdenum-enriched $MgMoO_4$ catalyst

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Abstract

Drastic activity increases were observed by the treatments of the magnesium-rich $MgMo_{0.99}O_y$ catalysts, which are poorly active for the oxidative dehydrogenation of propane, with inorganic or organic acid to remove excess magnesium on the surface. MoO_3 loading on magnesium-rich $MgMo_{0.99}O_y$ catalysts also resulted in drastic activity increases. The activity increases followed non-effective loadings of MoO_3 in the range 0–2 wt%, because it is necessary to neutralize the surface magnesium with MoO_3 before the formation of molybdenum-rich surface. The pH of the aqueous $(NH_4)_6Mo_7O_{24}$ solution for the MoO_3 loading apparently influenced the activity. Under the acidic conditions the MoO_3 loading resulted in the drastic activity increase but under the basic conditions the effect of the MoO_3 loading was poor, suggesting that a cluster-type MoO_3 on $MgMoO_4$ surface is responsible for the activity of propane oxidative dehydrogenation. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The catalytic oxidative dehydrogenation of propane has been extensively investigated and many catalysts and processes have been reported so far [1–11]. Recently we have investigated a variety of metal molybdate catalysts for the oxidative dehydrogenation of propane and found that most of the molybdates tended to show a high selectivity to propene and among them cobalt and magnesium molybdate catalysts revealed pronounced activity [12,13]. The most characteristic point in this magnesium molybdate catalyst system is that $MgMo_xO_y$ catalysts with slightly excess amount of molybdenum from stoichiometric $MgMoO_4$ compound showed pronounced activities for propene formation in the propane oxidative dehydrogenation, as reported in our previous papers [14]. Since the pure stoichiometric $MgMoO_4$ compound was intrinsically inactive, it was suggested that the surface excess MoO_3 plays important roles in the catalytic activation of propane and molecular oxygen, and in fact we were able to demonstrate in our recent paper [15] the roles of the surface excess MoO_3 in the oxidative dehydrogenation of propane. Here in this paper, we further demonstrate the importance of the surface excess MoO_3, particularly in the

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form of molybdenum oxide cluster, for the oxidative dehydrogenation of propane.

2. Experimental

2.1. Catalyst preparation and characterization

$MgMo_xO_y$. 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 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. The prepared $MgMo_{0.97}O_y$ and $MgMo_{0.99}O_y$ were immersed in an aqueous solution of $(NH_4)6Mo_7O_{24}\cdot 4H_2O$ under controlled pH conditions and dried up by evaporation of water at 40°C. Adjustment of pH was carried out using ammonia water and acetic acid. The loading amount of MoO_3 was varied in the range 0–4 wt%. The samples were calcined in air at 500°C for 20 h prior to the reaction.

Acid-treated catalysts. For removing surface magnesium, the prepared $MgMo_{0.97}O_y$ and $MgMo_{0.99}O_y$ were immersed in concentrated nitric acid, an aqueous solution of ascorbic acid (0.38 M), or acetic acid (neat) for desired hours at room temperature and then were filtered, washed with water, and dried at 150°C for 12 h. The samples were calcined in air at 500°C for 2 h prior to the reaction.

Phases of the prepared catalysts were identified by XRD measurement. Surface area of the catalyst powder was measured by BET method of nitrogen adsorption at liquid nitrogen temperature.

2.1.1. Catalytic oxidation procedure

The procedure and reaction apparatus have been reported in our previous reports [12]. 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 1620 cm^3 g-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).

3. Results and discussion

3.1. Effect of acid treatment on the catalytic activity of $MgMo_xO_y$

In order to create a molybdenum-rich surface on the $MgMo_xO_y$ catalyst, we conducted surface treatments of inactive $MgMo_{0.95}O_y$ and $MgMo_{0.97}O_y$ catalysts with inorganic or organic acid in aqueous conditions. By this treatment surface magnesium on the inactive catalysts will be removed, forming a molybdenum-rich surface, and then an activity increase could be expected since the $MgMo_xO_y$ catalysts with slightly excess amount of molybdenum from stoichiometric $MgMoO_4$ compound showed pronounced activities for propene formation in the propane oxidative dehydrogenation as reported previously [14]. The results of the acid treatment are shown in Table 1. As reported earlier [14] the $MgMo_{0.95}O_y$ catalyst and the $MgMo_{0.97}O_y$ catalyst are almost inactive or very poorly active for the oxidative dehydrogenation of propane. When the inactive $MgMo_{0.95}O_y$ catalyst was treated with acetic acid for 2 h, the activity apparently increased as expected, whereas the selectivity to propene was not affected much. Products besides propene at higher conversions are carbon oxides, and the formations of oxidized products such as acrolein were extremely small. When the catalyst was treated in acetic acid longer, the activity increased more. The surface area decreased slightly by this treatment and therefore, by comparing the activity per unit surface area, the activity changes by the treatments are much drastic. It was confirmed that neither the surface area nor the activity changed by treating the $MgMo_{0.95}O_y$ with pure water. Similar acid-treatment effects were also observed by using nitric acid and ascorbic acid as shown in Table 1. In these cases increases of the

Table 1
Effect of acid treatment on the catalytic activity of $MgMo_xO_y$

Acid	Sample	Treatment time (h)	Propane oxidation (480°C)			Surface area ($m^2\ g^{-1}$)
			Conversion of C_3H_8 (%)	Selectivity to C_3H_6 (%)	Rate of propene formation (μmol $min^{-1}\ m^{-2}$)	
	$MgMo_{0.97}O_x$	0	2.0	84.5	1.2	3.2
HNO_3	$MgMo_{0.97}O_x$	0.02	10.4	76.2	2.1	8.3
Ascorbic acid	$MgMo_{0.97}O_x$	0.5	12.4	81.0	2.4	9.3
	$MgMo_{0.95}O_x$	0	0.5	81.7	0.2	4.9
Acetic acid	$MgMo_{0.95}O_x$	2	1.5	85.0	—	—
Acetic acid	$MgMo_{0.95}O_x$	4	3.4	82.2	1.8	3.4

surface area were prominent, so that the propane conversion over these treated $MgMo_{0.97}O_y$ catalysts were very high. But again drastic activity increases by the treatments can be seen by comparing the activity per unit surface area. The selectivity to propene of the catalyst treated with nitric acid was slightly lower than the others, probably due to strong acid sites generated by quick removal of surface magnesium from the catalyst with nitric acid.

All the above results and the reported result [15] that the activity of the active $MgMo_{1.05}O_y$ catalyst remarkably decreased when treated with ammonia to remove surface excess molybdenum, strongly support the substantial role of the surface molybdenum oxide on selectively oxidizing propane. One of the things that cause ambiguity in the discussion of the activity increase is a structural effect. There are two observed structural phases in the catalysts prepared by the 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. Both the $MgMo_{0.95}O_y$ catalyst and the $MgMo_{0.97}O_y$ catalyst were α-phase rich and fortunately the initial structural phase compositions were kept completely after the acid-treatments 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 and so that the state of surface excess molybdenum oxide seems to be very important for the oxidation activity and propene selectivity. We, therefore, further testified the importance of the surface molybdenum oxide by demonstrating effects of MoO_3 loading on the inactive $MgMo_xO_y$ catalysts on the oxidation ability.

3.2. *Effect of MoO_3 loading on $MgMo_xO_y$ catalysts*

The catalytic activity and selectivity to propene formation in the oxidation of propane over the MoO_3 loaded $MgMo_{0.97}O_y$ and $MgMo_{0.97}O_y$ catalysts are shown in Figs. 1–3, where the effect of loading amount of MoO_3, temperature dependencies of the propane oxidation over the MoO_x loaded catalysts under various pH conditions, and the influence of pH condition during the loading on the rate of propene formation, respectively, are presented. Most of the MoO_3 loaded catalysts predominantly promoted the

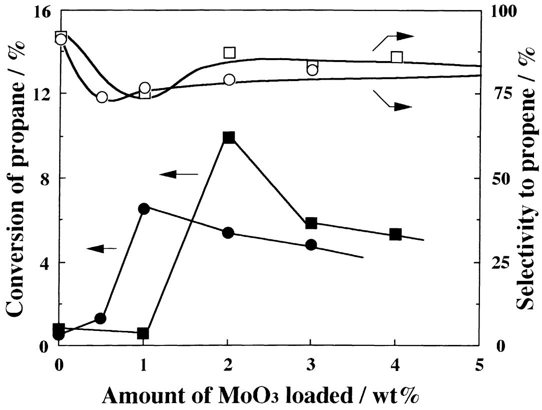

Fig. 1. Catalytic performance of MoO_3 loaded $MgMo_{0.97}O_x$ catalyst ((■) conversion, (□) selectivity) and $MgMo_{0.99}O_x$ catalyst ((●) conversion, (○) selectivity) for the oxidative dehydrogenation of propane at 430°C. MoO_3 was supported at pH=5 condition.

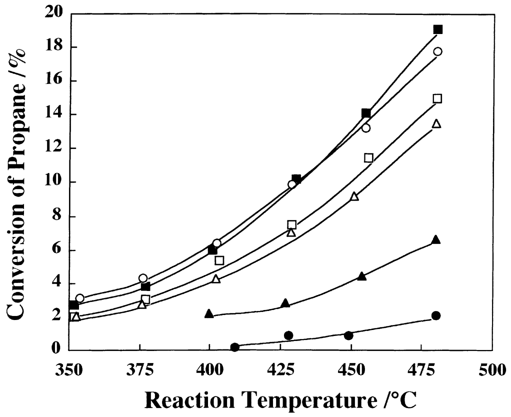

Fig. 2. Comparison of the propane conversions at different reaction temperatures over $MgMo_{0.97}O_y$ (▲), $MgMo_{1.05}O_y$ (●), and 2 wt% $MoO_3/MgMo_{0.97}O_y$ catalysts prepared under different pH conditions ((□) pH=4, (○) pH=5, (■) pH=7, (△) pH=8.5).

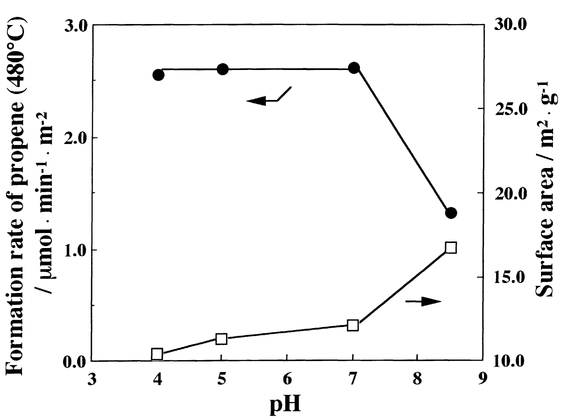

Fig. 3. Influences of pH condition in the preparation of 2 wt% $MoO_3/MgMo_{0.97}O_y$ catalyst on the formation rate of propene (●) in the oxidative dehydrogenation of propane at 480°C and surface area (□).

oxidative dehydrogenation of propane to propene. About 80% selectivity to propene was achieved irrespective of the loading amount of MoO_3 and the preparative pH condition. However, the activity for the propane oxidation is largely different: We observed that the activity of the $MgMo_{0.99}O_y$ catalyst did not change by the MoO_3 loading of 0.5 wt% but increased markedly with increasing the MoO_3 loading of 1 wt% and further loadings caused deceases in the activity as shown in Fig. 1. Similarly the activity of the $MgMo_{0.97}O_y$ catalyst did not change by the MoO_3 loading up to 1 wt% but increased markedly with increasing the MoO_3 loading of 2 wt% and further loadings caused deceases in the activity. Obviously the catalyst having the higher content of magnesium needs the higher loading of MoO_3 to be active, which simply implies that a molybdenum-enriched surface can be achieved by the excess addition of MoO_3 after the neutralization of surface magnesium with added MoO_3. Since the 1 wt% loading corresponds to less than double monolayer coverage with MoO_3, a cluster type of the surface molybdenum oxide is formed by the excess addition, where the high oxidation ability appears. Too much loadings of MoO_3 seem to result in the formation of MoO_3 crystallites which is obviously ineffective for the propane oxidation. That is the reason for the maximum activity observed in Fig. 1.

To get an insight about whether the surface molybdenum oxide cluster species are really active sites for the propane oxidation in the $MgMo_xO_y$ catalysts or not, we have investigated influences of pH condition during the loading of MoO_3 on the catalytic activity. As shown in Figs. 2 and 3, when MoO_3 was loaded under a basic condition, the resulting catalyst was definitely poor both in the propane conversion and in the rate of propene formation per surface area. On the other hand, the loading of MoO_3 at the pH range from neutral to acidic brought about highly active catalysts and interestingly the attained activities in terms of the formation rate of propene per surface area are almost constant irrespective of the pH value adjusted, as can be seen in Fig. 3. This result is interpreted as follows: since molybdenum oxo-anion in a basic aqueous solution is monomeric while polymeric in an acidic condition, the state of molybdenum oxide supported under a basic condition will be monomeric while under an acidic condition will be polymeric, in other words, of cluster type, if it can be assumed that the monomeric or polymeric molybdenum oxo-anion in the solutions is supported on the $MgMo_xO_y$ surface as it is. The fact seems to happen by this process and therefore it is reasonable to conclude that a cluster state of surface molybdenum oxide is responsible for the activity and selectivity of the $MgMo_xO_y$ catalysts for the propane oxidative dehydrogenation. This conclusion leads at the same time to an additional explanation about the effect of acid treatment (Table 1); that is, the activity increase by the treatment results not only from the molybdenum-enrichment by the removal of surface magnesium but also from the clustering of surface molybdenum oxide by action of the acid during the acid treatment.

The observed dependency on the loading amount in Fig. 1 is consistent with the composition effect of the $MgMo_xO_y$ catalysts on the activity, where $MgMo_xO_y$ catalysts with slightly excess amount of molybdenum from stoichiometric $MgMoO_4$ compound showed maximum activities for propene formation in the propane oxidative dehydrogenation [14]. Therefore, it can be speculated that the surface becomes molybdenum-enriched during the preparation of the active $MgMo_xO_y$ catalysts by coprecipitation and the active cluster-type molybdenum oxide species are formed. However, the generation of this active surface state is much effectively carried out by the MoO_3 loading, as presented in Fig. 2. The propane conversion over the 2 wt% $MoO_3/MgMo_{0.99}O_y$ catalyst was about three times higher than that over the $MgMo_{1.05}O_y$ catalyst at any reaction temperatures. We, therefore, believe that much active and selective catalysts based on molybdenum oxide for the oxidative dehydrogenation of propane are obtainable by the preparative and treatment procedure described in this paper.

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