Oxidative dehydrogenation of propane over magnesium molybdate catalysts

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Catalytic activities of magnesium molybdates were investigated for the oxidative dehydrogenation of propane with and without molecular oxygen under atmospheric pressure. Catalytic properties drastically changed with the catalyst composition, and it turned out that $Mg_{0.95}MoO_x$ catalysts having slight excess molybdenum showed the highest activity in the oxidative dehydrogenation of propane, which gave 61% selectivity to propene at 22% conversion of propane at 515°C. The catalytic activities strongly depended on the acidic properties of the catalysts. It was also revealed that the lattice oxide ions of the catalysts participated as an active oxygen in the oxidative dehydrogenation of propane.

Keywords: magnesium molybdates; oxidative dehydrogenation of propane; acidic properties; lattice oxide ions

1. Introduction

There is an increasing interest in the potential use of propane as a source of propene, which is an important starting material in the petrochemical industry [1]. The oxidative dehydrogenation of propane to propene is a promising reaction, because the reaction is thermodynamically feasible and can be carried out without carbon deposition problems [2].

Several catalysts and processes have been reported thus far for the oxidative dehydrogenation of propane to propene, including vanadium-based oxides [3–5], molybdenum-based oxides [6,7], and other oxide catalysts [8]. In a previous paper [6], we showed that various metal molybdate catalysts, including $MgMoO_4$, were highly active and selective for the oxidative dehydrogenation of propane to propene and the catalytic performances of $CoMoO_4$ and $MgMoO_4$ were comparable to those of other reported catalysts, such as V_2O_5–MgO and V_2O_5–Nb_2O_5 [1,2].

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In the present investigation, catalytic activities of magnesium molybdate catalysts of various compositions for the oxidative dehydrogenation of propane and their surface acidic properties are studied in detail. Furthermore, the involvement of lattice oxide ions in the oxidative dehydrogenation of propane is investigated by pulse reduction of the catalysts.

2. Experimental

2.1. CATALYST PREPARATION

Magnesium molybdate catalysts with various Mg/Mo ratios were prepared from aqueous solutions of appropriate amounts of magnesium nitrates with $pH = 2$ and ammonium paramolybdate with $pH = 9$. After mixing each solution, precipitates formed were solidified by evaporation of water at 80°C. The pH of the mixed solution was kept at ca. 5. The resulting slurry was dried at 110°C for 20 h and calcined stepwise at 200, 250 and 300°C for 0.5, 0.5 and 3 h in air. The resulting solid was ground into a fine powder and calcined again for 9 h at 600°C. The molybdenum oxide catalyst was prepared by the calcination of an ammonium paramolybdate under the above calcination conditions. The magnesium oxide catalyst was prepared by calcining magnesium hydroxide at 700°C for 3 h. Molybdenum oxide supported on silica gel (10 wt%) was prepared by the impregnation method. All catalysts were used in the form of powders of 100–200 mesh after dilution with quartz chips.

Chemical compositions of the catalysts were calculated on the basis of the amounts of the starting chemicals in the preparation. Phases of the catalysts were identified by XRD (Rigaku diffractometer RAD-1VB, Cu Kα) measurements. Surface area of the catalyst powder was measured by the BET method of nitrogen adsorption at liquid nitrogen temperature.

2.2. REACTION SYSTEM

Propane oxidation with molecular oxygen was carried out at an 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 of the reactor, except the catalyst zone, was minimized to prevent gas phase reactions. The standard conditions for the oxidation are as follows: the feed composition was 18 mol% of propane, 7 mol% of oxygen, the remainder being nitrogen. 4 g of the catalysts with 2 g of quartz chips were mounted in the middle of the reactor. The reaction temperature was varied in the range of 360–520°C and the space velocity was 810 cm^3 $g\text{-}cat^{-1}$ h^{-1}. Although a propane conversion of 0.5% was observed without catalysts at 520°C, this is considered negligible. The feed and products were analyzed by an on-line gas chromatograph operating with two sequential columns. A molecular sieve 13X, 1 m was used at 40°C to separate O_2, N_2, and CO, and a Gaskuropak 54, 6 m was used with increasing temperature from 60 to 160°C to separate the hydrocarbons, oxygen containing products and CO_2.

To investigate the acidity and basicity of the catalysts, 2-propanol dehydration/dehydrogenation (IPA reaction), which is the well-known method of acidity/basicity measurements, was carried out in a conventional pulse equipment using the TCD cell of a gas chromatograph. A PEG A20M, 3 m column was used for analysis and 6.5 μmol of 2-propanol was reacted 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 microreactor 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 min^{-1}) and reacted with lattice oxide ions of the catalyst (20 mg) at 550°C. The products were analyzed by on-line gas chromatography with a Unibeads 1S, 1 m column at 140°C.

3. Results and discussion

3.1. OXIDATIVE DEHYDROGENATION OF PROPANE OVER MAGNESIUM MOLYBDATE CATALYSTS

Table 1 shows the catalytic properties of various magnesium molybdate catalysts in the oxidative dehydrogenation of propane. The Mg/Mo ratio of the magnesium molybdate catalysts was varied in the range from 0 to 1.3. The catalyst system was composed of various complex oxides. At Mg/Mo = 0, the phase of the catalyst was MoO_3. Between Mg/Mo = 0 and 0.8, the catalyst was composed of MoO_3 and $Mg_2Mo_3O_{11}$ phases [9]. From Mg/Mo = 0.8 to 1.0, β-$MgMoO_4$, which has tetrahedral coordination around molybdenum and of which the structure is isotypic to α-$MnMoO_4$ [10], appeared with a small amount of $Mg_2Mo_3O_{11}$. Around Mg/Mo = 1, the phase formation is very critical, strongly depending on the preparation conditions. Just below the Mg/Mo ratio of 1, only the β-$MgMoO_4$ phase was formed and just above Mg/Mo = 1, the crystalline part of the catalyst consisted of α-$MgMoO_4$, of which the structure is isotypic to α-$ZnMoO_4$ and which has distorted tetrahedral coordination around molybdenum [11,12], and a small part of the β-$MgMoO_4$ phase. No MgO phase was detected, even at Mg/Mo = 1.3, by the XRD measurements.

As shown in table 1, the conversion of propane drastically changed depending on the chemical composition of the catalyst. Especially, when the Mg/Mo ratio exceeded 1 from the higher ratio, the catalytic activity steeply increased and then decreased in the narrow range of the Mg/Mo ratio. The products, besides propene, were CO_2, CO and small amounts of C_2H_4 and acrolein. The selectivity to propene

Table 1
Catalytic performance of various magnesium molybdates in the oxidative dehydrogenation of propane

Catalysts	Surface area ($m^2\ g^{-1}$)	Phase[b]	Reaction temp. (°C)	Conversion of propane (%)	Selectivity (%) to	
					propene	CO_x
MoO_3	0.3	MoO_3	480	0.0	–	–
$Mg_{0.5}MoO_x$	1.3	M, MoO_3	480	2.0	90	10
$Mg_{0.83}MoO_x$	2.9	M, B	480	9.7	75	23
$Mg_{0.95}MoO_x$	2.9	M, B	363	1.1	100	–
			388	1.8	96	4
			416	3.4	95	5
			442	6.1	85	15
			469	10.9	79	19
			480	12.5	74	23
			497	16.7	70	27
			515	22.0	61	35
$MgMoO_4$	4.2	A, B	480	6.0	75	23
$Mg_{1.03}MoO_x$	6.0	A, B	480	1.2	77	23
$Mg_{1.1}MoO_x$	7.9	A, B	480	0.4	65	35
$Mg_{1.3}MoO_x$	8.2	A, B	480	0.7	64	36
MgO	28.0	MgO	480	2.7	27	73
MoO_3/SiO_2[a]	–	MoO_3, S	455	9.7	17	60

[a] 10 wt% MoO_3/SiO_2.

[b] M = $Mg_2Mo_3O_{11}$; B = β-$MgMoO_4$; A = α-$MgMoO_4$; S = SiO_2.

decreased slightly with increasing content of magnesium, whereas the surface area increased. It turned out that the activity of $Mg_{0.95}MoO_x$ was highest for the propene formation and about 30 times higher than that of $Mg_{1.1}MoO_x$. Typical catalytic performance data obtained with the $Mg_{0.95}MoO_x$ catalyst at various reaction temperatures are also listed in table 1. The reaction of propane took place at about 360°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, a selectivity to propene of 61% was achieved at 22% conversion over the $Mg_{0.95}MoO_x$ catalyst at 515°C.

Like the pure MgO catalyst, which has no activity, the pure crystalline MoO_3 catalyst is also neither active nor selective in the oxidative dehydrogenation of propane under the reaction conditions. Since the MoO_3 catalyst has an extremely low surface area of less than 1 $m^2\ g^{-1}$, the MoO_3 catalyst supported on SiO_2 (10 wt%) was tested for the propane oxidation. As shown in table 1, this catalyst showed a high activity (9.7% conversion), but very low selectivity to propene of 17% at 455°C. Therefore, these pure metal oxides, MoO_3 and MgO, are inactive and non-selective phases for this reaction, whereas mixed metal oxides appeared to be active and selective for the catalytic oxidation.

Doroshenko et al. have studied the catalytic properties of several metal molybdates in the oxidative dehydrogenation of *n*-butane in the absence of gas phase oxygen. They found that the selectivity for the dehydrogenation products was highest on $MgMoO_4$, although the activity was low [13]. Stepanov et al. have tested the catalytic activity of binary oxide systems including the $MgMoO_4$–MoO_3 system in the *n*-butane oxidative dehydrogenation. They observed that the catalysts with atomic ratio $Mg/Mo > 1$ were most active and selective for the butadiene formation [14], which is completely different from our results described above. On the other hand, catalytic properties of the $MgMoO_4$–MoO_3 system containing various amounts of MoO_3 have been also studied in the oxidative dehydrogenation of ethylbenzene into styrene by Oganowski et al. [15]. They showed that the most active catalysts in the reaction were those which contain an excess of 1–3% of molybdenum trioxide. In addition, they reported that the active catalysts form a two-component solid solution $MgMoO_4$–MoO_3 where the main $MgMoO_4$ phase having a tetrahedral structure acts as a "carrier" of the active octahedral MoO_3 phase. Hasegawa et al. [16] also suggested that distorted MoO_x^{n-} polyhedra formed on the surface when the magnesium molybdates have excess molybdenum. The same situation may be present in our highly active $Mg_{0.95}MoO_x$ catalyst for the oxidative dehydrogenation of propane to propene. Molybdenum oxide or its polyhedra on the surface of the catalysts seems to play a key role in the oxidative dehydrogenation of propane. In addition, the catalytic properties of these surface molybdenum species seem to depend on the structure of the main catalyst particles, because molybdenum oxide supported on SiO_2 was less selective.

3.2. SURFACE ACIDIC SITES ON THE MAGNESIUM MOLYBDATE CATALYSTS

In the previous section, the surface state of molybdenum was suggested to be important for the active $MgMoO_4$ catalyst system. If it were indeed, some kinds of consideration for the acid–base properties of the catalysts should be given [17]. Therefore, the IPA reaction was adopted to investigate the active sites in terms of acid–base properties of the magnesium molybdate catalysts.

The main product in the IPA 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. In fig. 1 the formation rate of propene per surface area in the propane oxidation was plotted against the formation rate of propene per surface area in the IPA reaction on each catalyst. The $Mg_{0.95}MoO_x$ catalyst, which gives the highest propene formation (86.9 $\mu mol\ m^{-2}$) in the IPA reaction at 300°C, showed also the highest propene formation (2.85 $\mu mol\ min^{-1}\ m^{-2}$) in the propane oxidation at 460°C. On the other hand $Mg_{1.1}MoO_x$ reveals the lowest propene formations of 3.9 $\mu mol\ mol\ m^{-2}$ and 0.01 $\mu mol\ min^{-1}\ m^{-2}$ for both the reactions, respectively. Fig. 1 indicates well that the oxidation activities of catalysts linearly increase with increasing acidic properties of the magnesium molybdate catalysts. It is clear from this result that the acidic properties on the surface of the mag-

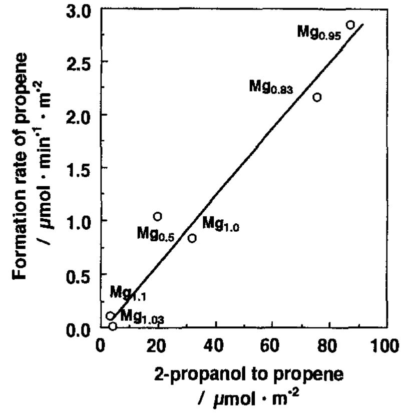

Fig. 1. Relationship between the catalytic activities of the magnesium molybdates for the oxidative dehydrogenation of propane (reaction temp.: 460°C, feed: $O_2 : N_2 : C_3H_8 = 7 : 75 : 18$ (%), SV: 810 cm^{-3} g-cat^{-1} h^{-1}) and for the 2-propanol dehydration (reaction temp.: 300°C, 2-propanol injected: 6.5 μmol, catalyst: 10 mg).

nesium molybdate catalysts are responsible for their activities in the oxidative dehydrogenation of propane. Presumably, the surface molybdenum species cause some acidic sites and activate adsorbed propane.

3.3. INVOLVEMENT OF LATTICE OXIDE IONS IN THE PROPANE OXIDATION

Active oxygen species would be important for deciding the catalytic activity and selectivity in the oxidative dehydrogenation of propane as well as surface acidic properties. The involvement of lattice oxide ions of the magnesium molybdate catalysts in the reaction was examined by pulse reduction of the catalyst with propane. In each propane pulse into the catalysts, propene was selectively formed. Since in this experiment water was formed but no hydrogen, the result indicates that the lattice oxide ions are active for the propene formation. Since the selectivity to propene increased with increasing extent of reduction and then reached constant selectivities, a slightly reduced surface, in other words, lower surface concentration of lattice oxide ions is preferable for the selective formation of propene. Presumably, the lower selectivity to propene at the beginning of pulsing is due to a higher probability for reaction of lattice oxide ions with propene once it is formed from propane. This situation may be close to the flow reaction condition where the feed contains gaseous oxygen. We thus compared the conversions of propane with (flow condition) and without (pulse condition, first pulse) gaseous oxygen over the magnesium molybdate catalysts. Both conversions are plotted against the Mg/Mo ratio in fig. 2. The conversions under both reaction conditions changed in a similar manner with catalyst composition irrespective of gaseous oxygen. This clearly demonstrates that the lattice oxide ion on the catalyst surface acts as an active oxygen species.

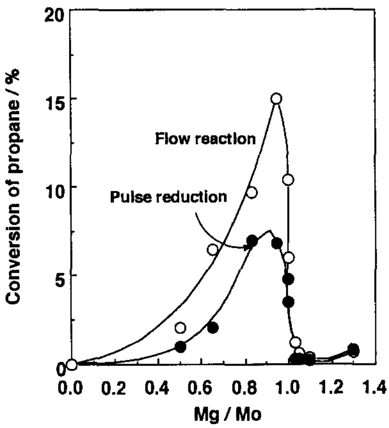

Fig. 2. Comparison of the propane conversions over the magnesium molybdate catalysts in the oxidative dehydrogenation of propane with (feed: $O_2 : N_2 : C_3H_8 = 7 : 75 : 18$ (%), SV: 810 cm^3 $g\text{-}cat^{-1}$ h^{-1}, reaction temp.: 480°C) and without gaseous oxygen (pulse size: 7.4 μmol, reduction temp.: 550°C).

4. Conclusions

From this study, it is concluded that: (1) the catalytic activities of the magnesium molybdate catalysts are very high in the oxidative dehydrogenation of propane; (2) among the magnesium–molybdenum oxide catalyst systems, the catalyst with excess molybdenum, the ratio of Mg/Mo = 0.9–1.0, presented the highest activity in the reaction, giving 60% selectivity to propene at 20% conversion of propane under optimum conditions; (3) it is strongly suggested that the acidic properties caused by excess molybdenum ions on the surface of the magnesium molybdate catalysts affected the catalytic activities in the oxidative dehydrogenation of propane; and (4) the lattice oxide ions of the catalyst surface act as active oxygen species for the oxidative dehydrogenation of propane to propene.

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