Structures and catalytic properties of magnesium molybdate in the oxidative dehydrogenation of alkanes

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Magnesium molybdates have been prepared from an aqueous solution of magnesium nitrate and ammonium paramolybdate under various pH conditions and used for the selective oxidation of propane and isobutane with gaseous oxygen under atmospheric pressure in the temperature range of 360–520 °C. The structure analyses by XRD and FT-IR showed the formation of three phases, α-$MgMoO_4$, β-$MgMoO_4$ and $Mg_2Mo_3O_{11}$, in the catalysts calcined below 550 °C. The catalyst prepared at pH = 5.7 showed the highest activity for the oxidative dehydrogenation of the alkanes as well as the strongest acidity. By XPS measurements, an excess amount of Mo compared to Mg was observed over the active catalysts. It is likely that the excess molybdenum species is present as molybdate and creates acidic sites over the catalyst surface.

Keywords: magnesium molybdates, catalyst preparation, pH conditions, selective oxidation, propane, isobutane, acidic properties

1. Introduction

Selective conversion of alkanes to more valuable chemicals is an important process in the chemical industry, in which the oxidative dehydrogenation of alkanes to alkenes is a promising reaction since it is thermodynamically feasible and can be carried out without carbon deposition [1]. For instance, the relatively abundant liquefied petroleum gas (LPG) contains mainly propane and butanes, among which isobutane might be converted to isobutene, since isobutene is a raw material for producing gasoline octane enhancers, i.e., methyl *tert*-butyl ether (MTBE) [2,3]. Catalytic oxidative dehydrogenation of low alkanes (C_3–C_5) has been extensively studied over molybdenum- [4–7] or vanadium-based [8–12] oxide. Ueda et al. [5,6] reported that the catalytic activities of magnesium molybdate drastically changed with catalyst composition, where the catalytic activity for the oxidative dehydrogenation of propane seemed to depend on surface acidic properties due to the existence of MoO_x clusters formed on the surface $MgMoO_4$. Similar phenomena were found by Oganowski et al. [13] in the oxidative dehydrogenation of ethylbenzene to styrene. Volta et al. [8] attributed the higher selectivity for propane dehydrogenation to propene to pyrovanadate, α-$Mg_2V_2O_7$, while orthovanadate, $Mg_3V_2O_8$, is the active phase for Kung et al. [9]. Furthermore, Delmon et al. [12] show that the selectivity of $Mg_3V_2O_8$ can be improved by the presence of an excess of MgO in intimate contact and that α-$Mg_2V_2O_7$ is the more selective phase compared with $Mg_3V_2O_8$ and β-$Mg_2V_2O_6$. It is likely that the activity of the molybdate or vanadate catalyst substantially depends on its surface structure, nonetheless the conclusions drawn on the activity and selectivity of these catalytic materials are still controversial.

It was reported that the molybdenum- [14,15] or vanadium-based [16,17] oxides change their structure depending on the polyacid precursor, which is affected by pH in the starting aqueous solution during the preparation of the catalysts. We reported that several chromium vanadates, the metavanadate ($Cr(VO_3)_3$), the pyrovanadate ($Cr_4(V_2O_7)_3$) and the polyvanadates of higher degree of condensation, are formed depending on pH value in the media of the catalyst preparation [16,17]. Also in the solution chemistry of molybdenum oxide, it is well known that the orthomolybdate (MoO_4^{2-}), paramolybdate ($Mo_7O_{24}^{6-}$) and octamolybdate ($Mo_8O_{26}^{4-}$) ions are stable depending on pH value [14]. In the present study, magnesium molybdate catalysts containing excess amount of Mo were prepared by changing pH of the starting aqueous solution and the calcination temperature of the catalysts. The structures and the catalytic activities for the oxidative dehydrogenation of propane and isobutane were studied in connection with the preparation conditions. Moreover, the catalytic activities were discussed in relation to the structure change and the surface acidic properties.

2. Experimental

2.1. Preparation and characterization of the catalyst

Magnesium molybdate catalysts were prepared from aqueous solutions of $Mg(NO_3)_2{\cdot}6H_2O$ and $(NH_4)_3Mo_7O_{24}{\cdot}$

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Table 1
The preparation conditions, surface area and analytical results by XPS of the $Mg_{0.92}MoO_x$ catalysts.[a]

pH of starting solution	Amount (ml)		Surface area ($m^2\,g^{-1}$)	Mo_{3d}/Mg_{2s} peak ratio by XPS
	63% aq. HNO_3	26% aq. NH_3		
1.5	5	0	1.9	1.338
4.4	5	5	2.4	1.264
5.7	2	12	3.5	1.277
6.6	0	40	2.0	1.397

[a] $Mg(NO_3)_2{\cdot}6H_2O$ (92.0 mmol) and $(NH_4)_3Mo_7O_{24}{\cdot}4H_2O$ (14.3 mmol) were used as the raw materials. The catalysts were calcined at 550 °C.

$4H_2O$ as the raw materials. The ratio of Mg/Mo was changed between 0.90 and 0.95, and finally fixed at 0.92 which showed the highest activity for the propane oxidation. Several $Mg_{0.92}MoO_x$ catalysts were then prepared by changing the pH of the starting aqueous solution, i.e., by varying the amount of each aqueous solution of 63% HNO_3 and 26% NH_3 added into an aqueous solution of the raw materials of $Mg(NO_3)_2{\cdot}6H_2O$ (92.0 mmol) and $(NH_4)_3Mo_7O_{24}{\cdot}4H_2O$ (14.3 mmol), as shown in table 1. After mixing the solution, the precipitate formed was solidified by evaporating water at 80 °C. The resulting slurry was dried at 110 °C for 20 h and was 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, calcined again for 5 h at 550 °C and used for the alkane oxidations. A part of the $Mg_{0.92}MoO_x$ powder precalcined at 300 °C for 3 h was then calcined at 450, 500, 550, 600 and 650 °C, respectively, for 5 h, and the molybdate samples thus prepared were analyzed to study the phase transition during the calcination.

Metal compositions of the catalysts were calculated on the basis of the amounts of the starting compounds in the preparation. Structures of the catalysts were identified by XRD (MAC Science, MXP18, Cu Kα) and FT-IR (JASCO, FT/IR-7000) measurements. Thermal analyses of the catalysts were carried out by TG/DTA (Shimadzu, TGA-50/DTA-50) measurements in order to clarify the phase transition during the calcination. Surface area of the catalyst powder was measured by using the BET method (Shimadzu, Flow Sorb II 2300). X-ray photoelectron spectra (XPS) were recorded on a Perkin–Elmer PHI 5500 ESCA system with Mg Kα as the X-ray source to investigate the catalyst surface compositions.

2.2. Catalytic reactions

The oxidations of propane and isobutane with gaseous oxygen were carried out at atmospheric pressure in a conventional flow system equipped with a Pyrex tube reactor. The volume of the reactor, excepting the catalyst zone, was minimized to prevent gas-phase reactions. The standard conditions for propane oxidation are as follows: the feed composition was 18 vol% of propane and 7 vol% of oxygen in helium. 4 g of the catalyst diluted 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 fixed at 810 cm^3 g-cat.$^{-1}$ h^{-1}. Although a propane conversion of 1.1% was observed without catalyst at 500 °C, this is considered negligible. The feed and products were analyzed by an on-line gas chromatograph operating with two sequential columns. A 2 m molecular sieve 13X column was used at 80 °C to separate O_2 and CO, a 5 m Gaschropak 54 column was used at 80 °C by TCD to separate the hydrocarbons and CO_2, and a 2 m PEG-6000 column was used at 80 °C by FID to analyze oxygenated products.

The reaction conditions for isobutane oxidation were as follows: the feed composition was 7.5 vol% of isobutane and 3.5 vol% of oxygen in helium. 1 g of the catalyst diluted with 2 g of quartz chips was used. Isobutane was more reactive than propane in the reactor and the space velocity was increased to 5400 cm^3 g-cat.$^{-1}$ h^{-1} to prevent the gas-phase reaction. In this instance, an isobutane conversion of 0.2% was observed without catalyst at 470 °C. The feed and products were analyzed by an on-line gas chromatograph operating with two sequential columns. A 2 m molecular sieve 13X column was used at 50 °C, a 6 m SM-pak column was used at 50 °C by TCD to separate the hydrocarbons and CO_2, and a 2 m Gaschropak 54 column was used at 160 °C by FID to analyze oxygenated products.

The reactions were carried out for 2 h at each temperature, during which no significant deactivation was observed.

To investigate acidity and basicity of the catalysts, 2-propanol dehydration/dehydrogenation (IPA reaction), which is a well-known method of acidity/basicity measurements, was carried out in a conventional pulse equipment with the TCD cell of a gas chromatograph. A 3 m PEG A20M column was used for analysis and 6.5 μmol of 2-propanol was reacted over 10 mg of the catalyst at 300 °C.

3. Results

3.1. Characterization of the magnesium molybdate catalysts

3.1.1. XRD measurements

XRD measurements of the $Mg_{0.92}MoO_x$ samples were carried out to study the transformation of bulk structure during the catalyst preparation. The samples were precipitated under the pH range from 1.5 to 6.6 and calcined at the temperature from 300 to 600 °C. Figure 1 shows the XRD patterns of the samples calcined at 550 and 600 °C, where three phases, α-$MgMoO_4$, β-$MgMo_3O_4$ and $Mg_2Mo_3O_{11}$, were detected. The samples are mainly composed of the α-$MgMoO_4$ and β-$MgMoO_4$ phases at the low calcination temperature below 550 °C and composed of the β-$MgMoO_4$ and $Mg_2Mo_3O_{11}$ phases at the high calcination temperature above 600 °C. No MoO_3 peaks were detected in the XRD measurements of all the samples although the ratio of Mo/Mg exceeded 1.0. This observation indicates that excess molybdenum ox-

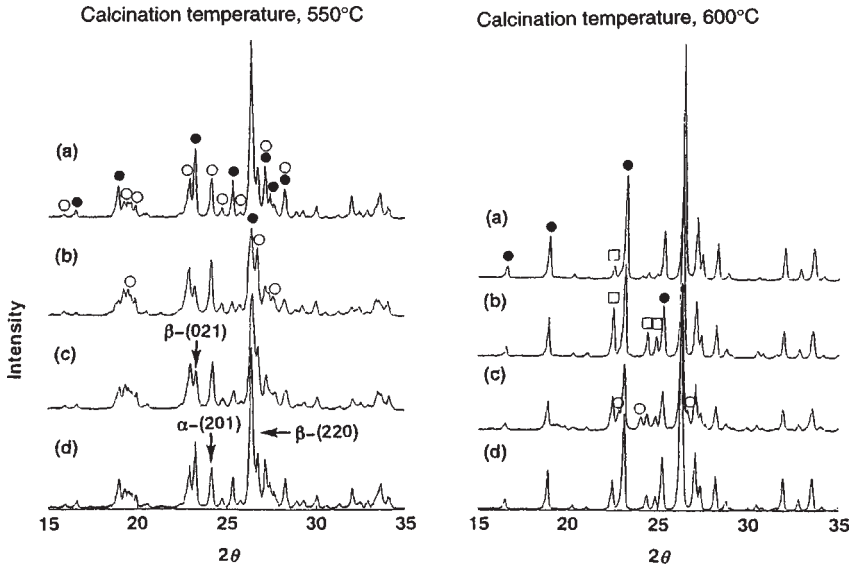

Figure 1. X-ray diffraction patterns of the $Mg_{0.92}MoO_x$ catalysts prepared from various pH solutions and calcined at 550 and 600 °C. (a) pH = 1.5, (b) 4.4, (c) 5.7, (d) 6.6. (○) α-$MgMoO_4$, (●) β-$MgMoO_4$, (□) $Mg_2Mo_3O_{11}$.

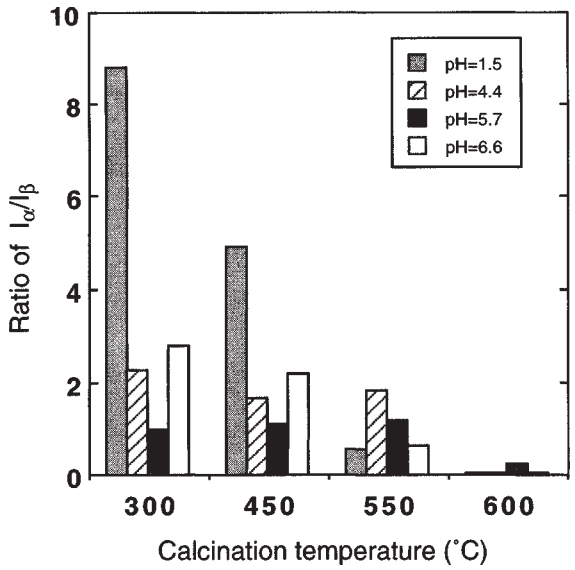

Figure 2. The intensity ratio of (201) line (α-$MgMoO_4$) to (021) line (β-$MgMoO_4$) from the XRD of the $Mg_{0.92}MoO_x$ catalysts.

ide spreaded quite well over the catalyst [18]. The intensity ratios (I_α/I_β) of the peaks of α-$MgMoO_2$ (201) and β-$MgMoO_4$ (021) in the XRD of the samples are shown in figure 2. The value of I_α/I_β substantially decreased with increasing the calcination temperature. When the sample was calcined at 300 °C, the ratio I_α/I_β is drastically decreased from 8.8 to 1.0 with increasing the pH of the starting solution from 1.5 to 5.7, and again increased to 2.8 at pH = 6.6. Both α-$MgMoO_4$ and β-$MgMoO_4$ phases were present in the samples calcined at 450 °C. The order of I_α/I_β in the samples calcined at 450 °C is almost similar to that of 300 °C. A different tendency of the order was observed for the samples calcined at the high temperature of 550 °C. The intensity ratio I_α/I_β was high with the samples prepared at pH = 4.4 and 5.7, i.e., α-$MgMoO_4$ was the main phase at pH = 4.4 and 5.7, while β-$MgMoO_4$ at pH = 1.5 and 6.6. At the calcination temperature of 600 °C, the new phase, $Mg_2Mo_3O_{11}$, appeared in place of α-$MgMoO_4$ in most of the samples except that of pH = 5.7, which is the most active catalyst for the selective oxidation of propane and isobutane. The main phase in all the samples changed from α-$MgMoO_4$ to β-$MgMoO_4$ with increasing the calcination temperature. The structure of α-$MgMoO_4$ is isotopic to α-$ZnMoO_4$ and has distorted tetrahedral coordination around molybdenum [19,20], while β-$MgMoO_4$ is isotopic to α-$MnMoO_4$ and has tetrahedral coordination around molybdenum [20,21]. Therefore, it is likely that the structure of the $Mg_{0.92}MoO_x$ sample was in the mixed state of distorted tetrahedral coordination around molybdenum at the low calcination temperature, and then changed to tetrahedral coordination with increasing the calcination temperature. The rate of phase transfer from α- to β-$MgMoO_4$ estimated from the change in XRD patterns during the calcination of the $Mg_{0.92}MoO_x$ samples substantially varied depending on the pH of the starting solution, and can be put in the following order: pH = 1.5 ⩾ pH = 6.6 > pH = 4.4 ⩾ pH = 5.7. It is noteworthy that the values of I_α/I_β in the samples of pH = 4.4 and 5.7 did not substantially change with increasing the calcination temperature compared to the others. In addition, it is considered that the α-$MgMoO_4$ phase is stable below 550 °C, but unstable above 600 °C. This instability was significantly observed with the samples prepared at pH = 1.5 and 6.6.

3.1.2. FT-IR and TG/DTA analyses

The change of crystal structure was also investigated by FT-IR measurement. $(NH_4)_3Mo_7O_{24}{\cdot}4H_2O$ shows an absorption band at about 890 cm^{-1} with two weak shoulders at 840 and 920 cm^{-1} for the Mo=O vibration, and NH_4^+ and HOH bands at 1405 and 1640 cm^{-1} [22], re-

Table 2
Absorption band of FT-IR spectra with changing the calcination temperature and the pH of the starting solution in the preparation of the $Mg_{0.92}MoO_x$ catalysts.

Calcination temp. (°C)	Assignment	pH of starting solution[a]			
		1.5	4.4	5.7	6.6
110	δ(HOH)	1638s	1635s	1635s	1635s
	$\nu(NO_3^-)$	1382vs	1382vs	1382vs	1382vs
				500–970vw	
300	δ(HOH)	1640s	1635m	1635s	1635m
	$\nu(NO_3^-)$	1382vs	1382m	1382m	1382m
	ν_{as}(Mo=O)	990sh	990sh	990sh	990sh
	ν_{as}(MoOMo)	965w	965w	965m	960s
		920w	940w	936m	932w
		900w	930w	–	902w
		885w	890m	890m	890m
		830w	830–800b	820m	820–800b
		780s	780m	780w	780s
				612m	
450	ν_{as}(Mo=O)	990sh	990sh	990sh	–
	ν_{as}(MoOMo)	960s	960m	960m	960m
		922s	945w	940sh	940sh
		902s	–	–	902sh
		885s	890m	890m	890m
		825w	830–810w	810m	820w
		775s	780m	775m	775s
		730w	730sh		
550	ν_{as}(Mo=O)	–	990sh	990sh	–
	ν_{as}(MoOMo)	970s	960s	960s	965s
		950s	940sh	940sh	940s
		902sh	902sh	–	–
		890s	890s	890s	890s
		830s	820w	825m	828s
		780s	775s	770s	775s
		740sh	740sh	730w	740sh
600	ν_{as}(MoOMo)	970s	970s	970s	970s
		942s	947s	948s	942s
		885s	880s	880s	880s
		840s	835s	835s	835s
		820s	815s	815s	815s
		–	775sh	780w	–
		725s	720s	720s	725s
650	ν_{as}(MoOMo)		968s		
				945s	
				890s	
				830s	
				740s	

[a] vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, b = broad.

spectively. The pure MoO_3 gives characteristic bands at 985(s), 845(m), 825(vs) and 500 cm^{-1}(s) attributed to crystalline MoO_3 vibrational modes [23,24]. $Mg(NO_3)_2{\cdot}6H_2O$ showed NO_3^- and HOH bands at 1385 and 1640 cm^{-1}, respectively. The pure MgO exhibits only broad bands at around 490 cm^{-1}.

The FT-IR spectra of the $Mg_{0.92}MoO_x$ samples prepared by changing the pH of the starting solution and the calcination temperature are shown in table 2. Strong absorption bands of NO_3^- and HOH at 1382 and 1635 cm^{-1}, respectively, were observed in all the samples after drying at 110 °C for 20 h. At the calcination temperature of 300 °C, the strong bands of NO_3^- and HOH still remained, and several bands assigned to Mo–O bonds appeared at 990, 965, 940–900, 890, 830–820, and 770 cm^{-1}. Meullemeestre et al. [20] studied the dehydration of $MgMoO_4{\cdot}zH_2O$ ($z = 1$, 2, 5 or 7) during the calcination by TG/DTA and IR measurements, and showed that a band at 612 cm^{-1} can be assigned to $MgMoO_4{\cdot}H_2O$. This well coincided with an increase in the temperature of dehydration from 70 to 110 °C observed as an endothermic peak in TG/DTA analyses. With the sample prepared at pH = 5.7 and calcined at 300 °C, the band at 612 cm^{-1} was clearly observed, suggesting that the monohydrate still remained. At the calcination temperature above 600 °C, the Mo–O absorption bands strongly appeared at 970, 945, 890, 835, 815, and 770 cm^{-1}. A band for the terminal Mo=O bond of MoO_3 was observed as a weak shoulder band at 990 cm^{-1} in the

samples calcined at 450 °C, and disappeared in the samples calcined above 500 °C. This suggests that the molybdenum species exists as well dispersed molybdate on the catalysts used in the alkane oxidation. The Mo–O absorption bands from 920 to 970 cm^{-1} and around 890 cm^{-1} were strengthened with increasing the pH of the starting solution and the calcination temperature. On the other hand, at the calcination temperature below 450 °C, the bands between 770 and 780 cm^{-1} were strong for the samples prepared at pH = 1.5 and 6.6, and oppositely were weak or medium for those prepared at pH = 4.4 and 5.7. The bands between 770 and 780 cm^{-1} were the strongest at the calcination temperature of 550 °C, and almost disappeared above 600 °C for all the samples.

Meullemeestre et al. [20] again reported that α-$MgMoO_4$ has the absorption bands at 994(sh), 958(s), 922(s), 890(s) and 780(vs) cm^{-1}, while β-$MgMoO_4$ has the bands at 995(sh), 965(s), 922(m), 821(s) and 720(s) cm^{-1}. Therefore, it is most likely that the absorption bands around 890 and 780 cm^{-1} are typically characteristic of α-$MgMoO_4$ having distorted tetrahedral coordination around Mo, while those around 821 and 720 cm^{-1} are of β-$MgMoO_4$ having tetrahedral coordination around Mo in the $Mg_{0.92}MoO_x$ catalysts. XRD measurements showed the clear phase transfer from α-$MgMoO_4$ to β-$MgMoO_4$ in the samples prepared at pH = 1.5 and 6.6 with increasing the calcination temperature (figures 1 and 2). When both samples were calcined at increasing temperature, their FT-IR spectra also showed the plain shift of absorption bands toward the lower wave number in the region between 700 and 900 cm^{-1} as follows: 890(m), 820–830(m-w) and 780(s) cm^{-1} at 300 °C; 885–890(m-s), 820(m-w) and 775(s-m) cm^{-1} at 450 °C; 890(s), 830(s), 780(s) and 740(sh) cm^{-1} at 550 °C; and 880(s), 840(s), 820(sh) and 720(s) cm^{-1} at 600 °C. A sharp and strong absorption band at 880 cm^{-1} observed at 600 °C calcination may be attributed to $Mg_2Mo_3O_{11}$. These shifts clearly suggest the phase transfer from α-$MgMoO_4$ to β-$MgMoO_4$, and finally to $Mg_2Mo_3O_{11}$ during the calcination.

3.2. Catalytic activity for the alkane oxidation

Typical catalytic performance data for the selective oxidation of propane over the $Mg_{0.92}MoO_x$ catalyst prepared at pH = 5.7 and calcined at 550 °C for 5 h as a function of the reaction temperature are shown in figure 3. The oxidation of propane took place at 380 °C and the conversion of propane increased with increasing the reaction temperature. The selectivity to propene decreased with increasing the reaction temperature, followed by the increases in the formations of other products such as CO_2, CO, C_2H_4 and oxygenates. In the literature, it is reported that the catalytic activity of magnesium molybdate strongly depended on the chemical composition over the catalyst surface in the oxidative dehydrogenation of propane [5,6] and of ethylbenzene [13], i.e., the catalyst having a small excess amount of molybdenum showed the maximum catalytic activity. In the present work, the magnesium molybdate catalysts having the ratio of Mg/Mo = 0.9, 0.92, 0.95 were prepared at the pH = 5.7 conditions and tested for the oxidation of propane (table 3). The $Mg_{0.92}MoO_x$ catalyst

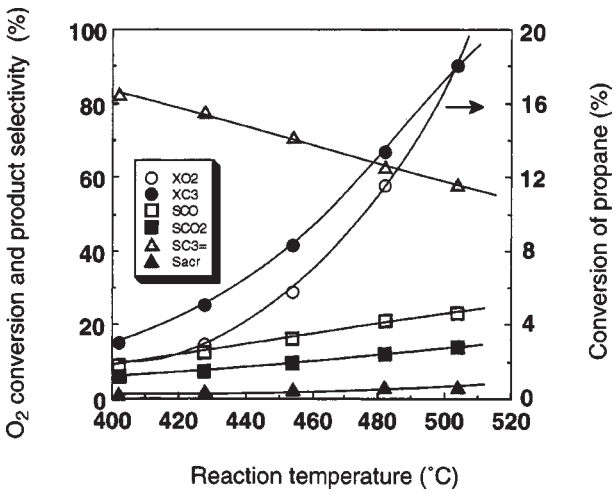

Figure 3. Propane oxidation over the $Mg_{0.92}MoO_x$ catalysts. C_3H_8 : O_2 : He = 10 : 4 : 40 (cm^3/min); SV = 810 $cm^3\,g^{-1}\,h^{-1}$; the $Mg_{0.92}MoO_x$ catalyst was prepared at pH = 5.7 and calcined at 550 °C.

Table 3
The oxidation of propane over the $Mg_{0.92}MoO_x$ catalysts.[a]

Catalyst	Phase from XRD[b]	Conversion[c] (%)		Selectivity[c] (%)					
		O_2	C_3	C_3	CO	CO_2	Ac.	Act.	Acr.
Empty	–	1.5	1.1	75.0	1.4	1.2	1.4	0.9	0.1
pH = 1.5	$\beta > \alpha$	4.0	1.6	76.0	9.0	10.0	0.4	0.4	1.2
pH = 4.4	$\alpha > \beta$	36.0	10.6	72.0	13.6	9.8	0.2	0.1	3.7
pH = 5.7	$\alpha \geqslant \beta$	84.0	17.4	58.0	22.0	13.0	0.1	0.1	3.4
pH = 6.6	$\beta > \alpha$	4.4	1.8	77.0	10.5	7.5	0.3	0.3	1.5
$Mg_{0.9}$[d]	$\alpha \geqslant \beta$	47.7	12.7	68.0	15.1	11.5	0.1	0.1	4.1
$Mg_{0.95}$[d]	$\beta \geqslant \alpha$	25.0	9.5	74.0	14.0	8.5	0.2	0.1	3.0

[a] C_3H_8 : O_2 : He = 10 : 4 : 40 (cm^3/min); catalyst, 4 g; reaction temperature, 500 °C.
[b] $\alpha = \alpha$-$MgMoO_4$, $\beta = \beta$-$MgMoO_4$.
[c] C_3 = propane, C_3' = propene, Ac. = acetaldehyde, Act. = acetone, Acr. = acrolein.
[d] $Mg_{0.9}$, $Mg_{0.9}MoO_x$ (surface area, 3.8 $m^2\,g^{-1}$); $Mg_{0.95}$, $Mg_{0.95}MoO_x$ (surface area, 3.3 $m^2\,g^{-1}$); both the catalysts were prepared under the conditions of pH = 5.7.

Table 4
The oxidation of isobutane over the $Mg_{0.92}MoO_x$ catalysts.[a]

Catalyst	Phase from XRD[b]	Conversion[c] (%)		Selectivity[c] (%)							
		O_2	i-C_4	C_3'	i-C_4'	CO	CO_2	Ac.	Act.	Acr.	MA
Empty[d]	–	10.7	3.8	19.1	69	6.5	0.6	0.2	2.7	0	2.0
Empty	–	0.5	0.2	21.4	74	–	0.9	0	1.2	0	2.0
pH = 1.5	$\beta > \alpha$	1.5	0.6	3.3	89	2.0	1.2	0.4	0	0	0
pH = 4.4	$\alpha > \beta$	11.3	2.4	3.1	63	12.0	15.4	0.3	2.1	0	0
pH = 5.7	$\alpha \geqslant \beta$	31.0	4.2	1.0	38	28.5	26.0	0.1	0.4	0.1	3.0
pH = 6.6	$\beta > \alpha$	0.7	0.3	3.7	93	1.3	0	0	0	0	0
pH = 5.7[e]	$\alpha > \beta$	65.0	7.5	0.8	28	35.0	30.5	0.1	0.4	0.1	2.5

[a] i-C_4H_{10} : O_2 : He = 7 : 3 : 80 (cm^3/min); catalyst, 1 g; reaction temperature, 470 °C.
[b] $\alpha = \alpha$-$MgMoO_4$, $\beta = \beta$-$MgMoO_4$.
[c] i-C_4 = isobutane, C_3' = propene, i-C_4' = isobutene, Ac. = acetaldehyde, Act. = acetone, Acr. = acrolein, MA = methacrolein.
[d] i-C_4H_{10} : O_2 : He = 10 : 4 : 40 (cm^3/min); 2 g of SiO_2 was packed in the reactor.
[e] 2 g of the catalyst was used.

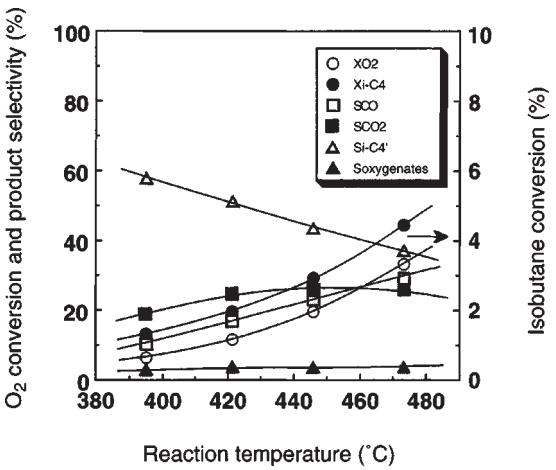

Figure 4. Isobutane oxidation over the $Mg_{0.92}MoO_x$ catalysts. i-C_4H_{10} : O_2 : He = 7 : 3 : 80 (cm^3/min); SV = 5400 $cm^3\,g^{-1}\,h^{-1}$; the $Mg_{0.92}MoO_x$ catalyst was prepared at pH = 5.7 and calcined at 550 °C.

showed the highest activity, resulting in the production of propene with the selectivity of 59% at the conversion of 17.4%.

Isobutane was more reactive than propane and was partly decomposed to propene (conversion 3.8%, selectivity 19.1%) even in the absence of catalyst when the reaction was carried out at the same space velocity and the same reaction temperature as the propane oxidation. Therefore, the oxidation of isobutane was carried out under the reaction conditions of a shorter contact time and a lower temperature than the propane oxidation (table 4). In the presence of the $Mg_{0.92}MoO_x$ catalysts, the decomposition to propene was substantially suppressed, resulting in the high selectivity to isobutene production. In the isobutane oxidation, however, both the conversion and the selectivity to isobutene were lower than those obtained in the propane oxidation (figure 4).

3.3. Effect of pH in the catalyst preparation

The catalysts prepared under the various pH conditions and calcined at 550 °C were tested for the propane and isobutane oxidations. The results of propane oxidation at 500 °C and of isobutane oxidation at 470 °C are shown in tables 3 and 4. The activities for both the propane and the isobutane oxidations drastically changed depending on the pH of catalyst preparation; the highest conversions of alkanes were observed over the catalyst prepared at pH = 5.7. In the propane oxidation, small amounts of ethene, acetaldehyde, acetone and acrylaldehyde besides CO_2 and CO were observed as the by-products. The surface area of the catalysts varied between 1.9 and 3.5 depending on the pH (table 1), and the highest activity was obtained over the catalyst having the largest surface area. However, the increase in the activity is not only due to the increasing surface area, but also due to the other effect, as observed in the following results. The catalytic activity for the propane oxidation increased drastically with increasing the pH of the catalyst solution from 1.5 to 5.7, and suddenly decreased with further increasing pH to 6.6. The activity of the catalyst prepared at pH = 5.7 was the highest and about ten times higher than that of the catalyst prepared at pH = 1.5 or 6.6. There was not observed a significant change in the selectivity to propene among the catalysts used. The oxidation of isobutane showed lower conversions of both oxygen and isobutane and lower selectivity to methacrylaldehyde, even at a shorter contact time and a lower reaction temperature, than that of propane. The main phase detected by the XRD measurements was α-$MgMoO_4$ in the catalysts prepared at pH = 4.4 and 5.7, and β-$MgMoO_4$ in those at pH = 1.5 and 6.6. Higher magnesium content resulted in a preferable formation of β-$MgMoO_4$.

3.4. Relationship between the activity and the surface acidity of the catalyst

Ueda et al. [5,6] reported the strong dependence of catalytic activity on surface acidic properties of the magnesium molybdate catalysts. We have studied the relationship between the catalytic activity for the selective oxidation of propane and isobutane and the surface acidic property obtained by the IPA reaction.

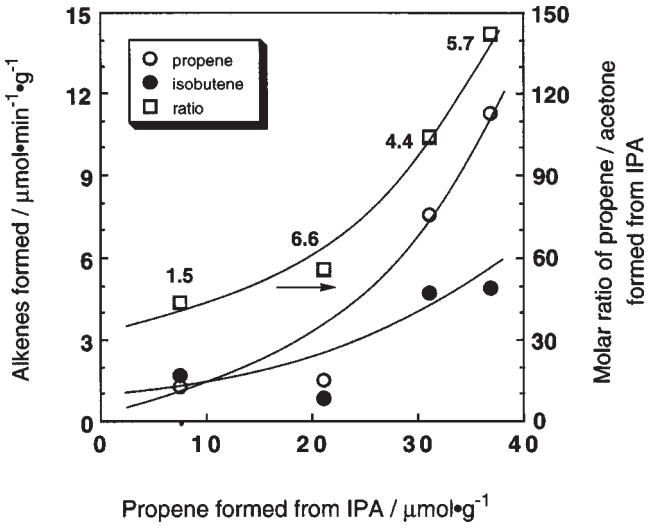

Figure 5. The catalytic activity and the acid–base property of the $Mg_{0.92}MoO_x$ catalysts in the oxidations of propane and isobutane. The numbers in the figure show the pH values where the catalysts were prepared. The alkanes oxidations were carried out as follows: (a) C_3H_8 : O_2 : He = 10 : 4 : 40 (cm^3/min); catalyst, 4 g; reaction temperature, 500 °C; (b) i-C_4H_{10} : O_2 : He = 7 : 3 : 80 (cm^3/min); catalyst, 1 g; reaction temperature, 470 °C. IPA reaction was carried out as follows: IPA (2-propanol), 6.5 μmol; catalyst, 10 mg; reaction temperature, 300 °C.

In the IPA reaction, the main product was propene and a negligible amount of acetone was observed over all the catalysts, indicating that the catalyst surface has mainly an acidic property. In figure 5, the formation rates of propene and isobutene per catalyst weight in the propane and isobutane oxidations, respectively, were plotted against the amount of propene formed per catalyst weight in the IPA reaction. The numbers in the figure show the pH values at which the catalysts were prepared. The $Mg_{0.92}MoO_x$ catalyst prepared at pH = 5.7 showed the strongest acidity, i.e., the highest amount of propene formation (36.9 μmol g^{-1}) from IPA at 300 °C. This catalyst also showed the highest rates of propene (11.3 μmol min^{-1} g^{-1}) and isobutene (4.9 μmol min^{-1} g^{-1}) formations in the oxidations of propane at 500 °C and isobutane at 470 °C, respectively. On the other hand, the catalyst prepared at pH = 1.5 gave the weakest acidity of the lowest amount of propene (7.5 μmol g^{-1}) from IPA reaction. The lowest rates of propene (1.2 μmol min^{-1} g^{-1}) and isobutene (1.7 μmol min^{-1} g^{-1}) formations were observed over the same catalyst. The catalysts prepared at pH = 6.6 and 4.4 showed the medium values of both the acidity and the activity. It is thus likely that the acidic properties of the catalyst surface are important for the activities of the magnesium molybdate catalysts for the selective oxidations of propane and isobutane.

The surface compositions of the catalysts were investigated by XPS measurements. The Mo_{3d}/Mg_{2s} peak ratios observed over the surface of the catalysts prepared at various pH conditions and calcined at 550 °C are shown in table 1. The ratios in all the samples gave higher values than the stoichiometric chemical composition (Mo/Mg = 1.087). The value of Mo_{3d}/Mg_{2s} obtained by XPS measurements was higher over the catalyst containing more amount of β-$MgMoO_4$ compared to α-$MgMoO_4$ phase (figure 2), i.e., surface segregation of molybdenum species takes place over the catalyst containing much β-$MgMoO_4$ phase. However, both the catalytic activity and the acidity were higher over the catalyst containing more amount of α-$MgMoO_4$ phase. The excess molybdenum species on α-$MgMoO_4$ phase over the catalyst surface produces some acidic sites and works for activating adsorbed lower alkanes.

4. Discussion

Since the catalysts used in the present study are prepared from aqueous solutions of molybdenum, it is instructive to review the solution chemistry of molybdenum oxide prior to the discussion. It is well known that the molecular structures of molybdenum oxides are very sensitive to pH value of the solution [14]. Orthomolybdate ion (MoO_4^{2-}) is stable at pH > 6.5. Acidification leads to the first polymeric species, paramolybdate ion ($Mo_7O_{24}^{6-}$), by the following reaction:

$$7MoO_4^{2-} + 8H^+ \rightleftharpoons Mo_7O_{24}^{6-} + 4H_2O \qquad (1)$$

This reaction is practically complete at pH = 4.5 and octamolybdate ion ($Mo_8O_{26}^{4-}$) forms at higher acidification (between pH = 2.9 and 1.5). At pH = 0.9, the isoelectric point of molybdic acid, molybdic acid ($MoO_3{\cdot}2H_2O$) precipitates. Haight et al. [15] also reported that at basic pH regions (pH > 6), tetrahedrally coordinated molybdate anions, MoO_4^{2-}, are generally present in solution, but at acidic pH regions (1 < pH < 6) MoO_4^{2-} gives polymeric and octahedrally coordinated molybdate anions, $Mo_7O_{24}^{6-}$ and $Mo_8O_{24}^{6-}$. Therefore, we can expect phase transition from the octahedral molybdates to the tetrahedral molybdates with changing the pH from 1.5 to 6.6 in the catalyst preparation.

Segawa et al. [25] reported that, in the Raman study of titania-supported molybdena catalysts, the surface molybdenum oxide species up to monolayer coverage possess a highly distorted MoO_6 octahedral structure with one short Mo=O bond. Gulari et al. [26] also reported that, in the IR bands of the model compounds, the tetrahedral species (MoO_4^{2-}) have a strong IR band at 833 cm^{-1} and the octahedral molybdates ($Mo_7O_{24}^{6-}$ or $Mo_8O_{24}^{6-}$) have strong IR bands at 883 and 940 cm^{-1}. The IR bands of the octahedral species have been assigned to continuous Mo–O and independent or terminal Mo–O bonds, respectively. Moreover, Chang et al. [14] reported that, at the molybdenum loading of 10% Mo/MgO, the structure of the surface molybdate species over the MgO support depends on the calcination temperature; the tetrahedrally coordinated molybdate species is observed below 400 °C (where MgO is hydrate) and the octahedrally coordinated molybdate forms above this temperature and is stable up to 700 °C.

We assume that excess molybdenum of the $Mg_{0.92}MoO_x$ catalysts is supported by $MgMoO_4$ as the carrier. A larger amount of molybdenum was observed on β-$MgMoO_4$ than on α-$MgMoO_4$ phase, as previously mentioned in the results of XPS measurements. However, distribution of molybdenum oxide seems not so good over the catalyst prepared at pH $=$ 1.5 and 6.6 because too much excess molybdenum on the catalyst surface aggregates to form MoO_3. Thus, it is likely that suitable excess molybdenum species over α-$MgMoO_4$ phase is effective for creating the active site composed of the molybdate.

Stepanov et al. [4] have tested the catalytic activity of binary oxide systems including the $MgMoO_4$–MoO_3 system in the oxidative dehydrogenation of n-butane. They observed that the catalysts with the atomic ratio Mg/Mo < 1 were the most active and selective for butadiene formation [1]. The 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. [13]. They showed that the most active catalysts for this reaction were those containing 1–3% of excess 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 molybdate phase. Hasegawa et al. [27] also suggested that a distorted MoO_x^{n-} polyhedron formed on the surface when the magnesium molybdates have excess molybdenum. These results also well correlate to the high activity of the present $Mg_{0.92}MoO_x$ catalyst prepared at pH $=$ 4.4 and 5.7 of the starting solution and calcined at 500–550 °C, where suitable excess molybdenum species over α-$MgMoO_4$ phase is considered to create the active site composed of molybdate. It is thus likely that the surface acidic property of the catalyst due excess molybdenum species played an important role in the oxidative dehydrogenation of propane and isobutane.

5. Conclusions

Magnesium molybdate catalysts have been prepared from an aqueous solution of magnesium nitrate and ammonium paramolybdate under different pH conditions and were calcined at different temperatures. The catalytic activities of the magnesium molybdates have been tested for the selective oxidation of propane and isobutane to propene and isobutene, respectively, with gaseous oxygen under an atmospheric pressure in the temperature range of 360–520 °C. The structure analyses by XRD and FT-IR showed the formations of three phases, α-$MgMoO_4$, β-$MgMoO_4$ and $Mg_2Mo_3O_{11}$, in the catalysts. By XPS measurements, an excess amount of Mo compared to Mg was observed over the active catalysts. It is likely that the molybdenum species exists as the molybdate. Moreover, a good correlation was observed between the catalytic activities and the acidities measured by isopropanol dehydration.

It has been concluded that the activities of the $Mg_{0.92}MoO_x$ catalysts strongly depended on the pH of the starting solution and the chemical composition. The surface acidic properties created by surface excess molybdenum species over the catalysts showed a definitive role in the selective oxidation of propane and isobutane. It is likely that suitable excess molybdenum species over α-$MgMoO_4$ phase is effective for creating the active site composed of molybdate. The catalyst prepared at pH $=$ 5.7 condition showed the highest activity for the oxidative dehydrogenation of alkanes as well as the strongest acidity.

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