

Dependence of reactivity on pretreatment in molybdena–alumina catalysts for propene metathesis

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Abstract

The $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalytic systems were studied. The catalysts were highly selective and moderately active in propene metathesis at a low temperature (303 K). It was shown by XPS that preliminary thermal treatment of the catalysts affects their final reactivity towards propene. The surface of the molybdena–alumina catalyst, which was evacuated at 523 K and then activated at 873 K in argon, underwent partial reduction to Mo^{V} phase under the influence of propene at 303 K. This effect was not observed in the case of the molybdena–alumina catalyst, which was calcinated at 823 K and then analogously activated. It was concluded that the reducibility of the surface molybdenum was connected with the activity of the catalyst in propene metathesis. It was proposed that the difference of the reactivity towards propene of both catalysts was caused by the difference in the homogeneity of the surface molybdenum. It was stated that the activation of the catalysts in argon at 873 K increased the homogeneity of the surface molybdenum. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Olefin metathesis can be carried out in the presence of both homogeneous and heterogeneous catalytic systems. The reaction proceeds according to the carbene mechanism [1] and active carbene complexes are present in the reaction environment [2]. On the surface of heterogeneous oxidic catalysts, alkylidene complexes are formed from precursors when the catalyst is brought into contact with olefin [2].

The role of the oxidation state and configuration of the active site precursors of heteroge-

neous metathesis catalysts is still a subject of debate. Different reports on the possible precursor structure have appeared in literature. EPR studies have shown a correlation between catalytic activity in olefin metathesis and the concentration of paramagnetic Mo^{V} centres in the catalyst [3–5]. On the other hand, on the basis of both XPS and EPR investigations of $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalyst, Grünert et al. [6,7] concluded that Mo^{V} species are inactive in propene metathesis. According to the authors, the precursors of the active sites contain Mo^{VI} and Mo^{IV} . Interesting results have been obtained from investigations of highly active photoreduced $\text{MoO}_3/\text{SiO}_2$ system [8–11]. Photoreduc-

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tion of the catalyst under CO atmosphere leads to generation of surface Mo^{IV} sites, which are the precursors of the active sites. In the case of $\text{MoO}_3/\text{Al}_2\text{O}_3$, Mo^{VI} species have been also reported as the active sites or their precursors [12].

The following two points are responsible for the above differences. First, the number of active sites is only a small fraction of the amount of molybdenum ions on the catalyst (the mentioned photoreduced $\text{MoO}_3/\text{SiO}_2$ system is an exception) [2,13]. So, the results that are obtained from spectroscopic study and concern the whole catalyst surface, need not be related to the active sites. Second, catalyst preparation, activation procedures and reaction conditions are different in different works. But there is no doubt that such factors as average oxidation state of molybdenum in the catalyst, structure and dispersion of the surface species and their reducibility influence activity of the catalyst [2].

In this work, $\text{MoO}_3/\text{Al}_2\text{O}_3$ catalytic systems have been studied. Two methods of preliminary thermal treatment were applied. Propene metathesis carried out at 303 K has been chosen as a test reaction. The catalysts have been characterised by XPS.

2. Experimental

2.1. Materials

Alumina (Table 1) and analytically pure ammonium heptamolybdate (AHM, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$) were used for the catalysts preparation. Argon (99.998 vol.%) was passed

through an oxygen trap and dried over 4A molecular sieve. The reactant (99.5 vol.% C_3H_6 or a propene–helium mixture containing 5 or 6.5 vol.% C_3H_6) was dried with 3A molecular sieve.

2.2. Preparation of the catalysts

The catalysts were prepared by impregnation of Al_2O_3 with an aqueous solution of AHM. AHM dissolved in doubly distilled water was added to the carrier. The amount of the impregnation solution was about $3.3 \text{ cm}^3 \text{ g}^{-1} \text{ Al}_2\text{O}_3$. The mixture was left in an open vessel at room temperature until excess water evaporated. It lasted about 72 h and during this time the mixture was gently stirred sometimes. Next, the precursor was further dried at 383 K for 4 h at a reduced pressure, using a vacuum drier. Subsequently, the precursor was divided into two parts and then two methods of preliminary thermal treatment (A and B) were applied — Table 2.

2.3. Propene metathesis reaction

Catalytic tests were carried out in a fixed-bed, electrically heated, stainless steel flow microreactor working on-line with a gas chromatograph. The microreactor was packed with 0.5 g of 0.2–0.3 mm catalyst grains. The catalyst was activated for 2 h at 873 K under argon and then was cooled in argon to the reaction temperature. Catalytic tests were carried out at 303 K under atmospheric pressure.

2.4. Gas chromatography (GC)

GC analysis was performed under the following conditions: column packed with sebacitrile supported on Chromosorbe P-NAW, room temperature, carrier gas; argon, detector; FID, gas chromatograph; GCHF 18.3. Chromatograms were collected and worked-up with a computer.

Table 1
Properties of the catalysts support (Al_2O_3)

Apparent density (g cm^{-3})	0.845 [14]
Support material density (g cm^{-3})	3.082 [14]
Porosity (%)	72.6 [14]
Pore volume ($\text{cm}^3 \text{ g}^{-1}$)	0.859 [14]
BET surface area ($\text{m}^2 \text{ g}^{-1}$)	210

Table 2
The catalysts studied

Code	MoO ₃ content [wt.%]	Details of the preliminary thermal treatment	BET surface area ^a [m ² /g]
MoA	10	Continuous evacuation for 4 h, $T = 523$ K, $p = 800$ Pa	196
MoB	10	Calcination in dry air for 4 h, $T = 823$ K, $p = 0.1$ MPa	204

^aThe catalysts heated at 873 K under argon atmosphere.

2.5. BET surface area

Prior to the measurements, the samples were evacuated at 473 K for 2.5 h. BET surface areas of the catalysts were determined by argon adsorption. The measurements were performed for the support (Table 1) and for MoA and MoB catalysts activated under argon atmosphere (Table 2).

2.6. XPS measurements

The XPS spectra were obtained with the ESCA-3 VG Scientific spectrometer using the AlK $\alpha_{1,2}$ X-ray source ($h\nu = 1486.6$ eV, 13 kV, 8–10 mA). Mo 3d, Al 2p, C 1s and O 1s bands were recorded with electron emission angle 45° at a pressure of $< 2 \times 10^{-8}$ Torr. Handling of spectra consisted of Shirley's background subtraction, K $\alpha_{3,4}$ satellite removing and fitting with Gauss–Lorentz peaks. The binding energies were referenced to the Al 2p line (74.9 eV) obtained for the support.

The samples studied by XPS are described in Table 3.

3. Results and discussion

3.1. Activity of the catalysts in propene metathesis

The catalysts were highly selective and moderately active at a relatively low temperature (303 K). Propene conversion was calculated from an amount of propene converted to ethylene and 2-butene, and the amount of propene in the feed.

The results shown in Table 4 indicate that the method of the preliminary thermal treatment affects the metathesis activity of the catalysts. Heating the precursor at 523 K under evacuation leads to a more active catalyst than calcinating the precursor at 823 K. This trend was reproducible and took place when the dilute substrate was applied.

Table 3
Details of the preparation of the samples studied by XPS

Code	Preparation
MoA-1	MoA catalyst after the preliminary thermal treatment (Table 2)
MoA-2	MoA-1 sample heated at $T = 873$ K, under argon atmosphere, for 2 h
MoA-3	MoA-2 treated with 99.5 vol.% propene at $T = 303$ K
MoB-1	MoB catalyst after the preliminary thermal treatment (Table 2)
MoB-2	MoB-1 sample heated at $T = 873$ K, under argon atmosphere, for 2 h
MoB-3	MoB-2 treated with 99.5 vol.% propene at $T = 303$ K
Al ₂ O ₃	Alumina (Table 1) continuously evacuated for 4 h ($T = 523$ K, $p = 800$ Pa) and then heated at $T = 873$ K, under argon atmosphere, for 2 h

Table 4

Propene conversion on MoO₃/Al₂O₃ catalysts prepared using two different methods of preliminary thermal treatment

Contact time [kg s mol ⁻¹]	C ₃ H ₆ content in the feed [mol%]	Propene conversion [%]	
		MoA	MoB
721	5	5.9	4.7
555	6.5	5.7	4.6
555	6.5	5.7 ^a	5.3 ^a
277	6.5	3	2.5

^aCatalysts obtained during another preparation, according to the method described in Section 2.2.

There were practically no differences between the catalyst activity when pure propene (99.5 vol.%) was used as the substrate [15].

3.2. XPS measurements

Al 2p line corresponding to binding energy 74.9 eV was estimated in the independent study. This value corresponds to the structure of the carrier surface similar to AlOOH [16].

In Fig. 1, Mo 3d spectra obtained for the molybdena–alumina catalysts of A series are presented. The curve fit envelopes are compared with the raw data and differences between the raw data points and the curve fitted points are plotted below each spectrum. Accuracy of the fitting procedure, in the case of the samples of B series, was similar.

Table 5 shows the XPS parameters, Mo 3d_{5/2} binding energy and full width at half maximum (FWHM), obtained for both series of molybdena–alumina catalysts. The difference between the binding energy values of Mo 3d_{3/2} and Mo 3d_{5/2} was kept in the range 2.95–3.00 eV, for all oxidation states. Therefore, the values of Mo 3d_{3/2} binding energies are not listed.

As the binding energy values listed in Table 5 indicate, three different Mo oxidation states were detected on the surface of the catalysts. Mo 3d_{5/2} binding energy in range 233.5–233.6

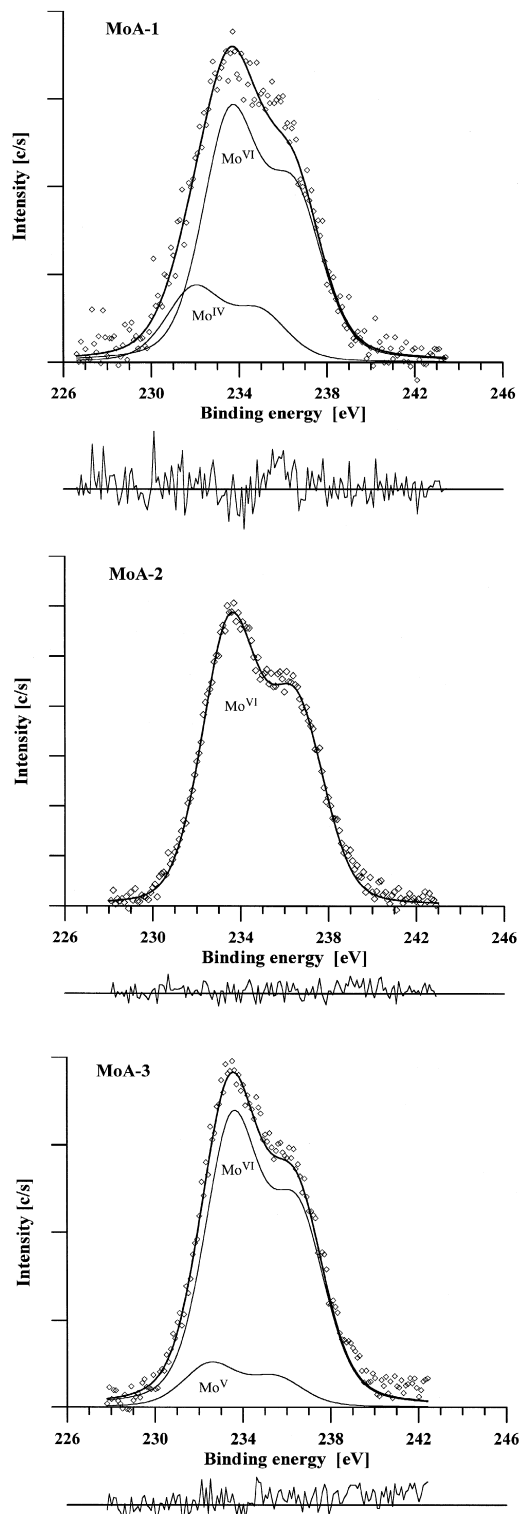


Fig. 1. Mo 3d curve-fitted spectra for molybdena-alumina catalysts of A series. Differences between the raw data points and the curve-fitted points are presented below each spectrum.

Table 5

XPS parameters derived for both series of the molybdena-alumina catalysts and percentage of each oxidation state
FWHM values [eV] used for deconvolution of the Mo 3d envelopes are given in parentheses. Splitting Mo 3d_{5/2}–Mo 3d_{5/2} distance was kept between 2.95 and 3.00 [eV].

Sample	Mo 3d _{5/2} binding energies [eV]			Percentage of each oxidation state		
	Mo ^{VI}	Mo ^V	Mo ^{IV}	Mo ^{VI}	Mo ^V	Mo ^{IV}
MoA-1	233.6 (3.0)	–	231.9 (3.0)	77	–	23
MoB-1	233.6 (2.8)	–	231.7 (2.8)	83	–	17
MoA-2	233.5 (3.0)	–	–	100	–	–
MoB-2	233.5 (3.0)	–	–	100	–	–
MoA-3	233.5 (3.0)	232.5 (2.9)	–	87	13	–
MoB-3	233.5 (2.9)	–	–	100	–	–

eV designates Mo^{VI} oxidation state. To identify other states, a linear relation between Mo 3d binding energies and molybdenum oxidation states with a slope of about 0.8 eV per oxidation state was assumed [17,18]. According to this assumption, Mo 3d_{5/2} binding energy of 232.5 eV should be attributed to Mo^V state. Finally, molybdenum species with binding energy of Mo 3d_{5/2} in the range 231.7–231.9 eV was attributed to monomeric Mo^{IV} ions [17–19].

To obtain relative abundance of each Mo oxidation state, the ratio of the Mo 3d area for a given Mo state and the total area of the Mo 3d envelope was calculated. The results expressed as percentages are given in the right section of Table 5.

As results from Table 5 and Fig. 1, the both initial forms of the catalysts, MoA-1 and MoB-1, contained mainly Mo^{VI} (Mo 3d_{5/2} binding energy is 233.6 eV). Reduced molybdenum species attributed to monomeric Mo^{IV} ions (Mo 3d_{5/2} binding energy 231.7–231.9 eV) were also present.

After thermal activation under argon atmosphere at 873 K, both samples (MoA-2 and MoB-2) contained only Mo^{VI} sites (Mo 3d_{5/2} binding energy is 233.5 eV). Oxidation of molybdenum under the influence of traces of oxygen is rather unlikely, because argon was deoxidised. On the other hand, oxidation of reduced MoO₃/Al₂O₃ surface by thermal treatment under inert atmosphere has been proved

and surface OH groups have been suggested to be the oxidising agents [6,20]:



As shown in the last two rows of Table 5, at 303 K, propene affected MoA-2 and MoB-2 samples in different ways, in spite of the fact that after the thermal activation in argon their surfaces were identical. In the case of the MoA-3 sample, partial reduction of molybdenum occurred after propene treatment. From the binding energy value of Mo 3d_{5/2} peak (232.5 eV) it can be concluded that Mo^V exists on the catalyst surface. However, the content of the Mo^V phase is small and Mo^{VI} phase is still dominant. On the other hand, no changes were detected on the surface of the MoB-3 sample treated with propene, in comparison with the MoB-2 sample activated in argon. EPR studies of heterogeneous molybdena catalysts indicate that under the influence of olefin, reduction of Mo^{VI} to Mo^V takes place [3,5]. But those investigations concerned processes carried out at higher temperatures than that have been applied in this work.

In Table 6, the surface Mo/Al atomic ratios, calculated for each sample, are shown.

As the results in Table 6 indicate, the surface content of molybdenum in MoA-1 sample was higher than in MoB-1 sample. Before the preliminary thermal treatment, the initial Mo loadings in both samples were identical, because

Table 6
The surface Mo/Al atomic ratios

Sample	MoA-1	MoB-1	MoA-2	MoB-2	MoA-3	MoB-3
Mo/Al	0.063	0.057	0.081	0.068	0.08	0.072

both originated from the same precursor. But after evacuating the precursor at $T = 523$ K, Mo in the catalyst was better dispersed than in the catalyst after conventional calcination at $T = 823$ K. Thermal activation of MoA-1 and MoB-1 catalysts at $T = 873$ K, under argon atmosphere, improves dispersion of surface molybdenum, and this effect is stronger in the case of MoA series. Generally, MoA samples had more a homogeneous distribution of surface molybdenum than respective MoB samples. These results can explain why propene affects in different ways the MoA-2 and MoB-2 catalysts, clearly modifying the surface of the former. Different reactivities of the catalysts towards propene at 303 K are caused by difference in the structure of the catalysts' surface.

The above results are consistent with the activity of the catalysts in propene metathesis. It was reported that better reducibility of the catalyst favours its activity in olefin metathesis [3,13]. MoA catalyst was more active than MoB when the process was carried out under low partial pressure of propene (Table 4). Catalysts obtained during another preparation, according to the method described in Section 2.2, also exhibited analogous behaviour (Table 4, the last but one row). Therefore, this trend is reproducible. Concurrently, as the results of XPS study show, MoA catalyst is more easily reduced than the MoB one. This explains the better activity of the catalysts pre-treated according to the A method.

The presence of Mo^{V} centres in the MoA-3 sample probably is not directly related to the occurrence of active sites, because Mo^{V} phase was not detected in MoB-3 catalyst, which was also active in propene metathesis. The number of active sites on the catalyst surface is only a small fraction of the number of molybdenum

atoms, so the results of the XPS investigations cannot lead to the determination of the molybdenum oxidation state in active sites or their precursors. However, the spectroscopic studies confirmed the relationship between the reducibility of the catalyst under the influence of propene and the activity of the catalyst in propene metathesis.

4. Conclusions

The present study on molybdena–alumina catalysts leads to the following conclusions.

(1) The preliminary thermal treatment of the molybdena–alumina catalyst affects its final reactivity towards propene. The surface of MoA catalyst, which was evacuated at 523 K and then activated at 873 K in argon, underwent partial reduction to Mo^{V} phase under the influence of propene at 303 K. This effect was not observed in the case of MoB catalyst, which was calcinated at 823 K and then analogously activated.

(2) The reducibility of the surface molybdenum is connected with the activity of the catalyst in propene metathesis.

(3) The difference in the reactivity of both catalysts towards propene is caused by the difference in their surface structure. After thermal activation in argon, surface molybdenum was better dispersed in the MoA catalyst than in the MoB one. The thermal activation of the catalysts increases the homogeneity of the surface molybdenum.

(4) Independent of the method of preliminary thermal treatment, activation of molybdena–alumina catalyst under argon atmosphere at 873 K leads to formation of Mo^{VI} surface phase.

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