Catalysis Letters Vol. 101, Nos. 1–2, May 2005 (© 2005)
DOI: 10.1007/s10562-005-3751-7

Comparison of metathesis activity of catalysts prepared by anchoring of $MoO_2(acac)_2$ on various supports

Jarosław Handzlik[a,]*, Jan Ogonowski[a], Jerzy Stoch[b], and Maciej Mikołajczyk[b]

[a]*Institute of Organic Chemistry and Technology, Cracow University of Technology, ul. Warszawska 24, PL 31-155 Kraków, Poland*
[b]*Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek 8, PL 30-239 Kraków, Poland*

Received 24 November 2004; accepted 2 January 2005

The properties and olefin metathesis activity of molybdena–alumina, molybdena–silica–alumina and molybdena–silica catalysts prepared by anchoring of $MoO_2(acac)_2$ complex were compared. The specific activity obtained for molybdena–silica–alumina system is higher than that of molybdena–alumina and molybdena–silica catalysts. This statement concerns also the catalysts treated with tetramethyltin

KEY WORDS: molybdenum; alumina; silica–alumina; silica; catalyst; tetramethyltin; metathesis.

1. Introduction

Activity of heterogeneous catalysts in olefin metathesis is influenced by the kind of the support [1, 2]. This effect is well recognised for supported rhenium catalysts. $Re_2O_7/Al_2O_3{\cdot}SiO_2$ systems are known to be more active than Re_2O_7/Al_2O_3 ones, whereas Re_2O_7/SiO_2 catalyst is inactive in olefin metathesis [1–6]. The difference between the activity of rhenium oxide supported on alumina and silica–alumina is explained by different local electronic properties of the carrier [6]. In the case of heterogeneous molybdena catalysts, the influence of the carrier on the catalytic activity in olefin metathesis is not so clear. Applying a suitable preparation and activation method, both highly active molybdena–alumina [7–11] and molybdena–silica [7,12–17] systems can be obtained. However, $MoO_3/SiO_2{\cdot}Al_2O_3$ catalysts were hardly investigated in olefin metathesis. The molybdena–silica–alumina systems prepared by anchoring of $MoOCl_4$ showed better performance than the analogous catalysts supported on alumina and silica [18]. Similar effects were reported for traditionally impregnated systems [19]. On the other hand, our previous studies concerning impregnated Mo catalysts showed that $MoO_3/SiO_2{\cdot}Al_2O_3$ systems are less or equally active, compared to the corresponding MoO_3/Al_2O_3 catalysts [20]. However, the preparation procedures and the supports applied were different in [19] and [20].

Previously, the detailed study of molybdena–alumina catalysts prepared by anchoring of $MoO_2(acac)_2$ complex were done [21]. In the present work, the properties and metathesis activities of anchored molybdena–silica–alumina and molybdena–silica catalysts are studied and compared with those of the molybdena–alumina system. The activity of the catalysts treated with tetramethyltin is also investigated. It was previously shown that activation of the molybdena–alumina catalysts with tetramethyltin causes an increase of the number of the metathesis active sites [22].

2. Experimental

2.1. Materials

Bis(acetyloacetonato)dioxomolybdenum (VI) $MoO_2(C_5H_7O_2)_2$ (Aldrich), dimethyloformamide (Polish Chemical Reagents, POCh), dried with 5 Å molecular sieve, and trichloromethane (POCh) were used for the catalysts preparation. As the catalysts supports, γ-Al_2O_3 (BET surface area 210 $m^2\ g^{-1}$, with other properties reported in the previous papers [21, 23]), amorphous silica–alumina (Aldrich, 475 $m^2\ g^{-1}$, pore volume 0.77 $cm^3\ g^{-1}$, Al_2O_3 content 13 wt%) and silica (BET surface area 335 $m^2\ g^{-1}$) were applied. Argon (99.998 vol.%) was passed through an oxygen trap and dried over 4 Å molecular sieves. The reactant (99.5 vol.% C_3H_6, 0.5 vol.% C_3H_8) was dried with 3 Å molecular sieves.

2.2. Catalysts preparation

$MoO_2(acac)_2$ was anchored to the supports from DMF solutions. The alumina support was earlier calcinated in air at 773 K [21], the silica–alumina support was dried at 373 K under vacuum, while the silica was treated with boiling HCl, washed with water and dried under vacuum at 423 K.

The carriers were contacted with the $MoO_2(acac)_2$ solutions (0.1 mol dm^{-3}) at room temperature, for 24 h.

---

* To whom correspondence should be addressed.
E-mail: jhandz@usk.pk.edu.pl

The slurry was shaken mechanically. Then, the excess solution was separated by filtration and the catalysts were washed, first with the pure solvent, then with trichloromethane. After that, the precursors were dried in air at room temperature for 24 h and subsequently, under vacuum, at 423 K for 6 h. Finally, the catalysts were calcinated in flowing dry air at 723 K, for 6 h. One sample of the molybdena–silica–alumina catalyst was continuously evacuated at 523 K, for 6 h, instead of the calcination step. In table 1, the molybdenum loadings in the catalysts are listed. The values were determined by ICP MS (ELAN 6100 spectrometer, Perkin Elmer).

2.3. Catalytic tests

Catalytic tests were performed 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 under argon at 873 K, for 2 h, and then cooled to the reaction temperature. As a test reaction, propene metathesis, carried out at 303 K under atmospheric pressure, was chosen. The flow rate of the reactant was 20 cm^3 min^{-1} (the contact time: 36.3 kg s mol^{-1}).

In the case of the molybdena–silica catalyst, the reaction temperature was changed in the range 303–673 K.

When the catalysts were activated with tetramethyltin, an injection of 0.5 cm^3 of diluted $SnMe_4$ solution in *n*-pentane at 303 K followed the thermal activation of the catalysts. After 30 minutes, the reactor was fed with propene (60 cm^3 min^{-1}, the contact time 12.1 kg s mol^{-1}).

2.4. XRD measurements

The molybdena–silica–alumina and molybdena–silica samples were analysed with the Philips XRD System X'PERT, using Cu Kα radiation. The analysis was performed for the samples that were calcinated and then heated at 873 K under argon. The XRD measurements of the molybdena–alumina sample were done previously [21] in the same conditions.

Table 1
The catalysts studied

Code	Support	Mo loading	
		[MoO_3 wt%]	[Mo atoms nm^{-2}][a]
MoAl[b]	Al_2O_3	7.1	1.5
MoSiAl	$SiO_2{\cdot}Al_2O_3$	2.0	0.2
MoSi	SiO_2	0.7	0.1

[a] Calculated from the amount of Mo deposited on the supports and from their surface areas.
[b] [21].

2.5. XPS measurements

The XPS analysis was done for the calcinated samples of the molybdena–silica–alumina and molybdena–silica catalysts. The molybdena–alumina sample were analysed previously [21]. The 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). Mo3d, Al2p, Si2p, C1s and O1s bands were recorded with electron emission angle 45° at a pressure of $< 2 \times 10^{-8}$ Torr. Handling of the spectra consisted of Shirley's background substraction, $K\alpha_{3,4}$ satellite removing and fitting with Gauss–(30%)Lorentz peaks. The binding energies were referenced to the C1s line (248.8 eV).

3. Results and discussion

3.1. XRD characterisation of the catalysts

The catalysts studied do not contain any Mo crystalline phases that could be detected by XRD. This is in accordance with other reported results, where no Mo crystallites were found on molybdena–alumina and molybdena–silica–alumina systems with a relatively low Mo loading [24–26]. As concerns the molybdena–silica catalyst, the Mo content is very low (table 1), what also explains the absence of the Mo crystallites.

The X-ray diffraction patterns of the molybdena–alumina sample exhibit broad peaks corresponding to microcrystallities of γ-Al_2O_3, which are dispersed in amorphous phase of alumina [21].

3.2. XPS characterisation of the catalysts

Binding energies $Mo3d_{5/2}$ and full width at half maxima (FWHM), obtained for the catalysts studied, are listed in table 2. As one can see, the binding energies are in the range of 232.8–233.0 eV. These values are attributed to Mo^{VI} surface species [10,24,27–30]. Other Mo oxidation states have not been detected.

3.3. Metathesis activity of the catalysts

The molybdena–alumina [21] and molybdena–silica–alumina catalysts are highly selective in the reaction conditions ($T = 303$ K) and the only products detected are ethene, *trans*-2-butene and *cis*-2-butene. In the case of the molybdena–silica catalyst, double-bond isomeri-

Table 2
$Mo3d_{5/2}$ binding energies [eV] of the catalysts. FWHM values [eV] used for deconvolution of the Mo3d envelopes are given in parantheses

MoAl[a]	232.8 (3.2)
MoSiAl	232.8 (3.0)
MoSi	233.0 (3.6)

[a] [21].

sation to 1-butene occurred at temperatures higher than 573 K. At 673 K, selectivity to 2-butene was ca. 80%.

The pre-treatment method affects the activity of the $MoO_3/SiO_2{\cdot}Al_2O_3$ catalysts (figure 1). The calcinated sample exhibits higher activity than the evacuated one. This effect is more evident than in the case of the MoO_3/Al_2O_3 systems [21]. Also, the $MoO_3/SiO_2{\cdot}Al_2O_3$ catalyst deactivates slower (fig. 1) than the MoO_3/Al_2O_3 one [21].

Molybdena–silica catalyst was inactive at temperatures lower than 573 K. At 673 K, this system exhibits good activity (figure 2). An induction period, similar as in the case of the molybdena–alumina catalysts [21], can be observed. What is interesting, when the reaction temperature was being decreased from 673 K, the MoO_3/SiO_2 catalyst still showed activity, even at 333 K (Fig. 2). This proves that the contact of the catalyst with olefin at high temperature is necessary to generate active metathesis sites and at least some of them can be still active at lower temperatures. Highly active at room temperature molybdena–silica systems were reported by Shelimov et al. [15–17]. However, those catalysts were obtained by photoreduction of surface Mo species under CO atmosphere.

In figure. 3, the specific activities of the $MoO_3/SiO_2{\cdot}Al_2O_3$, MoO_3/SiO_2 (working at low temperatures) and the most active sample among the previously studied MoO_3/Al_2O_3 catalysts [21] are compared. The catalysts have different surface Mo concentrations (table 1), because for each the support studied the Mo loading was obtained naturally during the anchoring process (there was an excess of the solution of the Mo complex). It was previously shown for the anchored molybdena–alumina systems that increase of the concentration of the $MoO_2(acac)_2$ in the solution almost do not affects the Mo content in the prepared catalysts [21].

As one can see from Fig. 3, the molybdena–silica–alumina catalyst exhibits much higher specific activity than the molybdena–alumina and molybdena–silica ones, both of similar activity. Either a higher percentage of the active sites or their higher activity, compared to the molybdena–alumina and molybdena–silica systems, can explain the enhanced specific activity of the $MoO_3/SiO_2{\cdot}Al_2O_3$ catalyst. Similarly to the Mo catalysts prepared by anchoring of $MoO_2(acac)_2$ complex on the support, the impregnated $Re_2O_7/SiO_2{\cdot}Al_2O_3$ systems with low rhenium loading are much more active in olefin metathesis than the corresponding Re_2O_7/Al_2O_3 catalysts [1–4,6]. In the case of the rhenium catalysts, the better activity of the systems supported on silica–alumina is explained by the fact that, at low loadings, rhenium species replace mainly the acidic Si–Al bridging hydroxyl groups, what results in electron-poor rhenium centres [6,31]. These centres are the active site precursors. On the other hand, ReO_4^{2-} ions on alumina support react predominantly with coordinatively unsaturated Al^{3+} Lewis acid sites and with the most basic OH groups. When the Re loading increases, the neutral and more acidic hydroxyl groups are replaced, resulting in the active site precursors [6,31]. By taking

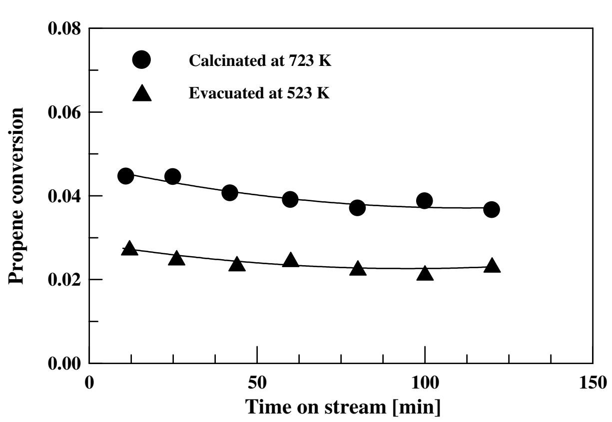

Figure 1. Activity of the molybdena–silica–alumina catalysts.

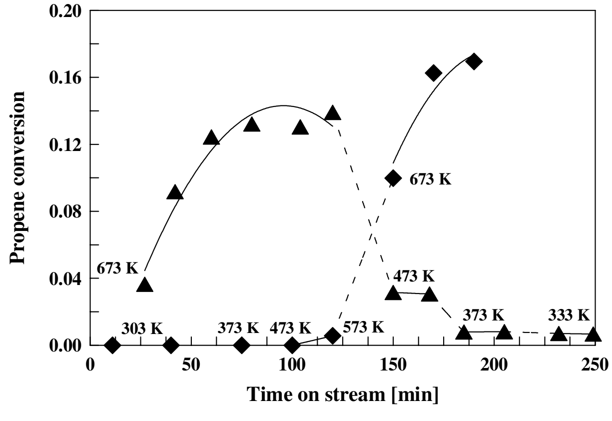

Figure 2. Activity of the molybdena–silica catalyst. Changes of the reaction temperature during each process are depicted.

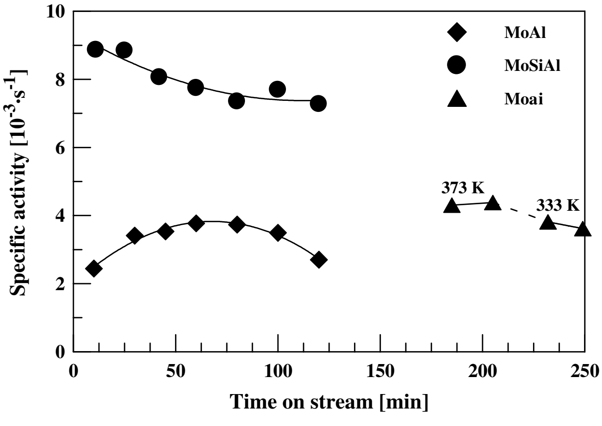

Figure 3. Comparison of the activity of the molybdena–alumina ($T = 303$ K), molybdena–silica–alumina ($T = 303$ K) and molybdena–silica ($T = 333$–373 K) catalysts.

into account that $MoO_2(acac)_2$ also reacts first with the Al^{3+} sites and basic OH groups of alumina [32,33], the behaviour of the anchored Mo catalysts can be explained in similar way as in the case of the rhenium systems. Thus, it seems that the local electronic properties of the support influence the metathesis activity of the Mo centres.

The catalysts treated with tetramethyltin show over one order of magnitude increased performance (Fig. 4), comparing to the untreated ones (Fig. 3). It was reported that an addition of tetramethyltin enables or significantly improves the activity of the supported Mo catalysts in olefin metathesis [21,23,34,35].

The specific activities of the MoO_3/Al_2O_3–$SnMe_4$ and MoO_3/SiO_2–$SnMe_4$ systems are similar, whereas the activity of the molybdena–silica–alumina catalyst treated with tetramethyltin is significantly higher (Fig. 4). This resembles the trend in the specific activities of the corresponding catalysts not treated with tetramethyltin (Fig. 3). On the other hand, the Sn:Mo molar ratios are not the same for the mentioned catalysts. It should be emphasised, however, that in Fig. 4 the performance of the most active MoO_3/Al_2O_3–$SnMe_4$ catalyst (with the optimal Sn:Mo ratio) is shown [21], while the amounts of the tetramethyltin added to the $MoO_3/SiO_2{\cdot}Al_2O_3$ and MoO_3/SiO_2 catalysts were not optimised. Thus, the efficiency of the latter two systems can be even improved and, without doubts, the $MoO_3/SiO_2{\cdot}Al_2O_3\text{-}SnMe_4$ system exhibits higher specific activity than the $MoO_3/Al_2O_3\text{-}SnMe_4$ one. Better performance after replacing alumina by silica–alumina was also reported for rhenium [3,5] and tungsten [18] systems treated with tetraalkyltin.

Therefore, applying the $MoO_2(acac)_2$ complex and the silica–alumina as a support leads to the Mo catalyst with higher specific activity than in the case of the molybdena–alumina systems prepared with the same precursor. This statement is true for both catalysts untreated and treated with tetramethyltin.

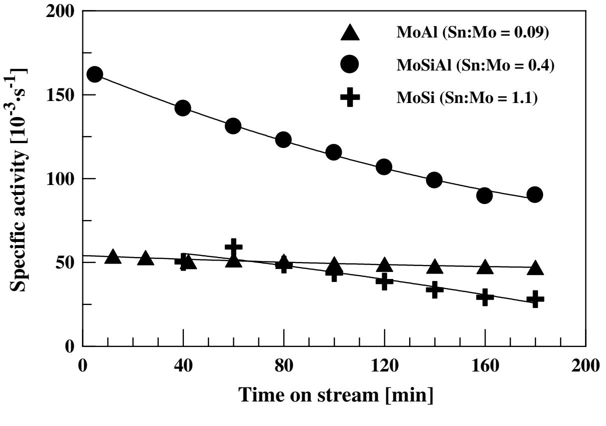

Figure 4. Comparison of the activity of the tetramethyltin treated catalysts on different carriers. $T = 303$ K.

3. Conclusions

In the present work, the properties and metathesis activity of molybdena–alumina, molybdena–silica–alumina and molybdena–silica catalysts prepared by anchoring of the $MoO_2(acac)_2$ complex were compared. It is shown that the specific activity of the molybdena–silica–alumina system is higher than the activity of the molybdena–alumina and molybdena–silica systems. In the case of the corresponding catalysts treated with tetramethyltin, the efficiency of the molybdena–silica–alumina system is also the best among the catalysts studied.

References

[1] K.J. Ivin and J.C. Mol, *Olefin Metathesis and Metathesis Polymerization* (Academic Press, London, 1997).

[2] J. Handzlik and J. Ogonowski,*Metateza Olefin, Monografia, Politechnika Krakowska*, Vol. 223 (Seria Inynieria i Technologia Chemiczna, Kraków, 1998).

[3] Xiaoding. Xu, C.. Boelhouwer, D. Vonk, J.I. Benecke and J.C. Mol, J. Mol. Catal. 36 (1986) 47.

[4] J.A.. Moulijn and J.C. Mol, J. Mol. Catal. 46 (1988) 1.

[5] M. Sibeijn and J.C. Mol, Appl. Catal. 67 (1991) 279.

[6] J.C. Mol, Catal. Today 51 (1999) 289.

[7] Y.. Iwasawa, H. Kubo and H. Hamamura, J. Mol. Catal. 28 (1985) 191.

[8] A.N.. Startsev, O.V. Klimov and E.A. Khomyakova, J. Catal. 139 (1993) 134.

[9] O.V. Klimov, E.A. Krivoshchekova and A.N. Startsev, React. Kinet. Catal. Lett. 43 (1991) 19.

[10] O.V.. Klimov, E.A. Krivoshchekova, A.V. Kalinkin and A.N. Startsev, React. Kinet. Catal. Lett. 43 (1991) 301.

[11] W. Yi, M. Schwidder and W. Grünert, Catal. Lett. 86 (2003) 113.

[12] M. Anpo, M. Kondo, Y. Kubokawa, C. Louis and M. Che, J. Chem. Soc., Faraday Trans. 184 (1988) 2771.

[13] K. Zama, Y.. Imada, A. Fukuoka and M. Ichikawa, Appl. Catal. A 194–195 (2000) 285.

[14] Q. Zhuang, A. Fukuoka, T. Fujimoto, K. Tanaka and M. Ichikawa, J. Chem. Soc. Chem. Commun. (1991) 745.

[15] B.N.. Shelimov, I.V. Elev and V.B. Kazansky, J. Catal. 98 (1986) 70.

[16] K.A. Vikulov, B.N. Shelimov and V.B. Kazansky, J. Mol. Catal. 65 (1991) 393.

[17] K.A. Vikulov, B.N.. Shelimov, V.B. Kazansky and J.C. Mol, J. Mol. Catal. 90 (1994) 61.

[18] P. Maksimowski and W. Skupiński, J. Mol. Catal. 65 (1991) 187.

[19] H. Aritani, O. Fukuda, T. Yamamoto, T. Tanaka and S. Imamura, Chem. Lett. (2000) 66.

[20] J. Handzlik, J. Ogonowski, E. Sikora and O. Vogt, Przem. Chem. 81 (2002) 184.

[21] J. Handzlik, J. Ogonowski, J.. Stoch and M. Mikoajczyk, Appl. Catal. A 273 (2004) 99.

[22] J.. Handzlik and J. Ogonowski, Catal. Lett. 88 (2003) 119.

[23] J. Handzlik and J. Ogonowski, Catal. Lett. 83 (2002) 287.

[24] E. Heracleous, A.F. Lee, I.A. Vasalos and A.A. Lemonidou, Catal. Lett. 88 (2003) 47.

[25] M.. Henker and K.-P. Wendlandt, Appl. Catal. 69 (1991) 205.

[26] S.. Rajagopal, H.J. Marini, J.A. Marzari and R. Miranda, J. Catal. 147 (1994) 417.

[27] J. Sarrín, O. Noguera, H. Royo, M.J. Pérez Zurita, C. Scott, M.R. Goldwasser, J. Goldwasser and M. Houalla, J. Mol. Catal. A 144 (1999) 441.

[28] D.S. Zingg, L.E. Makovsky, R.E. Tischer, F.R. Brown and D.M. Hercules, J. Phys. Chem. 84 (1980) 2898.

[29] W. Grünert, A.Yu. Stakheev, R. Feldhaus, K. Anders, E.S. Shpiro and K.M. Minachev, J. Phys. Chem. 95 (1991) 1323.

[30] I. Oliveros, M.J. Pérez Zurita, C. Scott, M.R. Goldwasser, J. Goldwasser, S. Rondón, M. Houalla and D.M. Hercules, J. Catal. 171 (1997) 485.
[31] R. Spronk, A. Andreini and J.C. Mol, J. Mol. Catal. 65 (1991) 219.
[32] J.A.R. Veen, G. Jonkers and W.H. Hesselink, J. Chem. Soc., Faraday Trans. 185 (1989) 389.
[33] J.A.R. Veen, P.C. Jong-Versloot, G.M.M. Kessel and F.J. Fels, Thermochim. Acta 152 (1989) 359.
[34] K. Tanaka and K. Tanaka, J. Chem. Soc., Chem. Commun. (1984) 748.
[35] K. Tanaka and K. Tanaka, J. Chem. Soc., Faraday Trans. 184 (1988) 601.