Activity of molybdena–alumina metathesis catalysts treated with tetramethyltin

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The MoO_3/Al_2O_3 catalytic systems treated with $SnMe_4$ were studied. Addition of tetramethyltin enhanced about 20 times the activity of the catalyst in propene metathesis ($T = 303$ K). The optimal Sn : Mo molar ratio was about 1 : 20. Increase of the activation temperature caused decrease of the catalyst activity.

KEY WORDS: molybdena–alumina; catalyst; tetramethyltin; propene; metathesis.

1. Introduction

Olefin metathesis has a great importance in organic synthesis, as well as having found many industrial applications [1–6]. The process can be carried out in the presence of both homogeneous and heterogeneous catalytic systems, containing transition metals, mainly Re, Mo, Ru and W [1,2]. Generally, heterogeneous catalysts are more favorable than homogeneous ones because of easier catalyst regeneration and the possibility of easy separation of a catalyst from the product mixture.

As has been generally accepted, olefin metathesis proceeds according to the carbene mechanism, and metal-alkylidene complexes must be present in the reaction environment [1].

Many studies have concerned heterogeneous rhenium-based catalysts [7–18] because of their high potential for practical applications [1,3]. Supported molybdenum catalysts can also be applied in industrial processes and an example is the large-scale Shell Higher Olefin Process (SHOP) for producing detergent-range alkenes from ethene [1,3]. Heterogeneous metathesis catalysts can be effectively promoted with tetraalkyltin [1–3,7–22]. Re_2O_7/Al_2O_3 and $Re_2O_7/SiO_2 \cdot Al_2O_3$ systems treated with tetraalkyltin are active for the metathesis of functionalized olefins [1,2,7,8,10,13,15]. On the other hand, only a few works concerning supported molybdenum catalysts promoted with tetraalkyltin have been published [19–22].

In previous works [23–25], we studied the effect of the catalyst preparation method, preliminary thermal treatment and *in situ* activation on the propene metathesis activity of molybdena–alumina systems, as well as the relationships between the details of the catalyst pretreatment and the composition of its structure. The purpose of the present work is to investigate the olefin metathesis activity of the MoO_3/Al_2O_3-$SnMe_4$ system and to optimize the amount of tetramethyltin added. Propene metathesis carried out at 303 K has been chosen as a test reaction.

2. Experimental

2.1. Materials

Alumina (table 1) and analytically pure ammonium heptamolybdate (AHM, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$) were used for the catalyst preparation. Tetramethyltin (99%, Merck) and *n*-pentane (p.a., Loba Feinchemie AG) were applied during the catalyst activation. Argon (99.998 vol.%) was passed through an oxygen trap and dried over a 4A molecular sieve. The reactant (99.5 vol.% C_3H_6, 0.5 vol.% C_3H_8) was dried with a 3A molecular sieve.

2.2. Preparation of the catalysts

The catalysts were prepared by impregnation of Al_2O_3 with an aqueous solution of ammonium heptamolybdate. AHM dissolved in distilled water was added to the carrier. The amount of the impregnation solution was about 3.3 cm^3 g–$Al_2O_3^{-1}$. The mixture was left in an open vessel at room temperature until excess

Table 1
Properties of the catalyst support (Al_2O_3).

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

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Table 2
The catalysts studied.

Code	MoO_3 content (wt%)	Details of the preliminary thermal treatment	BET surface area (m^2/g)[a]
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

[a] The catalysts heated at 873 K under argon atmosphere.

water evaporated. During this time the mixture was gently stirred sometimes. Next, the precursor was 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, B) were applied (table 2).

2.3. *Catalytic tests*

Catalytic tests were carried out in a fixed-bed 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. Before the reaction, the catalyst was *in situ* heated at 873 K under flowing argon for 2 h, and then it was cooled to 303 K. Next, tetramethyltin diluted with 0.5 cm^3 of *n*-pentane was injected into the microreactor, in flowing argon. The Sn : Mo molar ratios were 1 : 2, 1 : 5, 1 : 10, 1 : 15, 1 : 20, 1 : 30 and 1 : 50. Then, the temperature of the bed was raised to 313 K, 373 K, 473 K or 873 K (activation temperatures). After 30 min, the microreactor was cooled again to 303 K.

Propene metathesis was carried out at 303 K under atmospheric pressure. The flow rate of the reactant was 60 $cm^3 \, min^{-1}$ (the contact time was 12.1 $kg \, s \, mol^{-1}$).

The activity of the MoA catalyst not treated with tetraalkyltin was also measured. After *in situ* treatment at 873 K under argon, the catalyst was cooled to 303 K and then the reaction started.

2.4. *Gas chromatography*

The conditions of the GC analysis were described in the previous papers [23,25].

2.5. *BET surface area (tables 1 and 2)*

BET surface-area measurements were described in previous papers [23,25].

2.6. *XPS measurements*

A detailed XPS study on the MoA and MoB catalysts was described elsewhere [25].

3. Results and discussion

The catalysts treated with tetramethyltin were generally highly active and selective at $T = 303$ K. The only products were ethene, trans-2-butene, cis-2-butene and traces of 1-butene. Turnover frequency was defined as the number of propene molecules converted per Mo site per second. All molybdenum atoms were taken into account.

The activity of the MoO_3/Al_2O_3 catalysts increased about one order of magnitude after treatment of them with tetramethyltin, keeping at $T = 313$ K. In the case of the unpromoted catalysts, the break-in time was observed and the maximum of the catalyst activity was achieved after 40 min of the process. As concerns the MoO_3/Al_2O_3-$Sn(CH_3)_4$ systems, the catalyst break-in was not observed. However, the deactivation rates of the latter catalysts were higher than in the case of the catalysts that were not treated with tetramethyltin. These results are similar to the results reported for Re_2O_7/Al_2O_3 systems treated and not treated with tetraalkyltin [12]. It was proposed that intrinsically distinct active sites are present in the two rhenium-based catalysts [12,16,18]. Recently, on the basis of our kinetic studies, we also concluded that in the case of the molybdena–alumina systems the active sites generated by $SnMe_4$ are chemically different from those present on the catalyst not treated with the activator [26].

The results shown in figure 1 indicate that the optimal Sn:Mo molar ratio is about 0.05. Increase of the activator amount above this value causes gradual decrease of the catalytic activity, until the Sn : Mo molar ratio reaches a value of about 0.2. Further increase of the activator amount no longer influences the activity of the catalyst. Taking into account the fact that tetraalkyltins are human and environmental poisons, these results are important from the practical point of view. One can expect that for each Mo catalyst system treated with tetraalkyltin the optimal amount of activator added

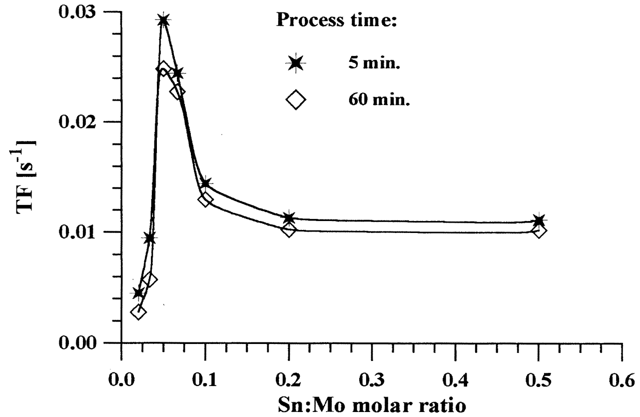

Figure 1. Dependence of the activity of the MoA–$Sn(CH_3)_4$ catalyst on the Sn : Mo molar ratio. $T_{act} = 303$ K.

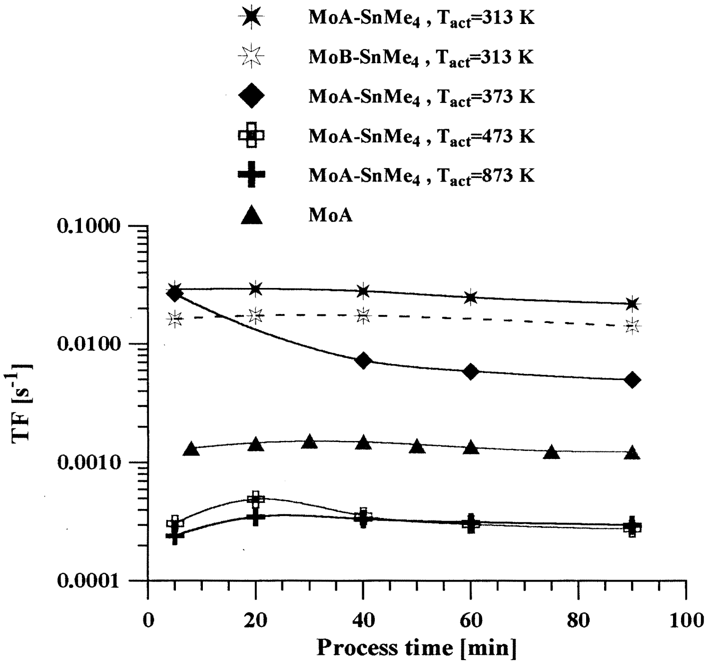

Figure 2. Influence of the activation temperature (T_{act}) on the activity of the MoA–$Sn(CH_3)_4$ catalyst. The efficiencies of the MoB–$Sn(CH_3)_4$ and MoA catalysts are also shown.

can be found. Therefore, there is no need to add more of the activator than is necessary.

It is interesting to compare the present results with those concerning optimization of the tetraalkyltin amount added to the Re_2O_7/Al_2O_3 system [8,18]. In the case of metathesis unsaturated esters, the activity of the rhenium–alumina system treated with tetramethyltin increased with increasing of the Sn : Re molar ratio to 0.015, and remained constant for the higher amounts of $SnMe_4$ [8]. Similar behavior was reported for the Re_2O_7/Al_2O_3–$SnBu_4$ catalyst in halogen-containing olefin metathesis; however, in that case the activity became constant for an Sn : Re molar ratio higher than 0.09 [18]. Thus, despite the fact that different systems are compared, our optimal Sn : Mo molar ratio value (0.05) is well consistent with the mentioned values of Sn : Re molar ratio. On the other hand, the dependency of the catalytic activity on the SnR_4 amount added to the Re_2O_7/Al_2O_3 system does not show a maximum, as was observed here for the molybdena–alumina catalyst. Probably the different structure and reactivity of the Mo and Re active-site precursors are responsible for the slightly different behavior of the two systems.

During treatment of the catalyst with tetramethyltin, before propene metathesis started, we had detected methane in the stream leaving the microreactor. This is in accordance with other reported results [22]. A part of the releasing methane can come from the reaction of methyl groups with hydrogen from the surface hydroxyl groups. However, large amounts of the releasing methane can be the product of the following reaction that explains the generation of the active metathesis sites on the catalyst surface [22]:

$$2CH_3 \rightarrow CH_4 + [CH_2].$$

If 100% of the $Sn(CH_3)_4$ molecules reacted according to the above scheme, two surface active sites would be generated per $SnMe_4$ molecule added. Therefore, the obtained optimal value of the Sn : Mo molar ratio (1 : 20) indicates that the number of active sites generated by tetramethyltin on the MoO_3/Al_2O_3 catalyst surface is no higher than 10% of the total Mo atoms in the catalyst. In fact, the number of active sites is less than 10% of the Mo atoms in the catalyst, because only a part of the methyl groups of the tetramethyltin react according to the above reaction.

Increasing the activation temperature, after treatment with tetramethyltin, caused a strong decrease of the catalyst activity (figure 2). Injecting of the activator, followed by heating the bed at $T_{act} = 473\,K$ or 873 K, results in a catalyst that is even less active than MoO_3/Al_2O_3 systems not treated with tetramethyltin. This is in contrast to other results reported for MoO_3/SiO_2–$SnMe_4$ systems [22]. Those catalysts were evacuated at raised temperatures after their treatment with tetramethyltin. The optimal evacuation temperature was 373 K, which allowed one to obtain a catalyst about 20 times more active than the catalyst evacuated at room temperature [22]. What is more, the evacuation temperature in the range 373–773 K was always more effective than the evacuation at room temperature. However, in ref. [22] the activation procedure was quite different: the catalysts were treated with an excess of $SnMe_4$ vapor. On the other hand, our method of tetramethyltin addition to the catalysts is very similar to the procedure commonly applied in the case of the rhenium-based catalysts, which are usually promoted at room temperature [8–16]. Recently, it was reported that the optimal activation temperature for the Re_2O_7/Al_2O_3 system after treatment with $SnBu_4$ was about 333 K, and increasing this value to 373 K caused considerable decreasing of the catalyst activity. Those results are quite similar to our results concerning molybdena–alumina systems.

The results shown in figure 2 indicate that the preliminary thermal treatment of the MoO_3/Al_2O_3 catalyst influences its further activity after adding $SnMe_4$. The precursor of the MoA catalyst had been evacuated at $T = 523$ K (table 2), whereas the precursor of the MoB catalyst had been calcinated at $T = 823$ K. As we can see from figure 2, the MoA–$SnMe_4$ catalyst is more active than the MoB–$SnMe_4$ one. That trend took place also in the case of non-activated $SnMe_4$ catalysts, if diluted propene was used as the reactant [23]. As was shown in the previous XPS study of the MoO_3/Al_2O_3 system [25], the kind of preliminary thermal treatment of the catalyst affects its final surface structure and reducibility. These differences can play a role during the reaction of $SnMe_4$ with the catalyst surface.

4. Conclusions

The present study on molybdena–alumina catalysts treated with tetramethyltin leads to the following conclusions:

1. The metathesis activity of MoO_3/Al_2O_3 catalyst treated with tetramethyltin is enhanced about 20 times compared to the non-activated catalyst. The optimal Sn : Mo molar ratio for MoO_3/Al_2O_3 catalysts is about 0.05.
2. The value of the optimal Sn : Mo molar ratio suggests that the amount of active sites generated by tetramethyltin on the MoO_3/Al_2O_3 surface is no higher than 10% of the total Mo atoms in the catalyst.

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