Dynamic chemical counting of active centers of molybdena–alumina metathesis catalysts

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A dynamic method of chemical counting of active centers of alkene metathesis is proposed and applied to study MoO_3/Al_2O_3 and $MoO_3/Al_2O_3-SnMe_4$ systems. For the MoO_3/Al_2O_3 catalyst, the estimated number of the active sites is less than 1% of the total number of the Mo atoms. $MoO_3/Al_2O_3-SnMe_4$ catalysts have a larger percentage of active centers, compared with the system not treated with $SnMe_4$. This increase of the active sites number approximately corresponds to improvement of the metathesis activity of the $MoO_3/Al_2O_3-SnMe_4$ catalyst.

KEY WORDS: molybdena–alumina; catalyst; tetramethyltin; metathesis; active centers.

1. Introduction

Alkene metathesis proceeds according to the carbene mechanism [1–3]. If the reaction is carried out on a heterogeneous catalyst, metal–alkylidene centers have to be present on its surface. These active sites are formed after the catalyst is brought into contact with alkene [2–5] or cycloalkane [6–8]. Heterogeneous metathesis catalysts are also effectively promoted with tetraalkyltin [9–18].

It seems that the surface concentration of the metathesis active centers is very small for the heterogeneous catalysts. Poisoning experiments using NO indicated that the fraction of the active sites is less than 1% of the total number of Re atoms for the supported rhenium catalysts [2]. Similar results were obtained during kinetic studies on Re_2O_7/Al_2O_3 system [19].

However, alkene metathesis gives an opportunity for direct counting of active sites present in the catalyst [20]. In the first step, the catalyst is contacted with an excess of so-called "activating alkene" (propene or 2-butene, for instance) and the active sites are generated. Then, the activating alkene is removed by pumping out and, in the second step, a second alkene (ethene) is fed. The second alkene reacts with the previously produced active sites, so new alkenes are generated and their amount is directly related to the number of the active centers. This method was applied to count active sites of Re_2O_7/Al_2O_3 catalysts, giving the percentage of active Re centers in the range 0.20 to 1.79 [20]. These results are quite consistent with the mentioned results of poisoning and kinetic experiments [2,19]. On the other hand, different and a bit surprising results were also reported for rhenium–alumina systems [21]. Applying the chemical counting method, the authors obtained the percentage of the active Re atoms as high as 18 to 35. It was mainly explained by a different method of catalyst preparation [21].

As alkene metathesis is a reversible reaction, a large excess of the second alkene should be added during the chemical counting. It was reported that the obtained percentage of the active sites depended on the ethylene pressure [20]. Another problem is intrinsic deactivation of alkene metathesis catalysts [2,3,20,22]. If the deactivation is caused by gradual loss of the active sites [22], the time of the evacuation between the first and the second step can influence the results. On the other hand, too short an evacuation period would remain in the catalyst a too high amount of the activating alkene adsorbed, which would also affect the obtained quantities.

In the present work, we have proposed the chemical counting of the metathesis active sites in dynamic conditions. Both steps take place in a flow microreactor. This approach eliminates the equilibrium problem and allows controlling the residual amount of the activating alkene. The method has been applied to determine the number of active sites of MoO_3/Al_2O_3 and $MoO_3/Al_2O_3-SnMe_4$ catalysts.

2. Experimental

2.1. Materials

Alumina (BET surface area 210 $m^2\ g^{-1}$; other properties were reported in the previous papers [18,23]) and analytically pure ammonium heptamolybdate $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ were used for the catalyst's preparation. Tetramethyltin (99%, Merck) and *n*-pentane (p.a., Loba Feinchemie AG) were applied during

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the catalyst's activation. Argon (99.998 vol.%) was passed through an oxygen trap and dried over a 4A molecular sieve. The alkenes (polymerization grade) were dried with a 3A molecular sieve.

2.2. *Preparation of the catalyst*

The 10 wt% MoO_3/Al_2O_3 catalyst was prepared by impregnation of Al_2O_3 with an aqueous solution of ammonium heptamolybdate. 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 water evaporated. During this time, the mixture was gently stirred occasionally. Next, the precursor was dried at 383 K for 4 h at a reduced pressure and continuously evacuated at 523 K and 800 Pa, for 4 h. The BET surface area of the obtained catalysts was $196\,m^2\ g^{-1}$ [24].

2.3. *Determination of the active sites number*

The reactions 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- to 0.3-mm catalyst grains. Before the reaction, the catalyst was heated *in situ* at 873 K under flowing argon, for 2 h, and then it was cooled to 303 K. After that, in the case of $MoO_3/Al_2O_3{-}SnMe_4$ catalyst, tetramethyltin diluted with $0.5\,cm^3$ of *n*-pentane was injected into the microreactor, in flowing argon. The Sn:Mo molar ratios were 1:20, 1:10, 1:5 or 1:2. Then, the temperature of the bed was raised to 313 K. After 30 min, the microreactor was cooled again to 303 K.

Next, the activating alkene (99.5 vol% propene or a propene–helium mixture containing 5 vol% C_3H_6) was delivered to the microreactor. The flow rate of the reactant was 10, 20 or $60\,cm^3\ min^{-1}$. Propene metathesis was carried out at 303 K under atmospheric pressure.

After 1 h of propene metathesis, the microreactor feed was changed to argon (10, 20 or $150\,cm^3\ min^{-1}$). The desorption temperature usually was fixed at 303 K, however, in some cases, it was risen to 373 K or 473 K. Then, the flow and temperature were established (10 or $20\,cm^3\ min^{-1}$, 303 K) and the gas mixture leaving the microreactor was analyzed by GC every 10 min. After several tens of minutes, the microreactor feed was changed to ethene–argon mixture (0.5 vol% C_2H_4) of the same flow rate as argon. The frequency of the GC analyses was initially increased to 1 per 90 s.

Two blind experiments were also performed. In the first case, alumina without any molybdenum deposited was placed into the microreactor and tetramethyltin was not added. In the second case, active MoO_3/Al_2O_3 catalyst was applied; however, during propene metathesis the catalyst was fully deactivated by treating it with moist air.

3. Results and discussion

During steady-state propene metathesis, two kinds of active centers should be present in the catalyst: $[Mo]=CH_2$ and $[Mo]=CHCH_3$. After treating the catalyst with ethene, the Mo-ethylidene centers are transformed into the Mo-methylidene ones and propene is released:

$$[Mo]=CHCH_3 + C_2H_4 \rightarrow [Mo]=CH_2 + C_3H_6 \quad (1)$$

Therefore, the amount of the released propene is related to the number of the Mo-ethylidene centers, which is half the number of all the active sites.

In all the experiments, when ethene was added, a residual stream of propene was leaving the microreactor together with argon. After the feed was changed to ethene, the molar flow rate of the releasing propene first increased dramatically and then decreased very quickly, thus giving an "impulse" of the "additional" propene. A typical experiment is shown in figure 1. The choice of the zero time is of course arbitrary. As it can be seen, it is very easy to distinguish the "additional" propene that released under the influence of ethene. The number of moles of the "additional" propene can be calculated by integrating the function:

$$n_{ap} = \int_{t_1}^{t_2} \left[N_p2(t) - N_p1(t)\right]dt \quad (2)$$

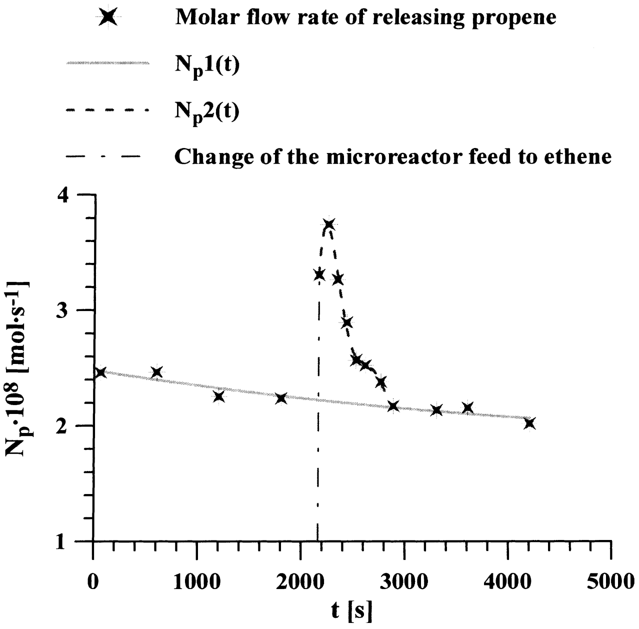

Figure 1. The molar flow rate of propene before and after change of the microreactor feed to ethene. Entry 8, table 1.

where

n_{ap}—the amount of the "additional" propene [mol];
t_1—a time when the microreactor feed was changed to ethene [s];
t_2—a time when the "additional" propene disappeared [s];
$N_p1(t)$—the molar flow rate of the desorbing propene [mol s^{-1}];
$N_p2(t)$—the total molar flow rate of the releasing propene in the time interval (t_1, t_2) [mol s^{-1}].

During both blind experiments, the flow rate of the residual, desorbing propene was in the same range as during the normal runs. However, no "impulse" of the "additional" propene was observed. This proves that the "additional" propene is related to the metathesis active sites.

Thus, according to (1), the number of moles of the active Mo-alkylidene centers is twice as many as the calculated value of n_{ap}. In table 1, such calculated number of the active sites, given as a percentage of all the Mo atoms deposited on the support, is presented. For each experiment, the conditions of the desorption steps are also described. As we can see from the table, both the desorption temperature and the argon flow rate do not influence the obtained results dramatically. This is because the amount of the "additional" propene is always obtained by subtraction of the "background" of the desorbing propene.

As it was mentioned before, during alkene metathesis the intrinsic deactivation of the catalyst takes place. It was proposed for supported rhenium catalysts that the most probable reason for the deactivation is a reductive elimination of the metallacyclobutane intermediate [22]. Thus, the following process cannot be excluded in the case of the presently studied catalysts:

$$[\mathrm{Mo}] = \mathrm{CH_2} + \mathrm{C_2H_4} \rightarrow [\mathrm{Mo}]\mathrm{C_3H_6} \rightarrow [\mathrm{Mo}] + \mathrm{C_3H_6} \qquad (3)$$

Releasing of propene in reaction (3) can influence the determination of the number of the active sites. However, this effect does not seem to be very significant, because after treatment with ethene the catalysts still show metathesis activity, which was checked in some experiments.

Therefore, we have assumed in table 1 that all the "additional" propene comes from reaction (1). As it can be seen from table 1, the estimated percentage of the active sites is very low for MoO_3/Al_2O_3 catalysts, in the range of 0.1 to 0.4. This is, however, quite consistent with the general opinion that the number of active sites in supported metathesis catalysts is very low, lower than 1% of all the transition metal atoms [2,19]. Moreover, the current findings also go with the results obtained for Re_2O_7/Al_2O_3 catalysts [20]. In the latter case, the reported numbers of active Re sites are in the range of

Table 1
The obtained percentage of the active sites, assuming that all the "additional" propene is generated according to (1). The Details column contains the molar flow rate of argon, a time of flushing with argon and the temperature of the catalytic bed

Entry	Catalyst	C_3H_6 content in the reactants (vol%)	Details of the desorption process	Active Mo sites (%)
1	MoO_3/Al_2O_3	5	150 cm^3 min^{-1} (30 min), 10 cm^3 min^{-1} (70 min), 303 K	0.3
2	MoO_3/Al_2O_3	5	150 cm^3 min^{-1} (30 min, 303 K), 10 cm^3 min^{-1} (60 min, 373 K), 10 cm^3 min^{-1} (60 min, 303 K)	0.4
3	MoO_3/Al_2O_3	5	150 cm^3 min^{-1} (30 min), 10 cm^3 min^{-1} (70 min), 303 K	0.3
4	MoO_3/Al_2O_3	5	10 cm^3 min^{-1} (100 min) 303 K	0.1
5	MoO_3/Al_2O_3	5	20 cm^3 min^{-1} (30 min), 10 cm^3 min^{-1} (70 min), 303 K	0.3
6	MoO_3/Al_2O_3	99.5	20 cm^3 min^{-1} (40 min, 303 K), 10 cm^3 min^{-1} (60 min, 473 K), 10 cm^3 min^{-1} (90 min, 303 K)	0.3
7	MoO_3/Al_2O_3-$SnMe_4$ (Sn:Mo=1:10)	5	10 cm^3 min^{-1} (115 min), 303 K	1.6
8	MoO_3/Al_2O_3-$SnMe_4$ (Sn:Mo=1:20)	99.5	20 cm^3 min^{-1} (30 min, 303 K), 20 cm^3 min^{-1} (30 min, 373 K), 20 cm^3 min^{-1} (60 min, 303 K)	2.4
9	MoO_3/Al_2O_3-$SnMe_4$ (Sn:Mo=1:5)	99.5	20 cm^3 min^{-1} (60 min), 10 cm^3 min^{-1} (80 min), 303 K	3.2
10	MoO_3/Al_2O_3-$SnMe_4$ (Sn:Mo=1:2)	99.5	150 cm^3 min^{-1} (10 min), 10 cm^3 min^{-1} (115 min), 303 K	4.6

1%. However, these percentages are generally sometimes higher than the corresponding quantities obtained in the present work, which seems to be connected with the higher activity of the rhenium catalysts, in comparison with the molybdenum systems.

In the case of $MoO_3/Al_2O_3{-}SnMe_4$ catalysts, the estimated number of the active sites is equal to several percent of the total number of the Mo atoms, which is about one order of magnitude higher than in the case of MoO_3/Al_2O_3 system (table 1). Thus, it has been proved that treating the catalyst with tetramethyltin leads to formation of the additional active sites during alkene metathesis. This increase of the active centers number is mainly, if not exclusively, responsible for about one order of magnitude higher activity of the $MoO_3/Al_2O_3{-}SnMe_4$ catalyst, in comparison with the MoO_3/Al_2O_3 system [18]. In the previous work [18], we also concluded that the optimal value of the Sn:Mo ratio indicated that the amount of active sites generated by tetramethyltin in the molybdena–alumina system was lower than 10% of total Mo atoms in the catalyst. The results presented in the current work confirm that statement.

4. Conclusions

In the present work, a new dynamic method of chemical counting of metathesis active centers is proposed and successfully applied to investigate MoO_3/Al_2O_3 and $MoO_3/Al_2O_3{-}SnMe_4$ systems.

In the case of the MoO_3/Al_2O_3 catalyst, the estimated number of the active sites is clearly less than 1% of the total number of the Mo atoms. Treating the molybdena–alumina catalyst with tetramethyltin causes an increase of the active sites percentage. This increment approximately corresponds to improvement of the metathesis activity of the catalyst.

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