ISSN 0023-1584, Kinetics and Catalysis, 2012, Vol. 53, No. 3, pp. 353–356. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.I. Bykov, B.A. Belyaev, T.A. Butenko, E.Sh. Finkelshtein, 2012, published in Kinetika i Kataliz, 2012, Vol. 53, No. 3, pp. 368–371.

Kinetics of α-Olefin Metathesis over the Heterogeneous Catalytic System $(MoOCl_4/SiO_2)–SnMe_4$

V. I. Bykov, B. A. Belyaev, T. A. Butenko, and E. Sh. Finkelshtein

Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, 119991 Russia
e-mail: bykov@ips.ac.ru

Received October 13, 2011

Abstract—The kinetics of 1-hexene and 1-octene metathesis over the $(MoOCl_4/SiO_2)–SnMe_4$ catalytic system at 27 and 50°C has been investigated. The rate constants of the forward and reverse reactions and the catalyst deactivation constants have been measured. The number of active sites has been determined to be 10–13 mol % of the total number of molybdenum atoms.

DOI: 10.1134/S0023158412030056

Olefin metathesis is finding increasingly wide application in organic synthesis. However, individual Schrock and Grubbs metallacarbene complexes used as metathesis catalysts [1] are very expensive and have drawbacks inherent in homogeneous catalysts: they are difficult to separate from the catalysate, undergo bimolecular deactivation, and so on.

Researchers of the Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, suggested a new, flexible, few-step strategy for the synthesis of a wide variety of pheromones and other natural compounds. This strategy is based on the cometathesis of a petrochemical feedstock (α-olefins, cycloolefins, cyclooctadiene, ethylene) [2–6] over efficient heterogeneous catalytic systems developed by us [7–9]. As compared to individual metallacarbene complexes, classical catalytic systems usually have a small number of active sites and are more fastidious about the nature of their functional groups. It is, therefore, a challenging problem to find efficient and inexpensive heterogeneous catalysts with a large number of active sites.

We have demonstrated in a recent work [10] that use of $MoOCl_4$ in place of $MoCl_5$ affords more active metathesis catalysts and that the activity and stability of the latter increases with an increasing silica gel calcination temperature (T_{calcin}) and with a decreasing catalyst immobilization temperature (T_{immob}). Here, we report kinetic data for 1-hexene and 1-octene metathesis in the presence of the most active and most stable $(MoOCl_4/SiO_2)–SnMe_4$ catalyst ($T_{calcin} = 460°C$, $T_{immob} = 25°C$).

EXPERIMENTAL

α-Olefin metathesis was carried out in a temperature-controlled glass reactor fitted with a magnetic stirrer, a dropping funnel, a backflow condenser, and a gas burette for measuring the volume of ethylene released during the reaction. A weighed sample of the catalyst prepared as described in our earlier publication [10] was placed in the reactor, and certain amounts of α-olefin and cocatalyst (Me_4Sn) were charged into the dropping funnel. All operations were performed in flowing predried argon (special-purity grade). Kinetic data were acquired by a volumetric method and were verified by chromatographic determination of the concentration of the symmetric olefin in the catalysate.

On the completion of the reaction, gas evolution practically ceased. The catalysate was removed, and a new, equal portion of the α-olefin was added to the catalyst partially deactivated during the reaction. This procedure was repeated 5–8 times. Special-purpose experiments demonstrated that the kinetics is independent of whether the cocatalyst is added to each new portion of the α-olefin or it is introduced only together with the first portion of the olefin. For this reason, in subsequent experiments tetramethyltin was added only with the first portion of the reactant.

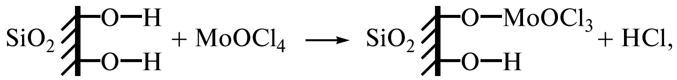
The purity of the initial and resulting compounds was determined and the reaction was monitored by GLC on an LKhM-8MD chromatograph (flame-ionization detector, 50 m × 0.2 mm i.d. quartz capillary column, SCTFP or SE-30 stationary phase, H_2 as the carrier gas). Analyses were performed in the linear temperature-programmed mode by heating the column from 35°C to the temperature 100°C below the boiling point of the symmetric olefin at a rate of 12 deg/min.

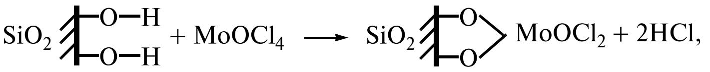
^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker MSL-300 spectrometer, with chemical shifts measured relative to Me_4Si. IR spectra were obtained from thin films on a Specord IR-75 spectrophotometer. Mass spectra were recorded on a Finigan MAT 95 XL 70 system (accelerating voltage of 70 eV).

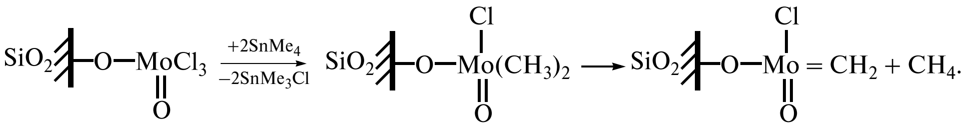
All reactions and pretreatment of the initial compounds (reagent-grade α-olefins from the Novocherkassk Plant of Synthetic Products) were performed in a special-purity argon atmosphere, using $LiAlH_4$ or Na as the drier. According to GLC data, the purity of the initial olefins was over 99.9%.

RESULTS AND DISCUSSION

We have recently demonstrated that, depending on the immobilization conditions and silica gel calcination temperature, $MoOCl_4$ can react with surface OH groups to release one or two equivalents of HCl (reactions (I) and (II), respectively). The latter reaction yields the catalytically inactive precursor of the metathesis catalyst, while $MoCl_5$, unlike $MoOCl_4$, forms the active precursor [8].


(I)


(II)


(III)

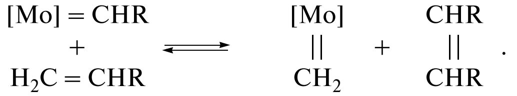
$$SiO_2-O-\underset{\underset{O}{\|}}{Mo}Cl_3 \xrightarrow[-2SnMe_3Cl]{+2SnMe_4} SiO_2-O-\overset{Cl}{\underset{\underset{O}{\|}}{Mo}}(CH_3)_2 \longrightarrow SiO_2-O-\overset{Cl}{\underset{\underset{O}{\|}}{Mo}}=CH_2 + CH_4.$$

The metathesis of the α-olefins is described by the stoichiometric equation (IV), according to which two α-olefin molecules yield an ethylene molecule and a symmetric olefin molecule:

$$2(R\text{-}CH{=}CH_2) = R\text{-}CH{=}CH\text{-}R + CH_2{=}CH_2, \quad (IV)$$

where $R = C_4H_9$ or C_6H_{13}.

The figure illustrates the kinetics of 1-hexene metathesis at 27°C. The 1-hexene conversion in all runs was below 100%. A plausible explanation of this fact is that the symmetric olefin– α-olefin equilibrium is established after a certain concentration of the symmetric olefin is reached and this equilibrium involves secondary and primary metallacarbene active sites:


(V)

$$\begin{array}{c} [Mo]=CHR \\ + \\ H_2C=CHR \end{array} \rightleftharpoons \begin{array}{c} [Mo] \\ \| \\ CH_2 \end{array} + \begin{array}{c} CHR \\ \| \\ CHR \end{array}. \quad (V)$$

The kinetic data presented below were obtained for the most active and longest storable sample of the $MoOCl_4/SiO_2$ catalyst [10].

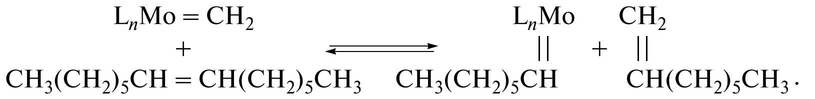
It was established earlier [8, 9] that the rate of reaction (IV) fits satisfactorily to the following differential rate equation:

$$r = (k_1C_\alpha - k_{-1}C_s)e^{-k_d\tilde{n}_{tot}}, \quad (1)$$

where r is the metathesis rate in (mol symmetyric olefin) L^{-1} s^{-1} (mol Mo)$^{-1}$ units, C_s is the concentration of the symmetric olefin (mol/L), C_α is the α-olefin concentration (mol/L), k_1 and k_{-1} are the rate constants of the forward and reverse reactions (s^{-1} (mol Mo)$^{-1}$), k_d is the catalyst deactivation constant (dimensionless quantity), and $\tilde{n}_{tot}$ is the total number of moles of the substances resulting from the metathesis of the symmetric olefin per mole of molybdenum atoms (in (mol symmetric olefin)/(mol Mo) units).

The processing of kinetic data for 1-octene and 1-hexene metathesis using the procedure described in our earlier publications [8, 9] enabled us to determine the numerical values of constants k_1, k_{-1}, and k_d (Tables 1, 2). It is clear from these data that the catalytic system based on molybdenum tetrachloride oxide is more active and more stable than the system based on molybdenum pentachloride.

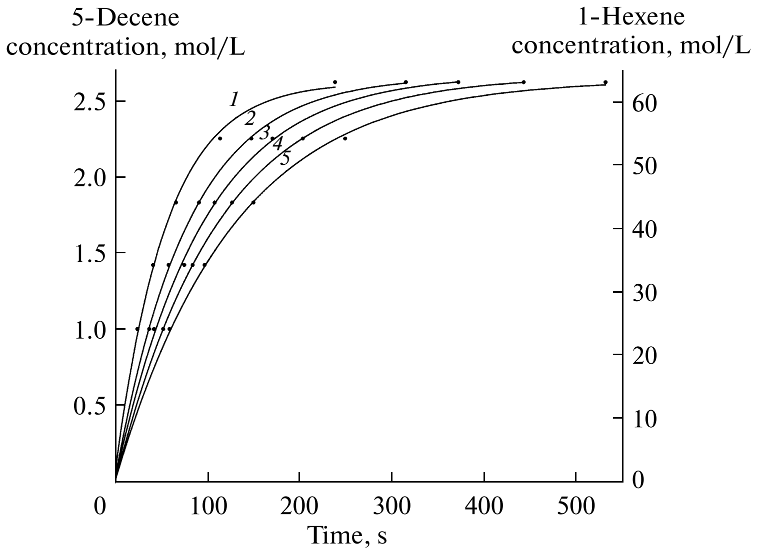
The number of active sites was determined in the same way as in our earlier work [8] under the assumption that the interaction of a primary metallacarbene site with excess 7-tetradecene yields 1-octene:


(VI)

$$\begin{array}{c} L_nMo=CH_2 \\ + \\ CH_3(CH_2)_5CH=CH(CH_2)_5CH_3 \end{array} \rightleftharpoons \begin{array}{c} L_nMo \\ \| \\ CH_3(CH_2)_5CH \end{array} + \begin{array}{c} CH_2 \\ \| \\ CH(CH_2)_5CH_3 \end{array}. \quad (VI)$$

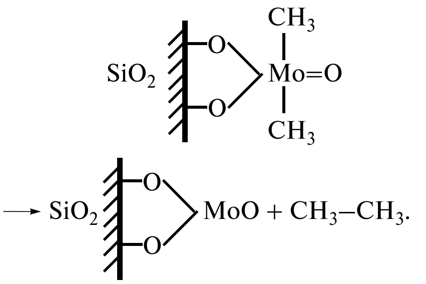
The latter can readily be quantified using n-octane as the internal standard.

According to GLC data, the proportion of these sites relative to the total number of molybdenum



1-Hexene metathesis kinetics observed upon successive addition of equal portions of 1-hexene to the catalytic systems (curves *1*–*5*). The points represent experimental data, and the curves represent the data calculated using Eq. (1). $T = 27°C$, $MoOCl_4 : SnMe_4$: 1-hexene molar ratio of 1 : 4 : 400.

atoms in $MoOCl_4$ is (10.4 ± 0.3)% at 27°C and (13.1 ± 0.3)% at 50°C. In the case of $MoCl_5$, this proportion is 5–6%. The fact that the $MoOCl_4$-based catalyst has more active sites than the $MoCl_5$-based catalyst can likely be explained as follows: in the case of $MoOCl_4$, α-elimination yielding a molybdenum–carbene site and methane proceeds more intensively than reductive elimination yielding ethane and inactive tetravalent Mo,



(VII)

The formation of methane and ethane was proved by the GC-MS method.

The deactivation constant, which characterizes the operating stability of the catalyst, is a measure of active site decay probability. The deactivation constants listed in Table 1, expressed in terms of moles of Mo divided by the total number of moles of symmetric olefin, allow the true deactivation constants to be determined as the number of moles of active sites per mole of symmetric olefin, provided that the number of active sites is known. The inverse of k_d is the total number of product (symmetric olefin) molecules forming on one active site before its decay. The true deactivation constants and their inverse values are listed in Table 3.

The slight increase in the deactivation constant observed on passing from 1-hexene to 1-octene is likely due to the fact that the probability of the asynchronous decomposition of metallacyclobutane increases with an increasing α-olefin chain length. The longer the carbon chain, the larger the number of its vibrational degrees of freedom and, accordingly, the stronger its destabilizing effect on the cyclic transition state. The same effect is exerted by an increasing temperature. Similar regularities were observed earlier for $MoCl_5$-based catalytic systems [8].

Knowing the rate constants of the reaction at different temperatures, we estimated the activation ener-

Table 1. 1-Hexene and 1-octene metathesis rate constants per mole of molybdenum at 27°C and catalyst deactivation constants for these reactions

Constant	1-Hexene metathesis		1-Octene metathesis	
	$MoOCl_4/SiO_2$	$MoCl_5/SiO_2$	$MoOCl_4/SiO_2$	$MoCl_5/SiO_2$
k_1, s^{-1} $(mol\ Mo)^{-1}$	32 ± 4	14 ± 2	26 ± 3	10 ± 1
k_{-1}, s^{-1} $(mol\ Mo)^{-1}$	30 ± 4	13 ± 2	24 ± 3	9.6 ± 1.2
$k_d \times 10^3$	1.3 ± 0.2	2.0 ± 0.3	1.6 ± 0.2	2.5 ± 0.3

Table 2. 1-Hexene and 1-octene metathesis rate constants per mole of molybdenum at 50°C and catalyst deactivation constants for these reactions

Constant	1-Hexene metathesis		1-Octene metathesis	
	$MoOCl_4/SiO_2$	$MoCl_5/SiO_2$	$MoOCl_4/SiO_2$	$MoCl_5/SiO_2$
k_1, s^{-1} (mol Mo)$^{-1}$	170 ± 18	50 ± 6	160 ± 17	39 ± 4
k_{-1}, s^{-1} (mol Mo)$^{-1}$	100 ± 11	33 ± 4	90 ± 10	26 ± 3
$k_d \times 10^3$	2.1 ± 0.3	3.2 ± 0.4	2.6 ± 0.4	4.1 ± 0.5

Table 3. True deactivation constants for the $NoOCl_4/SiO_2$ catalytic system at 27°C and their inverse values

Parameter	1-Hexene metathesis	1-Octene metathesis
$k_d \times 10^4$	1.4 ± 0.2	1.7 ± 0.2
$1/k_d$	7400 ± 700	5900 ± 600

Table 4. Activation energies of 1-hexene and 1-octene metathesis

Direction of the reaction	Activation energy, kJ/mol	
	1-hexene metathesis	1-octene metathesis
Forward	44.0 ± 5.3	47.1 ± 5.5
Reverse	32.3 ± 4.0	34.5 ± 4.2

gies for the forward and reverse metathesis reactions (Table 4).

Thus, we have investigated the kinetics of olefin metathesis over the most active and most stable $MoOCl_4$-based catalyst.

REFERENCES

1. *Handbook of Metathesis*, Grubbs, R.H., Ed., New York: Wiley-VCH, 2003, vol. 2.
2. Bykov, V.I., Butenko, T.A., Finkelshtein, E.Sh., and Henderson, P.T., *J. Mol. Catal.*, 1994, vol. 90, p. 111.
3. Bykov, V.I., Butenko, T.A., Kelbakiani, L.V., and Finkelshtein, E.Sh., *Russ. Chem. Bull.*, 1996, no. 2, p. 168.
4. Bykov, V.I., Butenko, T.A., Kelbakiani, L.V., and Finkelshtein, E.Sh., *Russ. Chem. Bull.*, 1996, no. 8, p. 2022.
5. Bykov, V.I. and Finkelshtein, E.Sh., *J. Mol. Catal. A: Chem.*, 1998, vol. 133, p. 17.
6. Bykov, V.I., Butenko, T.A., Petrova, E.B., and Finkelshtein, E.Sh., *Tetrahedron*, 1999, vol. 55, p. 8249.
7. Bykov, V.I., Butenko, T.A., and Finkel'shtein, E.Sh., USSR Inventor's Certificate no. 1666177, *Byull. Izobret.*, 1991, no. 28.
8. Bykov, V.I., Khmarin, E.M., Belyaev, B.A., Butenko, T.A., and Finkelshtein, E.Sh., *Kinet. Catal.*, 2008, vol. 49, no. 1, p. 11.
9. Bykov, V.I., Belyaev, B.A., Butenko, T.A., and Finkelshtein, E.Sh., in *Green Metathesis Chemistry: Great Challenges in Synthesis, Catalysis and Nanotechnology*, Dordrecht: Springer, 2009, p. 121.
10. Bykov, V.I., Belyaev, B.A., Butenko, T.A., and Finkelshtein, E.Sh., *Kinet. Catal.*, 2010, vol. 51, no. 4, p. 615.