

Kinetics of α -Olefin Metathesis on Binary and Ternary Catalytic Systems Based on $\text{MoCl}_5/\text{SiO}_2$: Determination of the Number of Active Centers and the Mechanisms of Their Formation, Deactivation, and Reactivation

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Abstract—The kinetics of α -olefin metathesis in the presence of binary ($\text{MoCl}_5/\text{SiO}_2\text{--Me}_4\text{Sn}$) and ternary catalytic systems ($\text{MoCl}_5/\text{SiO}_2\text{--Me}_4\text{Sn--ECl}_4$, $\text{E} = \text{Si}$ or Ge) was studied. It was found that reactivation in the course of metathesis occurred on the addition of a third component (silicon tetrachloride or germanium tetrachloride in combination with tetramethyltin) to a partially deactivated catalyst. The number of active centers was determined (5–6% of the amount of Mo), and the mechanisms of formation, deactivation, and reactivation were proposed for the binary and ternary catalytic systems. The roles of the individual components of the catalytic systems were revealed.

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INTRODUCTION

The catalytic metathesis of olefins is a very interesting and promising reaction in the chemistry of polymers, fine organic chemistry, and petroleum chemistry. This fact was acknowledged by the awarding of the Nobel Prize in Chemistry for the development of the metathesis method in organic synthesis in 2005. The contribution of the Nobel Prize Laureates to the development of a metathesis approach was primarily related to the discovery of a metal carbene mechanism (Y. Chauvin) and the development of efficient homogeneous catalysts containing 100% metal carbene active centers for metathesis: Ru carbene (R.H. Grubbs) and Mo(W) carbene (R.R. Schrock). These metal carbene complexes are capable of performing the metathesis of complex unsaturated structures containing various functional groups [1].

A new flexible strategy was proposed at the Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (Moscow), for the synthesis of a wide range of pheromones (environmentally appropriate insecticides) and other natural compounds in a few stages. This strategy is based on the cometathesis of raw materials of petroleum-chemical origin (α -olefins, cycloolefins, cyclooctadiene, and ethylene) [2–6] and the effective binary ($\text{MoCl}_5/\text{SiO}_2\text{--Me}_4\text{Sn}$) heterogeneous catalytic systems developed previously [7]. However, as well as all of the other catalysts, these catalytic systems gradually lose their activity in the course of the reaction. In his Nobel Lecture, Schrock referred to the prevention of catalyst deactivation and the devel-

opment of catalyst regeneration technologies as one of the most important and promising areas in the improvement of metathesis processes. A recent publication by Schrock et al. [8] was devoted to the design of heterogeneous catalysts based on individual tungsten carbene complexes and silica gel. Unlike metal carbene complexes, classical catalytic systems usually contain a low number of active centers and are less tolerant to the functional groups of a substrate. However, note that individual metal carbene complexes are very expensive and possess the disadvantages of homogeneous catalysts; in the case of complex substrates, a large catalyst amount (5–25 mol %) is required to perform metathesis [1]. The search for efficient and inexpensive heterogeneous catalysts remains a problem of considerable current interest. This problem can be solved only based on knowledge of the mechanisms of formation, deactivation, and effective reactivation of a deactivated center.

Previously, we found that experimental data on the kinetics of metathesis of 1-decene, 1-octene, and 1-hexene in the presence of the $\text{MoCl}_5/\text{SiO}_2\text{--SnMe}_4$ binary catalytic system are consistent with the rate equation for the formation of a symmetric olefin with consideration for the back reaction and catalyst deactivation [9, 10].

Here, we present experimental data to demonstrate that metal carbene active centers can be reactivated in the course of metathesis with the use of silicon tetrachloride or germanium tetrachloride as a third component. We determined the number of active centers and proposed the possible mechanisms of formation, deactivation, and reactivation of these active centers

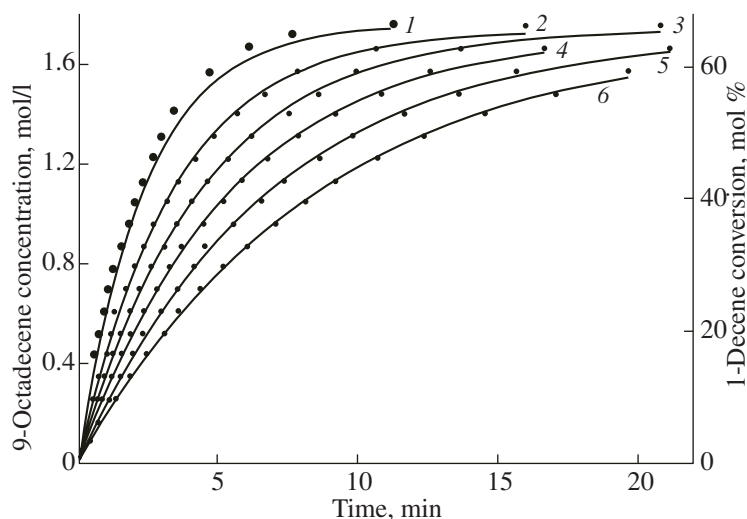


Fig. 1. Kinetics of 1-decene metathesis at 27°C (molar ratio 1-decene/Mo = 250 : 1 for each of the six portions). The numerals at the curves correspond to each new 1-decene portion, which was equal to the preceding one, added to the same catalyst.

for the binary ($\text{MoCl}_5/\text{SiO}_2\text{-SnMe}_4$) and ternary ($\text{MoCl}_5/\text{SiO}_2\text{-SnMe}_4\text{-ECI}_4$; E = Si, Sn) catalytic systems.

EXPERIMENTAL

The metathesis of α -olefins was performed in a thermostated glass reactor with a magnetic stirrer, which was equipped with a dropping funnel, a reflux condenser, and a gas burette for measuring the volume of ethylene released in the course of reaction. A weighed portion of the catalyst was loaded in the reactor, and specified amounts of an α -olefin, a cocatalyst (Me_4Sn), and a reactivator (SiCl_4 or GeCl_4) were placed in the dropping funnel. All of the operations were performed in a flow of dry argon of high purity grade. The kinetic data were obtained by volumetry and confirmed by the determination of the concentration of a symmetric olefin in the products of catalysis using GLC analysis.

After completion of the reaction, the gas evolution practically terminated. The products of catalysis were removed, and a new α -olefin portion, which was equal to the preceding portion, was added to the catalyst partially deactivated in the course of the reaction. The procedure was repeated five to eight times. In special experiments, we found that kinetic data were independent of the fact whether the cocatalyst was added with each new α -olefin portion or only with the first portion. Therefore, tetramethyltin was added only to the first reagent portion in all of the experiments.

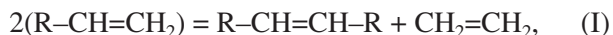
The purity of both starting and resulting compounds and the course of reactions were monitored using GLC analysis on an LKhM-8MD chromatograph with a flame-ionization detector (50 m \times 0.2 mm quartz capillary column); stationary phases were SKTFP and SE-30; H_2 was a carrier gas. The analyses were performed under conditions of linear temperature programming

(12 K/min) from 35°C to a temperature 100 K lower than the boiling temperature of the corresponding compound. The ^1H and ^{13}C NMR spectra were measured on a Bruker MSL-300 spectrometer in CDCl_3 with reference to Me_4Si . The IR spectra were obtained on a Specord IR-75 instrument in thin films. The mass spectra (electron impact) were measured on a Finnigan MAT 95 XL instrument (70 eV). All of the reactions, as well as the preparation of parent compounds (α -olefins of chemically pure grade from Novocherkassk plant), were performed in an atmosphere of high-purity argon with the use of LiAlH_4 or Na as a drying agent. According to GLC data, the purity of parent olefins was >99.9%.

RESULTS AND DISCUSSION

To understand the specific nature of α -olefin metathesis on ternary catalytic systems, we briefly consider the kinetics of α -olefin metathesis on binary ($\text{MoCl}_5/\text{SiO}_2\text{-Me}_4\text{Sn}$) systems.

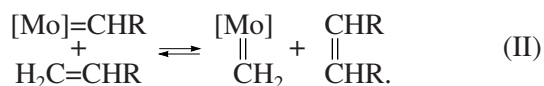
The metathesis occurs in accordance with the following stoichiometric equation to form a mole of ethylene and a mole of a symmetric olefin from two moles of an α -olefin:



where $\text{R} = \text{C}_8\text{H}_{17}$, C_6H_{13} , and C_4H_9 .

Figure 1 shows kinetic data on the metathesis of 1-decene at 27°C. The numerals at the curves correspond to each new 1-decene portion, which was equal to the preceding one, added to the same catalyst sample. Analogous experimental data were also obtained for the metathesis of 1-decene at 50°C and the metathesis of 1-octene and 1-hexene at the same temperatures. Although the liberated ethylene was removed from the reaction zone under experimental conditions, the conversion of 1-decene did not reach 100%, as can be seen

in Fig. 1. This is evidently due to the fact that, as a certain symmetric olefin concentration was reached, the following equilibrium between the final and parent olefins was established with the participation of secondary and primary metal carbene centers:



The experimentally found first kinetic orders with respect to the α -olefin and the catalyst correspond to the stoichiometric coefficients for these reactants in equilibrium (II). As can be seen in Fig. 1, in each particular series of experiments, the next α -olefin portion added to the same catalyst sample reacted more slowly. This was evidently due to catalyst deactivation. We found that a decrease in the number of active centers (n_{ac}) in the catalyst is adequately described by an exponential function of the form

$$n_{\text{ac}} = n_0 e^{-k_d \tilde{n}_{\text{tot}}}, \quad (1)$$

where n_0 is the initial number of active centers, which is proportional to the amount of molybdenum (n_{Mo} , mol), k_d is the catalyst deactivation constant ((mol Mo)/(mol symmetric olefin) $_{\text{tot}}$), and \tilde{n}_{tot} is the total amount of the symmetric olefin per mole of molybdenum atoms.

Thus, as found previously [9], the rate of the reaction can be expressed as the differential rate equation

$$w = (k_1 C_\alpha - k_{-1} C_s) e^{-k_d \tilde{n}_{\text{tot}}}, \quad (2)$$

where the rate of metathesis (w) is expressed in (mol symmetric olefin) $\text{l}^{-1} \text{s}^{-1}$ (mol Mo) $^{-1}$; k_1 and k_{-1} are the rate constants of the forward and back reactions, respectively; and C_α and C_s are the current concentrations of the α -olefin and the symmetric olefin, respectively.

According to the material balance condition at a constant liquid phase volume, $C_\alpha = C_\alpha^0 - 2C_s$, where C_α^0 is the initial α -olefin concentration. Substituting this relation into Eq. (2) gives the following equation for the rate of symmetric olefin formation, which contains only one of the two current concentrations, namely, the symmetric olefin concentration C_s :

$$w = \{k_1 C_\alpha^0 - (2k_1 + k_{-1}) C_s\} e^{-k_d \tilde{n}_{\text{tot}}}. \quad (3)$$

The treatment of kinetic data in accordance with a previously proposed procedure [9, 10] allowed us to determine all of the constants that appear in Eq. (3). The quantity k_d characterizes the stability of the catalyst and, in terms of physical meaning, equals the probability of decay of active centers.

We experimentally found that catalyst deactivation terminated upon completion of the metathesis reaction. Thus, we performed two series of experiments. In the first series, each portion of the products of catalysis was

separated from the catalyst immediately after equilibration. In the other series of experiments, the portions of the products of catalysis after equilibration were allowed to stand over the catalyst for a specified time. In both cases, identical kinetic data were obtained. The blocking of the active centers of the catalyst by impurities in α -olefins is not the main mechanism of deactivation because the additional purification of argon and α -olefins, as well as the repeated use of unreacted α -olefins, led to the same results. This suggests that the deactivation mechanism is related to the metathesis reaction. Spronk et al. [11], who studied the kinetics of 1-octene metathesis on the $\text{Re}_2\text{O}_7/\gamma\text{-Al}_2\text{O}_3$ catalyst, arrived at the same conclusion.

We found that germanium tetrachloride or silicon tetrachloride in combination with tetramethyltin can be used to regenerate catalytic activity. Reactivation at 50–80°C occurred with a noticeable rate. Figure 2 shows experimental data on the metathesis of 1-octene at 50°C. It can be seen that the successive addition of five portions of 1-octene resulted in a decrease in activity, whereas reactivation occurred on the addition of SiCl_4 with the sixth portion of 1-octene and, additionally, a cocatalyst (Me_4Sn) and the sixth kinetic curve was S-shaped because of the formation of additional active centers. It can be seen (Fig. 2) that the activity after 7-min operation was even higher than that in the metathesis of the third portion of 1-octene.

To reveal the roles of the third component and the cocatalyst in the course of reactivation, we performed experiments with different orders of introducing these components. Thus, in a series of experiments, the temperature was increased to 80°C after the conversion of five 1-octene portions on the catalyst sample at 27°C (Fig. 3, curves 1–5). Then, the sixth portion of 1-octene was subjected to metathesis at the specified temperature (Fig. 3, curve 6). Next, tetramethyltin was added with the seventh portion of 1-octene (Fig. 3, curve 7). In this case, the rate of metathesis did not increase. Finally, tetramethyltin and germanium tetrachloride were added with the eighth portion of 1-octene (Fig. 3, curve 8). In this case, the reaction of 1-octene metathesis significantly accelerated and equilibrium was established in 15 min.

In the other series of experiments, the temperature was increased to 80°C after the conversion of five 1-octene portions on a catalyst sample at 50°C (Fig. 4, curves 1–5); then, the sixth portion of 1-octene was subjected to metathesis at the specified temperature (Fig. 4, curve 6). Thereafter, germanium tetrachloride was introduced with the seventh portion of 1-octene (Fig. 4, curve 7). In this case, the metathesis process did not accelerate. At the end of the experiment, both germanium tetrachloride and tetramethyltin were added with the eighth portion of 1-octene (Fig. 4, curve 8). Because of the acceleration of the reaction of 1-octene metathesis, equilibrium was established in 15 min. Analogous results were obtained with the use of silicon tetrachloride. These experiments indicate that reactiva-

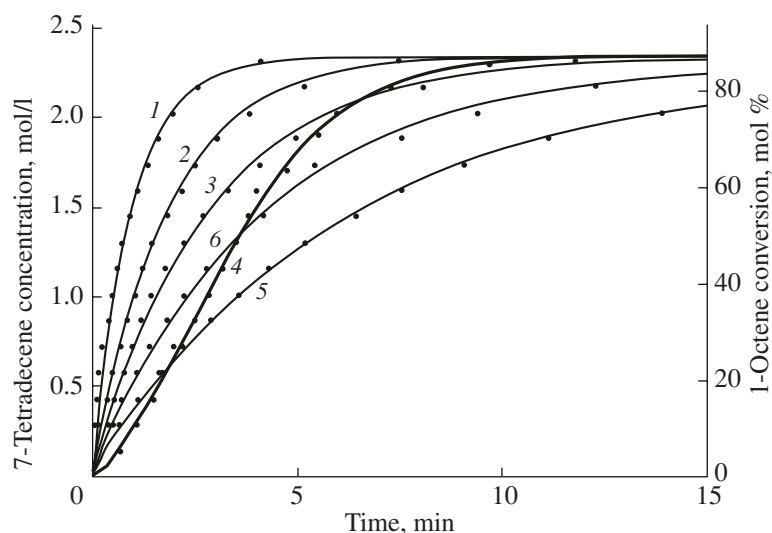


Fig. 2. Kinetics of 1-octene metathesis at 50°C (1–5) without and (6) with reactivation by tetrachlorosilane at 50°C.

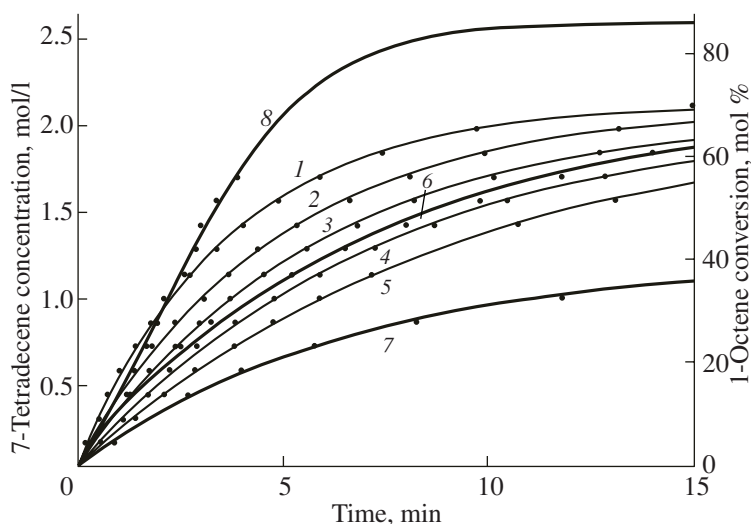
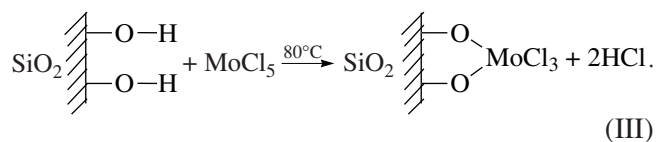


Fig. 3. Kinetics of 1-octene metathesis at (1–5) 27°C, (6) 80°C, (7) 80°C with the addition of Me_4Sn , and (8) 80°C with the addition of Me_4Sn and GeCl_4 .

tion occurred only in the simultaneous presence of tetramethyltin and a third component—germanium tetrachloride or silicon tetrachloride.

As hypothesized previously [12], the catalytic system was formed in the following manner: The interaction of molybdenum(V) chloride with the surface hydroxyl groups of silica gel at 80°C occurred with the release of two HCl molecules per each MoCl_5 molecule (reaction (III)). In this case, MoCl_5 was completely bound to the surface of silica gel.



It is believed that the fraction of molybdenum atoms bound to three oxygen atoms of silica gel is negligibly small. A temperature of 170°C is required for the release of three equivalents. At this temperature of the immobilization of MoCl_5 on the surface of silica gel, this latter is inactive in the metathesis reaction. It is of interest that an almost inactive catalyst was formed upon the immobilization of MoOCl_4 on the surface of silica gel with the release of two equivalents of HCl. According to mass spectrometric data, only trimethylchlorostannane (Me_3SnCl) was formed in the interaction of Me_4Sn with MoCl_5 immobilized on the surface of silica gel. In this case, as determined by gas-chromatographic analysis with consideration for the calibration factor, the amount of trimethylchlorostannane was close to two equivalents with respect to MoCl_5 .

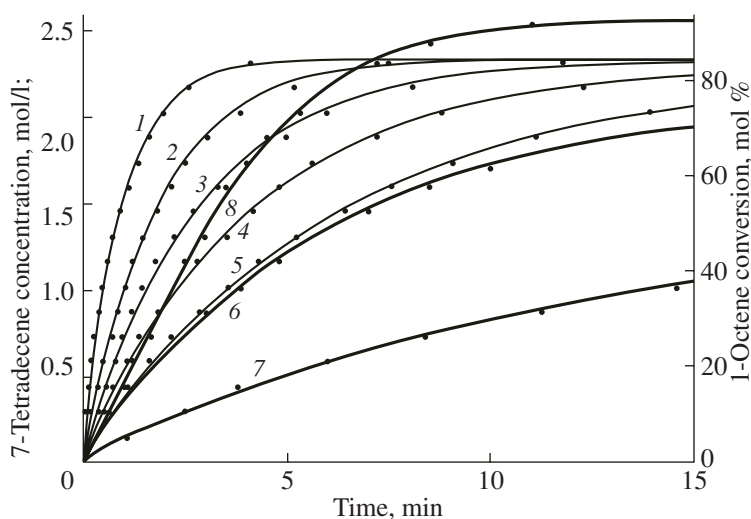
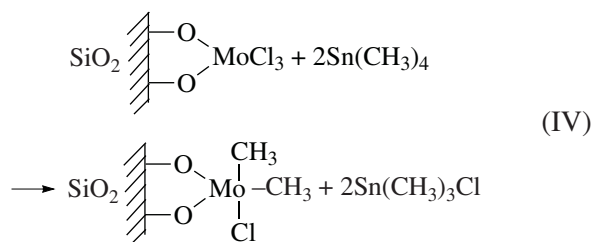
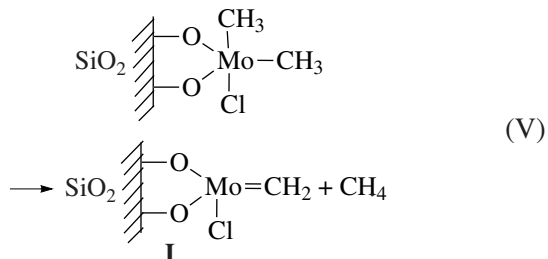


Fig. 4. Kinetics of 1-octene metathesis at (1–5) 50°C, (6) 80°C, (7) 80°C with the addition of GeCl_4 , and (8) 80°C with the addition of GeCl_4 and Me_4Sn .

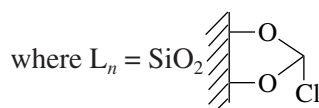
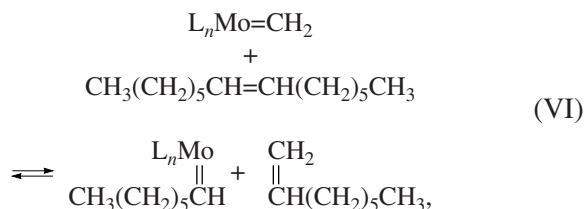
Thus, the stage of alkylation can be represented in the form



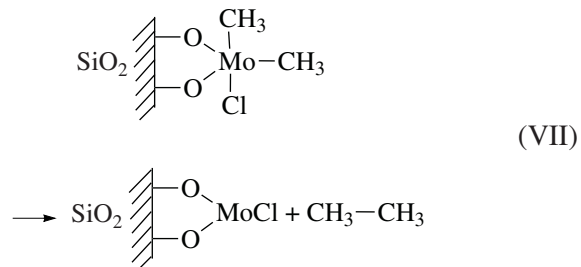
The dimethyl derivative spontaneously decomposed by α -H elimination to form a primary molybdenum carbene active center and methane:



The determination of the number of active centers is based on the fact that primary active center **I** reacts with a symmetric olefin to form a secondary active center and an α -olefin. In particular, 1-octene was formed by the interaction with 7-tetradecene; the amount of 1-octene can easily be determined using octane as an internal standard:



Because 7-tetradecene was taken in a large excess over MoCl_5 , the chemical equilibrium of reaction (VI) was strongly shifted to the right toward 1-octene formation. Thus, it is believed that the amount of 1-octene practically corresponds to the number of primary molybdenum carbene active centers. The GLC analysis demonstrated that the contribution of these centers to the total number of molybdenum atoms in MoCl_5 was $5.1 \pm 0.3\%$ at 27°C or $6.3 \pm 0.3\%$ at 50°C. Evidently, such a low number of active centers was related to the fact that the α -elimination process, which leads to the formation of a molybdenum carbene center and methane (reaction (V)), occurred to a lesser degree than the reductive elimination process to give ethane and inactive trivalent Mo

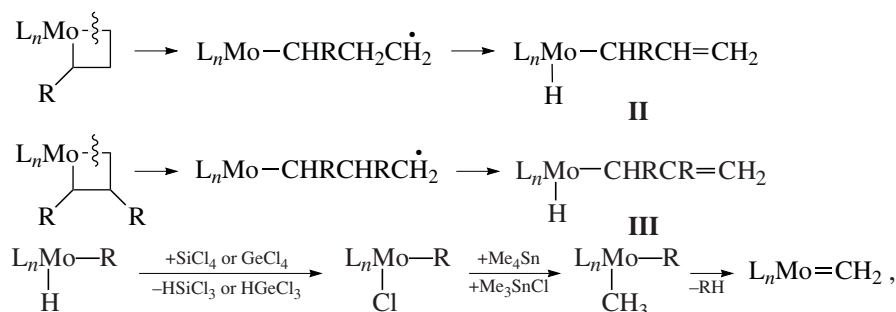


The formation of methane and ethane was determined using chromatography–mass spectrometry. The ratio between the amounts of methane and ethane was 0.07, which is consistent with reactions (V) and (VII) and data on the determination of the number of active centers.

As noted above, the constant of deactivation characterizes the stability of the catalyst and equals the probability of decay of active centers. The previously found [9, 10] constants of deactivation ((mol Mo)/(mol sym-

metric olefin)_{tot}) with consideration for data on the number of active centers allowed us to find the true values of deactivation constants expressed in (mol active centers)/(mol symmetric olefin)_{tot}). The reciprocal of k_d shows the total number of product (symmetric olefin) molecules formed at an active center of the catalyst before its decay. The table summarizes the true values and reciprocals of deactivation constants. It can be seen that the probability of decay of an active center

increases with temperature and exhibits maximum and minimum values in 1-decene and 1-hexene, respectively. Taking into account that the mechanism of deactivation is related to the metathesis reaction, we assume that the mechanism of deactivation can be represented by Scheme 1. There is a probability of the asynchronous degradation of metal cyclobutane with the formation of inactive hydride forms like **II** and **III**.



where $\text{R} = \text{CHRCH}=\text{CH}_2$ or CHRCRCH_2 .

Mechanism of the deactivation and reactivation of a metathesis catalyst.

It is evident that the constant of deactivation increased on going from 1-hexene to 1-decene because the probability of the asynchronous degradation of metal cyclobutane increases with increasing α -olefin chain length. The longer the carbon chain, the greater the number of its vibrational degrees of freedom; therefore, it more strongly destabilizes the cyclic transition state. An increase in the temperature leads to the same result.

Obviously, the reactivation mechanism (scheme) is related to the fact that silicon chloride or germanium chloride reacts with an inactive molybdenum hydride species by substituting chlorine for a hydrogen atom; in this case, silicon chloride or germanium chloride was converted into hydride forms. The formation of trichlorosilane hydride was demonstrated by mass spectrometry. The mass spectrum of the products of the interaction of SiCl_4 with a deactivated catalyst exhibited peaks

due to ions with $m/z = 99$ and 101 , which are characteristic of HSiCl_3 . These ions were practically absent from the mass spectra of parent SiCl_4 and the products of the interaction of SiCl_4 with the undeactivated catalyst. The ions $^{28}\text{SiH}^{35}\text{Cl}_2^+$ and $^{28}\text{SiH}^{35}\text{Cl}^{37}\text{Cl}^+$ made the main contribution to the intensities of signals with $m/z = 99$ and 101 . Trace amounts of ions with $m/z = 99$ and 101 in the parent SiCl_4 were due to the isotopic fragments $^{29}\text{Si}^{35}\text{Cl}_2^+$ and $^{29}\text{Si}^{35}\text{Cl}^{37}\text{Cl}^+$. Thus, mass-spectrometric data unambiguously demonstrate the presence of silane hydride in the products of the interaction of SiCl_4 with the deactivated catalyst.

Next, the chloride species (scheme) underwent alkylation by tetramethyltin followed by the regeneration of a primary carbene center as a result of α -H-elimination in accordance with a reaction scheme analogous to reaction (V) of the formation of an active center. The scheme explains the set of all of the experimental results, in particular, the fact that both a reactivator and a cocatalyst are required for regenerating the catalytic activity of the catalyst.

Thus, we were the first to develop self-reactivating ternary catalytic systems for metathesis ($\text{MoCl}_5/\text{SiO}_2\text{-Me}_4\text{Sn-ECl}_4$; $\text{E} = \text{Si}$ or Ge), in which the active center was reactivated in the course of metathesis. We determined the number of active centers in heterogeneous catalysts and proposed mechanisms for their formation, deactivation, and reactivation with consideration for the role of each particular component in the binary and ternary catalytic systems for metathesis.

Catalyst deactivation constants and the reciprocal values

α -Olefin	$T, ^\circ\text{C}$	$k_d \times 10^4$, (mol active centers)/(mol symmetric olefin) _{tot}	$1/k_d$, (mol symmetric olefin) _{tot} /(mol active centers)
1-Decene	27	1.6	6250
	50	3.3	3000
1-Octene	27	1.3	7700
	50	2.6	3850
1-Hexene	27	1.0	10000
	50	2.0	5000

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