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Olefin Metathesis Catalyst Systems Based on Molybdenum Halides and Organosilicon Compounds

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Abstract—The catalytic activity of heterogeneous catalytic systems based on molybdenum halides immobilized onto the silica gel surface in combination with organosilicon cocatalysts has been studied in a model reaction of hexene-1 metathesis at 27 and 50°C. It has been established that quite active catalysts are formed when using 1,1,3,3-tetramethyl-1,3-disilacyclobutane or triethylsilane as cocatalysts. Tetramethylsilane has exhibited no marked activity, while tetramethyltin has turned out to be the most effective cocatalyst. Possible routes of formation of active centers have been proposed for organosilicon cocatalysts.

Keywords: olefin metathesis, organosilicon compounds, heterogeneous catalysts

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Olefin metathesis is of interest for modern petroleum chemistry and fine organic synthesis. Several industrial processes have been implemented on the basis of this reaction [1], and also effective syntheses of natural compounds, in particular, insect pheromones have been developed [2–4].

Heterogeneous catalytic systems possess a number of technological advantages as compared to homogeneous catalytic systems, in particular, they open opportunities to carry out the process in the absence of solvent and to take catalyst-free samples, thereby allowing their easy analysis by gas–liquid chromatography (GLC) and thus monitoring chemoselectivity and stereoselectivity during the course of the reaction [5]. Earlier, we studied the kinetics of α-olefin metathesis in the presence of two- and three-component heterogeneous catalytic systems on the basis of $MoCl_5$ or $MoOCl_4$ immobilized onto the silica gel surface [6–8] in combination with tetramethyltin (Me_4Sn).

In this paper, we report data on the activity and stability of catalysts in combination with organosilicon compounds in a model reaction of hexene-1 metathesis. Apparently, the search for sufficiently active organosilicon cocatalysts that are less toxic than organotin compounds is a reasonable and relevant task.

EXPERIMENTAL

Hexene-1 metathesis was carried out in a thermostated glass reactor equipped with a magnetic stirrer, a dropping funnel, a reflux condenser, and a gas burette for measuring the volume of ethylene evolving during the reaction. A weighed amount of the catalyst was charged into the reactor, and certain amounts of hexene-1 and a cocatalyst, selected from 1,1,3,3-tetramethyl-1,3-disilacyclobutane, triethylsilane, and tetramethylsilane, were loaded into the dropping funnel. All the operations were performed in a flow of dried argon of the special purity grade. The volumetric data were confirmed by determining the concentration of decene-5 in the catalyzate using GLC analysis.

At a defined conversion of hexene-1, the catalyzate was separated from the catalyst, and a new portion of hexene-1 equal to the previous portion was added to the partially deactivated catalyst. The procedure was repeated two–five times.

The purity of initial hexene-1 and the cocatalysts was monitoring using GLC analysis on an LKhM-8MD chromatograph equipped with a flame ionization detector (FID) (50 m × 0.2 mm quartz capillary column coated with the SKTFP or the SE-30 stationary phase, and H_2 as the carrier gas). The analyses were performed in the linear temperature programming mode (12°C/min). Electron ionization mass spectra (70 eV) were recorded on a Finnigan MAT 95 XL 70 instrument. All the reactions, as well as the preparation of reactants (reagent grade hexene-1, Novocherkassk plant), were performed in the atmosphere of special-purity argon using $LiAlH_4$, Na, or CaH_2 as a drying agent. The purity of initial hexene-1 and cocatalysts was 98–99% according to GLC data.

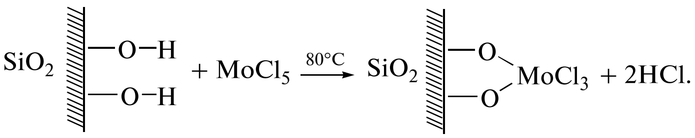
RESULTS AND DISCUSSION

The metathesis of hexene-1, like that of all other α-olefins, proceeds in accordance with the stoichiometric equation of formation of one symmetric olefin molecule and one ethylene molecule from two α-olefin molecules (reaction (1)):

$$2\,(R{-}CH{=}CH_2) = R{-}CH{=}CH{-}R + CH_2{=}CH_2, \quad (1)$$

where $R = C_4H_9$.

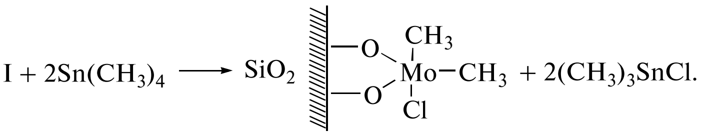
The precursor of active centers of the olefin metathesis catalyst is molybdenum(V) chloride, which interacts with surface hydroxyl groups of silica gel at 80°C to release two HCl molecules per $MoCl_5$ molecule (reaction (2)).



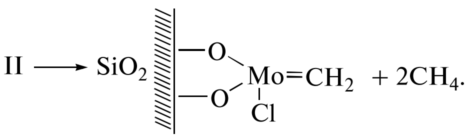
(2)

It can be assumed that the fraction of molybdenum atoms bound to three oxygen atoms of silica gel is quite insignificant because this requires a temperature above 150°C. If the immobilization is carried out at or higher than 150°C, inactive precursors of catalytic systems for metathesis are formed. It should be noted that molybdenum(V) chloride interacts with hydroxyl groups of γ-aluminum oxide at 80°C in the same manner as with SiO_2, with the evolution of two HCl molecules; however, an inactive sample is formed in this case.

During the interaction of Me_4Sn with the precursor of the active center (reaction (3)), dimethyl derivative **II** is formed, which decomposes via α-H elimination to give the primary carbene active center and methane (reaction (4)).



II (3)



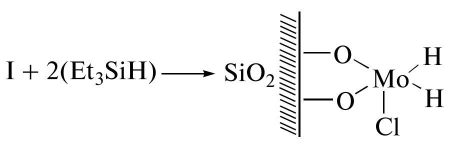
III (4)

When tetramethylsilane is used instead of tetramethyltin, no metathesis reaction occurs. only It is only after treating the precursor with Me_4Si vapor at 110°C that nonselective catalysts having low activity are formed.

When organosilicon compounds, such as 1,1,3,3-tetramethyl-1,3-disilacyclobutane ($[Me_2SiCH_2]_2$) or triethylsilane (Et_3SiH), are used as a cocatalyst, the resulting catalysts are quite active. The table shows the results of some experiments on the metathesis of hexene-1 at 27 and 50°C.

A comparison of the experimental results presented in the table shows that a more active catalytic system is formed when $[Me_2SiCH_2]_2$, rather than Et_3SiH, is used as the cocatalyst. Thus, a hexene-1 conversion of 67% is reached within 6.2 min (T = 27°C, $[Me_2SiCH_2]_2$) versus 63% within 16 min in the case of Et_3SiH. The catalytic system based on $[Me_2SiCH_2]_2$ is more stable than that with Et_3SiH. For example, the time to reach the conversion specified in the table is 32 min for the second portion of hexene-1, whereas that in the case of $[Me_2SiCH_2]_2$ is 13.2 min for the third portion of hexene-1.

By using gas chromatography–mass spectrometry, it was found that the only product of Et_3SiH interaction with **I** is triethylchlorosilane (Et_3SiCl), the amount of which was close to two equivalents per equivalent of molybdenum. Traces of hexane were detected in the first portion of the catalyzate. In the case of Et_3SiH used as the cocatalyst, the formation route for the active center can be represented by reactions (5)–(7). First, active-center precursor **I** interacts with triethylsilane to form dihydride derivative **IV** (reaction (5)), to which two molecules of hexene-1 add, thus forming dihexyl derivative **V** (reaction (6)). This derivative degrades via α-H elimination to form a secondary carbene center and a hexane molecule (reaction (7)).

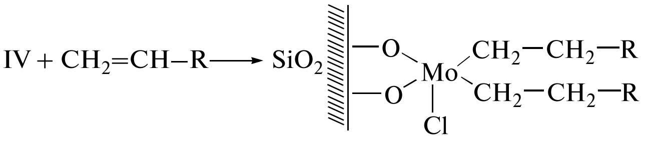


IV (5)

Dependence of hexene-1 conversion on the reaction time for various cocatalysts at 27 and 50°C

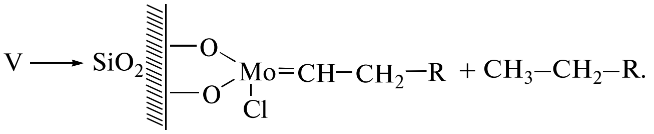
Hexene-1 portion number	Conversion of hexene-1		Time to reach specified conversion, min					
			cocatalyst $[Me_2SiCH_2]_2$		cocatalyst Et_3SiH		cocatalyst Me_4Sn	
	$T = 27°C$	$T = 50°C$	$T = 27°C$	$T = 50°C$	$T = 27°C$	$T = 50°C$	$T = 27°C$	$T = 50°C$
1'	63	58	–	–	16	28	–	–
2'	58	23	–	–	32	12	–	–
1	67	36	6.2	1.5	–	–	4.0	0.5
2	62	42	8.2	3.3	–	–	3.0	0.8
3	62	49	13.2	4.7	–	–	3.9	1.7
4	62	49	34.0	6.0	–	–	4.8	2.7
5	52	50	33.0	6.5	–	–	3.3	3.9

* Hexene-1 : Mo : cocatalyst = 300 : 1 : 4 for all the cocatalysts at $T = 27°C$; hexene-1 : Mo : Et_3SiH = 900 : 1 : 4 at $T = 50°C$.



V

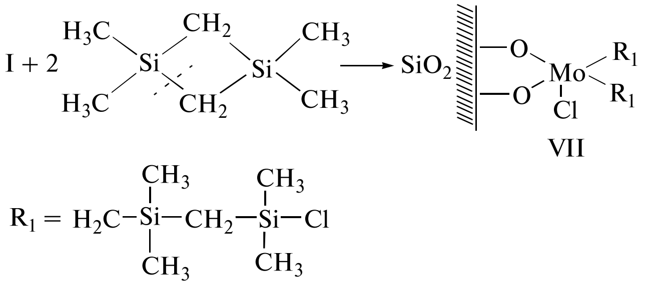
(6)



VI

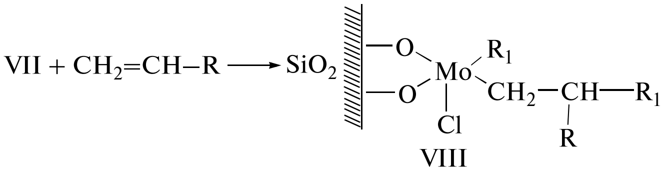
(7)

It is known [9] that 1,1,3,3-tetramethyl-1,3-disilacyclobutane reacts with Ti, Zr, Hf, W, and Mo chlorides with the cleavage of the cyclic Si–C bond to form derivative **VII** (reaction (8)), to which a hexene-1 molecule adds to form derivative **VIII** (reaction (9)). This derivative degrades, like in other cases, via α-H elimination to give carbene complex **IX** and [trimethylsilyl(chlorodimethylsilyl)]methane **X** (reaction (10)).



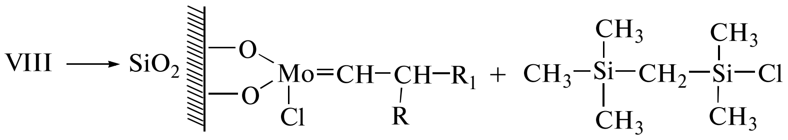
VII

(8)



VIII

(9)



IX X

(10)

In summary, it has been shown that organosilicon cocatalysts (1,1,3,3-tetramethyl-1,3-disilacyclobutane and triethylsilane) can be used for the formation of quite active heterogeneous catalysts for olefin metathesis. Unlike tetramethyltin, tetramethylsilane is not a cocatalyst. Possible routes for the formation of active centers in the case of organosilicon cocatalysts have been proposed.

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