4. E. M. Flanigen, H. Khatami, and H. A. Szymanski, Adv. Chem. Ser., 101, 201 (1971).
5. K. V. Topchieva and Ko Shu Tkoang, The Activity and Physicochemical Properties of High-Silicon Zeolites and Zeolite-Containing Catalysts [in Russian], Izd. Mosk. Gos. Univ., Moscow (1976).
6. T. G. Alkhazov and A. E. Lisovskii, The Oxidative Dehydrogenation of Hydrocarbons [in Russian], Khimiya, Leningrad (1980).
7. D. B. Tagiev and Kh. M. Minachev, Usp. Khim., 50, 1929 (1981).

HETEROGENIZED TRANSITION METAL HALIDES IN THE PREPARATION

OF HIGHLY DISPERSED METAL AND METAL COMPLEX CATALYSTS.

COMMUNICATION 5. LIQUID-PHASE EPOXIDATION OF CYCLOHEXENE

IN THE PRESENCE OF MOLYBDENUM PENTACHLORIDE HETEROGENIZED

ON SILICA

A. Ya. Yuffa, A. A. Slinkin, V. V. Berentsveig,   UDC 541.128:547.592.2
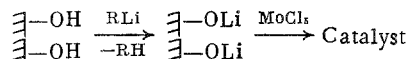A. V. Kucherov, V. V. Ryabova, and A. Yu. Stakheev

Homogeneous molybdenum catalysts are effective in the epoxidation of olefins using hydroperoxides [1]. These catalytic systems which have high catalytic activity and selectivity also have the disadvantages typical of homogeneous catalysts [2].

One method for the elimination of such disadvantages is chemical fixation of catalytically active transition metal complexes on a support surface. In our previous work [3, 4], we described a method for the fixation of nickel, copper, and cobalt halides on a silica surface modified by lithium. In the present work, this method was used for the preparation of heterogeneous olefin epoxidation catalysts with $MoCl_5$ fixed on silica.

EXPERIMENTAL

Catalyst Preparation. Silochrom S-120 with 120 m^2/g specific surface and 3.7 nm^{-2} OH group surface concentration was taken as the support. The OH group concentration was found by titration of the silica sample using methyllithium.

The heterogenization of $MoCl_5$ on the silica surface was carried out by the scheme

$$\begin{matrix} \text{≡—OH} \\ \text{≡—OH} \end{matrix} \xrightarrow[\text{−RH}]{\text{RLi}} \begin{matrix} \text{≡—OLi} \\ \text{≡—OLi} \end{matrix} \xrightarrow{\text{MoCl}_5} \text{Catalyst}$$

Detailed methods for the lithiation of silica are described in our previous work [3] and by Fripiat [5]. The deposition of Mo(V) was carried from an ethereal (A) or benzene (B) solution. The $MoCl_5$ concentration in the solution from which the complex was heterogenized was $2.96 \cdot 10^{-2}$ (in case A) and $1.43 \cdot 10^{-2}$ mole/liter (in case B).

A solution of 1.49 g $MoCl_5$ in 184 ml anhydrous ether or 380 ml benzene was added to 5 g lithium modified silica. The suspension was stirred at from 30° to 40°C in an atmosphere of thoroughly dried argon. The solution is decolored and the support becomes highly colored. The samples were washed for an extended period in a Soxhlet apparatus and in vacuum at 40–70°C. Sample A was light brown while sample B was blue. The molybdenum content in the samples found by neutron activation was 3.93 and 4.96 mass %, respectively, which corresponds to surface concentrations of 2.1 and 2.6 nm^{-2}.

ESR and XPE Spectroscopic Study of the Surface Complexes. The electron spin resonance spectra of the heterogenized molybdenum pentachloride samples were taken on a reflection-type instrument with $\lambda = 3$ cm.

TABLE 1. Parameters of the X-Ray Photoelectronic Spectra of Molybdenum Epoxidation Catalysts

Catalyst type	Bond energy, eV			Ratio of the surface atom concentrations		
	$Mo3d_{5/2}$	Cl $2p$	Si $2p$	Si/Mo	Si/Cl	Cl/Mo
A	234,0	199,5	103,5	24,4	2,7	9,1
A *	233,5	199,0	103,5	71,4	35,5	2,0
B	233,0	199,0	103,5	18,9	17,0	1,1
B*	233,1	199,0	103,4	19,1	18,5	1,0

*Catalysts after completion of the first catalytic cycle.

TABLE 2. Catalytic Activity of Heterogeneous Catalysts Consisting of $MoCl_5$ Supported on Silica (A and B) in the Epoxidation of Cyclohexene by Cyclohexenyl Hydroperoxide at 70°C, 3 h

Catalyst type	$[CHHP]_0$, mole/liter	m_{cat}, g/liter	CHHP conversion, %	Product yield, mole/liter		Selectivity relative to epoxide, %	$W^0_{epox} \times 10^4$, mole/liter·sec·g (Mo)
				cyclo-hexenol	epoxide		
A	1,16	9,6	93,1	1,1	0,79	73,5	0,6
	1,16	3,2	94,8	0,96	0,73	66,7	3,3
	1,16	1,6	94,0	1,1	1,09	100	6,9
	0,60	3,2	93,1	1,08	0,54	100	2,1
B	0,50	9,6	88,0	0,75	0,09	20,5	0,06
	0,50	3,2	72,0	0,40	0,32	88,3	0,5
A *	0,60	3,2	20,0	0,20	0,02	12,5	0,09
B*	0,92	3,2	82,6	0,75	0,73	96,1	8,4

*Repeated experiments with catalysts A and B.

The ESR spectra of samples A and B differ significantly both in intensity and line shape. The ESR spectrum of sample B taken at 20°C under argon is an anisotropic signal with $g_\| = 1.96$ and $g_\perp = 1.93$ and intensity of $2 \cdot 10^{19}$ spins/g, which indicates the presence of a significant amount of Mo(V) ions. The introduction of air at 20°C does not immediately affect the ESR intensity and line shape. The intensity begins to drop markedly only after several days. Heating of sample B in argon for 30 min at 200°C does not lead to a significant change in the signal intensity. Sample A shows an anisotropic signal with the same ESR spectra parameters. The signal intensity in this case ($\simeq 4 \cdot 10^{17}$ spins/g) is almost two orders of magnitude less than for sample B. Thus, upon the deposition of $MoCl_5$ from ether, the Mo(V) concentration on the SiO_2 surface found by the ESR method is much less than upon deposition from benzene solution and is only about 8% of the total amount of molybdenum supported on the silica surface. For sample B, almost all the Mo(V) ions were revealed by the ESR measurement, which probably indicates the lack of aggregation of these ions on the silica surface.

The x-ray photoelectron (XPE) spectra were taken on an ES-200B spectrometer. The aluminum K_α line with 1486.6-eV energy was the inducing radiation. Prior to the recording, the sample was pressed into a copper matrix in an atmosphere of purified argon without contact with the air using a special chamber located within the probe. Table 1 gives the XPE spectral parameters for samples A and B of silica-supported $MoCl_5$ before and after use in the catalytic epoxidation of cyclohexene. The C1s line with $E_b = 285$ eV was used as the standard.

The higher value for E_b of $Mo3d_{5/2}$ in sample A relative to catalyst B may be attributed to the higher oxidation state of the metal in sample A.

Study of the Catalytic Activity of the Mo Catalysts. The liquid-phase epoxidation of cyclohexene by cyclohexenyl hydroperoxide (CHHP) was studied at 70°C under argon in cyclohexene (Table 2) in a steady-state system in a long-necked two-chamber reactor attached to a rapid shaker. The volume of the reaction mixture was 5 ml and the catalyst concentration was varied from 1.6 to 9.6 g/liter. The CHHP concentration was found idometrically, while the concentrations of the other components of the reaction mixture were found by gas—liquid chromatography on a Vyrukhrom chromatograph using a column packed with 10% tricyanoethoxypropane on Chromaton.
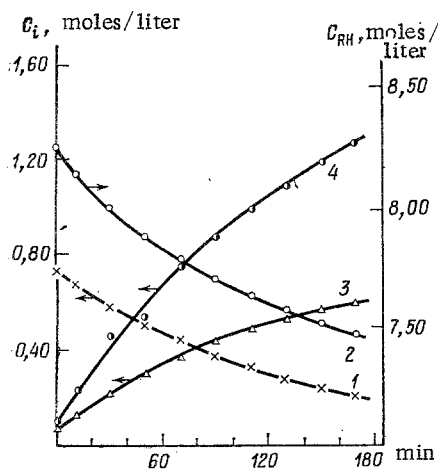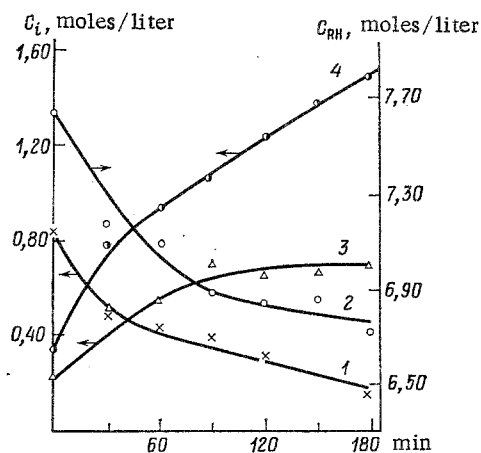
Fig. 1

Fig. 2

Fig. 1. Kinetic curves for the consumption of CHHP (1) and cyclohexene (2) and the accumulation of the reaction products: epoxycyclohexene (3) and cyclohexanol (4) in the presence of 9.6 g/liter catalyst A, C°_{CHHP} = 0.74 mole/liter at 70°C in an argon atmosphere.

Fig. 2. Kinetic curves for the consumption of the starting reagents and accumulation of the reaction products in the presence of catalyst B. The numbering of the curves and the conditions were the same as in Fig. 1 with the exception of C°_{CHHP} = 0.84 mole/liter.

The total conversion of hydroperoxide (α) was calculated using the formula ($\Delta CHHP/CHHP$)·100%. The selectivity (β) was found using the equation ($\Delta R > 0/\Delta CHHP$)·100% ($\Delta R > 0$ indicates an increase in the epoxycyclohexene concentration in solution).

The kinetic data given in Figs. 1 and 2 and Table 2 show that some excess in the cyclohexenol yield relative to the cyclohexene oxide yield (the product accumulation curves do not arise from the origin since we used solutions of previously oxidized cyclohexene containing some prior amounts of these products) is characteristic for both types of catalysts. The lack of balance in the stoichiometry of the bimolecular hydroperoxide epoxidation of cyclohexene may be attributed to decomposition of CHHP induced by the catalyst with the formation of the alcohol and, possibly, of O_2. Table 2 indicates that the rate of the desired reaction increases with decreasing catalyst concentration. The rates of side reactions such as the induced decomposition of CHHP likely increase to a greater extent with an increase in the catalyst concentration.

The initial rates of cyclohexene oxide formation relative to 1 g Mo (see Table 2) are similar or even greater than the initial rates of cyclohexene epoxidation by cyclohexenyl hydroperoxide in the presence of homogeneous $Mo(CO)_6$ catalyst [6], which are on the order of $5 \cdot 10^{-4}$ mole/liter·sec·g(Mo) for [CHHP] = 0.2, [C_6H_{10}] = 2.0, and [$Mo(CO)_6$] = $2 \cdot 10^{-3}$ mole/liter at 75°C.

In order to study the stability of the catalysts prepared, repeat experiments with catalysts previously used in the epoxidation reaction were carried out (see Table 2). The results obtained indicate that catalyst A sharply loses catalytic activity and selectivity upon repeated use, while the activity and selectivity for catalyst B increase upon repeated use. A large portion of the molybdenum in catalyst A is likely transferred to the homogeneous phase during the reaction and is irreversibly lost.
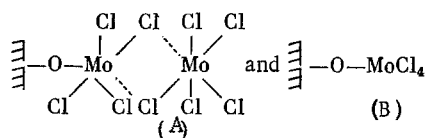
RESULTS AND DISCUSSION

The results indicate the factors accounting for the different behavior of the catalysts consisting of $MoCl_5$ deposited on lithium-modified silica from ethereal and benzene solution.

According to Opalovskii et al. [7], molybdenum pentachloride is monomeric in anhydrous solution while it exists in ether mainly as a dimer with about 5% of the monomeric form.

The significantly more intense ESR signal found for sample B relative to A indicates a markedly higher surface concentration of paramagnetic Mo(V) sites in sample B.

The intensity of the ESR signal for MoCl$_5$ heterogenized from benzene solution onto the lithium-modified silica surface does not change over a prolonged period in the air. This behavior indicates high stability of form B relative to hydrolysis and oxidation by oxygen. Such high stability may be explained by the isolation of the individual Mo(V) complexes supported on the surface. For comparison, we note that the introduction of a small amount of unpurified air onto sample A leads to disappearance of the ESR signal.
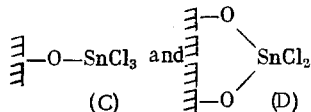
The literature data and our results indicate that the heterogenization of MoCl$_5$ from ethereal and benzene solution leads to the predominant formation of surface complexes

$$
\begin{array}{c}
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \\
\equiv\!-\!O\!-\!Mo \qquad Mo \qquad \text{and} \equiv\!-\!O\!-\!MoCl_4 \\
\text{Cl} \quad \text{Cl} \ \text{Cl} \quad \text{Cl} \quad \text{Cl} \\
(A) \qquad\qquad (B)
\end{array}
$$

The formation of the products of the two-center chemisorption of Mo(V) chloro complexes on the surface is also not excluded.

The proposed structure for the heterogenized complexes permits us to explain the low stability for the action of catalyst A: Decomposition of the surface dimers accompanied by washing out of a portion of the active component into solution occurs during the reaction. According to the XPE spectral data, only about 34% of the initial molybdenum remains on the surface after completion of the first catalytic cycle (see Table 1). The total CHHP conversion in the repeat experiment was only about 22% of the initial value (see Table 2).

The increase in the activity and selectivity of catalyst B during the reaction is apparently related to a change in the chemical composition and structure of the active site. It is not excluded that the change in the structure of the surface sites upon heating in an argon atmosphere reduces to an increase in the number of two-center chemisorbed Mo(V) chloro complexes. This hypothesis is supported by the finding that SnCl$_4$ is deposited from solution onto silica as single-site chemisorbed molecules (C), while it is deposited upon heterogenization from the gas phase at high temperatures in the two-site chemisorbed form (D) [8].

$$
\equiv\!-\!O\!-\!SnCl_3 \quad \text{and} \quad
\begin{array}{c}
\equiv\!-\!O \\
\equiv \quad\quad SnCl_2 \\
\equiv\!-\!O
\end{array}
$$

$$(C) \qquad\qquad (D)$$

CONCLUSIONS

1. The preparation was described for an effective catalyst for the epoxidation of cyclohexene by hydroperoxides consisting of molybdenum pentachloride heterogenized onto a lithium-modified silica surface.

2. The structure of the surface catalytic complexes depends on the nature of the solvent from which the deposition of MoCl$_5$ is carried out.

LITERATURE CITED

1. V. N. Sapunov, J. Mol. Catal., 7, 149 (1980).
2. G. V. Lisichkin and A. Ya. Yuffa, Heterogeneous Metal Complex Catalysts [in Russian], Khimiya, Moscow (1981).
3. A. Ya. Yuffa, L. M. Ryazanova, G. M. Gvozdeva, and M. Yu. Turova, Kinet. Katal., 23, 1465 (1981).
4. A. Ya. Yuffa, V. V. Berentsveig, G. V. Kudryavtsev, and G. V. Lisichkin, Kinet. Katal., 23, 1469 (1981).
5. G. G. Fripiat and G. Uytterhowen, J. Phys. Chem., 66, 800 (1962).
6. V. A. Proskuryakov, A. M. Syroezhko, and R. M. Azhikova, Zh. Prikl. Khim., 53, 1126 (1980).
7. A. A. Opalovskii, I. I. Tychinskaya, Z. M. Kuznetsova, and P. P. Samoilov, Molybdenum Halides [in Russian], Nauka, Novosibirsk (1972), p. 132.
8. V. B. Aleskovskii, The Chemistry of Building Materials [in Russian], Vestn. Akad. Nauk SSSR, No. 6, 45 (1975).