Copperphenylsiloxane as a new structurally organized catalyst for isomerization of chloroolefins

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Polynuclear copper complexes, in which the metal atoms are linked by chlorine bridges, are efficient catalysts for allyl isomerization of dichlorobutenes (DCB).

$$CH_2=CH-CHCI-CH_2CI \longrightarrow CH_2CICH=CHCH_2CI \qquad (1)$$

The activity of these catalysts is many times greater than the activity of their mononuclear analogs.¹ It is also retained for deposition on mineral carriers,² which is rather important because reaction (1) is the stage of the production of chloroprene rubber performed to date in the presence of the low-efficiency and nonselective catalyst, copper naphthenate.³ It is of interest to use polynuclear structures of other types, for example, complexes with oxygen bridges, in the catalysis of isomerization. The characteristic example of such compounds is structurally organized copperphenylsiloxane (CPSO) containing Cu-O-Cu fragments.⁴

In this work, the catalytic activity of silica gelsupported CPSO was studied. For comparison under the same conditions, the efficiency of another heterogeneous catalyst was studied: silica gel-supported polynuclear copper chloride complex with triethylamine (CTEA),² whose activity exceeds considerably that of the known heterogeneous catalysts of reaction (1). Both complexes were deposited on silica gel (fraction 6-8 mm) with a specific surface of 250 m² g⁻¹, which was obtained free from Fe ions and dried in vacuo at 200 °C. The content of copper in the sample with CTEA was 1.1% and 0.8% for the sample with CPSO. Reaction (1) was performed by keeping 3.4-DCB over the layer of the catalyst (10 wt.%, which corresponds to 0.08-0.11 wt.% copper of DCB) at 100 °C in rotating sealed tubes. The change in the composition of the reaction mixture in time from GLC data for typical experiments is presented in Table 1. Unlike the reaction in the presence of the homogeneous industrial catalyst, no side products were observed when the deposited systems were used, *i.e.*, the

Table 1. Isomerization of DCB at 100 °C

t/min	Conversion of 3,4-DCB to 1,4-DCB (%)	
	CTEA	CPSO
0	0.4	0.4*
20	5.0	33.6
40	10.7	54.6
60	17.5	72.0

* Admixture of 1.4-DCB in the initial 3,4-DCB.

process occurs with 100% selectivity (within the accuracy of measurements). Almost identical results were obtained for the reaction repeated three to five times with the same sample of the catalyst.

It follows from the data of Table 1 that when CPSO is used, the concentration of 1,4-dichlorobut-2-ene approaches the equilibrium concentration (78%) in 1 h. The conversion is fourfold lower under the same conditions in the presence of CTEA. Thus, CPSO has high catalytic activity in the isomerization of chloroolefins, which is noticeably greater than the efficiency of the heterogeneous systems described previously.

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