Kinetics and Catalysis, Vol. 44, No. 4, 2003, pp. 572–574. Translated from Kinetika i Kataliz, Vol. 44, No. 4, 2003, pp. 625–628.
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HIGHLY ORGANIZED CATALYTIC SYSTEMS

Structural Regulation of the Catalytic Activity of Polymetalorganosiloxanes

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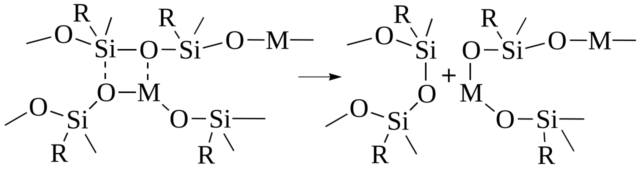
Received September 25, 2002

Abstract—Linear polycopperorganosiloxanes (PCOSs) with phenyl and nonyl substituents at the silicon atom immobilized on oxide supports catalyze the addition of CCl_4 to alkenes. It was found that PCOSs with nonyl substituents supported on zirconia exhibited a maximum catalytic activity, whereas catalysts containing phenyl fragments were less active. Supporting PCOSs on titania resulted in a complete loss of activity.

INTRODUCTION

Linear polymetalorganosiloxanes (PMOSs) with the general formula $(SiR_2–O–M)_n$ (where M = Cu, Ni, Co, or Mn and R is a hydrocarbon radical) immobilized on the surface of silica exhibited high activity in the reactions of halogenated hydrocarbons (the addition of CCl_4 to olefins, exchange interactions with alkanes, and the isomerization of dichlorobutenes) [1]. The catalytic properties of PMOSs mainly depend on the coordination number of metal ions (in a linear metal siloxane molecule in the absence of external complexing agents, the coordination number can be as unusually low as 2). The reason for the coordinative unsaturation of a metal ion in the siloxane structure consists in the extremely low basicity of siloxane oxygen, which is incapable of occupying vacancies in the coordination sphere of the metal [2]. It is not surprising that no data were reported on the preparation of at least one stable metal organosiloxane in which the siloxane oxygen of the Si–O–Si fragment occurred in the coordination sphere of a polyvalent metal [3]. The coordinative unsaturation of a metal ion is of particular importance for the catalysis of reactions involving halogenated hydrocarbons, substrates that are not at all prone to coordinate transition metal ions. Previously, we found that a decrease in the surface concentration of metal siloxane oligomers is favorable for increasing the activity [1, 4, 5]. However, a number of factors hinder the production of catalysts with low metal coordination numbers. This is primarily the interaction of siloxane chains with each other; at the stage of siloxane synthesis, it can result in the rearrangement As a result, the fraction of M–O–M–O– fragments increased. Because of this, taking into account the subsequent formation of intrachain and interchain clusters, the metal ion occurred in a rigid environment of several oxygen atoms. This structure of a coordination center hinders the reduction of the metal ion, which is a necessary step in a catalytic process, and the interaction with reactant molecules; consequently, it decreases the catalytic activity [4].

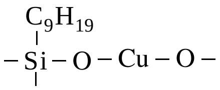
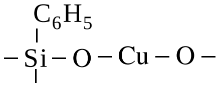


The interaction of chains to form interchain clusters can be significantly weakened by the introduction of bulky substituents at the silicon atom. Previously, we found that the catalytic activity of phenyl derivatives was higher than that of methyl derivatives, all other factors being the same. In this work, we synthesized siloxanes with a more bulky nonyl substituent and performed a comparative study of the catalytic activity of these siloxanes and the activity of phenyl-substituted systems.

Not only the interaction of chains with each other but also the insertion of the surface hydroxyl groups of the support into the coordination sphere prevent coordinatively unsaturated metal ions from stabilizing in the siloxane chains of an immobilized catalyst. A low concentration of the surface hydroxyl groups is optimum from the standpoint of specific catalytic activity. This decreases the contribution of hydroxyls to the occupation of the coordination sphere and simultaneously facilitates the uniform distribution of chains on the surface and decreases their interactions with each other. Thus, in addition to the structure of the initial oligomer, the nature of the mineral support can be another important factor responsible for the catalytic properties of immobilized PMOSs.

In this work, we examined the effects of various supports on the activity of phenyl and nonyl copper organosiloxanes under identical conditions. Along with Silochrome, titania and zirconia were used as the supports.

Table 1. Composition of polycoppernonylsiloxane and polycopperphenylsiloxane fractions

Catalyst	Composition of a unit	Fraction composition			
		fraction	Si, wt %	Cu, wt %	Si/Cu atomic ratio
Polycoppernonylsiloxane	 $-\overset{C_9H_{19}}{\overset{\vert}{Si}}-O-Cu-O-$	1	11.98	13.08	2.07
		2	12.05	11.98	2.27
		3	12.55	9.97	2.84
Polycopperphenylsiloxane	 $-\overset{C_6H_5}{\overset{\vert}{Si}}-O-Cu-O-$	1	13.42	30.41	0.98
		2	16.43	19.51	1.90
		3	18.10	13.21	3.10

EXPERIMENTAL

The following mineral supports were used for the synthesis: Silochrome S-80 (fraction of 6–8 mm), CS-200 TiO_2 (specific surface area of 35 m^2/g), and ZrO_2 promoted with 6% Y_2O_3 (specific surface area of 190 m^2/g).[1] All the supports were prepared in accordance with a standard procedure: calcined in air and then in a vacuum at 400–450°C for several hours.

The phenylsiloxanes were synthesized and supported on a carrier in accordance with the previously described procedure, starting from the sodium derivatives of diphenyloligosiloxanediols and $CuCl_2$ [4]. Polycoppernonylsiloxane was synthesized in accordance with the following reaction scheme, which includes the hydrolysis of nonyltrichlorosilane, the alkaline cleavage of the resulting polysiloxane with the formation of an organosilanolate, and the subsequent exchange reaction of the organosilanolate with a copper halide:

$$nC_9H_{19}SiCl_3 \xrightarrow[HCl]{H_2O} [C_9H_{19}SiO_{1.5}]_n$$

$$\xrightarrow{NaOH} [C_9H_{19}Si(ONa)O]_n \xrightarrow[NaCl]{CuCl_2} [(C_9H_{19}SiO_{1.5})_m(CuO)]_n.$$

The supported catalysts were prepared by mixing a mineral support with a PMOS solution in toluene in a vacuum; next, an excess of the solvent was slowly removed at 180°C [4].

The catalytic experiments were performed in sealed thick-walled glass ampules in the absence of air at 110–150°C for several hours. The contents of the ampules were continuously stirred to provide the kinetic regime of reactions. The experiments were performed at stirring rates that provided the kinetic regime of reactions (the rate of reaction was independent of the rate of stirring). The reaction mixtures were analyzed by GLC on an LKhM 3700 chromatograph with a flame-ionization detector [6]. The standard CCl_4/1-octene volume ratio was equal to 9 : 1; this ratio was varied from 20 : 1 to 1 : 5 in determining the order of reaction, and saturated hydrocarbons were used as solvents. The orders of reactions were determined by the method of initial rates.

RESULTS AND DISCUSSION

A study of the fraction composition of polycoppernonylsiloxane demonstrated that the above rearrangement process, which is typical of PMOSs with other substituents, was noticeably inhibited in this case. Table 1 summarizes the composition of fractions obtained by the fractional reprecipitation of polycoppernonylsiloxane and polycopperphenylsiloxane. It can be seen that on going from the first to the last fraction the Si/Cu atomic ratio in polycoppernonylsiloxane changed by a factor of 1.4 or lower, whereas a change by a factor of more than 3 was observed in polycopperphenylsiloxane. Note that, in the majority of PMOSs with no bulky substituents tested to date, this value changed from the first to the subsequent fractions by a factor of 4–5 (sometimes 7–8) [7]. The inhibition of a rearrangement to M–O–M–O– clusters in polycoppernonylsiloxane can be explained by a much stronger shielding action of this organic radical, as compared with phenyl. As will be considered below, this positively affects the catalytic properties of the prepared samples.

Thus, the phenyl group shields a metal atom in the siloxane chain to a much lesser extent than the nonyl group; consequently, it prevents the coordination interaction of the metal oxide fragments of neighboring chains to a lesser extent. Nonyl groups, which exhibit the flexibility of a polymer segment, produce much greater steric hindrances. At the same time, it is believed that they do not prevent the interaction of reactants with the metal center too severely because of high lipophilicity and spatial flexibility in an organic medium. This assumption was supported by a comparative study of the catalytic activity of copper-containing phenyl- and nonylsiloxanes.

In this case, the reaction of CCl_4 with 1-octene in the presence of copper complexes was chosen as a model because of its high selectivity for the target product [6]. In this reaction, 1,1,1,3-tetrachlorononane was formed in a >90% yield, whereas the formation of by-products in commensurable amounts was observed only at

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[1] ZrO_2 was provided by Leading Researcher P.A. Chernavskii, Faculty of Chemistry, Moscow State University.

Table 2. Initial rates of the PMOS-catalyzed reaction of CCl_4 with 1-octene per mole of Cu

Composition of a unit	Initial rates, mol product (mol Cu)$^{-1}$ h^{-1}		
	TiO_2	SiO_2	ZrO_2*
$(C_6H_5)_2SiOCu$	0	15	21
$(C_9H_{19})_2SiOCu$	0	29	41

Note: The reaction temperature was 130°C; the CCl_4/octene volume ratio was 9 : 1; the catalyst content was 0.1 g/(ml solution); and the metal content was 5×10^{-4} g/ml.

* When calculating PMOS activity on this support, the proper activity of pure ZrO_2 was subtracted.

$T > 150°C$. Previous data [1, 4] unambiguously demonstrated that the reaction occurred by a chain-radical mechanism and surface copper complexes played the role of a renewable initiator. In this case, the total concentration of active catalyst species remained approximately constant for a long time. Thus, this reaction combined the special features of chain-radical and heterogeneous catalytic processes. The reaction kinetics was studied in detail using polycopperphenylsiloxane supported on Silochrome as an example. In the concentration ranges of 0.8–8 M CCl_4, 0.1–1 M octene, and 10–300 mg of the catalyst per milliliter of solution, the process is adequately described by the following equation at conversions of up to 70% (orders of reaction were determined to within ±0.1):

$$w = k[\mathrm{Ol}][\mathrm{Cat}]^{0.8}[\mathrm{CCl_4}], \quad (1)$$

where [Ol], [Cat], and $[CCl_4]$ are the initial concentrations (mol/l) of the olefin, the catalyst, and CCl_4, respectively. The effective activation energy was equal to 100 ± 8 kJ/mol, as determined from the linear $\ln w_0 - 1/T$ relationship within the temperature range 110–150°C under conditions of a first-order reaction with respect to CCl_4. These rate laws are characteristic of the specified reaction in the presence of metal complexes in homogeneous solutions [8].

Table 2 summarizes data on the activity of the resulting catalysts in the addition of CCl_4 to 1-octene. The activity was determined as the initial rate of the process per mole of copper in solution. As can be seen in Table 2, nonyl derivatives exhibited the highest activity; this is consistent with the above assumptions about the role of a bulky substituent, which prevents the formation of interchain clusters.

Surprisingly, we found that PMOSs supported on TiO_2 were fully inactive. High metal contents of reaction solutions after heating in the presence of a reaction mass suggested that the strong Ti–O–Si covalent bond was not formed in the course of the standard procedure of oligomer immobilization on the surface, and PMOS was physically adsorbed on the support. As a result, oligomers actively interacted with each other, and further polymerization and formation of interchain clusters occurred; ultimately, the samples completely lost catalytic activity.

Among all the catalysts tested, an oligomer supported on ZrO_2 exhibited the highest activity; in this case, not only PMOS samples supported on ZrO_2 but also the pure support were active. The activity of ZrO_2 in the test reaction, which was ~20% of the total activity of the catalyst, is an unexpected fact that calls for further investigation. The high activity of PMOSs on this support can be explained by the much more developed surface of this oxide, as compared with the samples of SiO_2 used (the specific surface area was greater by a factor of ~2.5). With equal weight metal contents of catalysts, this suggests a considerable decrease in the density of surface coverage with oligomer chains and consequently a decrease in their interactions with each other to form interchain clusters. Another reason consists in the low concentration of surface hydroxyl groups as compared with SiO_2; this is responsible for the “brush” structure of the grafted layer [9]. This structure, in which siloxane chains practically do not interact with the surface, except for immobilization sites, is most favorable for the free coordination of reactants and hence for the occurrence of a catalytic reaction.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 03-00-32211).

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