

# Catalytic Activity of Polymetalorganosiloxanes Supported on Silica in the Metathesis of a C–Cl Bond

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**Abstract**—The catalytic activity of structurally different Cu- and Ni-containing polymetalorganosiloxanes supported on silica was studied using the reaction of C–Cl bond metathesis in the carbon tetrachloride–saturated hydrocarbon (*n*-decane) system as an example. Catalysts with low metal contents were found to exhibit the highest activity; an increase in the metal content resulted in a decrease in both conversion and specific activity. At the initial portions of kinetic curves, the reaction was described by first-order rate equations with respect to *n*-decane; the reaction was of fraction order with respect to  $\text{CCl}_4$  and catalyst. The activation energy of the process in the *n*-decane–carbon tetrachloride system on a copper-containing network catalyst was  $23 \pm 2$  kcal/mol. The mechanism of catalysis on immobilized catalysts from the above class is discussed.

## INTRODUCTION

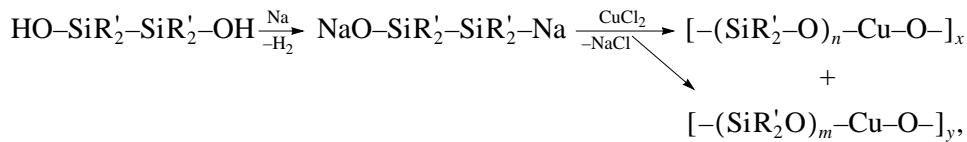
Polymetalorganosiloxanes (PMOSs) immobilized on silica catalyze a number of reactions with the participation of halogenated hydrocarbons [1, 2]. In particular, they are active in the metathesis of a C–Cl bond [3]



where R is an alkyl, cycloalkyl, or arylalkyl. This reaction is of considerable interest as a route for the effective conversion of carbon tetrachloride and other polyhalogenated derivatives. PMOSs exhibit reasonably high stability and can retain their catalytic activity for a long time. At the same time, the specific activities of previously studied copper-containing catalysts in the metathesis of a C–Cl bond were low; values lower than 1 mol of product (mol of metal) $^{-1}$  h $^{-1}$  at 180°C were obtained by calculation using published data [3]. In this work, for developing catalytic systems that are more active, we studied the behavior of a number of supported copper- or nickel-containing PMOSs with different metal contents and structures in the reaction of  $\text{CCl}_4$  with *n*-decane.

## EXPERIMENTAL

Oligomeric network and linear PMOSs were prepared according to well-known procedures [4, 5] by the hydrolysis of compounds with the general formula  $\text{R}'\text{SiCl}_3$  (where  $\text{R}' = \text{Ph}$  or  $\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ ), the subsequent treatment of the resulting polysiloxanes ( $\text{R}'\text{SiO}_{1.5}\text{}_n$ ) with sodium hydroxide, and the exchange reaction of the sodium derivative  $[\text{R}'\text{Si}(\text{ONa})\text{O}]_3$  with copper(II) chloride or nickel(II) chloride. The figure demonstrates a structural unit of this type of PMOS. As a rule, hydroxyls are terminal groups. The structure of the prepared PMOS was supported by spectroscopic (characteristic bands of Si–O–Si, Si–O–M (M is a transition metal), and Ph–Si groups in the vibrational spectra) and elemental analysis data (in full agreement with the structural formula, the Si/M atomic ratio was close to 2 in all of the compounds). The compounds with linear metal–siloxane chains (also shown in the figure) containing two organic substituents at each silicon atom were prepared by the interaction of a sodium metal with diorganooligosiloxanes [6, 7] followed by the reaction of the sodium derivative with a metal halide



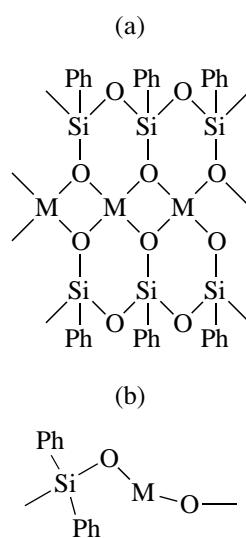
in this case,  $n = 4.2\text{--}6.5$  and  $m = 0.2\text{--}0.4$ . The simultaneous production of two PMOSs which are dramatically different in metal content is due to the disproportionation of initially formed compounds with a Si/M molar ratio of  $\sim 2$  under the conditions of synthesis. The

compounds with different Si/M ratios are significantly different in solubility in organic solvents. This fact provides an opportunity to separate fractions with approximately constant metal contents. The values of  $x$  and  $y$  determined by ebullioscopy lie within the range 12–20 [1].

The synthesis and structural identification of oligomeric PMOSs were described in more detail in [8].

Supported catalysts were prepared as described below. A weighed portion of Silochrome S-80 (fraction of 6–8 mm) was dried in a thermostat at 180°C and then evacuated at a pressure of 4 torr or lower. Next, a measured amount of a toluene solution of the corresponding PMOS was added to a reaction vessel with Silochrome and the solvent was slowly removed by evacuation and then pumping out on a rotary evaporator. The resulting samples were dried at 160°C for 1 h and stored in an inert atmosphere or in sealed ampules under a vacuum. Control experiments demonstrated that the samples were free from toluene and almost nonhygroscopic in air; in contact with nonpolar organic solvents, they did not release any organometallic or organic compounds into solution. Similarly, metals also did not pass into solution after performing a reaction (6–8 cycles of duration 1 h at 180°C in a decane–CCl<sub>4</sub> mixture). These data demonstrate that both metal and siloxane components of the catalysts are firmly bonded to the support, and they do not pass into solution in the course of the catalytic process. Table 1 summarizes the composition of particular test catalysts.

The catalytic experiments were performed in rotating sealed ampules. The products were analyzed by GLC. The procedures of kinetic experiments, in particular, tests for the kinetic reaction regime, were described in detail in [1, 2]. In the majority of experiments, the molar ratio between CCl<sub>4</sub> and a hydrocarbon (*n*-decane) was 4 : 1; this ratio was varied from 10 : 1 to 1 : 10 in determining the order of reaction. The orders of reaction were determined by the method of initial rates.



Polymetalphenylsiloxane fragments: (a) oligomeric network PMOS and (b) linear PMOS.

## RESULTS AND DISCUSSION

At 150–190°C, PMOS supported on silica (samples 1–10) exhibited catalytic activity in the reactions of CCl<sub>4</sub> with decane, cyclohexane, and other hydrocarbons. In the case of toluene, the substitution almost completely occurred at the side chain. To perform a more detailed study, we chose the CCl<sub>4</sub>–*n*-decane system, which was examined previously [9] with other copper-containing catalysts. As on immobilized copper complexes with dimethylformamide, the reaction in the presence of PMOS afforded chloroform and a mixture of secondary monochlorodecane isomers. Hexachloroethane was detected in minor amounts (less than 1%).

**Table 1.** Composition and structure of test PMOS

| Sample no.        | Metal | R'  | Element content, wt % |                |                 | Si/M in initial PMOS, atom/atom |  |
|-------------------|-------|---|-----------------------|----------------|-----------------|---------------------------------|--|
|                   |       |   | M                     |                | Si initial PMOS |                                 |  |
|                   |       |   | initial PMOS          | supported PMOS |                 |                                 |  |
| Network compounds |       |   |                       |                |                 |                                 |  |
| 1                 | Cu    | Ph  | 18.1                  | 2.30           | 17.3            | 2.15                            |  |
| 2                 | Cu    | Ph  | 17.0                  | 0.11           | 15.4            | 2.05                            |  |
| 3                 | Ni    | Ph  | 17.0                  | 4.00           | 16.5            | 2.03                            |  |
| 4                 | Cu    | NH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> | 20.1                  | 0.10           | 18.6            | 2.10                            |  |
| 5                 | Cu    | NH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> | 21.2                  | 0.50           | 18.2            | 1.95                            |  |
| 6                 | Ni    | NH <sub>2</sub> (CH <sub>2</sub> ) <sub>3</sub> | 17.1                  | 0.16           | 16.3            | 2.05                            |  |
| Linear oligomers  |       |   |                       |                |                 |                                 |  |
| 7                 | Cu    | Ph  | 39.8                  | 1.60           | 7.0             | 0.40                            |  |
| 8                 | Cu    | Me  | 11.2                  | 0.60           | 34.3            | 6.50                            |  |
| 9                 | Cu    | Me  | 15.2                  | 0.13           | 31.0            | 4.60                            |  |
| 10                | Cu    | Ph  | 6.3                   | 0.02           | 13.1            | 4.70                            |  |

At low conversions (up to 20%), the selectivity for both of the products was 97–98%; the yield of 1-chlorodecane was no higher than 2–3%. As the conversion increased, an amount of dichlorodecanes was formed (up to 3–5% conversion).

The reaction kinetics was studied in detail using catalyst 4 (Table 1) as an example. In the  $\text{CCl}_4$  and decane concentration ranges 0.5–7.0 and 1.5–4.7 mol/l, respectively, at the effective concentration of the heterogeneous catalyst in solution  $[\text{Cat}] = 10\text{--}300 \text{ mg/ml}$ , the process is adequately described by the following equation at conversions up to 50% (orders of reaction were determined to within  $\pm 0.1$ ):

$$w = k[\text{RH}][\text{CCl}_4]^{0.5}[\text{Cat}]^{0.6}. \quad (1)$$

At higher conversions, the kinetic curves cannot be linearized in coordinates that correspond to Eq. (1). We failed to fit an exponential rate law suitable for describing the entire kinetic curve. The effective activation energy for catalyst 4 is equal to  $23 \pm 2 \text{ kcal/mol}$ , as determined from the linearized  $\ln w_0 - 1/T$  relationship ( $w_0$  is the initial rate of reaction) within the range  $150\text{--}190^\circ\text{C}$ .

The activity of catalysts was characterized by the values of conversion and specific activity. These values were determined under identical conditions:  $180^\circ\text{C}$ ; reaction time, 8 h;  $\text{CCl}_4$ /decane molar ratio of 4; catalyst weight, 100 mg of supported catalyst per 1 ml of solution. Small variations in the total catalyst content in particular experiments were taken into account in the data processing. Conversion  $x$  was determined on the basis of decane, which was taken in a deficiency; the specific activity  $A$  was calculated as the number of moles of formed monochlorodecane (chloroform) per mole of metal per hour. Table 2 summarizes the data on

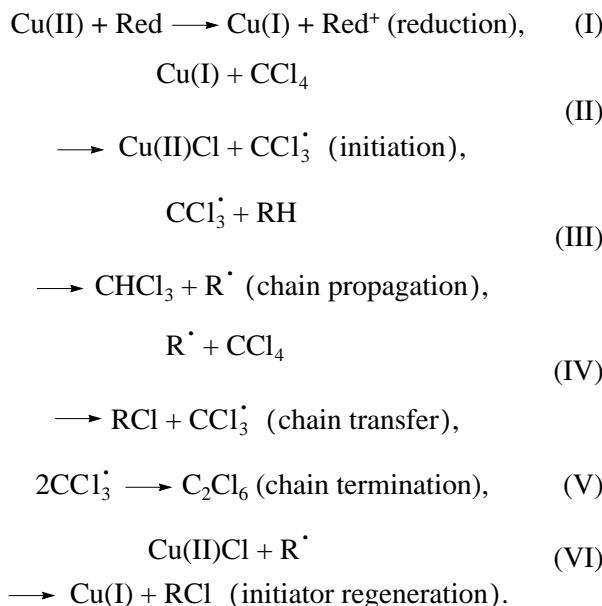
the activity of catalysts (run-to-run coefficients of variation averaged over three experiments were 10–15%).

The data suggest that the metal content of a heterogeneous catalyst is a factor responsible for the catalytic activity of PMOSs. A decrease in this content by two orders of magnitude leads to a considerable increase in the activity. This fact is surprising; in principle, it might indicate that the support or a product of its modification by high-temperature treatment rather than the supported metal exhibits a catalytic activity. To test this hypothesis, the process was performed under standard conditions (see above) in the presence of the properly treated Silochrome and the product of its reaction with the metal-free polysiloxane ( $\text{PhSiO}_{1.5}{}_n$ ). Both of these substances exhibited activity; however, it was much lower than that in the samples with low metal contents. Thus, supported PMOSs with low copper or nickel contents do exhibit high catalytic activity. Under conditions of the test reaction, structural factors are of little importance. Thus, the activity of network and linear PMOSs was almost equal at close metal contents. The metal content of the parent PMOS before the interaction with silica is also of no significance (cf. catalysts 1 and 7). No significant changes were observed on the replacement of a phenyl substituent at silicon by methyl or aminopropyl either. The replacement of copper with nickel affected the activity only slightly.

Let us consider conceivable causes for this unusual behavior. It should be borne in mind that, as found previously [3], the metathesis of a C–Cl bond occurs by a chain-radical mechanism. It is commonly supposed that the first step of radical reactions of  $\text{CCl}_4$  in the presence of copper complexes is the reduction of  $\text{Cu(II)}$  to  $\text{Cu(I)}$ , which further reacts with  $\text{CCl}_4$  to form the trichloromethyl radical [10]. Taking into account the above, the reaction scheme can be presented in the form

**Table 2.** Activity of supported PMOS catalysts in the reaction of  $\text{CCl}_4$  with decane under standard conditions

| Catalyst  | Catalyst type | Metal content, wt % | X, % | A, mol product $(\text{mol M})^{-1} \text{ h}^{-1}$ |
|-----------|---------------|---------------------|------|---|
| <b>1</b>  | Network       | 2.30 (Cu)           | 13   | 0.6   |
| <b>2</b>  | "             | 0.11 (Cu)           | 30   | 45.0  |
| <b>3</b>  | "             | 4.00 (Ni)           | 15   | 0.45  |
| <b>4</b>  | "             | 0.10 (Cu)           | 53   | 73.0  |
| <b>5</b>  | "             | 0.50 (Cu)           | 24   | 16.0  |
| <b>6</b>  | "             | 0.16 (Ni)           | 35   | 27.0  |
| <b>7</b>  | Linear        | 1.60 (Cu)           | 13   | 2.0   |
| <b>8</b>  | "             | 0.60 (Cu)           | 15   | 3.0   |
| <b>9</b>  | "             | 0.13 (Cu)           | 44   | 44.0  |
| <b>10</b> | "             | 0.02 (Cu)           | 46   | 320.0   |



Here, Cu(I), Cu(II), and Cu(II)Cl are copper-containing fragments of the heterogeneous catalyst, in which copper is coordinated to oxygen atoms of the  $-\text{O}-\text{Si}-$  groups or to chlorine in the case of Cu(II)Cl and Red is a system component required for the reduction of copper. In this case, it is most likely that organic groups of PMOSs (Ph,  $\text{NH}_2(\text{CH}_2)_3$ , and Me), which easily lose electrons, serve as reducing agents. Rather than the recombination of R or cross termination, reaction (V) was chosen as the step of chain termination because hexachloroethane was detected in the reaction products. Rate law (1) describes the above reaction scheme on the assumptions that reaction (I) is fast and the rate of reaction (VI) is much lower than that of (IV). Both of these assumptions seem reasonable. Thus, the derived rate equation is consistent with the probable scheme of the chain process. A change in the kinetics at high conversions can be explained by the consumption of organic groups adjacent to metal ions and capable of reducing these metal ions (Red in the reaction scheme). In this case, it is likely that the regeneration of active centers of the catalyst by the interaction with radicals comes into play to change the rate law.

An inverse relationship between the catalytic activity and the metal content cannot be explained by the fact that the metal plays the role of an inhibitor. Indeed, if we assume, for example, that chain termination occurs in the reaction of radicals with Cu(II)



rather than in reaction (V), it is easy to see that the steady-state treatment with respect to organic radicals leads to the expression

$$k_1[\text{Cu(II)}][\text{Red}] = k_7[\text{Cu(II)}][\text{R}^{\cdot}]$$

Consequently, the concentration of radicals and the rate of the overall reaction  $w$  ( $w = k_4[\text{R}^{\cdot}][\text{CCl}_4] =$

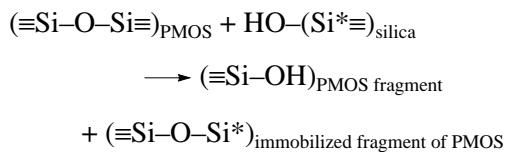
$k_4 k_1 k_7^{-1} [\text{Red}][\text{CCl}_4]$ ) would be independent of the total amount of the catalyst and the metal content.

It is our opinion that the observed facts can be explained on the assumption that the association of copper-containing fragments via bridge bonds dramatically inhibits redox processes required for the appearance of radicals. Indeed, in network PMOSs, a metal atom is strongly coordinated to at least four oxygen atoms. Electron transfer from a reducing agent (Red) to the metal will result in the formation of a negatively charged fragment that contains the metal with a lower oxidation number. However, it is well known that in negatively charged species Cu(I) always exhibits a coordination number of two. The formation of species with higher coordination numbers is energetically unfavorable [11]. Thus, two additional firmly bound ligands will destabilize the ion in the lowest oxidation state and prevent reduction. The same or a similar situation also occurs in the case of linear PMOSs. Here, the coordination number of the metal in an oxidized state increases because of coordination to the oxygen atoms of neighboring chains. This coordination will also take place in solution and in immobilized catalysts with high surface coverages where the oligomeric chains are arranged within reach of one another. Fragments containing the metal with an anomalously low coordination number of two, which are most favorable for the reduction of Cu(II) and the formation of Cu(I) ions active in the reaction of C-Cl bond metathesis, can be produced only when oligomeric PMOS chains immobilized on a surface are widely spaced, that is, at very low surface coverages.

The mechanism of metathesis in the presence of nickel derivatives is still unclear. A nonchain mechanism with the intermediate formation of Ni(III) derivatives was suggested [12] for a similar reaction of carbon tetrachloride addition to a multiple bond. It is likely that in this case a decrease in the coordination number of the metal is also favorable for the reaction because of the stronger interaction between the metal ion and the polyhaloalkane. However, to draw final conclusions, the evolution of nickel-containing catalysts in the course of the reaction should be studied in more detail.

The assumptions made for copper-containing PMOSs are consistent with data for linear oligomers. At the same time, at first glance, it seems impossible to understand why immobilized network PMOSs, in which the coordination number of copper is strongly determined by the network structure (see the figure), also exhibit a reasonably high activity at a low metal content. It is our opinion that this behavior of oligomeric network PMOSs can be associated with network degradation in the reaction with the surface of silica. We may believe that in a large excess of surface hydroxyl groups of silica with respect to the hydroxyls of the initial PMOS (this is the case on supporting small amounts of PMOS), the hydroxyls of silica react not only with terminal OH groups of the oligomer but also

with siloxane fragments in the course of high-temperature treatment. For example, these reactions can be represented as follows:



( $\text{Si}^*$  is the silicon ion in the structure of the support).

As a result, along with unchanged PMOS oligomers, fragments with distorted network structures can be formed on the surface of the support. The coordination number of copper is lowered in these fragments. Of course, this is possible only at low PMOS concentrations. With an increase in the surface coverage, the interaction of the metal with oxygen atoms of the neighboring fragments will restore the initially high coordination number. This explanation is preliminary; the observed interesting behavior should be studied in more detail. In any case, the results will be helpful in the development of a new type of active and stable heterogeneous catalysts with low metal contents on the basis of PMOSSs.

#### ACKNOWLEDGMENTS

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