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LETTERS TO THE EDITOR

Activity of Immobilized Catalytic Compounds in the Oxidation of 1-Octene with Molecular Oxygen

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Communications [1–3] have described the results of the studies of catalytic activity of a number of rhodium, palladium, iridium, and ruthenium complex compounds in the reaction of liquid-phase oxidation of 1-octene with molecular oxygen. In this communication we present the data on the catalytic properties of some of these metal complexes in an immobilized form. The principle of immobilization of metal complexes is based on the known ability of the transition metals (M) cyanides to act as metal-containing ligands coordinating to other transition metals (M') through the nitrogen atom of the cyanide groups to form M–CN–M' bridges [4–9]. The catalysts studied in this work were prepared by fixing a metal on the surface of the carrier (alumina), on which Ni(II) cyanide was preliminary applied. Thus, the data presented here characterize the catalytic activity of immobilized bimetallic compositions Ni–CN–M'L_n, where L_n is a set of the ligands forming the coordination sphere of the transition metal M'. As a quantitative characteristic of the catalytic activity of the compositions we used, as in [1, 2], the initial rate of oxidation of 1-octene (W_0) determined from the curve of the rate of oxygen consumption extrapolated to zero time.

The experimental procedure has been described previously [1, 2]. The oxidation of 1-octene with molecular oxygen in the presence of immobilized catalyst compositions (1 g l^{-1}, which corresponds to the concentration of deposited metal complex 1.8×10^{-4} M) was carried out in a thermally controlled reactor equipped with magnetic stirrer, at 333 K, oxygen pressure 90 kPa, solvent chlorobenzene. The stirrer rotation rate 1000 rpm is sufficient to ensure the reaction to proceed in the kinetic regime. Oxygen consumption was determined using a gasometric unit [1, 2]. Preliminary experiments showed that all studied catalysts influence the oxidation of 1-octene only in the presence of hydroperoxides. Therefore, in the homogeneous reaction system was introduced *tert*-butyl hydroperixide as an initiator, to the concentration in the reaction mixture 0.05 M.

The immobilized catalyst compositions were prepared as follows. Aluminum oxide (γ-form, Woelm) was dried at 100°C, degassed, and saturated with dry argon. To thus prepared aluminum oxide (27 g) was added a solution of $NiSO_4\cdot7H_2O$ (1.31 g) in water (20 ml). The resulting mixture was dried at 100°C to the loose state. To the obtained material was added a solution of KOH (0.64 g) in water (30 ml), the mixture was stirred for 30 min, the product, $Ni(OH)_2/Al_2O_3$, was filtered off and washed with water (10 ml). To obtain the desired composition $Ni(CN)_2/Al_2O_3$, the material obtained was treated with a solution of acetone (1 ml) in water (10 ml) (stirring at 70°C for 1 h), the principle of the method has been described previously [10]. The product was filtered off, washed with water (4×15 ml), and dried in a thermostat (100°C) to constant weight. To obtain immobilized bimetallic compositions, to a weighed sample (2 g) of the $Ni(CN)_2/Al_2O_3$ carrier prepared by the above method was added a solution of the corresponding compound in water (compositions **I, II**, and **IV**) or chloroform (composition **III, V**, and **VI**) in an amount corresponding to a molar ratio M'/Ni = 1. After stirring for 1 h, the solvent

was removed by evaporation on a water bath (**I, II, IV**) or in a vacuum (**III, V, VI**). The product was dried in a thermostat (100°C) to constant weight.

The obtained $W_0 \times 10^5$ values, mol l^{-1} s^{-1}, are listed below (Cod is 1,5-cyclooctadiene, COE is cyclooctene).

No catalyst	0.10
$Ni(CN)_2 – VO(SO_4)\cdot 7H_2O$ (**I**)	0.46
$Ni(CN)_2 – RuOHCl_3$ (**II**)	2.66
$Ni(CN)_2 – [Rh(CO)_2Cl]_2$ (**III**)	1.00
$Ni(CN)_2 – RhCl_3\cdot 4H_2O$ (**IV**)	0.69
$Ni(CN)_2 – [Rh(Cod)Cl]_2$ (**V**)	1.04
$Ni(CN)_2 – [Rh(COE)_2Cl]_2$ (**VI**)	0.80

The results obtained showed that the initial rate of oxidation of 1-octene in the presence of any studied catalyst compositions is significantly higher than the rate of the non-catalytic process. Highest catalytic activity among the six investigated compositions showed the composition **II** containing immobilized ruthenium complex. According to the preliminary data obtained in the study of the dependence of 1-octene oxidation on the concentration of the immobilized catalyst (for example, the most active composition **II**), the immobilization does not lead to a decrease in catalytic activity at the initial stage of reaction. We can expect some advantages of the immobilized form of the catalyst compositions at higher degrees of conversion, when an important role belongs to the ability of the catalyst to conserve the activity in the reaction for a long period.

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