

LETTERS  
TO THE EDITOR

**Palladium Nanoparticles in Homo-  
and Heterogeneous Oxidation of Lower Olefins  
with Fe(III) Aqua Ions in a Chloride-Free System**

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We studied previously [1–3] the kinetics and mechanism of a number of homogeneous redox processes involving organic and inorganic substances, occurring in the presence of the Pd(II) tetraaqua complex. We concluded that the catalytically active species are Pd nanoparticles formed from Pd(II) by reduction with one of the substrates. It is known that the redox potential of metal nanoparticles is considerably lower than that of the corresponding bulk metals [4, 5]. This fact made it possible to perform some oxidation processes in the catalytic mode with the Pd(II) tetraaqua complex as oxidant and Fe(III) ions and/or molecular oxygen, as cooxidant [2].

Here we demonstrated for the first time the possibility of catalytic oxidation of lower olefins (ethene, propene, 1-butene) to the corresponding carbonyl compounds with Fe(III) aqua ions in the absence of chloride ions, both in a homogeneous system with the Pd(II) tetraaqua complex and in a heterogeneous system with Pd(0) on an “inert” support.

A TEM examination of the homogeneous catalytic system (JEOL-1200EXII electron microscope, 100 kV) revealed formation in solution of Pd nanoparticles with a mean size of 5 nm.

From the scientific and applied viewpoint, it is important to deposit the arising Pd nanoparticles on a support. We chose acidic supports  $ZrO_2/SO_4$ ,  $\gamma-Al_2O_3$ , and  $SiO_2$ . To obtain a supported Pd(0) catalyst, the Pd(II) tetraaqua complex was reduced with Fe(II) aqua ions in the presence of appropriate support. Binding of Pd nanoparticles formed in this reaction [3] with the acid centers of the support prevents the diffusion of the nanoparticles over the support surface and their aggregation with the formation of crystals.

The catalytic activity of the heterogeneous Pd catalysts obtained ( $Pd/ZrO_2/SO_4$ ,  $Pd/Al_2O_3$ ,  $Pd/SiO_2$ , 1 wt % Pd) was tested in oxidation of lower olefins,

methanol, hydrogen, and CO with Fe(III) aqua ions (0.01–0.12 M) in an  $HClO_4$  solution (0.1–3 M) at 25–80°C. In all cases, we observed selective oxidation of the starting substances, accompanied by reduction of Fe(III) to Fe(II), with almost 100% conversion.

In the experiments on oxidation of olefins, a TEM examination of the reaction solutions showed that, in the presence of the heterogeneous catalyst, the carbonyl compounds are formed in the bulk with the participation of Pd nanoparticles; these particles are the catalytically active species in the process.

In particular, we found that the olefin oxidation rate depends on the acid properties of the support and increases with an increase in the acidity of the medium ( $HClO_4$ ,  $H_2SO_4$ ) and in the order  $C_2H_4 < C_4H_8 < C_3H_6$ . As shown by the example of ethylene, the oxidation rate decreases in the order  $ZrO_2/SO_4 > Al_2O_3 > SiO_2$ . In the case of 1-butene, the oxidation is accompanied by concurrent migration of the double bond with formation of 2-butene, as proved by  $^1H$  NMR spectroscopy (Bruker DPX-300) and gas chromatography–mass spectrometry (Agilent-6890/5973, Network  $100 \times 0.25 \times 0.5$ ). The ratio between *cis*- and *trans*-2-butenes was 1 : 2, which corresponded to the thermodynamic equilibrium. No isomerization occurred in the absence of Fe(III).

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