



## Short communication

# New approach for highly selective hydrogenation of phenol to cyclohexanone: Combination of rhodium nanoparticles and cyclodextrins

Sergey Kuklin <sup>a</sup>, Anton Maximov <sup>a,b</sup>, Anna Zolotukhina <sup>a</sup>, Eduard Karakhanov <sup>a,\*</sup><sup>a</sup> Department of Chemistry, Moscow State University, Moscow 119991, Russian Federation<sup>b</sup> Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Leninskii pr. 29, Moscow 119991, Russian Federation

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## ABSTRACT

The effect of cyclodextrins on the activity and selectivity of a catalytic system based on rhodium nanoparticles stabilized by polyacrylic acid (PAA) in the hydrogenation of phenol in aqueous solution and ionic liquid was reported. It was found that the reaction medium and the nature of the cyclodextrin (CD) essentially affect the rate of reaction and the distribution of reaction products. The use of the system based on rhodium nanoparticles stabilized by cyclodextrins makes it possible to rapidly and efficiently prepare cyclohexanone from phenol with yields up to 100% under relatively mild conditions (1 h;  $T = 80^{\circ}\text{C}$ ,  $p(\text{H}_2) = 10\text{--}40$  bars).

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## 1. Introduction

The hydrogenation of phenols and their derivatives is one of the most important processes in industrial organic chemistry and the renewable feedstock processing. The reduction of phenol to cyclohexanone or cyclohexanol is the primary stage of the production of adipic acid and caprolactam [1]. Thus, in the hydrogenation of phenol, it is reasonable to obtain cyclohexanone, which can be further directly converted into cyclohexanone oxime and caprolactam [1–2].

As a rule, the hydrogenation of phenol is carried out in the presence of different platinum group metals (palladium, rhodium, and ruthenium) supported onto silicon oxide, aluminum oxide, or activated carbon [3–4]. The reaction occurs by a consecutive-parallel mechanism: cyclohexanol is formed both as a result of the direct hydrogenation of phenol and from cyclohexanone, an intermediate product of the reaction [5–7]. In this context, the selective production of cyclohexanone (>90%) at a high phenol conversion (>80%) is a nontrivial problem.

Earlier, it was found that the high yields of cyclohexanone can be reached in the presence of a bimetallic palladium–gold catalyst supported on the mesoporous hollow spheres of silica (Pd–Au/MHSS) [8]: the selectivity of this catalyst for the ketone was 95–97% at a 93–97% conversion in 45 min at  $50^{\circ}\text{C}$  and 10 atm of  $\text{H}_2$ . This catalyst was much superior to both corresponding monometallic catalysts and traditional Pd/

C in terms of activity. Analogous results were obtained for the Pd/ $\text{Al}_2\text{O}_3$  catalyst doped with  $\text{AlCl}_3$  in supercritical carbon dioxide [6].

Palladium supported onto mesoporous aluminum oxide made it possible to obtain cyclohexanone in high yields (98% selectivity at a 96% conversion) even after half an hour at a temperature of  $100^{\circ}\text{C}$  and a hydrogen pressure of 5 bars [9]. A special feature of this catalytic system was the use of water as a solvent: taken in a large excess relative to the substrate, water readily displaced less polar cyclohexanone from the hydrophilic surface of mesoporous aluminum oxide. Aqueous solution was also used for the hydrogenation of phenol and its derivatives in the presence of a palladium catalyst supported onto poly(s-triazine) (Pd@mpg- $\text{C}_3\text{N}_4$ ) [10].

The dispersions of metal nanoparticles in a reaction medium stabilized by surfactants and polymers are an alternative to supported systems in the hydrogenation of aromatic compounds and phenols [11–13]. Thus, it was found that phenol was hydrogenated to cyclohexanol on catalysis by Rh nanoparticles stabilized with tetraalkylammonium [14] and tetraalkylphosphonium [15] ionic liquids. In the latter case, the reaction occurred much more slowly, with hydrogenolysis. With the use of Rh nanoparticles stabilized by polymers [16–17], cyclohexanol was the main reaction product. Simultaneously, high selectivity for cyclohexanone was observed at the slow hydrogenation of phenol in the presence of Pd nanoparticles stabilized by polyvinylpyrrolidone in water [18] and on Pd nanoparticles stabilized by a polymer based on ionic liquid modified with sulfogroups in the presence of heteropolyphosphoric acid [19].

\* Corresponding author.

E-mail address: [kar@petrol.chem.msu.ru](mailto:kar@petrol.chem.msu.ru) (E. Karakhanov).

The selectivity of hydrogenation can be affected with the use of additional ligands capable of forming inclusion complexes of the host-guest type [20–23]. Cyclodextrins and calixarenes belong to ligands of this type [20,21]. Noël et al. [21,24] studied the stabilization of rhodium nanoparticles by a polymer consisting of carboxylic acid and  $\beta$ -cyclodextrin ( $\beta$ -CD) fragments. In this case, the rhodium nanoparticles exhibited high stability and catalytic activity in the hydrogenation of olefins and aromatic compounds (xylenes and styrene) in aqueous solutions. Depending on the Rh/ $\beta$ -CD ratio, styrene could be hydrogenated to ethylbenzene or ethylcyclohexane.

Cyclodextrins can serve as effective phase-transfer agents not only in water but also in ionic liquids [20]. Here, we report the results of the selective hydrogenation of phenol to cyclohexanone in water and a tetraalkylammonium ionic liquid in the presence of rhodium nanoparticles and cyclodextrins (free or immobilized on a polymer).

## 2. Experimental

Commercial reagents from Fluka, Aldrich, Reachem, and Acros Organics were used in this study. The *n*-hexyltriethylammonium bromide ionic liquid ( $N_{6222}Br$ ) was synthesized in accordance with a published procedure [25]. The synthesis of poly(mono-( $\beta$ -cyclodextrin-2-yl)-maleate-alt-maleate-alt-methyl vinyl ether) (polymer **1**) was carried out using a published procedure [24]. The structures of the ionic liquid and polymer **1** were confirmed by  $^1H$  and  $^{13}C$  NMR spectroscopy.

The catalyst in the ionic liquid was prepared in accordance with a previously reported procedure [26]. Then, corresponding cyclodextrin (200 mg) was added to the system. The catalyst in water was prepared analogously. On the stabilization of rhodium nanoparticles with polymer **1**, this polymer (200 mg) was added in place of PAA without the use of free cyclodextrin in this case. For details, please see Supplementary Material.

The studies by X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) were performed on a Kratos Axis Ultra DLD instrument equipped with an OPX-150 analyzer of photoelectrons with retarded potential and on a LEO912 AB OMEGA transmission electron microscope with a cathode potential of 100 kV, respectively.

The catalytic experiments on the hydrogenation of phenols were carried out according to a procedure described elsewhere [26]. The reaction products were analyzed by gas–liquid chromatography on a Chrompack CP9001 instrument with an SE-30 column (30 m  $\times$  0.2 mm) and a flame-ionization detector.

The catalyst activity (turnover frequency, TOFs) was defined as the number of moles of the substrate converted per mole of surface rhodium per unit of time from the formula:

$$TOFs(substr) = \frac{conv. \cdot C_{substr.}}{V_{RH-t}} \cdot \frac{1}{D_M},$$

where  $D_M$  is the ratio of surface Rh atoms to the total number of Rh atoms in nanoparticles.  $D_M$  was calculated as  $d/0.901$ , where  $d$  is a nanoparticle diameter [27]. Also  $TOFs(H_2)$  for the hydrogen consumed has been calculated. In this case the TOF value obtained was multiplied on 3 for the cyclohexanol as product and for 2 for the cyclohexanone, taking into account the corresponding selectivities. All the reactions, both in water and ionic liquid, in presence and in the absence of CD, were conducted under the kinetic control, where the reaction rate has not already depended on the stirring rate.

## 3. Results and discussion

The system based on rhodium nanoparticles stabilized by polyacrylic acid (PAA) and modified with cyclodextrins was used as a catalyst for the hydrogenation of phenol. An analogous catalytic system without cyclodextrins was successfully used previously in an aqueous-alcoholic solution and ionic liquids [26,28–29]. The rhodium nanoparticles were

synthesized in a tetraalkylammonium ionic liquid by the reduction of an aqueous solution of rhodium trichloride with sodium borohydride in the presence of polymer at the ratio Rh: COOH = 1: 4 (Scheme 1) with the subsequent addition of  $\beta$ -CD.

According to the TEM data, the particle size distribution in the system obtained in the absence of  $\beta$ -CD was monomodal and unsymmetrical, with particle size of 1.5 nm [26; also see Fig. S1 in the Supplementary material]. Upon the addition of free cyclodextrin to the system, the average size considerably increased to reach 4.2 nm (Fig. 1, top); the distribution became more symmetrical. We assume that this phenomenon is related to the formation of inclusion complexes between cyclodextrins and the hydrophobic fragments of the tetraalkylammonium constituents of ionic liquids. In this case, a cyclodextrin molecule can form an inclusion complex simultaneously with two tetraalkylammonium ions (Fig. 1, bottom) [30]. Consequently, this latter leaves the near-surface layer to cause an increase in the average particle size (the local ligand/metal ratio decreases). For polymer **1** the average size was 1.5 nm in ionic liquid and 2.7 nm in water that corresponded to the Noël et al. data [21].

The XPS data for the sample containing cyclodextrin (Table 1; Figs. S2–S5 in the Supplementary Material) confirm the above hypothesis on the structure of the Rh–PAA–ionic liquid–CD system. Thus, the 3d signal of rhodium was very weak, and its atomic surface concentration was only 0.16%. Rhodium predominantly occurred in an oxidized form, which corresponds to its stabilization by polyacrylic acid [31] and, as a result, to the formation of Rh–O bonds, as additionally confirmed by the deconvolution of the 1s spectrum of oxygen [32; Fig. S3 in the Supplementary Material]. Cyclodextrins can also take part in the stabilization of rhodium nanoparticles [33] due to adsorption and charge transfer from donor OH groups. The low nitrogen content of the catalyst surface and the almost complete absence of metal–nitrogen bonds are also indicative of the predominant occurrence of ionic liquid in an interlayer between PAA and cyclodextrin molecules.

Cyclohexanone was the only product of the reaction performed in the ionic liquid in the presence of  $\beta$ -CD (Fig. 2b). We found that a conversion of about 80% at 100% selectivity for cyclohexanone could be reached even in 1 h; in this case, a further increase in the reaction time did not lead to the formation of cyclohexanol. As the pressure of hydrogen was decreased to 10 bars, the degree of conversion insignificantly decreased to 70–80% in 3 h. Note that the addition of cyclodextrin led to an increase in the overall rate of the reaction, as compared with an analogous system without cyclodextrin [26]. Thus, the TOF values were 401 h<sup>−1</sup> and 104 h<sup>−1</sup> for the reactions with and without cyclodextrin correspondingly.

Cyclohexanone can also be selectively prepared in the presence of various  $\beta$ -CD derivatives (Table 2). We found that the use of cyclodextrins containing polar modifying groups ( $SO_3^-$  and maltosyl – Entries 7–8 and 10–11 respectively, Table 2) increased the rate of hydrogenation, as compared with unmodified  $\beta$ -CD, whereas, on the contrary, hydrophobic cyclodextrins (methyl- $\beta$ -cyclodextrin and heptakis(2,6-di-O-methyl)- $\beta$ -cyclodextrin – Entries 3–6 and 9 respectively, Table 2) considerably inhibited the process. The activity for system with 6-O-Maltosyl- $\beta$ -CD was 1827 h<sup>−1</sup> at 40 bars and 988 h<sup>−1</sup> at 10 bars. The conversion was 98% for 0.5 h at pressure of 40 bars. It is likely that this tendency is related to an increase in the stability constants of the inclusion complexes of phenol with hydrophobic cyclodextrins and, as a result, the hindered adsorption of phenol on the surface of metal nanoparticles.

It is likely that the high selectivity for cyclohexanone reached in ionic liquids in the presence of cyclodextrins can be explained by the structure of a near-surface layer of ligands adjacent to rhodium nanoparticles (Scheme 2). Cyclohexenol, which is an intermediate product of phenol hydrogenation, forms an inclusion complex with cyclodextrin; as a consequence, it is desorbed from the metal surface. The probability of the repeated adsorption of cyclohexenol is very small because of a high stability constant of this complex with cyclodextrin [34]. The isomerization

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