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Hydrogenation of Phenols in Ionic Liquids on Rhodium Nanoparticles

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Abstract—A new catalyst system based on rhodium nanoparticles stabilized by polyacrylic acid have been suggested for the hydrogenation of phenols in ionic liquids. It has been shown that high near-quantitative yields of reaction products are achieved in ionic liquids containing a tetraalkylammonium cation. By the TEM and XPS techniques it has been revealed that the use of ionic liquids substantially decreases the particle size and reduces the aggregation of nanoparticles through the inclusion of the ionic liquid cations into the surface layer along with polyacrylic acid.

Keywords: hydrogenation, phenols, rhodium nanoparticles, ionic liquids

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Hydrogenation of phenols plays an important role both in the petrochemical industry and in the processing of various types of renewable raw materials. This reaction is the first stage of the commercial-scale production of caprolactam, adipic acid, and polyamide resins. Hydrogenation products of phenol derivatives are used as feedstock for the manufacture of synthetic lubricants, oil and fuel additives, special solvents, surfactants, and synthetic fragrances. Upon processing of biological feedstock, the hydrogenation of various types of substituted phenols plays an important role to produce hydrocarbons or alcohols. In the latter case, works aimed at processing phenols which are models of lignin fragments deserve consideration [1–2]. Systems containing metal nanoparticles, either supported or immobilized in alternative media, exhibit a high catalytic activity in the hydrogenation of phenols [3–10].

When the reaction is carried out in water, various stabilizing ligands may be used; however, it is necessary to use a number of special stabilizers to create stable hydrogenation nanocatalysts in the case of ionic liquids (ILs) [11–12]. Thus, the catalytic activity of rhodium nanoparticles in nonfunctionalized imidazolium ionic liquids without further stabilization by ligands decreased sharply because of aggregation into larger particles [13]. Successful hydrogenation of phenol and other arenes over rhodium nanoparticles using special polymers as stabilizers was described in [11]. In [12], preliminary modification of ionic liquids was proposed for the dissolution in them of conventional stabilizers of nanoparticles, such as polyvinylpyrrolidone.

In this study, we have examined a catalytic system, based on rhodium nanoparticles, stabilized with polyacrylic acid, in the hydrogenation of phenols. Such systems have been shown [14–15] to have a high activity in the hydrogenation of phenols and other aromatic compounds in the aqueous medium.

EXPERIMENTAL

To carry out the hydrogenation of phenols, two types of ionic liquids containing imidazolium and tetraalkylammonium cations were chosen as solvents (Fig. 1). Tetrabutylammonium bromide $(C_4H_9)_4NBr$ ($\mathbf{N_{4444}Br}$) Aldrich, 99%, methyltri(*n*-octyl)ammonium chloride $(CH_3(C_8H_{17})_3NCl$ ($\mathbf{N_{8881}Cl}$)) Aldrich, cetyltrimethylammonium bromide $(C_{16}H_{33}(CH_3)_3NBr$ ($\mathbf{N_{16111}Br}$)), Merck, 97%, were used without previous purification. The synthesis of 1-butyl-3-methylimidazolium chloride ($\mathbf{[Bmim]^+[Cl]^-}$) was performed according to [16]; 1-butyl-3-methylimidazolium tetrafluoroborate ($\mathbf{[Bmim]^+[BF_4]^-}$), according to [17];, *n*-hexyltriethylammonium bromide ($\mathbf{N_{6222}Br}$), according to [18]. The structure of the ionic liquids was confirmed by ^{1}H and ^{13}C NMR spectroscopy. The obtained data were consistent with the literature.

Triethyl(propyl-3-sulfonyl) ammonium hydrogen sulfate ($\mathbf{[Et_3N^+(CH_2)_3SO_3H]HSO_4^-}$) was prepared as follows. 1,3-propanesultone (12.2 g), triethylamine (15.3 mL), and toluene were placed in a 100 mL flask. The mixture was refluxed for 12 h at 90°C and constant stirring. After the completion of the reaction, toluene was removed on a rotary evaporator to the complete drying of the resulting white amorphous precipitate. 22.3 g of zwitterion was obtained, the yield was 100%. The obtained zwitterion (5 g) and H_2SO_4 conc. (1.2 mL) were placed into a flask. The reaction mixture was refluxed twenty-four hours at 70°C. 7 g of a substance was obtained, the yield was 99%.

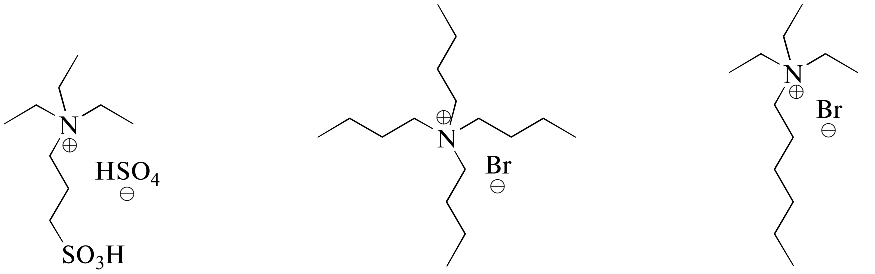
^{1}H NMR (DMSO-D6), δ, ppm: 1.2 (t, 9H, $CH_2C\underline{H}_3$); 1.9 (m, 2H, $CH_2C\underline{H}_2CH_2$); 2.5 (t, 4H,

$[Bmim]^+[Cl]^-$

1-butyl-3-methylimidazolium chloride

$[Bmim]^+[BF_4]^-$

1-butyl-3-methylimidazolium tetrafluoroborate



$[Et_3N^+(CH_2)_3SO_3H]HSO_4^-$

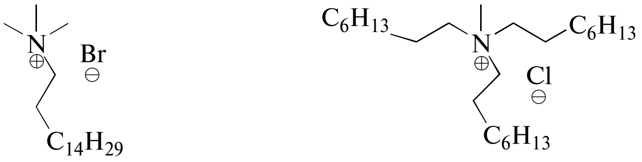
triethyl(propyl-3-sulfonyl) ammonium hydrosulfate

$N_{4444}Br$

tetrabutylammonium bromide

$N_{6222}Br$

hexyltriethyl-ammonium bromide



$N_{16111}Br$

cetyltrimethylammonium bromide

$N_{8881}Cl$

methyltri(*n*-octyl)ammonium chloride

Fig. 1. Structures of the ionic liquids used in the study.

$C\underline{H}_2CH_2C\underline{H}_2$); 3.1 (m, 6H, $NC\underline{H}_2CH_3$); 3.2 (m, 2H, $NC\underline{H}_2CH_2$); 3.3 (quartet, 6H, NCH_2CH_3).

^{13}C NMR (DMSO-D6), δ, ppm: 7.5 ($NCH_2\underline{C}H_3$); 18.4 ($NCH_2\underline{C}H_2$) 47.7 ($NCH_2CH_2\underline{C}H_2$); 52.2 ($N\underline{C}H_2CH_3$) 55.5 ($N\underline{C}H_2CH_2$).

The study of the obtained samples of nanoparticles by X-ray photoelectron spectroscopy (XPS) was carried out using a LAS_3000 electronic device equipped with a photoelectron analyzer with an OPX-150 retarding potential. The photoelectron excitation was carried out using X-ray emission of an aluminum anode (Al $K\alpha$ = 1486.6 eV) with a tube voltage of 12 kV and an emission current of 20 mA. Photoelectron peaks were calibrated by carbon C 1*s* line with binding energy 285 eV. The studies by the method of transmission electron microscopy (TEM) were performed using a LEO912 AB Omega transmission electron microscope.

Procedure for Catalytic Experiments

Catalytic experiments on hydrogenation of phenols were carried out at an elevated pressure and vigorous stirring of the reaction mixture in a stainless steel autoclave under a hydrogen atmosphere. A constant temperature of the reaction mixture was maintained using a thermostat with an accuracy of no less than 0.5°C. The catalyst was prepared in situ: 5 mg of polyacrylic acid was dissolved in 150 μL of water with stirring, an ionic liquid (~0.5 mL) and 3 mg of rhodium chloride were added. Red coloring of the solution was observed upon the dissolution of rhodium chloride. Then 2 mg of $NaBH_4$ was dissolved in 100 μL of water and added to the solution of rhodium chloride, the solution turned black.

During the catalytic experiments the following order of operations was used: a catalyst in the form of rhodium nanoparticles immobilized in an ionic liquid and stabilized by polyacrylic acid, and a substrate (1.06×10^{-3} mol of substrate per 1.06×10^{-5} mol of the catalyst) were placed into a glass cartridge of an autoclave. The autoclave was sealed, filled with hydrogen to a pressure of from 5 to 40 bar and then thermostated for 0.5–3 hours at 80°C. After the experiment the reactor was cooled and an excess pressure was relieved. The reaction products were analyzed by GLC using a ChromPack CP9001 gas chromatograph with a flame ionization detector and a column 30 m × 0.2 mm coated with SE-30 stationary phase. Chromatograms were recorded and analyzed on a computer using a Maestro

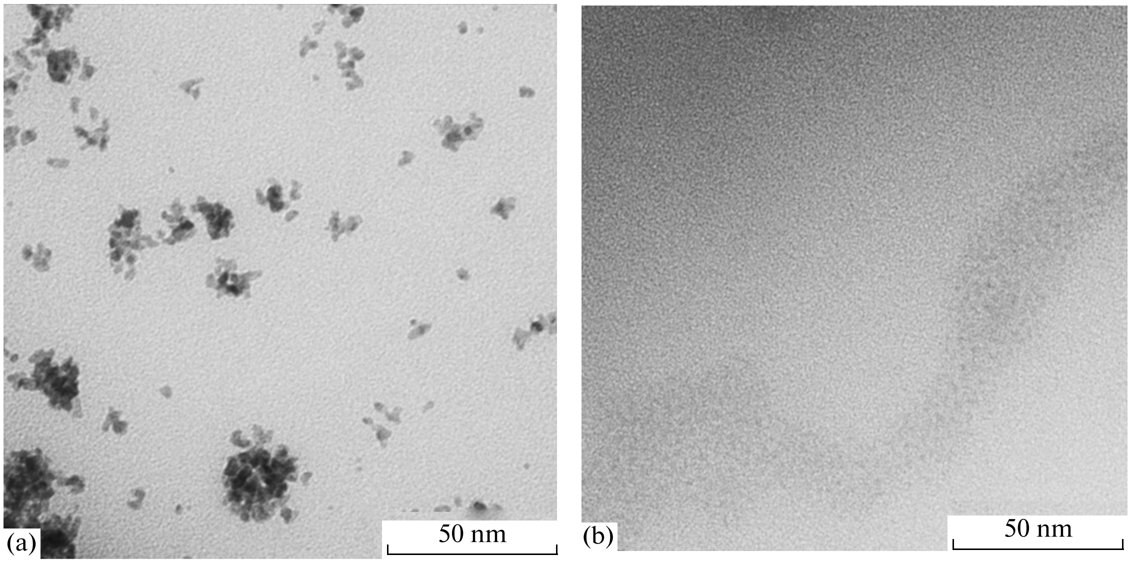
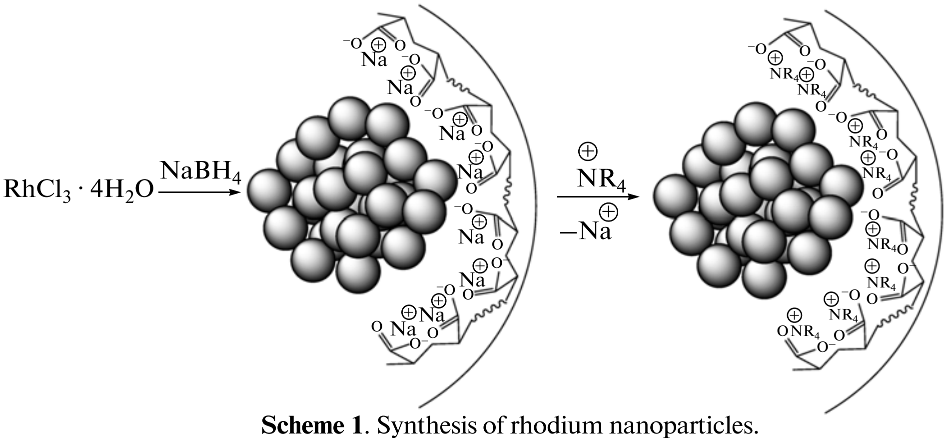


Fig. 2. Micrographs of rhodium nanoparticles stabilized by PAA in (a) water and (b) the ionic liquid $N_{4444}Br$.

1.4 program. The conversion was monitored using nonane as an internal standard.

RESULTS AND DISCUSSION

A well-established earlier for the use in an aqueous–alcoholic medium system based on rhodium nanoparticles stabilized by polyacrylic acid (PAA) was used as a catalyst system for the hydrogenation of phenol [14–15]. The synthesis of nanoparticles was carried out in an aqueous medium by the reduction of a rhodium trichloride solution with sodium borohydride in the presence of the polymer at a Rh : COOH ratio = 1 : 4 (scheme 1).



Scheme 1. Synthesis of rhodium nanoparticles.

The resulting dispersion was added to the corresponding ionic liquids for subsequent reaction. Rhodium nanoparticles synthesized were characterized using transmission electron microscopy (TEM) (Fig. 2). The average size of the particles in water is 2.2 nm, while in the ionic liquid it was 1.3 nm (Fig. 3). It is substantial that in water the association of metal nanoparticles is observed to occur in a significantly greater extent. This suggests that the ionic liquids act as not only solvent, but also as a stabilizer of metal nanoparticles. X-ray photoelectron spectroscopy data for particles isolated from $N_{4444}Br$ (Fig. 4) evidence in favor of the suggestion that on the surface of the particles a layer of polyacrylic acid and its associates with cations of ionic liquids is formed in the ionic liquid, which prevents the aggregation of the nanoparticles. Additionally, the surface layer contains a small amount of carboxylate complexes of rhodium (II) $[Rh_2(CH_3COO)_4]ClO_4$ [19]. A signal corresponding to $3d_{5/2}$ binding energy for both the metal, and the complex of rhodium is present in the spectrum. The C : O : N ratio indicates that polyacrylic acid on the surface is in the form of associates with cations of the ionic liquid.

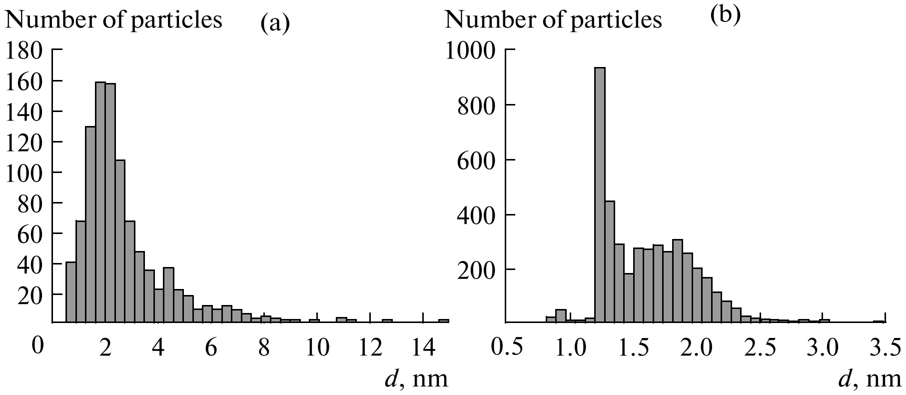


Fig. 3. Size distribution of rhodium nanoparticles stabilized by PAA in (a) water and (b) the ionic liquid $N_{4444}Br$.

Phenol was chosen as a model substrate for the hydrogenation reaction. It has been shown that the use of ionic liquids based on imidazolium cation does not make it possible to achieve acceptable yields in the reaction of phenol hydrogenation. The conversion of the substrate for 3 h is only a few percent.

Note that according to published data, acceptable conversions of the substrate by catalysis with nanoparticles of platinum metals in imidazolium ionic liquids can be attained only over a very long reaction time (more than 20 h). Apparently, this is caused by the interaction of NCN carbenes formed in the reaction conditions with the metal surface, which results in the blocking of the surface of metal nanoparticles. When replacing the imidazolium ionic liquids by tetraalkylammonium ILs, the rate of the reaction increases by two or more orders of magnitude and quantitative conversion is achieved. Cyclohexanol and cyclohexanone are formed as the main reaction products. The alcohol/ketone ratio differed significantly depending on the ionic liquid nature (Table 1). Unusual results were obtained using methyl(trioctyl)ammonium chloride ($N_{8881}Cl$) and acidic ionic liquids. In the case of the first ionic liquid, cyclohexanone was formed with 100% selectivity. When using an acidic ionic liquid, cyclohexanol (selectivity 54%), and cyclohexane (selectivity 46%) were formed as the main products.

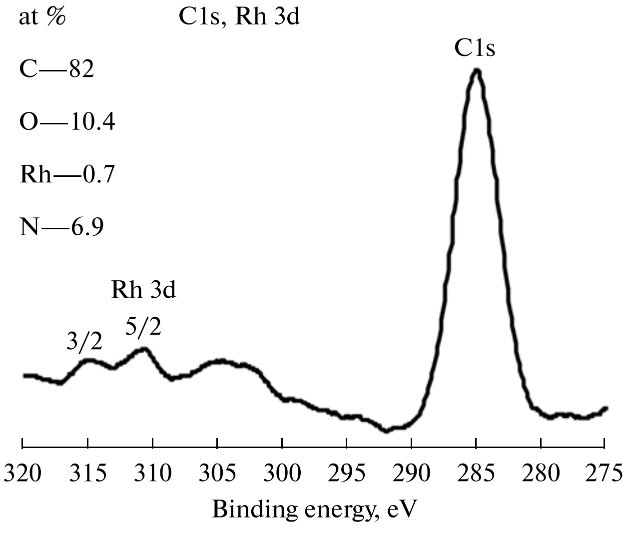


Fig. 4. XPS data for a sample of the catalyst.

The separation of the catalyst after the reaction in the ionic liquid showed that the particles are in a finely dispersed state (Fig. 5). According to the TEM data, the size distribution of the nanoparticles is bimodal (average size, 0.9 nm and 2.1 nm). In water, insignificant aggregation of small nanoparticles is detected (Fig. 6). Apparently, the ionic liquid exerts an additional stabilizing effect on the nanoparticles in this case.

The study of the kinetics of the process shows that both cyclohexanol and cyclohexanone are formed already in the first period of the reaction; cyclohexanone is then slowly hydrogenated to the corresponding alcohol (Table 2).

Special experiments have shown that even for three hours of the reaction with cyclohexanone as a substrate the rate of its hydrogenation was low, the yield of alcohol was less than 1%. Apparently, most of the cyclohexanol is formed via a parallel route.

A similar pattern is observed when using cetyltrimethylammonium bromide ($N_{16111}Br$) (Table 3). In this case, the conversion reached 60% for half an hour, and the selectivity for cyclohexanone is 100%.

It has been shown that the used catalyst system is active in the hydrogenation of substituted phenols and phenol derivatives. Upon the hydrogenation of *para*- and *ortho*-ethylphenol the conversion achieved 100% for 3 h. The hydrogenation of cresols proceeds at much lower rates. Upon the hydrogenation of anisole and phenetole 36% selectivity for cyclohexanone is observed, for diphenyl ether, it is 10% (Table 4). These data indicate the occurrence of hydrogenolysis.

When using ($N_{16111}Br$) as an ionic liquid, the selectivity for methoxycyclohexane, the product of anisole hydrogenation, was substantially higher than when using $N_{6222}Br$ and was more than 80%.

We also investigated the effect of pressure on the reaction of hydrogenation (Table 5). Upon carrying out

Table 1. Phenol hydrogenation in various ionic liquids

Run no.	Ionic liquid	Product	Selectivity, %	Conversion, %
1	$N_{6222}Br$	cyclohexanone	36	100
		cyclohexanol	64	
2	$N_{8881}Cl$	cyclohexanone	100	100
3	$N_{16111}Br$	cyclohexanone	51	100
		cyclohexanol	49	
4	$N_{4444}Br$	cyclohexanone	32	100
		cyclohexanol	68	
5	$[Et_3N^+(CH_2)_3SO_3H]HSO_4^-$	cyclohexane	46	91
		cyclohexanol	54	
6	$[Bmim]^+[Cl]^-$	cyclohexanone	–	1–3
		cyclohexanol	–	
7	$[Bmim]^+[BF_4]^-$	cyclohexanone	–	1–3
		cyclohexanol	–	

Reaction conditions: $T = 80°C$, $p(H_2) = 40$ bar, 3 h, substrate/Rh ratio = 100.

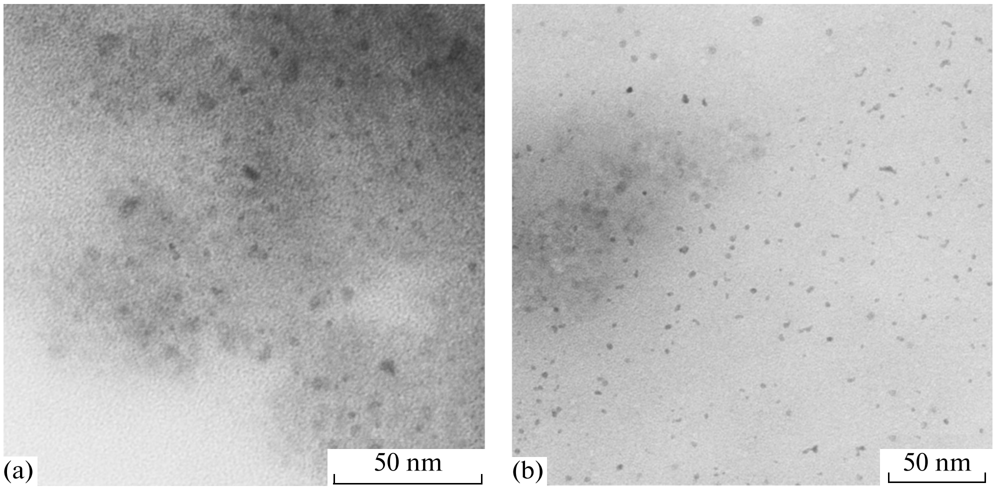


Fig. 5. Micrographs of rhodium nanoparticles stabilized by PAA in (a) water and (b) the ionic liquid $N_{4444}Br$ after the reaction.

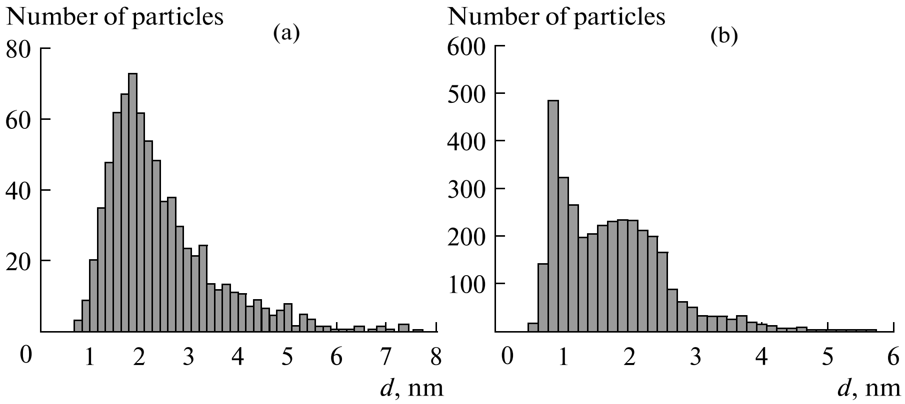


Fig. 6. Size distribution of rhodium nanoparticles stabilized by PAA in (a) water and (b) the ionic liquid $N_{4444}Br$ after the reaction.

Table 2. Kinetics of phenol hydrogenation in $N_{6222}Br$

Run no.	Time, h	Products	Selectivity, %	Conversion, %	TOF*, h^{-1}
1	0.5	cyclohexanone	68	46	213
		cyclohexanol	32		
2	2	cyclohexanone	70	90	104
		cyclohexanol	30		
3	2.5	cyclohexanone	40	96	100
		cyclohexanol	60		
4	3	cyclohexanone	36	100	88
		cyclohexanol	64		

Reaction conditions: $T = 80°C$, $p(H_2) = 40$ bar, substrate/Rh ratio = 100.

$$* \text{ TOF} = \frac{n_{\text{consumed } H_2}}{n_{\text{catalist}} \times t}.$$

Table 3. Phenol hydrogenation in $N_{16111}Br$

Run no.	Time, h	Products	Selectivity, %	Conversion, %	TOF, h^{-1}
1	0.5	cyclohexanone	100	59	236
2	3	cyclohexanone	51	100	83
		cyclohexanol	49		

Reaction conditions: $T = 80°C$, $p(H_2) = 40$ bar, substrate/Rh ratio = 100.

Table 4. Hydrogenation of various substrates in $N_{6222}Br$

Run no.	Substrate	Products	Selectivity, %	Conversion, %
1	phenol	cyclohexanone	36	100
		cyclohexanol	64	
2	anisole	methylcyclohexyl ether	64	100
		cyclohexanone	36	
3	benzene	cyclohexane	100	100
4	*o*-cresol	2-methylcyclohexanol	100	38
5	*p*-cresol	4-methylcyclohexanol	100	9
6	*o*-ethylphenol	2-ethylcyclohexanol	100	84
7	*p*-ethylphenol	4-ethylcyclohexanol	100	99
8	phenetole	cyclohexanone	36	27
		ethoxycyclohexane	64	
9	diphenyl ether	cyclohexanone	10	50
		dicyclohexyl ether	21	
		phenylcyclohexyl ether	69	

Reaction conditions: $T = 80°C$, $p(H_2) = 40$ bar, 3 h, substrate/Rh ratio = 100.

Table 5. Effect of pressure on the process of phenol hydrogenation in $N_{6222}Br$

Run no.	Pressure, bar	Products	Selectivity, %	Conversion, %	TOF, h^{-1}
1	5	cyclohexanone	84	57	41
		cyclohexanol	16		
2	10	cyclohexanone	66	98	76
		cyclohexanol	34		
3	40	cyclohexanone	36	100	88
		cyclohexanol	64		

Reaction conditions: $T = 80°C$, 3 h, substrate/Rh = 100.

Table 6. Effect of the IL/water ratio on phenol hydrogenation in $N_{6222}Br$

Run no.	IL/water ratio	Products	Selectivity, %	Conversion, %	TOF, h^{-1}
1	1/1	cyclohexanone	72	100	76
		cyclohexanol	28		
2	2/1	cyclohexanone	36	100	88
		cyclohexanol	64		
3	4/1	cyclohexanone	100	40	27

Reaction conditions: $T = 80°C$, $p(H_2) = 40$ bar, 3 h, substrate/Rh = 100.

the reaction for three hours the conversion was close to 100%, right up to 10 bar. Significant is the fact that the selectivity for alcohol increases (from 16% to 64%) as the pressure increases.

It has been shown that when running the reaction in the presence of water an increase in its quantity results in an increased conversion of the substrate (Table 6). Apparently, at high concentrations of the ionic liquid in water a partial blocking of the surface by the formation of a double adsorption layer of organic cations is observed.

Thus, it has shown that the proposed rhodium-containing system is superior to the polyvinylpyrrolidone-based catalysts known in the literature in the activity in the hydrogenation of phenols in ionic liquids.

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