



Ruthenium nanoparticles prepared from ruthenium dioxide precursor: Highly active catalyst for hydrogenation of arenes under mild conditions

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ABSTRACT

The hydrogenation of benzene and benzene derivatives was studied using Ru(0) nanoparticles prepared by a very simple method based on the in situ reduction of the commercially available precursor ruthenium dioxide under mild conditions (75 °C and hydrogen pressure 4 atm) in imidazolium ionic liquids. Total turnovers (TTO) of 2700 mol/mol Ru were obtained for the conversion of benzene to cyclohexane under solventless conditions and TTO of 1200 mol/mol Ru were observed under ionic liquid biphasic conditions. When corrected for exposed ruthenium atoms, TTO values of 7940 (solventless) and 3530 (biphasic) were calculated for benzene hydrogenation. These reaction rates are higher than those observed for Ru nanoparticles prepared from decomposition of an organometallic precursor in similar conditions. The presence of the partially hydrogenated product cyclohexene was also detected at low conversion rates.

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1. Introduction

Hydrogenation of benzene conventionally occurs under drastic temperature and pressure conditions over metal-supported heterogeneous catalysts, such as Rh/Al₂O₃ or Raney nickel [1]. Recently, soluble transition metal nanoparticles stabilized in ionic liquids, polyoxoanions, quaternary ammonium salts or soluble polymers, have shown enhanced lifetime and activity in benzene hydrogenation under mild reaction conditions [2–15]. Ionic liquids are outstanding solvents for the synthesis and stabilization of metal nanoparticles of 2–3 nm particle size and allow easy product recovery and catalyst recycling. The catalyst-containing ionic liquid forms a biphasic reaction mixture with both substrate and hydrogenated products that can be easily separated by simple decantation. Hydrogenation of olefins and arenes catalyzed by metal nanoparticles soluble in ionic liquids has received increasing attention [3,6,11,13,15–19]. Rhodium(0), iridium(0), platinum(0) and ruthenium(0) nanoparticles of 2–3 nm diameter with narrow size distribution have been synthesized in 1-*n*-butyl-3-methylimidazolium ionic liquids by reduction with molecular hydrogen of metal complexes [6,16] or controlled decomposition of organometallic compounds [3,13] under mild reaction condi-

tions (75 °C and hydrogen pressure 4 atm). It is worth to mention the results of benzene hydrogenation by iridium(0) nanoparticles stabilized by ionic liquid with total turnover (TTO) of 3509 in solventless mild reaction conditions (corrected for exposed atoms) [6]. The hydrogenation of benzene by rhodium(0) nanoparticles stabilized by ionic liquid under forcing conditions of 40 bar of hydrogen attained the unprecedented TTO of 20,000. However, the turnover frequency (TOF) of benzene hydrogenation by those catalytic systems was not higher than 250 h⁻¹, which necessitates long reaction times. Stabilized aqueous colloidal suspensions of metallic nanoparticles have also been reported as reusable catalyst for arene hydrogenation in biphasic conditions (water/hydrocarbons) [10,12,20].

More elegant is the use of ionic liquids to modulate product selectivity based on different substrates, reaction intermediates and products solubilities in the ionic liquid phase. Although the selective hydrogenation of benzene to cyclohexene seems to be a property characteristic of heterogeneous catalysts, the partially hydrogenated product cyclohexene was observed during the hydrogenation of benzene by Ru nanoparticles stabilized in ionic liquids [3].

We have previously prepared ruthenium(0) nanoparticles by reduction of the corresponding commercially available ruthenium dioxide in 1-*n*-butyl-3-methylimidazolium ionic liquids at 75 °C and 4 atm hydrogen pressure. The resulting ruthenium(0) nanoparticles, characterized by XRD, TEM and XPS, are a highly active and

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re-usable catalyst for hydrogenation of 1-hexene under mild reaction conditions with TTO up to 110,000 (based on total Ru atoms) and 320,000 (based on exposed Ru atoms) [18]. We also argue that the use of the commercially available catalyst precursor ruthenium oxide is very advantageous compared to the organometallic precursor Ru(COD)(COT) usually required for the preparation of Ru nanoparticles by reduction in mild conditions with H₂ [3,4]. The preparation of that compound is laborious, giving low yield and the compound itself is very sensitive to air and requires very careful handling. Moreover, in the same reaction conditions (75 °C and 4 atm hydrogen pressure), the RuCl₃ precursor is not reduced to give Ru(0) nanoparticles and requires the use of other reducing agents, such as NaBH₄ [17].

Because of these promising catalytic results on olefin hydrogenation catalyzed by our Ru(0) nanoparticles, we now investigate the use of Ru(0) nanoparticles prepared from the RuO₂ precursor for catalytic hydrogenation of benzene and benzene derivatives. Preliminary results concerning selective hydrogenation of benzene will also be given.

2. Experimental

2.1. Materials and instrumentation

RuO₂ hydrate was purchased from Aldrich Chem. Co. By following previously reported procedures [21], 1-*n*-butyl-3-methylimidazolium ionic liquids BMI-PF₆, BMI-BF₄ and BMI-CF₃SO₃ were prepared. The absence of Cl⁻ was verified by an Ag⁺ test and the water content (<0.1%, v/v) was checked by cyclic voltammetry of an authentic sample and after the addition of water [22]. All manipulations were carried out using Schlenk techniques. Gas chromatographic analyses were performed on a Shimadzu GC 14B gas chromatograph equipped with a 30-m capillary column with a dimethylpolysiloxane stationary phase, with the parameters set as follows—initial temperature: 50 °C, initial time: 5 min, ramp: 10 °C min⁻¹, final temperature: 250 °C, final time: 5 min, injector and detector temperature: 250 °C, injection volume: 2 μL. Gas chromatographic analyses for detection of cyclohexene were performed on a Varian Star 3400 gas chromatograph equipped with Petrocol DH 100 m × 0.25 mm × 0.5 μm column with the parameters set as follows—initial temperature: 100 °C, initial time: 20 min, ramp: 20 °C min⁻¹, final temperature: 250 °C, final time: 10 min, injector temperature: 250 °C, detector temperature: 250 °C, injection volume: 2 μL.

Transmission electron microscopy (TEM) micrographs were taken on a JEM-2010 microscope operating at an accelerating voltage of 200 kV. Samples for TEM observations were prepared by placing a thin film of the ionic liquid containing the ruthenium nanoparticles in a holey carbon grid. The metal particle size distribution was estimated from the measurement of about 200 particles, assuming a spherical shape, found in an arbitrary chosen area in enlarged micrographs.

2.2. Nanoparticles preparation and hydrogenation experiments

In a typical experiment, RuO₂·3H₂O (3 mg, 0.0225 mmol) and 1.17 g of benzene (15 mmol) were added to a Fischer–Porter reactor under inert atmosphere. In biphasic experiments, the RuO₂ was dispersed in 1 mL of room temperature ionic liquid (BMI-PF₆, BMI-BF₄ or BMI-CF₃SO₃) prior to the addition of the substrate. The reactor was submitted to vacuum, placed in an oil bath at 75 °C under stirring (700 rpm) and connected to the hydrogen gas reservoir. The reaction was initiated by the admission of H₂ gas of 4 atm (constant). The reaction was monitored by the fall in hydrogen pressure

in the H₂ reservoir as a function of time. H₂ uptake was measured at 1 min intervals with a Huba Control pressure transducer interfaced via a Novus Field Logger converter to a computer. The pressure versus time data were collected by the FieldChart Novus Software, stored as a data file and exported to MicroCal Origin 7.0 for hydrogenation rates calculations. The products were separated by decantation and the organic phase was analyzed by GC and GC–MS. The Ru(0) nanoparticles were isolated by precipitation with acetone and centrifugation (3500 rpm) for 3 min. The solid was washed with acetone (3 × 15 mL) and dried under reduced pressure. The samples thus obtained were prepared for TEM analysis.

Partial hydrogenation of benzene to cyclohexene was performed in a Fischer–Porter reactor under H₂ constant pressure (4 atm) and heating. In a typical experiment, RuO₂·3H₂O (3 mg, 0.0225 mmol) was dispersed in 1 mL of room temperature ionic liquid (BMI-BF₄) and 5.85 g (75 mmol) of benzene was added to the reactor under inert atmosphere. The reactor was submitted to vacuum, placed in an oil bath at 75 °C under stirring (700 rpm) and connected to the hydrogen gas unit. The reaction was initiated by the admission of H₂ gas of 4 atm (constant). The conversion and selectivity in cyclohexene was estimated by GC analysis of aliquots collected in desired time intervals.

2.3. Hg(0) poisoning test

The catalytic reactions were carried out in the same standard hydrogenation conditions, except for the addition of elemental Hg (1.4 g, 300 equiv.) to the reaction mixture at 10% conversion of benzene to cyclohexane. The reaction was monitored by the fall in hydrogen pressure in the H₂ reservoir as a function of time before and after the addition of Hg. The products were separated by decantation of the nanoparticles and the organic phase was analyzed by GC and GC–MS.

2.4. CS₂ poisoning test

The catalytic reactions were carried out under the same standard hydrogenation conditions, except for the addition of 0.5 equiv. of CS₂ (1.7 mg) dissolved in an additional 1.17 g of benzene to the reaction mixture at 10% of conversion. The reaction was monitored by the fall in hydrogen pressure in the H₂ reservoir as a function of time before and after the addition of CS₂. The products were separated by decantation of the nanoparticles and the organic phase was analyzed by GC and GC–MS.

3. Results and discussion

We have previously reported that Ru(0) nanoparticles of small size and narrow size distribution can be easily prepared by in situ H₂ reduction of RuO₂·3H₂O dissolved in room temperature ionic liquids, under mild reaction conditions (75 °C and hydrogen pressure 4 atm) [18]. The Ru(0) nanoparticles stabilized by 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ionic liquid (BMI-PF₆) are very stable in the biphasic and recyclable catalytic systems for the hydrogenation of 1-hexene. In an extension of that work, we investigate the formation of Ru(0) nanoparticles and their catalytic performance in the hydrogenation of benzene and other aromatic compounds in solventless and ionic liquid biphasic conditions. For solventless hydrogenation of benzene, RuO₂ hydrate powder was added to the reactor containing benzene (molar ratio 1/667) under inert atmosphere, and the system was subjected to hydrogen pressure and heating. After 42 min we observed >99% of conversion to cyclohexane corresponding to a TOF = 953 h⁻¹ (based on total Ru). This turnover frequency is about 10 times higher than that observed for Ru(0) nanoparticles prepared from Ru(COD)(COT)

Table 1
Hydrogenation^a of arenes by RuO₂ hydrate pre-catalyst.

Entry	Substrate	Product	Stabilizing agent	Time (h)	Conv. ^b (%)	TOF ^c (h ⁻¹)
1	Benzene	Cyclohexane	None (solventless)	0.7	100	953 (2803)
2	Benzene	Cyclohexane	BMI·PF ₆	13	96	49 (144)
3	Benzene	Cyclohexane	BMI·BF ₄	20	46	15 (44)
4	Benzene	Cyclohexane	BMI·CF ₃ SO ₃	12	40	22 (65)
5	Toluene	Methylcyclohexane	None (solventless)	1.2	100	556 (1635)
6	Toluene	Methylcyclohexane	BMI·PF ₆	20	54	18 (53)
7	Styrene	Ethylcyclohexane	None (solventless)	4	100	168 (494)
8	<i>p</i> -Xylene	1,4-Dimethylcyclohexane	None (solventless)	4.3	97 ^d	150 (441)

^a Conditions: catalyst/substrate ratio = 1/667, temperature = 75 °C, hydrogen pressure = 4 atm.

^b Measured by GC.

^c Catalytic turnover frequency: moles of substrate transformed per mole of catalyst per hour (total metal) and in parentheses TOF corrected for exposed metal.

^d *cis/trans* 3:2.

in similar conditions [3]. Under biphasic ionic liquid conditions, slower reaction rates were obtained (Table 1, entries 2–4), and only the reaction performed in BMI·PF₆ reached 96% of conversion in 13 h. The turnover frequency of our catalyst is about two times that observed for Ru(0) nanoparticles prepared from the Ru(COD)(COT) precursor in ionic liquids [3].

Further experiments under identical hydrogenation conditions, but with catalyst to substrate molar ratio of 1/1330, were performed to investigate the catalyst lifetime in solventless and BMI·PF₆ biphasic conditions. After each reaction in biphasic conditions, the hydrogenated product was easily separated by simple decantation and the ionic liquid phase containing the catalyst could be reused in successive reactions. Under solventless conditions, the hydrogenated product was distilled from the mixture and the resulting powder could be reused in successive reactions. TTO of 2700 was obtained in solventless conditions after three successive runs (the reaction reached >99% conversion in 3 h (first cycle) and 4.6 h (second cycle) and only 10% conversion after 12 h in the third cycle), when deactivation of the catalyst had occurred. Under BMI·PF₆ biphasic conditions, total turnovers of 1200 were observed with 83% conversion to cyclohexane in 17 h (first run) and 10% conversion in 15 h (second run). The catalyst deactivation occurred before the third cycle both in solventless and in ionic liquid biphasic conditions. We expected to find in this study a more pronounced difference in the stability of the Ru(0) nanoparticles in solventless and in ionic liquid conditions, especially because particles aggregation is less probable in the ionic liquid phase. As reported in our previous work [18], the same catalyst was reused for up to 4 and 17 successive cycles in solventless and BMI·PF₆ biphasic conditions, respectively, during hydrogenation of 1-hexene. By approximating the Ru(0) average nanoparticles (2.6 ± 0.4 nm) as close-packed clusters with the same density as bulk Ru metal, it is possible to estimate, by means of “magic numbers” approach [23], that roughly 34% of the Ru atoms should be on the surface; 22–30 Å Ru nanoclusters correspond to 6 (923 atm)–9 shell (2869 atm) nanoclusters with ca. 39–28% of metal atoms on the surface, respectively. Considering that only the Ru atoms on the surface are available for catalysis in the nanocluster, the total turnovers corrected for exposed Ru atoms reach the values of 7940 in solventless and 3530 in biphasic reactions. The catalytic lifetime values presented here are far superior to that of other soluble ruthenium nanoparticle catalysts previously reported by us [3] in solventless (TON = 450 after 5.5 h at 75 °C, 4 atm H₂) or biphasic (TON = 365 after 18.5 h at 75 °C, 4 atm H₂ and BMI·PF₆) conditions and by Chaudret and co-workers [4] (TON = 410 after 14 h at 80 °C, 20 atm H₂). We also mention here that the Ru nanoparticles were prepared by reduction of the commercially available precursor, RuO₂·3H₂O, which avoid the laborious and expensive preparation of the very unstable organometallic precursor Ru(COD)(COT) used in the above-mentioned reports.

The Ru(0) nanoparticles dispersed in ionic liquid or in solventless conditions are also efficient catalysts for the hydrogenation of other aromatic compounds (Table 1, entries 5–8). It is worth to note that the hydrogenation of toluene to methylcyclohexane occurred under mild conditions (75 °C, 4 atm H₂) with a turnover number of 667 mol of substrate converted per mol of metal in 70 min of reaction (not optimized) which gives a TOF of 556 h⁻¹ or 1635 h⁻¹ (corrected for exposed Ru(0) atoms). This is an outstanding result if we consider that one of the most active catalysts for benzene hydrogenation reported elsewhere [11] hydrogenates toluene with a TOF of 158 h⁻¹ under forcing conditions (40 atm H₂) [15]. The Ru nanoparticles prepared from Ru(COD)(COT) precursor [3] hydrogenates toluene with TOF of 45 h⁻¹ under the same conditions used in this study.

Additional experiments were carried out in order to characterize our nanocluster catalyst in more detail and to establish whether the present system works as a homogeneous or as a heterogeneous metal particle catalyst [2,5,24,25]: (i) the observation of a sigmoidal curve for the H₂ consumption as a function of time during the hydrogenation of benzene is the first evidence for the in situ formation of the true catalyst by H₂ reduction of RuO₂ precatalyst prior to the hydrogenation of the substrate—sigmoidal kinetic curves for hydrogenation reaction have been attributed to transition metal nanocluster catalysis; (ii) transmission electron microscopy analysis performed directly in the ionic liquid catalyst containing phase detected the presence of ruthenium nanoparticles. After a hydrogenation reaction performed following the standard conditions, the product was evaporated to dryness and the ionic liquid phase, containing the ruthenium nanoparticles, was placed as a thin film in a holey carbon grid and immediately analyzed. The TEM photography obtained in the ionic phase 1-*n*-butyl-3-methylimidazolium tetrafluoroborate (BMI·BF₄) is shown in Fig. 1. An average diameter of 2.6 ± 0.4 nm was estimated from the measurement of about 200 particles diameters, assuming spherical shape, found in an arbitrary chosen area in enlarged microphotographs.

(iii) Poisoning tests with elemental Hg were examined as it is a well-known metal-heterogeneous catalyst poison through efficient adsorption on the surface of transition metal(0) catalysts [24]. In the hydrogenation of benzene in BMI·PF₆ performed under standard conditions, excess Hg⁰ (300 equiv.) was added to the reaction mixture after about 10% conversion and the catalytic activity was suppressed in a few minutes; (iv) fractional poisoning experiments were examined by addition of 0.5 equiv. of CS₂ to the reaction mixture after about 10% conversion of benzene under the standard BMI·PF₆ biphasic hydrogenation conditions. The catalytic activity was immediately suppressed (Fig. 2). The poisoning test with CS₂ suggests that we have a heterogeneous catalyst with only a fraction of metal atoms on the surface and available for catalysis, since the catalyst was completely poisoned with <1 equiv. of added CS₂.

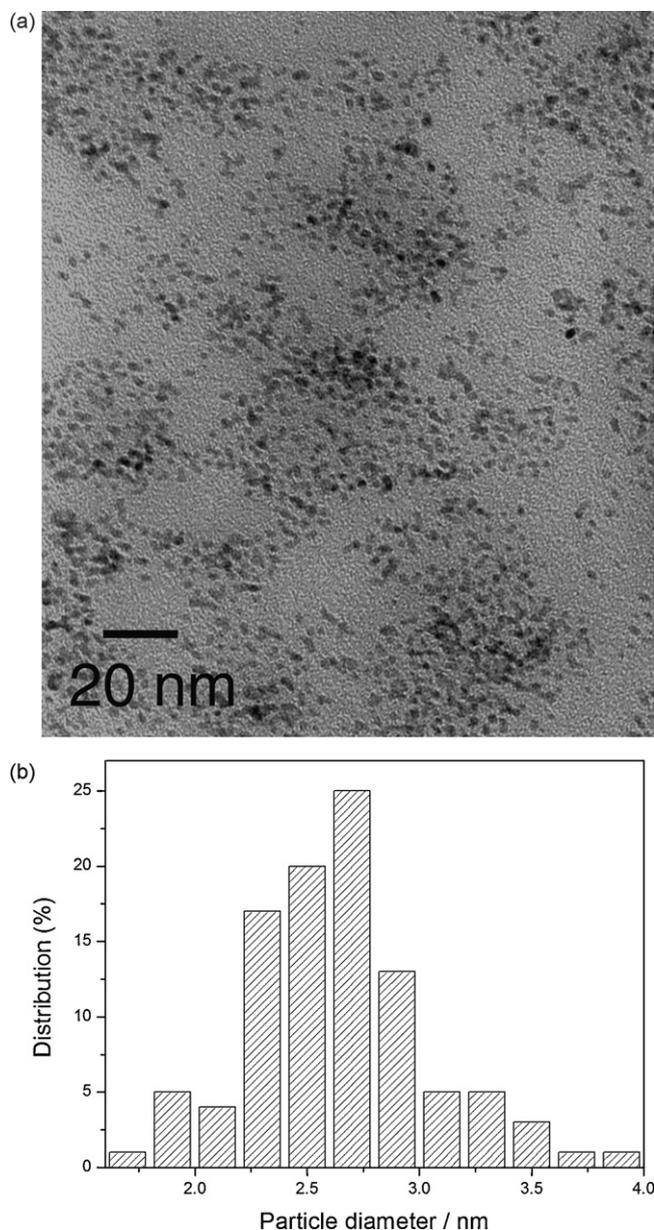


Fig. 1. (a) TEM of ruthenium nanoparticles in the ionic liquid BMI-BF₄ after hydrogenation of benzene under biphasic standard conditions and (b) histogram illustrating the particle size distribution.

As an initial attempt to identify cyclohexene in the hydrogenation of benzene, the reactions performed under standard hydrogenation conditions (catalyst/substrate = 1/667, 75 °C and 4 atm hydrogen pressure) were stopped at low benzene conversion and analyzed by GC. The results were 4% of cyclohexene selectivity at 10% of benzene conversion in BMI-PF₆, 13% of cyclohexene selectivity at 7% of benzene conversion in BMI-BF₄ and 8% of cyclohexene selectivity at 9% of benzene conversion for the catalytic hydrogenations performed in BMI-CF₃SO₃. Cyclohexene selectivity was expressed as the ratio of the formed cyclohexene and the benzene converted to products. After these preliminary results, BMI-BF₄ was elected for further experiments. In order to identify cyclohexene intermediate in the hydrogenation of benzene, the reaction conditions were changed to keep the reaction sufficiently slow to permit careful analysis of the intermediate at very low conversion rates. As shown in Fig. 3, high cyclohexene selectivity was attained at a very low benzene conversion (<2%).

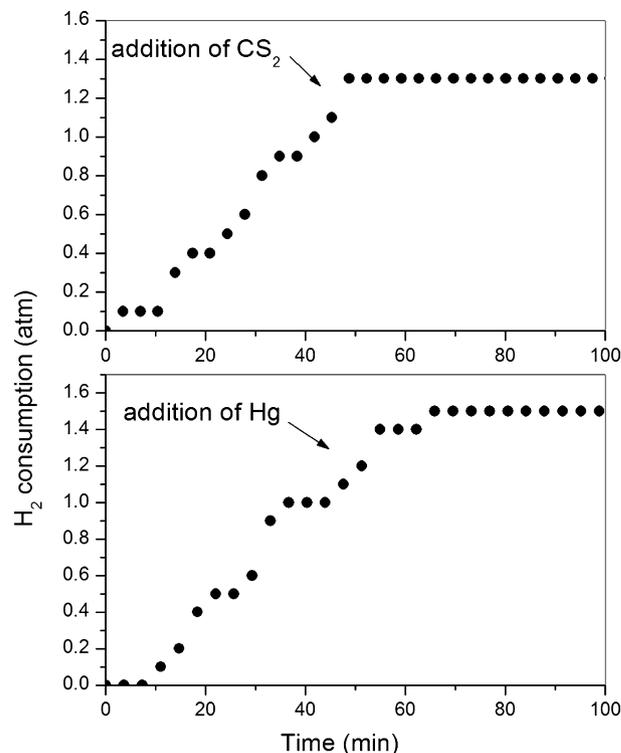


Fig. 2. Hydrogenation of benzene by ruthenium nanoparticles in BMI-PF₆ biphasic conditions with addition of CS₂ (0.5 equiv.) and Hg⁰ (300 equiv.) at about 10% conversion.

The influence of the temperature on cyclohexene selectivity and reaction rates in the hydrogenation of benzene using our Ru(0)/BMI-BF₄ catalytic system was examined. The reaction rate rose by a factor of 15 with the temperature increase from 50 °C to 75 °C. The reaction rate diminished at 120 °C, probably due to catalyst deactivation and was null at 150 °C and 180 °C. The cyclohexene selectivity was increased with the temperature increase from 75 °C (maximum selectivity of 53% at 0.2% benzene conversion) to 120 °C (maximum selectivity of 65% at 0.3% benzene conversion). However, our Ru(0)/BMI-BF₄ system deactivates at 150 °C. In the experiments above 150 °C, neither cyclohexane nor cyclo-

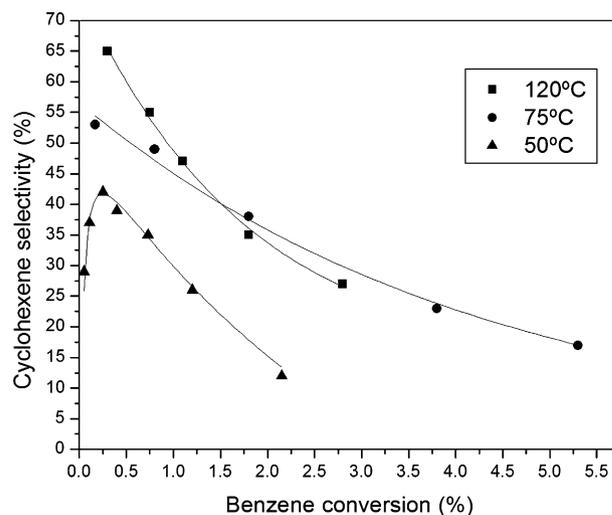


Fig. 3. Selectivity to cyclohexene as a function of benzene conversion at 120 °C (square), 75 °C (circle) and 50 °C (triangle). Conditions: catalyst/substrate ratio = 1/3333, BMI-BF₄, P_{H₂} = 4 atm.

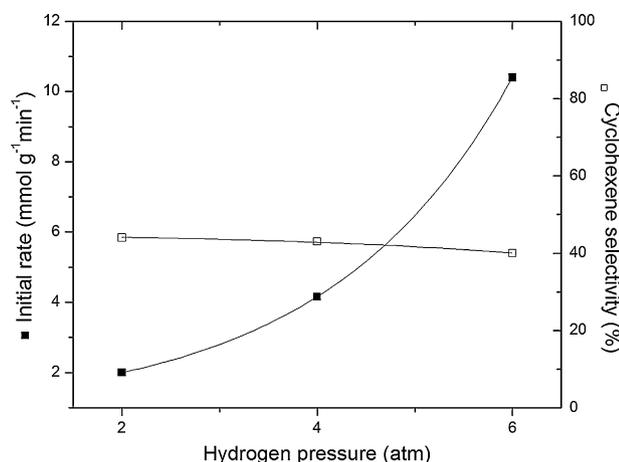


Fig. 4. Selectivity to cyclohexene and initial rate of hydrogenation of benzene as a function of hydrogen pressure at 75 °C in BMI-BF₄ (catalyst/substrate ratio = 1/3333).

hexene was formed. Most 1,3-dialkylimidazolium ILs are stable towards temperature and many organic and inorganic substances [26]. However, under certain reaction conditions, the cation and anion undergo degradation reactions and this might be the reason for catalyst deactivation observed above 150 °C [27]. On the other hand, the deactivation of the catalytic system can also be due to the poor solubility of the substrate in this phase. At 150 °C the benzene is in the vapor phase, which decreases its miscibility in the ionic liquid phase and, consequently, deactivates the catalytic system [28].

The influence of H₂ pressure on the partial hydrogenation of benzene over Ru(0)/BMI-BF₄ catalytic system was also examined. The plot of the initial rate of benzene conversion and the initial selectivity to cyclohexene as a function of hydrogen pressure (Fig. 4) showed the reaction rate being proportional to the pressure, which meant that hydrogen mass transfer should govern the overall reaction rate, and that the selectivity is not influenced by the hydrogen pressure in the studied pressure range.

4. Conclusion

In summary, the Ru(0) nanoparticles prepared by a very simple method based on H₂ reduction of the commercially available precursor RuO₂·3H₂O, which avoids the use of an organometallic precursor, has proved to be an efficient catalyst for hydrogenation of benzene and other benzene derivatives. We also demonstrated by poisoning experiments and TEM that the catalyst behaves as an heterogeneous metal nanoparticle catalyst. The partially hydrogenated product cyclohexene was also detected in certain reaction conditions. The maximum selectivity to cyclohexene (65% at 0.3% of benzene conversion) was reached at 120 °C and 4 atm hydrogen pressure in the BMI-BF₄ ionic liquid biphasic system. Although the maximum yield of cyclohexene is too low for practical applications, the use of reaction modifiers such as methanol [29], ZnSO₄ [30] or NaOH [31] has been suggested to enhance selectivity to cyclohexene and will be the subject of further investigation in our catalytic system. Such modifiers to enhance the selectivity must stimulate desorp-

tion of cyclohexene and/or slow down its further hydrogenation to cyclohexane.

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