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On the use of ruthenium dioxide in 1-*n*-butyl-3-methylimidazolium ionic liquids as catalyst precursor for hydrogenation reactions

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The H_2 reduction of RuO_2 hydrate "dissolved" in 1-*n*-butyl-3-methylimidazolium ionic liquids with different counterions, hexafluorophosphate ($BMI \cdot PF_6$), tetrafluoroborate ($BMI \cdot BF_4$) and trifluoromethane sulfonate ($BMI \cdot SO_3CF_3$), is a simple and reproducible method for the preparation of ruthenium nanoparticles of 2.0–2.5 nm diameter size and with a narrow size distribution. The Ru nanoparticles were characterized by TEM and XRD. The isolated Ru nanoparticles are reoxidized in air, whereas they are less prone to oxidation when imbibed in the ionic liquids. These nanoparticles are active catalysts for the solventless or liquid–liquid biphasic hydrogenation of olefins under mild reaction conditions (4 atm, 75 °C). The catalytic system composed of nanoparticles dispersed in $BMI \cdot PF_6$ ionic liquid is very stable and can be reused several times without any significant loss in the catalytic activity. Total turnover numbers greater than 110 000 (based on total Ru) or 320 000 (corrected for exposed Ru atoms) were attained within 80 h for the hydrogenation of 1-hexene.

KEY WORDS: ionic liquids; ruthenium oxide; hydrogenation; nanoparticles; TEM; XRD.

1. Introduction

Ruthenium dioxide is one of the most simple and employed catalyst precursor for various oxidation reactions, such as, carbon monoxide to carbon dioxide [1], water to O_2 [2], methanol to formaldehyde and CO_2 [3], cleavage of alkenes [4], and, more recently, the aerobic transformation of alcohols to the corresponding carbonyl compounds [5]. In opposition, the use of RuO_2 as catalyst precursor in hydrogenation reactions has been exploited to a lesser extent. It is known in these cases that ruthenium oxide is easily reduced to ruthenium metal at room temperature but apparently only large metal particles are formed and their surface ruthenium atoms are reoxidized in air [6].

Although nanoscale Ru(0) particles can be prepared by decomposition of Ru(0) organometallic precursors or reduction of $RuCl_3$ in the presence of stabilizing agents such as polymers or ligands [7], the development of a more simple and efficient method for the preparation of Ru nanoparticles is still a challenge in nanocatalysis. We have recently demonstrated that the Ir(0) and Rh(0) nanoparticles of 2–3 nm diameter can be easily prepared by reduction with molecular hydrogen of standard metal salts dissolved in room-temperature ionic liquids [8]. The intrinsic ionic charge and polymeric nature of 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMI \cdot PF_6$) ionic liquid [9] provide a unique electronic and steric protection environment for transition-metal nanoparticles [10]. It was therefore of interest to verify whether these liquids could be used for the generation of stable Ru nanoparticles through the reduction of RuO_2.

We report herein that indeed Ru nanoparticles with a narrow size and distribution are easily accessible by the reduction of RuO_2 dissolved in imidazolium ionic liquids and that these nanoparticles are active catalysts for the solventless or two-phase hydrogenation of olefins [11]. We also show that these nanoparticles can be characterized *in situ* by transmission electron microscopy (TEM).

2. Experimental

2.1. Materials and Instrumentation

RuO_2 hydrate was purchased from Aldrich Chem. Co. 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMI \cdot PF_6$), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BMI \cdot BF_4$), and 1-*n*-butyl-3-methyl imidazolium triflate ($BMI \cdot SO_3CF_3$) were prepared following previously reported procedures [12]. The absence of Cl^- was checked by Ag^+ test and the content of water ($<0.1\%$ v/v) was checked by cyclic voltammetry of an authentic sample and after addition of water [13]. All manipulations were done using Schlenk techniques. Gas chromatography was performed using a Shimadzu GC 14B with the following parameters: initial temperature: 50 °C, initial time: 5 min, ramp: 10 °C / min, final temperature: 250 °C, final time: 5 min,

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injector temperature: 250 °C, detector temperature: 250 °C, and injection volume: 2μL. Transmission electron microscopy photographs were taken on a JOEL JEM-2010 transmission electron microscope operating at an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were recorded by a Philips X'PERT MRD X-ray diffractometer equipped with curved graphite crystal. The diffraction data were collected at room temperature in a Bragg–Brentano $\theta - 2\theta$ geometry. The equipment was operated at 40 kV and 40 mA with scan range between 20° and 100°.

2.2. Transmission electron microscopy measurements

Samples for TEM measurements 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 particle diameters, assuming spherical shape, found in an arbitrary chosen area in enlarged microphotographs.

2.3. X-ray diffraction measurements

Samples analyzed under oxygen-free conditions were prepared in a glovebox and covered with Kapton tape. The indexation of Bragg reflections was obtained by a pseudo-Voigt profile fitting using the FULLPROF code.

2.4. Hydrogenation experiments

The catalytic reactions were carried out in a Fischer–Porter reactor connected to a H_2 reservoir. In a typical experiment, RuO_2 (3 mg, 0.0225 mmol) and 15 mmol of substrate (1.26 g of 1-hexene) are added to the reactor under an inert atmosphere. In biphasic experiments, the ruthenium oxide is dispersed in 1 mL of room-temperature ionic liquid ($BMI \cdot PF_6$, $BMI \cdot SO_3CF_3$ or $BMI \cdot BF_4$) prior to the addition of the substrate. The reactor is submitted to vacuum, placed in an oil bath at 75 °C under stirring (700 rpm) and connected to the hydrogen gas unit. The reaction is initiated by the gas admission at 4 atm (constant). The reaction is monitored by the fall in hydrogen pressure in the H_2 reservoir as a function of time. H_2 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 are collected by the Field Chart Novus Software, stored as a data file, and exported to MicroCal Origin 5.0 for hydrogenation rates calculations. The products are separated by decantation of the nanoparticles and the organic phase is analyzed by GC and GC-MS.

2.5. Catalyst lifetime experiments

The catalyst lifetime experiments were performed as for the hydrogenation experiments, except for the catalyst-to-substrate molar ratio of 1/6667 for each charge. In a typical experiment, RuO_2 (2 mg, 0.015 mmol) and 1-hexene (8.4 g, 100 mmol) are added to the Fischer–Porter reactor under an inert atmosphere. In biphasic experiments, 0.5 mL of room-temperature ionic liquid ($BMI \cdot PF_6$) are added prior to the addition of the substrate. The reactor is submitted to vacuum, placed in an oil bath at 75 °C under stirring (700 rpm), and connected to the hydrogen gas unit. The reaction is initiated by the gas admission at 4 atm (constant). The reaction is monitored by the fall in hydrogen pressure in the H_2 reservoir, measured via a computer-interfaced pressure transducer, as a function of time. At the end of the reaction (when stopped the H_2 uptake), the reactor is cooled to room temperature and depressurized. An aliquot of the product is collected, under inert atmosphere, to be analyzed by GC. If all the 1-hexene was converted to hexane, the maximum turnover would be attained. The remaining amount of hexane is evaporated in vacuum and an additional 8.4 g of 1-hexene (100 mmol) is added to the reactor that is evacuated and reattached to the hydrogen unit. The pressure is reestablished to 4 atm of H_2 (constant) and a new recording of H_2 uptake versus time starts. The same procedure is repeated until a significant loss of activity is observed. In each experiment, a maximum of 6667 turnovers are possible.

2.6. Hg poisoning test

Poisoning experiments with Hg^0 were examined as it is a well-known "Homogeneous versus Heterogeneous" catalysts test. The catalytic reactions were carried out using the same standard hydrogenation conditions. In the first run, RuO_2 (3 mg; 0.0225 mmol) and 1.26 g (15 mmol) of 1-hexene were added to the Fischer–Porter reactor under an 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 gas admission at 4 atm (constant). The reaction was monitored by the fall in hydrogen pressure in the H_2 reservoir as a function of time. At the end of the reaction (when the H_2 uptake had stopped), the reactor was cooled to room temperature and depressurized. An aliquot of the product was collected, under an inert atmosphere, to be analyzed by GC. The remaining amount of hexane was evaporated under vacuum and an additional 1.26 g of 1-hexene (15 mmol) were added to the reactor, which was evacuated and reattached to the hydrogen unit. The pressure was reestablished to 4 atm of H_2 (constant) and a new monitoring of H_2 uptake versus time started. The reaction was stopped when 50% of the 1-hexene was converted and elemental Hg (1.4 g, 300 equiv) was added to the reaction mixture. The pressure was reestablished to 4 atm of H_2 (constant) and the recording of H_2 uptake versus time continued. In biphasic experiments, the RuO_2 was dispersed in 1 mL of $BMI \cdot PF_6$ room-temperature ionic liquid. The products were separated by decantation of the nanoparticles and the organic phase was analyzed by GC and GC-MS.

2.7. CS_2 poisoning test

Poisoning experiments with CS_2 were examined. The catalytic reactions were carried out in the same hydrogenation standard conditions. RuO_2 (6 mg, 0.045 mmol) dispersed in 1 mL of $BMI \cdot PF_6$ room-temperature ionic liquid and 1.26 g (15 mmol) of 1-hexene were added to the Fischer–Porter 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 gas admission at 4 atm (constant). The reaction was monitored by the fall in hydrogen pressure in the H_2 reservoir as a function of time. The reaction was stopped when 50% of the 1-hexene was converted and 0.5 equivalents of CS_2 (1.7 mg) dissolved in an additional 1.26 g of 1-hexene was added to the reaction mixture. The pressure was reestablished to 4 atm of H_2 (constant) and the recording of H_2 uptake versus time continued. The products were separated by decantation of the nanoparticles and the organic phase was analyzed by GC and GC-MS.

3. Results and discussion

RuO_2 hydrate dissolved in the ionic liquids (figure 1) 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMI \cdot PF_6$), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BMI \cdot BF_4$), and 1-*n*-butyl-3-methylimidazolium trifluoromethane sulfonate ($BMI \cdot CF_3SO_3$) promotes the hydrogenation of 1-hexene under mild reaction conditions (table 1). It is worth noting that the hydrogenation of 1-hexene is complete in 12 min with hydrous RuO_2, whereas it takes 10 h to complete when anhydrous RuO_2 is employed as the catalyst precursor. It is clear from data in table 1 that RuO_2 hydrate under solventless conditions is more active in the hydrogenation of 1-hexene than the corresponding reactions performed in ionic liquids (compare entry 1 with entries 2–4, table 1). Under solventless conditions, the conversion of 1-hexene to hexane, at 75 °C and 4 atm (constant pressure) of H_2 (entry 1, table 1), is complete within 12 min corresponding to a catalytic turnover frequency (TOF) of 3300 h^{-1}.

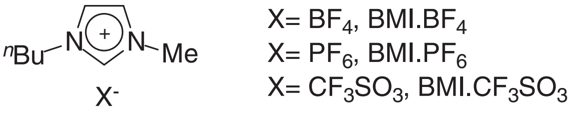

Figure 1. Imidazolium room-temperature ionic liquids.

In biphasic catalysis carried out with the addition of 1 mL of $BMI \cdot PF_6$, $BMI \cdot BF_4$ or $BMI \cdot SO_3CF_3$ ionic liquids, the reaction time increases, resulting in catalytic turnover frequencies of 943 h^{-1}, 388 h^{-1}, and 147 h^{-1} respectively (entries 2–4, table 1). This difference in catalytic activity can be ascribed to the typical biphasic conditions of the reactions performed in the ionic liquid, which can be a mass-transfer-controlled process[8]. Despite the relatively lower reaction rates, the recovered catalytic ionic liquid "solution" can be reused several times without any significant loss in catalytic activity, (figure 2) in opposition to those performed in solventless conditions that show significant loss in catalytic activity. The catalyst lifetime was estimated in a separate set of experiments by means of successive reactions performed under identical conditions of the standard hexane hydrogenations, except for the catalyst-to-substrate molar ratio of 1/6667 for each charge. After the first cycle, the product was separated and the isolated black material (solventless reaction) or ionic liquid catalyst containing layer (biphasic reaction) was reused in a second run by addition of an additional 8.4 g of 1-hexene (100 mmol). The same procedure was repeated until a significant loss of activity had been observed in the case of solventless reactions. In these experiments, a good catalytic performance in biphasic conditions was attained without significant loss in activity after 17 recycles, which corresponds to a total turnover number

Table 1

Hydrogenation[a] of 1-hexene to hexane by RuO_2 hydrate catalyst precursor under solventless conditions and in imidazolium ionic liquids

Entry	Stabilizing agent	Time (h)	Conv.[b] (%)	TOF[c] (h^{-1})
1	None	0.2	> 99	3300
2	$BMI \cdot BF_4$	1.7	> 99	388
3	$BMI \cdot PF_6$	0.7	> 99	943
4	$BMI \cdot CF_3SO_3$	4.5	> 99	147

[a] Conditions: catalyst/substrate ratio = 1/667, temperature = 75° C, hydrogen pressure = 4 atm. [b] Measured by GC.

[c] Catalytic turnover frequency: mol of substrate transformed per mole of catalyst per hour.

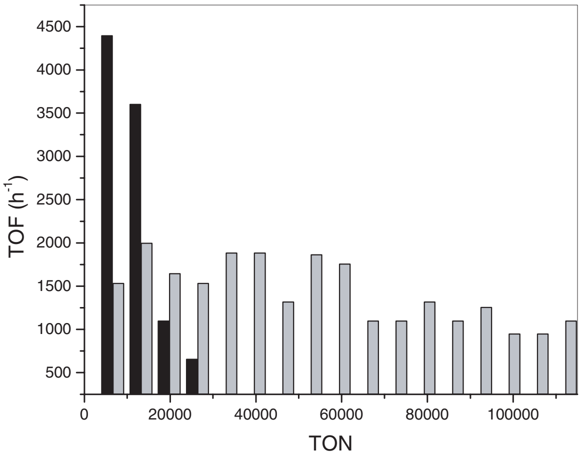

Figure 2. Turnover frequency (TOF) versus turnover number (TON) for the catalytic hydrogenation of 1-hexene by RuO_2 hydrate catalyst precursor in solventless (black) and BMI · PF_6 biphasic (gray) conditions.

greater than 110 000 (based on total Ru), compared to only 4 recycles in solventless conditions (total TON (based on total Ru) = 26 400). Approximating the Ru(0) average nanoparticles (2.5 ± 0.4 nm, estimated by TEM) as hexagonal-close-packed spheres, it is possible to estimate, by means of a "magic numbers" approach, that roughly 35% of the Ru atoms should be on the surface. Considering that all surface Ru atoms are active, it is possible to have the total turnover number corrected for exposed Ru atoms of 320 000 within 80 h of reaction for the hydrogenation of 1-hexene under biphasic BMI · PF_6 conditions. These results clearly show the beneficial effect of the ionic liquid in the stabilization of the catalytic active Ru species.

In order to check the involvement of metallic Ru in the hydrogenation reactions, Hg and CS_2 tests were undertaken (figure 3) [14]. An excess of Hg° (300 equiv) was added to the reaction mixture performed under standard hydrogenation conditions using 1-hexene as substrate. In solventless experiments, Hg° was added to the mixture after about 50% conversion and this immediately deactivated the catalyst. In a subsequent run, no catalytic activity was observed. In biphasic experiments, a decrease in the catalyst activity was observed only in a second catalytic cycle after the addition of Hg. In both cases, the results corroborate the presence of Ru(0) as the true hydrogenation catalyst. In order to achieve additional evidence that a dispersed Ru nanoparticle catalyst is involved, we carried out poisoning experiments with CS_2. Addition of 0.5 equivalents of CS_2 to the reaction mixture after about 50% conversion, performed under standard BMI · PF_6 biphasic hydrogenation conditions using 1-hexene as substrate, immediately suppressed the catalytic activity.

It is clear that the poisoning effect in both cases indicating the presence of metallic Ru (solventless and in ionic liquids) and that RuO_2 is easily reduced under these reactions conditions (4 bar of H_2 and 75°C). Moreover, the nature of Ru material formed in these reactions was further characterized by XRD and TEM analysis.

Samples for X-ray diffraction measurements were prepared under oxygen-free conditions. Thus, after the reaction was performed in the ionic liquid (BMI · PF_6), a black solution was formed from which ruthenium material was separated by centrifugation in acetone and evaporated to dryness under an inert atmosphere. In the solventless hydrogenation, the solid was easily isolated by evaporation of the product to dryness. The isolated solids were placed in the sample holder and covered by a Kapton tape in a glove box. In both cases, i.e., samples obtained by reduction of RuO_2 in (1) solventless conditions and (2) dissolved in BMI · PF_6, the X-ray diffraction pattern showed the predicted lines of the Ru hcp structure (figure 4). The material isolated after BMI · PF_6 biphasic hydrogenation conditions was con-

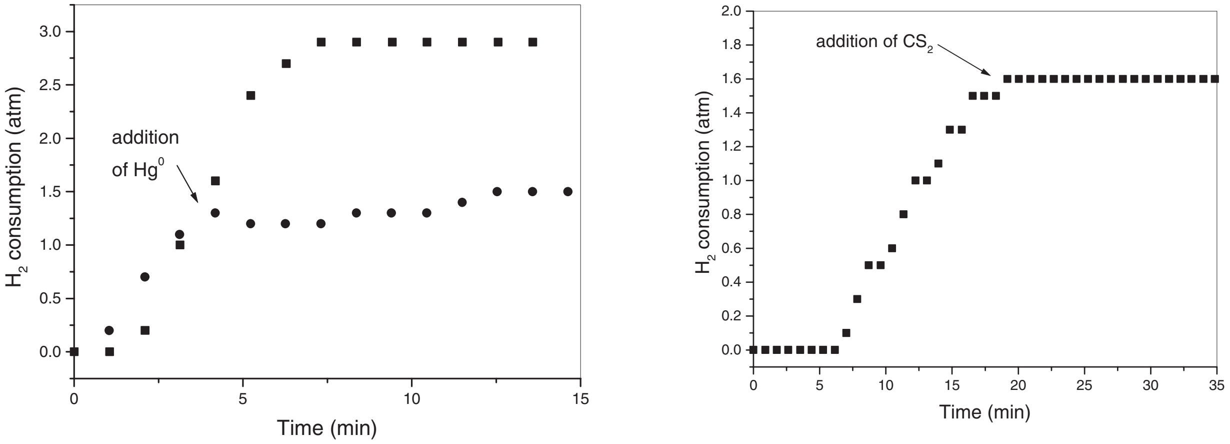

Figure 3. Hg and CS_2 poisoning experiments in the hydrogenation reaction. (a) Hydrogenation of 1-hexene by RuO_2 hydrate catalyst precursor under standard solventless conditions with addition of Hg°; (300 equivalents) at < 50% of conversion ((■) first cycle with conversion to hexane = 99% and (●) second cycle of hydrogenation with addition of Hg°). (b) Hydrogenation of 1-hexene by RuO_2 hydrate catalyst precursor under standard BMI · PF_6 biphasic conditions with addition of 0.5 equivalent of CS_2 at about 50% of conversion.

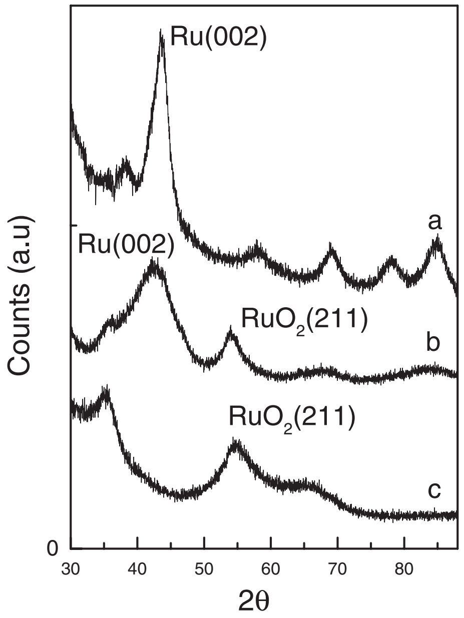

Figure 4. XRD of Ru material isolated under an inert atmosphere after hydrogenation of 1-hexene (a) in solventless conditions, (b) in $BMI \cdot PF_6$ biphasic conditions, and (c) of $RuO_2 \cdot xH_2O$.

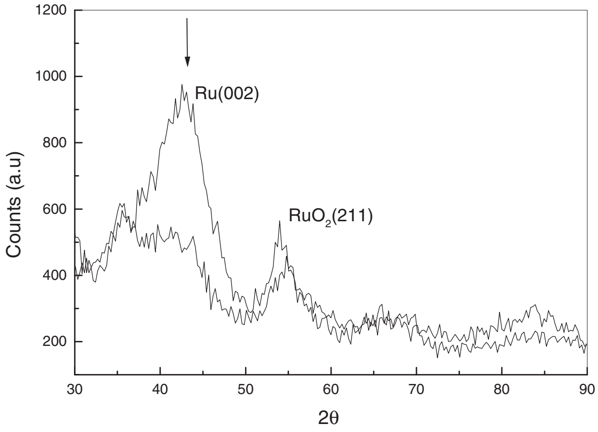

Figure 5. X-Ray diffraction pattern of the material isolated after hydrogenation of 1-hexene by $RuO_2 \cdot xH_2O$ in $BMI \cdot PF_6$ ionic liquid under inert atmosphere and after exposure to air (1 day).

taminated by small amounts of RuO_2 (RuO_2 (211) reflection at $2\theta = 53°$). Surface reoxidation during the isolation procedure was most probably the origin of such a RuO_2 reflection. Indeed, it was confirmed that the Ru metal surface can be reoxidized by O_2 since the Ru(002) metal peak at $2\theta = 42°$ decreases and the RuO_2

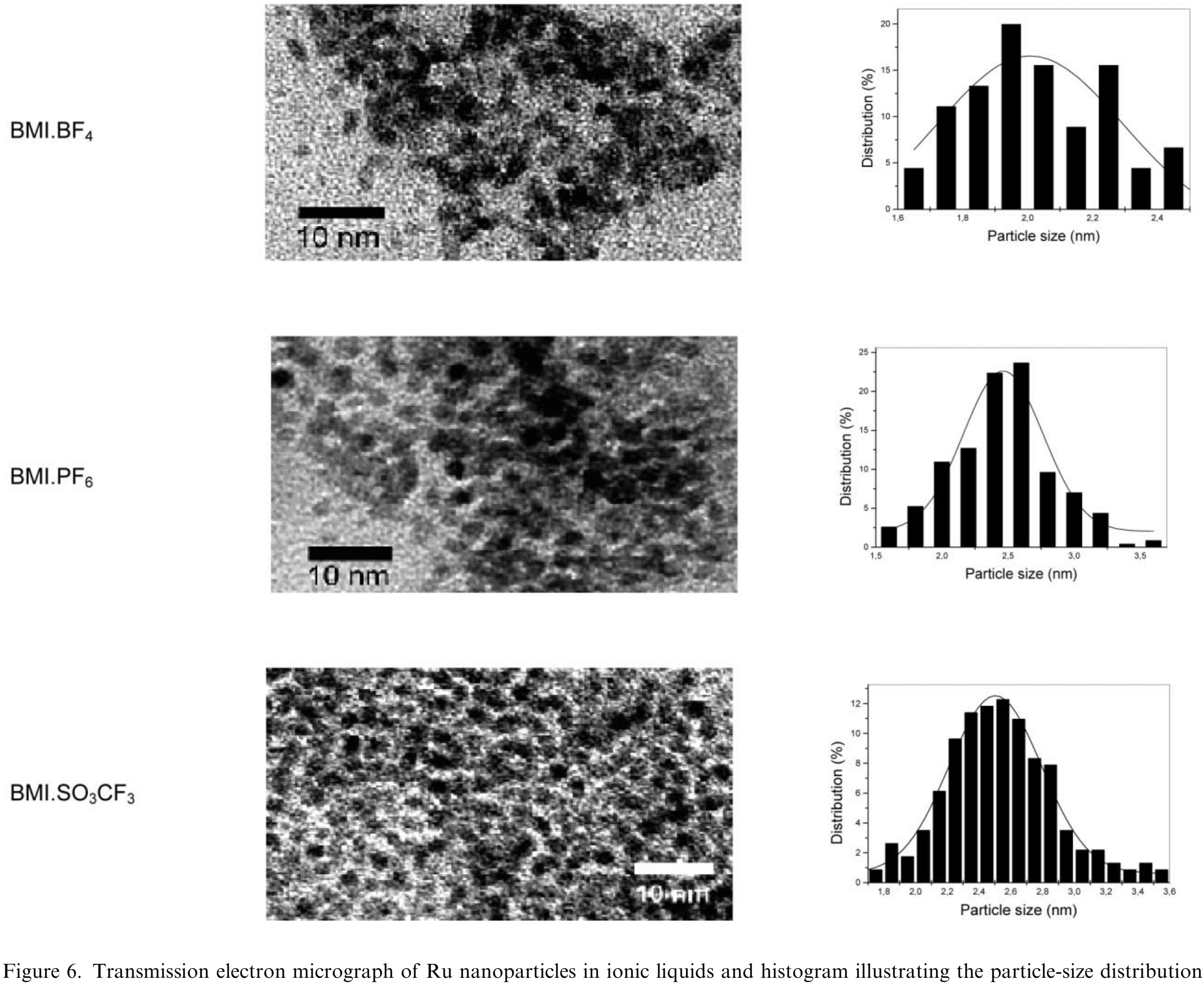

Figure 6. Transmission electron micrograph of Ru nanoparticles in ionic liquids and histogram illustrating the particle-size distribution.

reflections increase in a new XRD recorded after exposure of the same sample to air for 1 day (figure 5). It is worthy of note that the Ru samples in the ionic liquids are more reluctant to oxidation compared to those prepared in solventless conditions.

Inasmuch as the imidazolium ionic liquids possess no measurable vapor pressure and a relatively high viscosity (2–3 poises) [15], the nanoparticle size and morphology could be investigated *in situ* by transmission electron microscopy (TEM). Thus, after the hydrogenation reactions, the volatiles were removed under reduced pressure and the ionic liquid phase containing the ruthenium nanoparticles was placed as a thin film in a holey carbon grid and immediately analyzed. TEM micrographs were obtained in the ionic phases 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($BMI \cdot PF_6$), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($BMI \cdot BF_4$), and 1-*n*-butyl-3-methylimidazolium triflate ($BMI \cdot SO_3CF_3$) (figure 6). The metal particle-size distribution was estimated from the measurement of about 200 particles diameters, assuming a spherical shape, found in an arbitrary chosen area in enlarged microphotographs. These particles display a monomodal size distribution and can be classified as "near" monodispersed [16] (average diameters of 2.5 ± 0.4 nm were calculated in $BMI \cdot PF_6$ and $BMI \cdot SO_3CF_3$, and 2.0 ± 0.2 nm in $BMI \cdot BF_4$). Therefore, the particle size and size distribution are apparently independent of the nature of the ionic liquid anion.

3. Conclusions

In summary, we have shown that Ru nanoparticles of small size and narrow size distribution can be easily prepared by H_2 reduction of hydrous RuO_2 in room-temperature ionic liquids, under mild reaction conditions. In particular, Ru-immobilized in $BMI \cdot PF_6$ is a very stable, biphasic, and recyclable catalytic system for the hydrogenation of olefins that eliminates the need for classical organic solvents in the hydrogenation reactions and provides a medium for the extrastabilization of the Ru surface atoms.

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