

Shape- and Size-Selective Preparation of Hectorite-Supported Ruthenium Nanoparticles for the Catalytic Hydrogenation of Benzene

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Abstract The cationic organometallic aqua complexes formed by hydrolysis of $[(C_6H_6)_2RuCl_2]_2$ in water, mainly $[(C_6H_6)Ru(H_2O)_3]^{2+}$, intercalate into white sodium hectorite, replacing the sodium cations between the anionic silicate layers. The yellow hectorite thus obtained reacts in water with molecular hydrogen (50 bar, 100 °C) to give a dark suspension containing a black hectorite in which large hexagonally shaped ruthenium nanoparticles (20–50 nm) are intercalated between the anionic silicate layers, the charges of which being balanced by hydronium cations. If the reduction with molecular hydrogen (50 bar, 100 °C) is carried out in various alcohols, spherical ruthenium nanoparticles of smaller size (3–38 nm depending on the alcohol) are obtained. In alcohols other than methanol, the reduction also works without H_2 under reflux conditions, the alcohol itself being the reducing agent; the ruthenium nanoparticles obtained in this case are spherical and small (2–9 nm) but tend to aggregate to form clusters of nanoparticles. Whereas the ruthenium nanoparticles prepared by reduction of the yellow hectorite in refluxing alcohols without hydrogen pressure are almost inactive, the nanoparticles formed by hydrogen reduction catalyze the hydrogenation of benzene to give cyclohexane under mild conditions (50 °C) with turnover frequencies up to 6500 catalytic cycles per hour, the best solvent being ethanol.

Dedicated to Professor C. N. R. Rao, pioneer of nanocluster chemistry, on the occasion of his 75th birthday.

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Introduction

The design of nanocomposites consisting of functional metals and adequate matrices is a challenge for the fabrication of recyclable catalysts. Highly active metallic nanoparticles must be stabilized by a suitable support in order to prevent aggregation to bulk metal [1]. Hectorite is, just as montmorillonite, a naturally occurring clay, which can be defined as layers of negatively charged two-dimensional silicate sheets held together by cationic species in the interlaminal space, which are susceptible to ion exchange [2–4]. Ruthenium-supported hectorite obtained by ion exchange has been reported by Shimazu et al. using $[\text{Ru}(\text{NH}_3)_6]^{2+}$ cations [5] and by our group using $[(\text{C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$ cations [6] or $[(\text{C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]^{2+}$ cations [7] for the intercalation. These materials show high catalytic activity for the hydrogenation of olefins [5] and aromatic compounds (catalytic turnover frequency up to 7000 h^{-1}) [8]. Ruthenium nanoparticles intercalated in montmorillonite were also found to efficiently catalyze the hydrogenation of benzene ($110\text{ }^\circ\text{C}$), the catalytic activity (4000 h^{-1}) being somewhat lower than the one of hectorite-supported ruthenium nanoparticles [9]. In this paper, we report on the influence of solvent and reducing agent on the shape and size of the ruthenium nanoparticles intercalated in hectorite and on the catalytic performance of the materials obtained for the hydrogenation of benzene.

Experimental Section

Synthesis

White sodium hectorite (**1**) was prepared according to the method of Bergk and Woldt [10]. The sodium cation exchange capacity, determined according to the method of Lagaly [11], was found to be 104 mEq per 100 g. The dimeric complex $[(\text{C}_6\text{H}_6)_2\text{RuCl}_2]_2$ was synthesized following the procedure reported by Arthur and Stephenson [12].

Preparation of the Ruthenium(II)-Containing Hectorite **2**

The neutral complex $[(\text{C}_6\text{H}_6)_2\text{RuCl}_2]_2$ (83.8 mg, 0.17 mmol) was dissolved in distilled and Ar-saturated water (50 mL), giving a clear yellow solution after intensive stirring for 1 h. The pH of this solution was adjusted to 8 (using a glass electrode) by adding the appropriate amount of 0.1 M NaOH. After filtration this solution was added to 1 g of finely powdered and degassed (1 h high vacuum, then Ar-saturated) sodium hectorite **1**. The resulting suspension was stirred for 4 h at $20\text{ }^\circ\text{C}$. Then the yellow ruthenium(II)-containing hectorite **2** was filtered off and dried *in vacuo*.

Preparation of the Ruthenium(0)-Containing Hectorite 3 by Reduction with Molecular Hydrogen

The ruthenium(0)-containing hectorite **3** was obtained by reacting a suspension of the yellow ruthenium(II)-containing hectorite **2** (50 mg, 0.01592 mmol Ru) in a magnetically stirred stainless-steel autoclave (volume 100 mL) under a pressure of H₂ (50 bar) at 100 °C for 14 h using water or different alcohols (2.5 mL) as solvent. After pressure release and cooling, **3** was isolated as a black material.

Preparation of the Ruthenium(0)-Containing Hectorite 3 by Reduction with Refluxing Alcohols

Alternatively, the ruthenium(0)-containing hectorite **3** was prepared by reducing yellow hectorite **2** (50 mg, 0.01592 mmol Ru) without hydrogen in refluxing alcohols (10 mL), the reaction time varying from 12 to 96 h for completion, depending on the alcohol.

Catalysis

The catalytic hydrogenation of benzene was carried out in a magnetically stirred stainless-steel autoclave. The conversion of benzene to cyclohexane was determined by ¹H NMR spectroscopy in [D₆]-acetone.

Benzene Hydrogenation with Freshly Prepared Ruthenium(0)-Hectorite 3 in the Original Solvent

A freshly prepared suspension (2.5 mL) of ruthenium(0)-containing hectorite **3** was used, 2.5 mL of the same solvent as well as 5.0 mL of benzene were added. Then the autoclave was heated under rigorous stirring to 50 °C for 2 h (preheating period) and then pressurized with hydrogen (50 bar). When the pressure had dropped to 35 bar (15 min to 4 h), the autoclave was cooled in an ice-bath. After pressure release, the solution was decanted from the solid and analyzed.

Benzene Hydrogenation with Ruthenium(0)-Hectorite 3 in Ethanol

A freshly prepared suspension (2.5 mL) of ruthenium(0)-containing hectorite **3** was allowed to settle down, the black precipitates were isolated by decanting and washing with ethanol (3 times, 10 mL) without drying. Then **3** was suspended in 5 mL of ethanol. After addition of 5 mL of benzene, the autoclave was heated under rigorous stirring to 50 °C for 2 h (preheating period) and then pressurized with hydrogen (50 bar). When the pressure had dropped to 35 bar (20 min to 57 h), the autoclave was cooled in an ice-bath. After pressure release, the solution was decanted from the solid and analyzed.

Instrumentation

NMR spectra were measured using Bruker DRX-400 MHz spectrometer. For the particle size determination, a transmission electron microscope Philips CM 200 operating at 200 kV was used, the hectorite sample being deposited on a 300 mesh copper grid covered by a carbon thin film.

Results and Discussion

Synthetic sodium hectorite (**1**) is a white solid which presents an idealized cell formula of $\text{Mg}_{5.5}\text{Li}_{0.5}\text{Si}_8\text{O}_{20}(\text{OH})_4\text{Na} \cdot n\text{H}_2\text{O}$. It has a three-layer sheet-like morphology which results from the two-dimensional condensation of silicic acid, two layers of SiO_4 tetrahedra being connected by a layer of MgO_6 octahedra. Partial replacement of the Mg^{2+} cations in the octahedral layers by Li^+ cations leads to an excess of anionic charges of the layers, which are compensated by Na^+ cations in the interlamellar space (Fig. 1). Hydratisation of the interlamellar sodium cations to give $[\text{Na}(\text{H}_2\text{O})_n]^+$ is responsible for the swelling of hectorite in water, since the interlamellar space is widened [13].

Contrary to the magnesium and lithium cations in the octahedral layer, the sodium cations in the interlamellar space are not bound to the silicate framework. For this reason, the Na^+ cations can easily be exchanged in water by other water-soluble inorganic, organic or organometallic cations. The dinuclear complex benzene ruthenium dichloride dimer dissolves in water with hydrolysis to give, with successive substitution of chloro ligands by aqua ligands, a mixture of mononuclear benzene ruthenium complexes being in equilibrium [13]. The benzene ^1H NMR signals of the D_2O solution have been assigned to $[(\text{C}_6\text{H}_6)\text{RuCl}_2(\text{H}_2\text{O})]$ ($\delta = 5.89$ ppm),

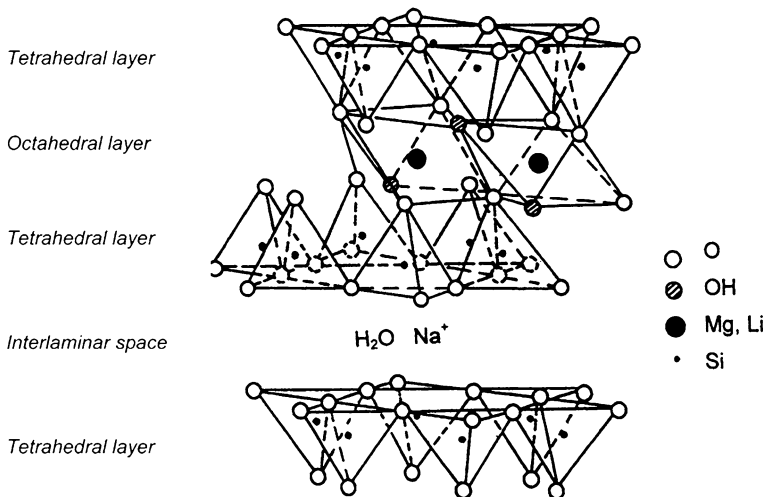
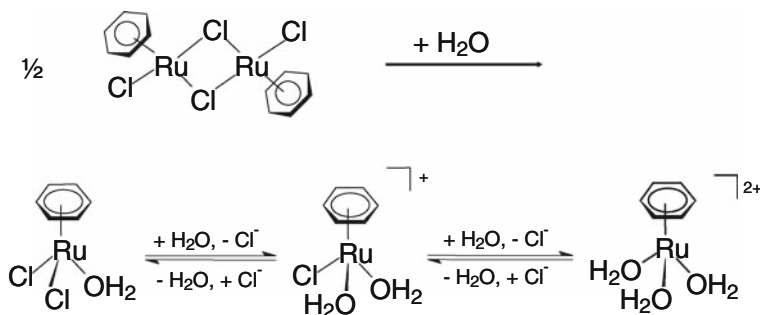


Fig. 1 Structural model according to Grim [13] of sodium hectorite $\text{Mg}_{5.5}\text{Li}_{0.5}\text{Si}_8\text{O}_{20}(\text{OH})_4\text{Na} \cdot n\text{H}_2\text{O}$, showing the anionic three-layer sheets and the interlamellar space containing sodium cations and water molecules



Scheme 1 Hydrolysis of the dinuclear complex $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ in water to give a mixture of mononuclear benzene ruthenium complexes, the dicationic triaqua complex $[(\text{C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$ being the major product

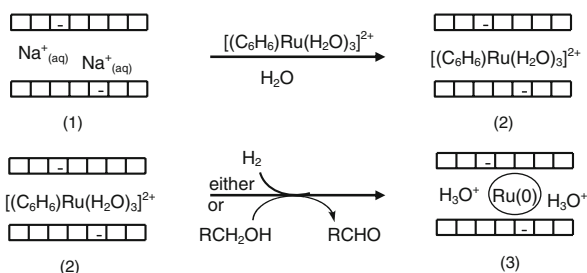
$[(\text{C}_6\text{H}_6)\text{RuCl}(\text{H}_2\text{O})_2]^{2+}$ ($\delta = 5.97$ ppm), and $[(\text{C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$ ($\delta = 6.06$ ppm) (Scheme 1) [14]. The dication $[(\text{C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$, which has been isolated as the sulfate and structurally characterized [15], is the major species present in the hydrolytic mixture over the pH range from 5 to 8 according to the NMR spectrum.

When the yellow solution obtained from dissolving the dinuclear complex $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ in water after adjusting the pH to 8 by NaOH is added to white sodium hectorite (**1**), the main hydrolysis product $[(\text{C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$ intercalates into the solid, replacing the appropriate amount of sodium cations, to give the yellow ruthenium(II)-modified hectorite **2**. This material, which can be dried and stored in air, reacts either with hydrogen under pressure (50 bar) at 100 °C or refluxing alcohols by reduction of $[(\text{C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$ to give the black ruthenium(0)-modified hectorite **3** (Scheme 2). The ruthenium loading of the black hectorite **3** was assumed to be 3.2 wt% [6], based upon the molar ratio of $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$ used (corresponding to 75% of the experimentally determined [11] cation exchange capacity of **1**), and the presence of metallic ruthenium was proven by its typical reflections in the X-ray diffraction pattern. The specific surface of **3** was determined by low-temperature nitrogen adsorption to be 207 m²/g, which is significantly higher than for the unmodified hectorite **1** (87 m²/g), the pore size distribution in **3** showing a maximum of 1.98 nm [7].

The size distribution of the ruthenium(0) nanoparticles in **3** was studied by transmission electron microscopy (TEM) using the “ImageJ” software [16] for image processing and analysis. The micrographs show particles varying from 2 to 60 nm depending on method of reduction and nature of solvent used. At the edges of superimposed silicate layers nanoparticles are visible, the lighter tone of which is typical for intercalated particles. The mean particle size and standard deviation (σ) were estimated from image analysis of *ca.* 100 particles at least.

Formation of Hectorite-Stabilized-Ru(0) Nanoparticles under Hydrogen Pressure

When yellow ruthenium(II)-containing hectorite **2** is reduced in an aqueous medium, a black suspension is obtained, which represents a stable dispersion of



Scheme 2 Ion exchange of Na^+ cations in sodium hectorite **1** (white) against $[(\text{C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$ cations to give ruthenium(II)-modified hectorite **2** (yellow) and reduction of $[(\text{C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$ in **2** either by molecular hydrogen or by refluxing alcohols to give ruthenium(0)-containing hectorite **3**

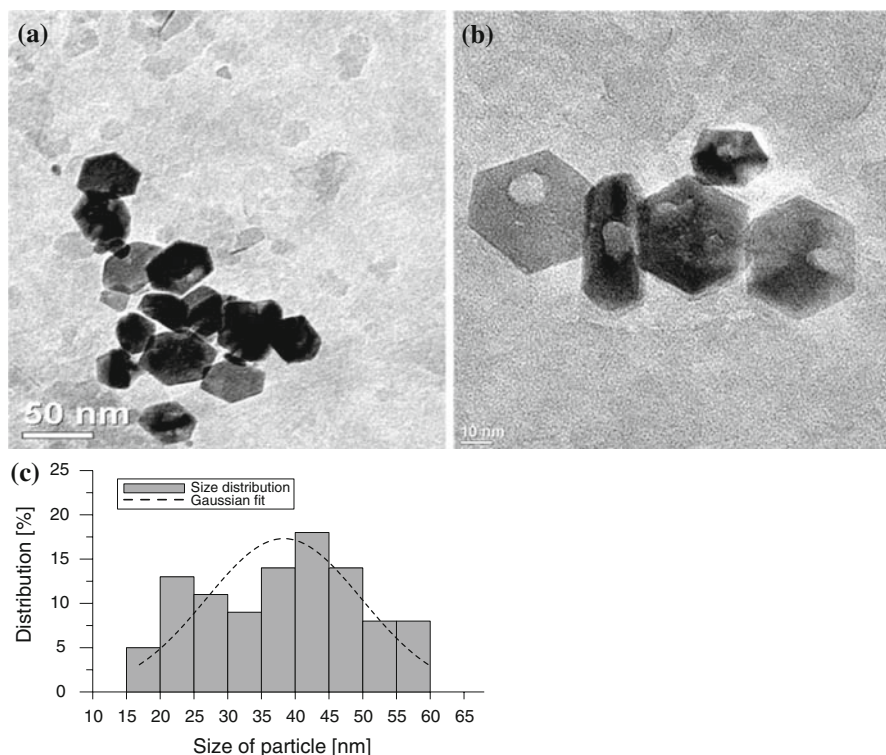


Fig. 2 TEM micrographs (**a** and **b**) and histogram (**c**) of hectorite-supported hexagonally shaped ruthenium nanoparticles prepared by reduction of **2** with H_2 in water

ruthenium(0)-containing hectorite **3** in water. Even after storage for several weeks, the dispersed solid does not precipitate. The TEM analysis of this material shows the presence of hexagonally shaped ruthenium nanoparticles intercalated in hectorite, the nanoparticles having mean size of 38 nm with a wide range of size distribution ($\sigma = 11.6$), see Fig. 2.

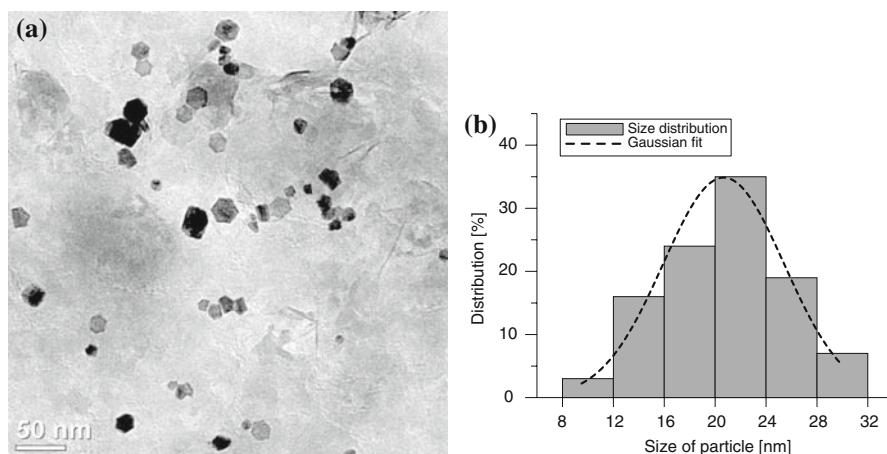


Fig. 3 TEM micrograph (a) and histogram (b) of hexagonally shaped ruthenium nanoparticles prepared in a water/methanol (1:1) mixture

Hexagonally shaped ruthenium nanoparticles are also obtained in water/methanol mixtures, indicating that water is essential for the formation of hexagons in hectorite **3**. Whereas the reduction with H_2 in alcohols alone produces more or less spherically shaped ruthenium particles (see below), the nanoparticles obtained in aqueous methanol are also hexagonally shaped, the size of which depends on the ratio of methanol/water: For example, the reduction of **2** in an aqueous solution containing 50% methanol results in a hectorite **3** containing relatively small hexagons with an average size up to 20.7 nm having a standard deviation $\sigma < 25\%$ of the mean particle size (Fig. 3), which is fairly narrow as compared to that observed in pure water (Fig. 2). If the water content is inferior to 20%, hexagonally shaped nanoparticles are not observed any more.

The reduction of **2** with molecular hydrogen in different alcohols was studied as well. The TEM micrographs in these cases reveal the black hectorite **3** to contain smaller ruthenium nanoparticles as those observed in aqueous media, see Fig. 4. When **2** is reduced in primary alcohols, well separated particles are observed, the average size ranging from 9.4 nm (ethanol) to 12.3 nm (1-propanol) with a fairly wide particle size distribution as shown in the histograms. In the case of 1-butanol, two kinds of particles are observed with an average size of 3 nm and of 26.7 nm. In secondary alcohols, the reduction of **2** with H_2 results in well separated and even smaller particles (Figs. 4 and 5).

Formation of Hectorite-Stabilized Ru(0) in Refluxing Alcohols

We found out that in refluxing alcohols other than methanol, the Ru(II) complex in **2** is reduced to Ru(0) nanoparticles to give **3** even without hydrogen being present, which shows that, in this case, the alcohol itself functions as reducing agent (Scheme 2). This can be observed very easily by the color change of the refluxing hectorite suspension in various alcohols from yellow to black. In the case of primary

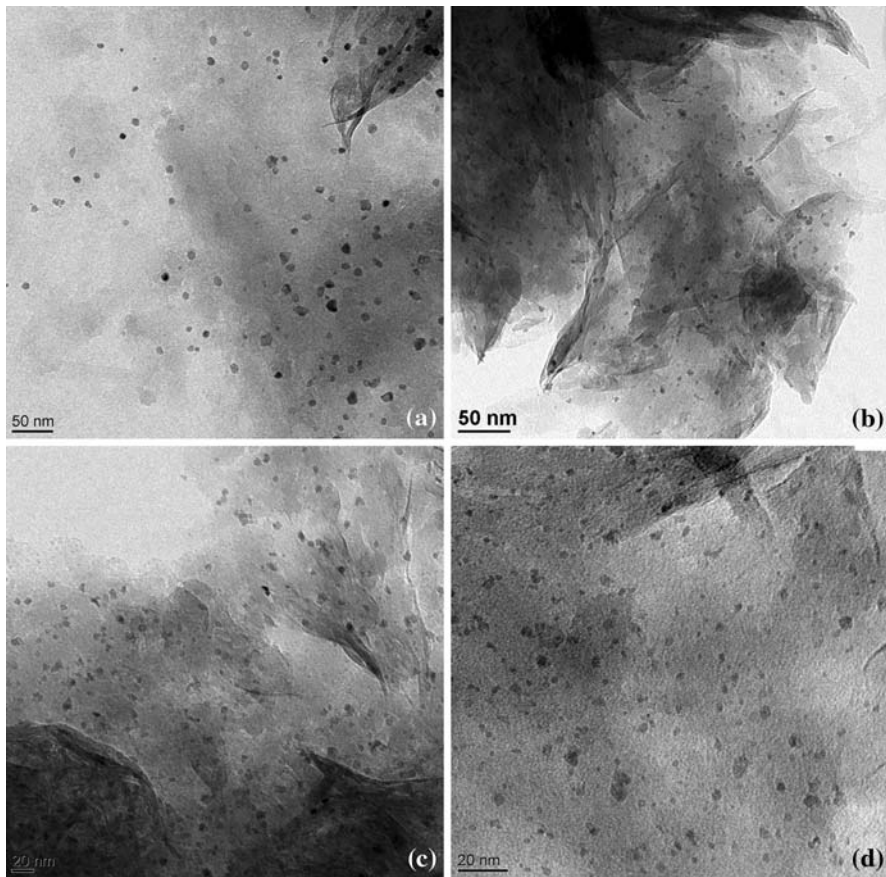


Fig. 4 TEM micrographs of hectorite-stabilized ruthenium nanoparticles prepared from H_2 reduction of yellow ruthenium(II)-modified hectorite **2** in different alcohols: methanol (a), ethanol (b), 2-propanol (c), 2-butanol (d)

alcohols, the refluxing time necessary for completion varies from 96 h (ethanol) to 12 h (1-butanol), indicating that long-chain alcohols are better reducing agents for **2** to **3**. The same applies to secondary alcohols which are, however, less efficient than primary alcohols (67 h for 2-propanol and 24 h for 2-butanol). Once the reduction is complete, an increased refluxing time has no effect on particle size. However, hectorite-stabilized ruthenium nanoparticles obtained this way tend to aggregate to form clusters of nanoparticles. In every case, the mean particle size is always less than 10 nm with a standard deviation (σ) generally greater than 18% of mean particle size (Figs. 6 and 7).

Catalysis

Ruthenium nanoparticles intercalated in hectorite are highly active hydrogenation catalysts: Ruthenium(0)-containing hectorite **3** efficiently reduces even benzene to

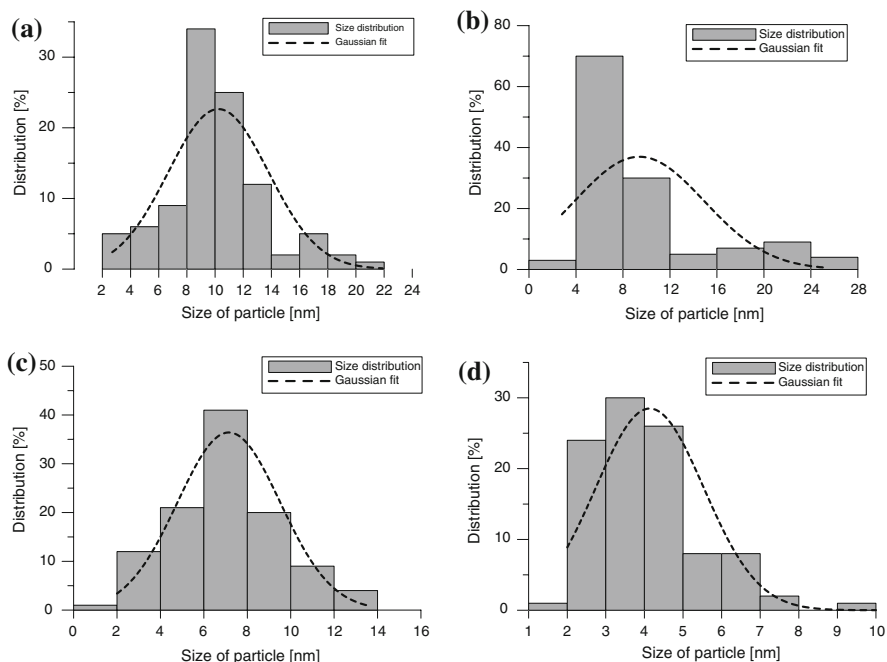


Fig. 5 Histograms of hectorite-stabilized ruthenium nanoparticles prepared by H_2 reduction in methanol (a), ethanol (b), 2-propanol (c), 2-butanol (d) showing the particle size distribution

give cyclohexane under mild conditions (50 °C). However, the catalytic activity of **3** crucially depends on the way how the ruthenium(0)-containing hectorite **3** is prepared and conditioned as well as on the solvent used for benzene hydrogenation.



The catalytic activity of the various Ru(0)-hectorite **3** samples obtained by different synthesis and conditioning for the hydrogenation of benzene was studied in various alcohols or in water under a hydrogen pressure of 50 bar at 50 °C. It turned out that ethanol is by far the best solvent for catalytic benzene hydrogenation (Table 1).

Otherwise, no clear correlation between the catalytic activity and the size nor the shape of the ruthenium(0) nanoparticles intercalated in hectorite can be established. The way how **3** is prepared and conditioned is much more important than particle size and shape. Thus, the Ru(0)-hectorites **3** obtained by reduction of **2** in refluxing alcohols (in the absence of hydrogen) are almost inactive in the original alcohol and become only slightly active after being transferred to ethanol (Table 2).

By contrast, the Ru(0)-hectorites **3** prepared by reduction of **2** with H_2 in ethanol or other alcohols are more or less catalytically active in the original reaction medium and become even more active if transferred to ethanol, whatever the size

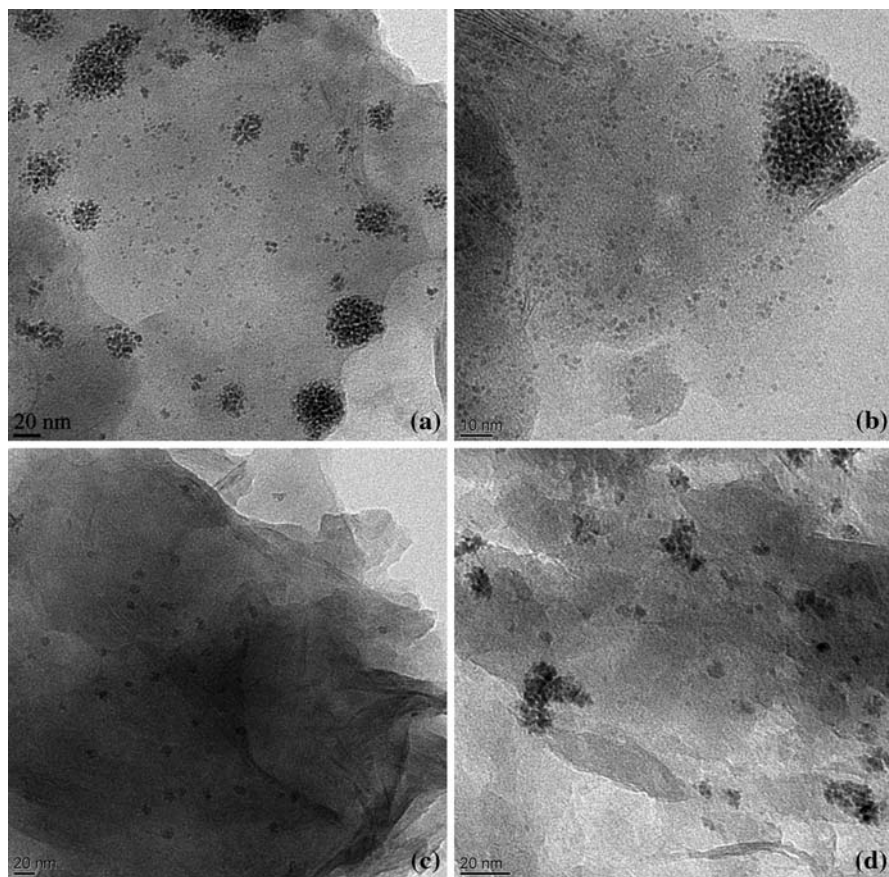


Fig. 6 TEM micrographs of hectorite-stabilized ruthenium nanoparticles prepared by the reduction of yellow ruthenium(II)-modified hectorite **2** in different refluxing alcohols without H_2 being present: ethanol (a), 1-propanol (b), 2-propanol (c), 2-butanol (d)

(mean values varying from 3 to 27 nm) of the ruthenium nanoparticles is (Table 1). The highest catalytic activity is observed with **3** being prepared with H_2 in ethanol (TOF 6531 h^{-1}). This suggests that the highly active ruthenium nanoparticles (made by H_2 reduction of **2**) contain hydrogen adsorbed at the surface or in the interior.

A special case are the large and medium-sized hexagonally shaped ruthenium-nanoparticles obtained in hectorite by reduction of **2** with molecular hydrogen in water or in aqueous methanol. Despite their regular shape and their size, they are quite active for benzene hydrogenation in an aqueous system (TOF 3670 h^{-1} in H_2O or 1874 h^{-1} in $H_2O/MeOH$, 1:1), but their activity drops sharply by transferring them to ethanol (Table 1). A possible explanation might be that the hexagonal nanoparticles exclusively obtained in the presence of water contain water or hydroxyl groups at the surface which may be blocked or replaced by alcohols.

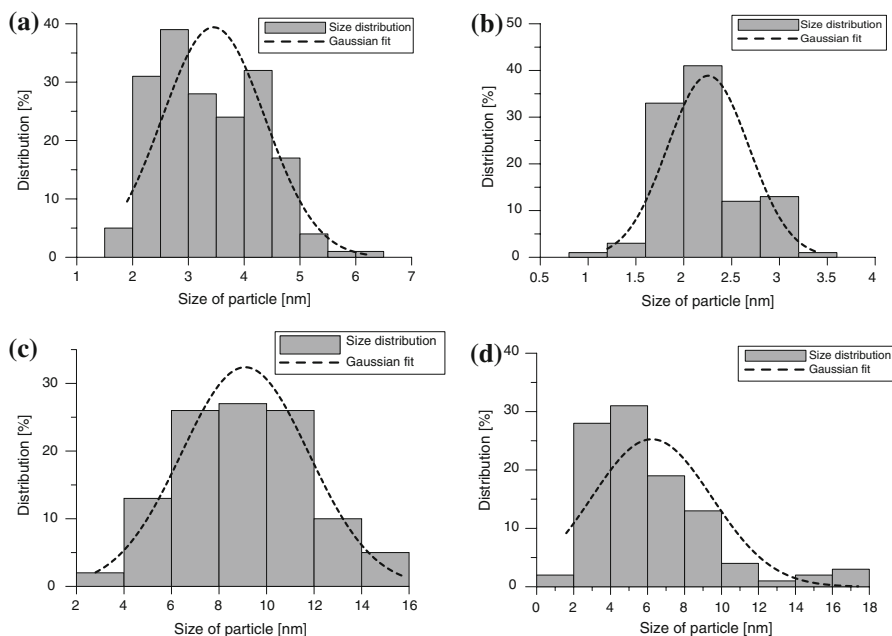


Fig. 7 Histograms showing the particle size distribution of hectorite-stabilized ruthenium nanoparticles prepared by the reduction of yellow ruthenium(II)-modified hectorite **2** in different refluxing alcohols without H_2 being present: ethanol (a), 1-propanol (b), 2-propanol (c), 2-butanol (d)

Table 1 Benzene hydrogenation using Ru(0)-hectorite **3** prepared by reduction of Ru(II)-hectorite **2** with H_2

Medium for catalyst preparation	Mean particle size (nm)	Solvent for catalytic reaction	Reaction time (h)	Conversion (%)	Activity TOF (h^{-1}) ^a
H ₂ O	38	H ₂ O	0.5	63	3670
		EtOH	2.2	56	839
H ₂ O/MeOH (1:1)	21	H ₂ O/MeOH (1:1)	1.1	71	1874
		EtOH	1.7	39	883
MeOH	10	MeOH	1.9	47	893
		EtOH	0.3	46	5060
EtOH	9	EtOH	0.2	38	6531
Pr ⁿ OH	12	Pr ⁿ OH	1.3	64	1553
		EtOH	0.5	39	3278
Pr ⁱ OH	7	Pr ⁱ OH	0.3	34	4753
		EtOH	0.3	60	5732
Bu ⁿ OH	3 and 27	Bu ⁿ OH	1.4	56	1354
		EtOH	0.6	70	3508
Bu ⁱ OH	4	Bu ⁱ OH	0.4	41	4125
		EtOH	0.2	18	5564

^a TOF, turnover frequency was calculated as moles of converted benzene per mol Ru per hour

Table 2 Benzene hydrogenation using Ru(0)-hectorite **3** prepared by reduction of Ru(II)-hectorite **2** in refluxing alcohols

Medium for catalyst preparation	Mean particle size (nm)	Solvent for catalytic reaction	Reaction time (h)	Conversion (%)	Activity TOF (h ⁻¹) ^a
EtOH	3	EtOH	4.7	34	301
Pr ⁿ OH	2	Pr ⁿ OH	72	0	0
		EtOH	3.2	53	564
Pr ⁱ OH	9	Pr ⁱ OH	72	0	0
		EtOH	57	21	20
		Bu ⁿ OH	182	14	5
Bu ⁿ OH	4	EtOH	2.6	53	684
		Bu ⁱ OH	3.1	37	479
Bu ⁱ OH	6	EtOH	6.9	35	208

^a TOF, turnover frequency was calculated as moles of converted benzene per mol Ru per hour

Conclusion

In conclusion, we have shown that large hexagonally shaped ruthenium nanoparticles intercalated in hectorite can be produced by reducing hectorite containing $[(C_6H_6)Ru(H_2O)_3]^{2+}$ cations under hydrogen pressure in water. If the reduction with hydrogen is carried out in various alcohols, almost spherical ruthenium nanoparticles of various sizes intercalated in hectorite are obtained. All these Ru(0)-containing hectorite materials are active catalysts for the hydrogenation of benzene to cyclohexane, the highest activity being observed in ethanol. However, black hectorite materials obtained by reducing Ru(II)-containing hectorite in refluxing alcohols without hydrogen pressure are almost inactive for benzene hydrogenation, although they contain small spherical ruthenium nanoparticles. These results suggest the active ruthenium nanoparticles obtained by hydrogen reduction to contain hydrogen at the surface or in the interior, which conditions them as hydrogenation catalysts.

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