

## Ruthenium Nanoparticles Intercalated in Hectorite: A Reusable Hydrogenation Catalyst for Benzene and Toluene\*

Georg Süss-Fink,<sup>1,6</sup> Birgit Mollwitz,<sup>1</sup> Bruno Therrien,<sup>1</sup> Massoud Dadras,<sup>2</sup>  
Gabor Laurency,<sup>3</sup> Annette Meister,<sup>4</sup> and Götz Meister<sup>5</sup>

The cationic organometallic aqua complexes formed by hydrolysis of  $[(C_6H_6)RuCl_2]_2$  in water, mainly  $[(C_6H_6)Ru(H_2O)_3]^{2+}$ , intercalate into sodium hectorite by ion exchange, replacing the sodium cations between the anionic silicate layers. The yellow hectorite thus obtained reacts in ethanol with molecular hydrogen (50 bar, 100°C) with decomposition of the organometallic aqua complexes to give a black material, in which ruthenium(0) nanoparticles (9–18 nm) are intercalated between the anionic silicate layers, the charges of which being balanced by hydronium cations. The black ruthenium-modified hectorite efficiently catalyses the hydrogenation of benzene and toluene in ethanol (50 bar  $H_2$ , 50°C), the turnover frequencies attaining 7000 catalytic cycles per hour.

**KEY WORDS:** Ruthenium nanoparticles; ruthenium-modified hectorite; benzene hydrogenation.

\*Dedicated to Professor Günter Schmid, pioneer of nanocluster chemistry, on the occasion of his 70th birthday

<sup>1</sup>Institut de Chimie, Université de Neuchâtel, CH-2009, Neuchâtel, Switzerland.

<sup>2</sup>Institut de Microtechnique, Université de Neuchâtel, CH-2009, Neuchâtel, Switzerland.

<sup>3</sup>Institut des Sciences et Ingénierie Chimiques, Ecole Polytechnique Fédérale, CH-1015, Lausanne, Switzerland.

<sup>4</sup>Institut für Physikalische Chemie, Martin-Luther-Universität Halle-Wittenberg, D-06108, Halle, Germany.

<sup>5</sup>Fachgruppe Landschaftsökologie, Unabhängiges Institut für Umweltfragen, D-06108, Halle, Germany.

<sup>6</sup>To whom correspondence should be addressed. E-mail: georg.suess-fink@unine.ch

## 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 interlaminar space, which are susceptible to ion exchange [2]. Ruthenium-supported hectorite obtained by ion exchange has been reported by Shimazu *et al.* using  $[\text{Ru}(\text{NH}_3)_6]^{2+}$  cations [3] and by our group using  $[(\text{C}_6\text{H}_6)\text{Ru}(\text{H}_2\text{O})_3]^{2+}$  cations [4] or  $[(\text{C}_6\text{H}_6)_4\text{Ru}_4\text{H}_4]^{2+}$  cations [5] for the intercalation. These materials show high catalytic activity for the hydrogenation of olefins [3] and aromatic compounds [4, 5]. A recent communication by Liu and co-workers on ruthenium nanoparticles immobilized on montmorillonite as highly efficient benzene hydrogenation catalysts [6] prompted us to revisit our study on hectorite-supported ruthenium as hydrogenation catalyst [4], to analyze the nanoparticles present in the catalyst with new analytical methods and to study their hydrogenation potential as well as their activity for the hydrogenation of benzene and toluene.

## EXPERIMENTAL SECTION

### Synthesis

White sodium hectorite (**1**) was prepared according to the method of Bergk and Woldt [7]. The sodium cation exchange capacity, determined according to the method of Lagaly [8], was found to be 104 mEq per 100 g. The dimeric complex  $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$  was synthesized following the procedure reported by Arthur and Stephenson [9].

The neutral complex  $[(\text{C}_6\text{H}_6)\text{RuCl}_2]_2$  (83.8 mg, 0.17 mmol) was dissolved in distilled and  $\text{N}_2$ -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  $\text{N}_2$ -saturated) sodium hectorite **1**. The resulting suspension was stirred for 4 h at 20°C. Then the yellow ruthenium-complex-containing hectorite **2** was filtered off and dried *in vacuo*.

The ruthenium-metal-containing hectorite **3** was obtained by reacting a suspension of the yellow ruthenium-complex-containing hectorite **2** (50 mg, 0.01592 mmol Ru) in absolute ethanol (2.5 mL) in a magnetically stirred stainless-steel autoclave (volume 100 mL) with  $\text{H}_2$  (50 bar) at 100°C for

14 h. After pressure release and cooling, the black hectorite **3** was isolated by filtration and dried *in vacuo*.

## Catalysis

The catalytic hydrogenation of benzene and toluene was carried out in a magnetically stirred stainless-steel autoclave (working volume 100 mL), for the first run charged with freshly prepared hectorite **3**, made from 50 mg of hectorite **2** (0.01592 mmol Ru) in 2.5 mL ethanol under a hydrogen pressure of 50 bar. After 14 h at 100°C, the autoclave was cooled, and the pressure was released. Then 2.5 mL of absolute ethanol and 5 mL of the aromatic substrate were added, and the autoclave was heated under rigorous stirring to 50°C for 2 h (preheating period) and then pressurized again with hydrogen (50 bar). When the pressure had dropped to 35 bar (typically after 15 min), the autoclave was cooled in an ice-bath. After pressure release, the solution was decanted from the solid and analyzed by <sup>1</sup>H NMR.

For further catalytic runs, the solid catalyst residue was used without drying by adding 5 mL of absolute ethanol and 5 mL of the aromatic substrate prior to pressurizing with hydrogen (50 bar) and heating to 50°C.

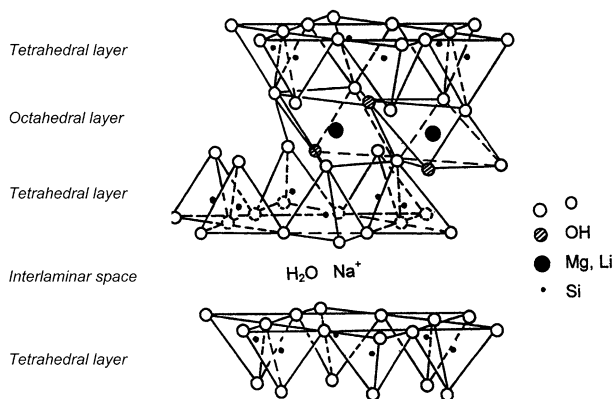
## Instrumentation

NMR spectra were measured in [D<sub>6</sub>]-acetone using a VARIAN Gemini 200 MHz spectrometer. High-pressure NMR spectra were recorded with a Bruker DRX-400 instrument using a sapphire tube assembly according to published methods [10, 11].

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

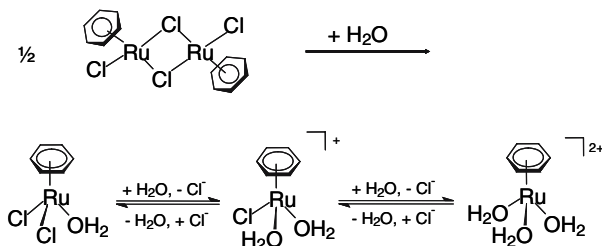
Synthetic sodium hectorite (**1**) is a white solid which presents an idealized cell formula of Mg<sub>5.5</sub>Li<sub>0.5</sub>Si<sub>8</sub>O<sub>20</sub>(OH)<sub>4</sub>Na · n H<sub>2</sub>O. It has a three-layer sheet-like morphology which results from the two-dimensional condensation of silicic acid, two layers of SiO<sub>4</sub> tetrahedra being connected by a layer of MgO<sub>6</sub> octahedra. Partial replacement of the Mg<sup>2+</sup> cations in the octahedral layers by Li<sup>+</sup> cations leads to an excess of anionic charges of the layers, which are compensated by Na<sup>+</sup> cations in the interlaminar space (Fig. 1). Hydratisation of the interlaminar sodium cations to give [Na(H<sub>2</sub>O)<sub>n</sub>]<sup>+</sup> is responsible for the swelling of hectorite in water, since the interlaminar space is widened [12].



**Fig. 1.** Structural model according to Grim [12] of sodium hectorite  $Mg_{5.5}Li_{0.5}Si_8O_{20}(OH)_4 Na \cdot n H_2O$ , showing the anionic three-layer sheets and the interlaminar space containing sodium cations and water molecules.

Contrary to the magnesium and lithium cations in the octahedral layer, the sodium cations in the interlaminar 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 [12]. The benzene  $^1H$  NMR signals of the  $D_2O$  solution have been assigned to  $[(C_6H_6)RuCl_2(H_2O)]$  ( $\delta = 5.89$  ppm),  $[(C_6H_6)RuCl(H_2O)_2]^+$  ( $\delta = 5.97$  ppm), and  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  ( $\delta = 6.06$  ppm) (Scheme 1) [13]. The dication  $[(C_6H_6)Ru(H_2O)_3]^{2+}$ , which has been isolated



**Scheme 1.** Hydrolysis of the dinuclear complex  $[(C_6H_6)RuCl_2]_2$  in water to give a mixture of mononuclear benzene ruthenium complexes, the dicationic triaqua complex  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  being the major product.

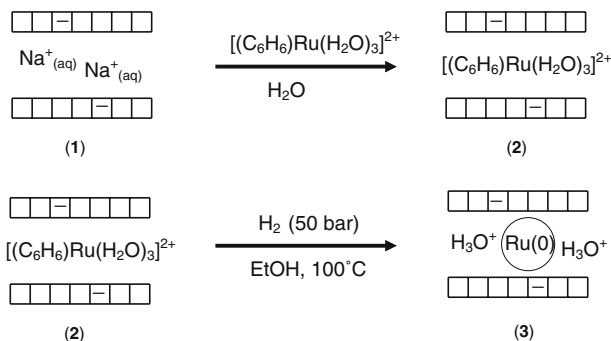
as the sulfate and structurally characterized [14], is the major species present in the hydrolytic mixture over the pH range from 5 to 8 according to the NMR spectrum.

When the yellow solution obtained from dissolving the dinuclear complex  $[(C_6H_6)RuCl_2]_2$  in water after adjusting the pH to 8 by NaOH is added to white sodium hectorite (**1**), the main hydrolysis product  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  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 with hydrogen under pressure (50 bar) at  $100^\circ C$  by reduction of  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  to give the black ruthenium(0)-modified hectorite **3** (Scheme 2).

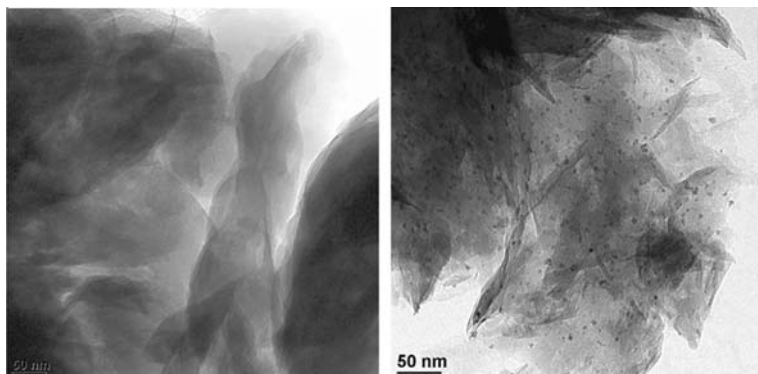
The ruthenium loading of the black hectorite **3** was assumed to be 3.2 wt%, based upon the molar ratio of  $[(C_6H_6)RuCl_2]_2$  used (corresponding to 75% of the experimentally determined [8] cation exchange capacity of **1**), and the presence of metallic ruthenium was proven by its typical reflections in the X-ray diffraction pattern. The specific surface of **3** was determined by low-temperature nitrogen adsorption to be  $207\text{ m}^2/\text{g}$ , which is significantly higher than for the unmodified hectorite **1** ( $87\text{ m}^2/\text{g}$ ), the pore size distribution in **3** showing a maximum of 1.98 nm [5].

The size distribution of the ruthenium(0) nanoparticles in **3** was studied by transmission electron microscopy (TEM). The micrographs of **3** show particles varying from 9 to 18 nm (Fig. 2). At the edges of superimposed silicate layers nanoparticles are visible, the lighter tone of which is typical for intercalated particles.

The ruthenium(0)-modified hectorite **3** is an excellent hydrogenation catalyst; its catalytic activity was studied for the hydrogenation of benzene

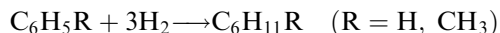


**Scheme 2.** Ion exchange of  $Na^+$  cations in sodium hectorite **1** (white) against  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  cations to give ruthenium(II)-modified hectorite **2** (yellow) and reduction of  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  in **2** by molecular hydrogen to give ruthenium nanoparticles in the ruthenium(0)-modified hectorite **3**.



**Fig. 2.** TEM micrographs of hectorite **1** (left) showing only the silicate sheets and of the ruthenium(0)-modified hectorite **3** (right) showing metallic nanoparticles (darker colored ones at the surface and lighter colored ones in between the silicate layers).

and toluene in ethanol solution. For the first catalytic run, **3** was freshly prepared from the air-stable precursor **2**. For further catalytic runs, the solid **3** was reused without drying after decantation of the ethanol solution.



The mean catalytic activity (turnover frequency) of **3** was found to be around 7000 cycles per hour for benzene hydrogenation and 3500 cycles per hour for toluene hydrogenation (Table I). The decrease in the turnover frequencies after several catalytic runs in the case of toluene hydrogenation is not clear, it may be due to a more pronounced bulk metal formation from the nanoparticles situated at the outside of the hectorite layers.

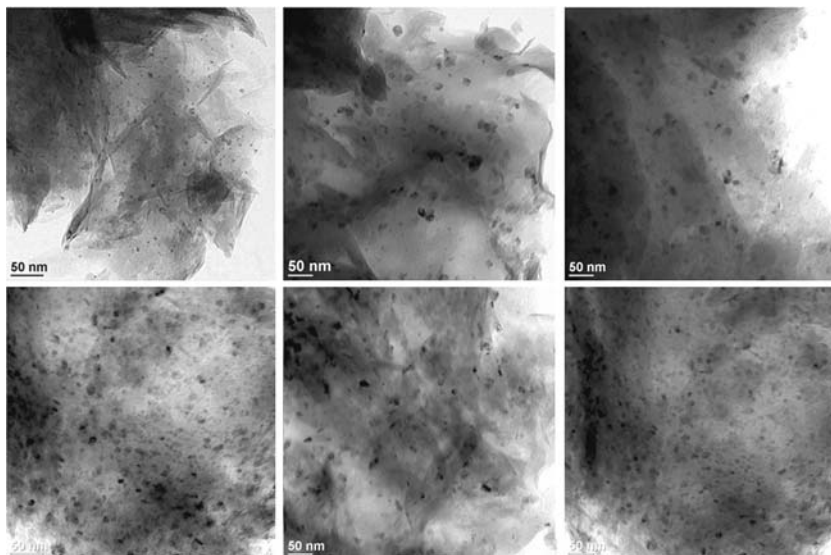
The persistence of the ruthenium(0) nanoparticles in **3** after the catalytic reaction was verified by TEM: Figure 3 shows five TEM micrographs of the same hectorite **3** after the first, second, third, fourth and fifth catalytic run of benzene hydrogenation, each time after 15 min at

**Table I.** Turnover frequencies<sup>a</sup> for arene hydrogenation<sup>b</sup> catalyzed by hectorite **3**

Substrate	Product	1st run	2nd run	3rd run	4th run	5th run
Benzene	Cyclohexane	6140	7500	7160	7280	7650
Toluene	Methylcyclohexane	3550	5700	4380	3200	2400

<sup>a</sup> TOF = mol product per mol ruthenium.

<sup>b</sup> Conditions: precatalyst (**2**) 50 mg, ethanol 5 mL, substrate 5 mL, H<sub>2</sub> 50 bar, 50°C, 15 min.

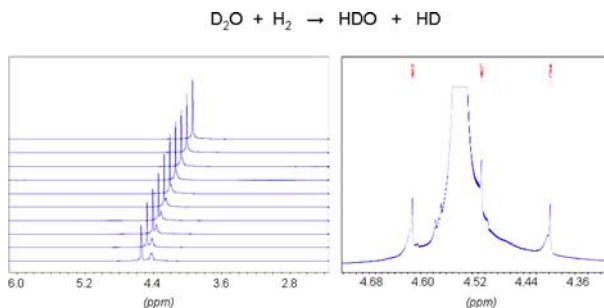


**Fig. 3.** TEM micrographs (from the upper row on the left side to the lower row on the right side) of hectorite **3** used as catalyst for the hydrogenation of benzene in ethanol before catalysis and after 1, 2, 3, 4 and 5 catalytic runs (50°C, 50 bar H<sub>2</sub>).

50°C under a hydrogen pressure of 50 bar, as compared to the first TEM micrograph showing the same hectorite **3** before catalysis.

The hydrogenation potential of **3** was studied by *in situ* high-pressure NMR spectroscopy of the H/D exchange between molecular hydrogen and deuterated water, which takes place only in the presence of a powerful hydrogenation catalyst. For this purpose, 15 mg (0.00522 mmol Ru) of the yellow precursor **2**, suspended in 2.0 mL of D<sub>2</sub>O, have been pressurized with molecular hydrogen (50 bar) in a high-pressure NMR tube, and the <sup>1</sup>H NMR spectra have been recorded at 50°C over a period of 10 min with a time interval of 1 min, then repressurized with H<sub>2</sub> (50 bar) and remeasured at 50°C. The results are shown in Fig. 4.

The conversion of ruthenium(II)-modified hectorite **2** into the ruthenium(0)-modified hectorite **3** under hydrogen pressure also takes place under these conditions (water, 100 bar, 50°C), as the color change of the suspension from yellow to black indicates. Once ruthenium nanoparticles are present in the hectorite, the H/D exchange between molecular hydrogen and deuterated water becomes very rapid: The <sup>1</sup>H NMR signal of H<sub>2</sub> decreases, while the HDO and HD signals increase.



**Fig. 4.**  $^1H$  NMR spectra of a  $D_2O$  suspension of **2** under a  $H_2$  pressure of 100 bar at  $50^\circ C$ . Left-hand figure: Spectral evolution during the formation of **3**, showing the increase of the HDO signal (left) and the rapid decrease of the  $H_2$  signal (right) over a period of 10 min, the time interval being 1 min. Right-hand figure: Spectrum after repressurizing the sample with  $H_2$  (50 bar) at  $50^\circ C$ , showing the triplet signal of HD ( $J = 43$  Hz) besides the large (central) HDO signal.

## CONCLUSION

In conclusion, we have shown that a highly active and reusable benzene and toluene hydrogenation catalyst, formed by intercalation of  $[(C_6H_6)Ru(H_2O)_3]^{2+}$  cations into sodium hectorite followed by reaction with molecular hydrogen (50 bar,  $50^\circ C$ ), contains ruthenium(0) nanoparticles (9 to 18 nm) which are stabilized by the hectorite layers.

## ACKNOWLEDGMENTS

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