

Highly selective low-temperature hydrogenation of furfuryl alcohol to tetrahydrofurfuryl alcohol catalysed by hectorite-supported ruthenium nanoparticles

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ABSTRACT

Metallic ruthenium nanoparticles intercalated in hectorite (particle size ~4 nm) were found to catalyse the hydrogenation of furfuryl alcohol to give tetrahydrofurfuryl alcohol in methanolic solution under mild conditions. The best results were obtained at 40 °C under a hydrogen pressure of 20 bar (conversion 100%, selectivity >99%). After a total turnover number of 1423, the hectorite supported ruthenium nanoparticles are deactivated but can be recycled and regenerated.

Keywords

Ruthenium nanoparticles, Ruthenium-modified hectorite, Furfuryl alcohol hydrogenation

1. 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 [2–4]. 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 of aromatic compounds [8,9].

The hydrogenation of furfuryl alcohol (FA) to give tetrahydrofurfuryl alcohol (THFA) is of great importance [10–13], but little information is available in this regard. A brief literature survey shows that nickel-based catalysts (alloys or Raney-nickel, promoted or supported) are generally used for this reaction. With these catalysts, the yields are generally high, but the reaction is not very selective. Moreover, drastic pressure and temperature conditions are

required. Nobel metals (Pd, Pt and Rh) supported catalysts are less efficient than Ni-supported catalysts [14–19]. In this paper, we report ruthenium nanoparticles (~4 nm) intercalated in hectorite to be a highly efficient (conversion 100%, turnover number 1423) and highly selective (selectivity >99%) reusable catalyst for the hydrogenation of FA to give THFA under mild conditions (methanol solution, 40 °C, 20 bar H_2).

2. Experimental section

2.1. Syntheses

White sodium hectorite (**1**) was prepared according to the method of Bergk and Woldt [20]. The sodium cation exchange capacity, determined according to the method of Lagaly [21], 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 [22].

2.1.1. 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 °C. Then the yellow ruthenium(II)-containing hectorite **2** was filtered off and dried *in vacuo*.

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2.1.2. Preparation of the ruthenium(0)-containing hectorite **3**

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 different solvents and different volumes. After pressure release and cooling, **3** was isolated as a black material.

2.1.3. Regeneration of the ruthenium(0)-containing hectorite **3**

Regenerated ruthenium(0)-containing hectorite **3** was obtained by reacting a suspension of recycled ruthenium(0)-containing hectorite in a magnetically stirred stainless-steel autoclave (volume 100 mL) under a pressure of H₂ (50 bar) at 100 °C for 14 h using methanol (18 mL).

2.2. Catalysis

The selective hydrogenation of FA was carried out in a magnetically stirred stainless-steel autoclave. The air in the autoclave was displaced by purging three times with hydrogen prior to use. The experiments were carried out at different operating conditions. Quantitative chemical analysis of hydrogenation products was done by ¹H NMR spectroscopy in CDCl₃ using Bruker® DRX-400 MHz spectrometer and by GC-MS analysis. The GC separation was carried out on a ZB-5MS column (30 m x 0.25 mm, 0.25 μm) using a temperature program of 25–200 °C at 5 °C/min. The instrument used was a ThermoFinnigan® Trace GC-Polaris Q. The data was collected by using extracted ion chromatograms of marker m/z values for each molecule from the total ion chromatograms (TIC).

2.2.1. Catalytic hydrogenation of FA with freshly prepared **3**

A freshly prepared suspension (10 mL) of the ruthenium(0)-containing hectorite **3** in the appropriate solvent was introduced into 100 mL stainless-steel autoclave and 1.0 mL of FA was added. After pressurizing with hydrogen (15–30 bar), the autoclave was subjected to rigorous stirring at 40–60 °C. After 2 h, the pressure was released, and the autoclave was cooled in an ice-bath. Then the solution was decanted from the solid and analyzed.

In order to determine the catalytic productivity and selectivity, a freshly prepared suspension of ruthenium(0)-containing hectorite **3** in methanol (18 mL) was used, 0.2 mL of FA was added, pressurized with hydrogen (20 bar) and subjected to rigorous stirring at 40 °C. After 1 h, pressure was released, and the autoclave was cooled in an ice-bath. Then a sample was taken, filtered and analyzed. The turnover number was determined by adding 0.2 mL of FA after regular intervals (1 h) until the catalyst became inactive, the total volume of substrate added being 2 mL. The selectivity was checked by GC-MS.

The same catalytic procedure was followed for the recycled and regenerated ruthenium(0)-containing hectorite **3**.

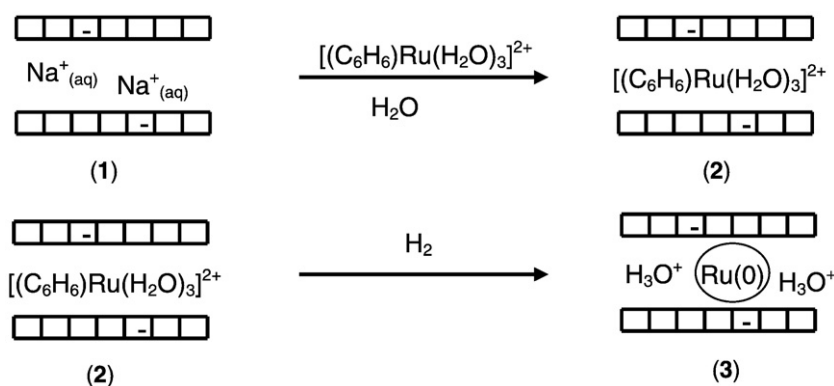
3. Results and discussion

Synthetic sodium hectorite (**1**) is a white solid of the general formula Mg_{5.5}Li_{0.5}Si₈O₂₀(OH)₄Na · n H₂O which contains Na⁺ cations in the interlaminar space. These 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 a mixture of mononuclear benzene ruthenium complexes being in equilibrium [23]. The dication [(C₆H₆)Ru(H₂O)₃]²⁺, which has been isolated as the sulfate and structurally characterized [24], 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 [(C₆H₆)RuCl₂]₂ in water after adjusting the pH to 8 by NaOH is added to white sodium hectorite (**1**), the main hydrolysis product [(C₆H₆)Ru(H₂O)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 methanolic solution of **2** under hydrogen pressure (50 bar) at 100 °C by reduction of [(C₆H₆)Ru(H₂O)₃]²⁺ to give the black ruthenium(0)-modified hectorite **3** (Scheme 1).

The ruthenium loading of the black hectorite **3** was assumed to be 3.2 wt% [6], based upon the molar ratio of [(C₆H₆)Ru(H₂O)₃]²⁺ used (corresponding to 75% of the experimentally determined [21] cation exchange capacity of **1**), and the presence of metallic ruthenium was proven by its typical reflections in the X-ray diffraction pattern. The size distribution of the ruthenium(0) nanoparticles in **3** was studied by a Philips CM 200 transmission electron microscope operating at 200 kV and the "ImageJ" software [25] was used for image processing and analysis. The mean particle size of ruthenium(0) nanoparticles in **3** was found to be ~4 nm having σ > 25% of the mean particle size (Fig. 1).

Ruthenium nanoparticles intercalated in hectorite are highly active and selective hydrogenation catalysts: Ruthenium(0)-containing hectorite **3** efficiently reduces FA to give THFA under mild conditions, the formation of the usual side-product 2,5-bis(trimethyleneoxy)-1,4-dioxane being avoided.

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 FA hydrogenation. The effects of various factors on the course of FA hydrogenation were evaluated in order to determine suitable conditions for maximum FA conversion and highest possible selectivity towards THFA. The catalytic reaction was studied using different polar solvents: In acetonitrile, chloroform, dioxane and



Scheme 1. Ion exchange of Na⁺ cations in sodium hectorite **1** (white) against [(C₆H₆)Ru(H₂O)₃]²⁺ cations to give ruthenium(II)-modified hectorite **2** (yellow) and reduction of [(C₆H₆)Ru(H₂O)₃]²⁺ in **2** by molecular hydrogen gives ruthenium nanoparticles in the ruthenium(0)-containing hectorite **3**.

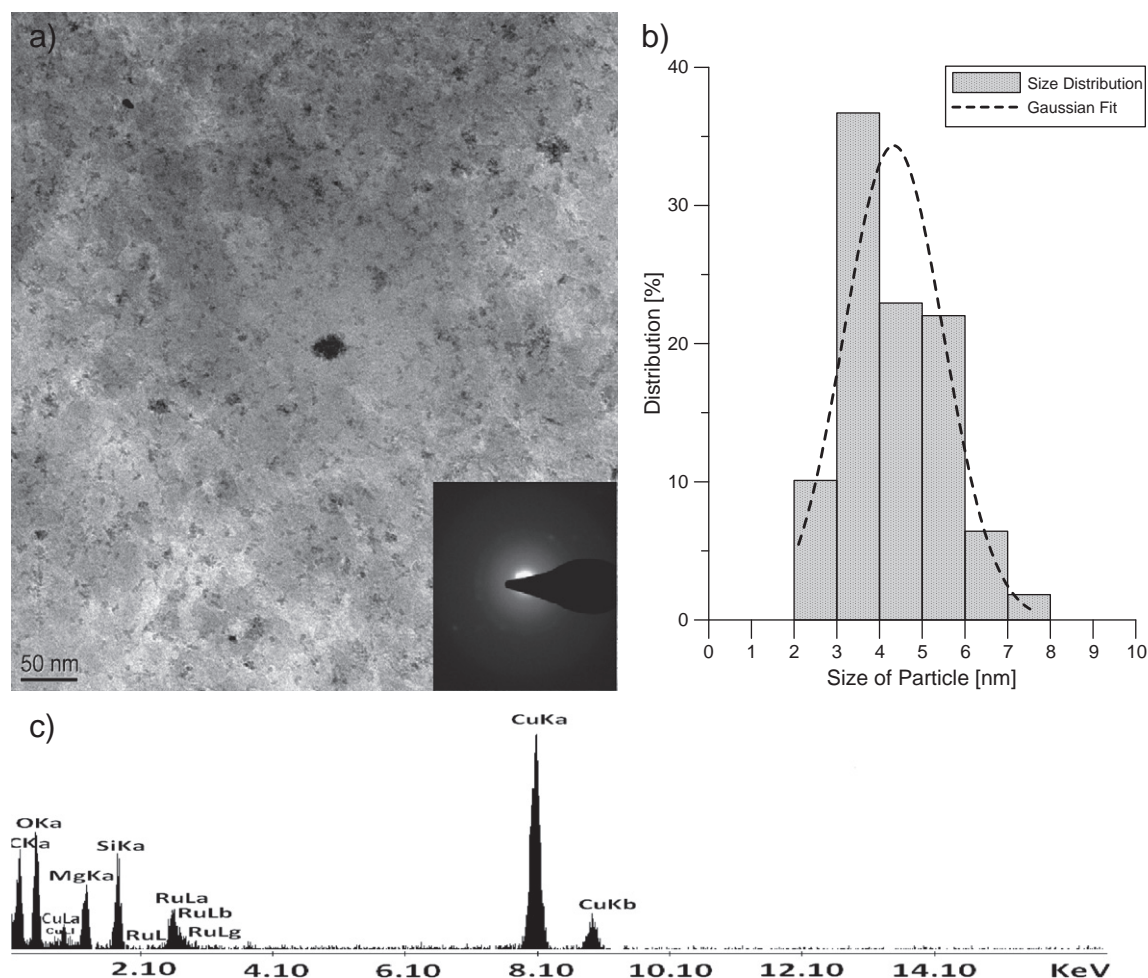


Fig. 1. TEM micrograph with SAED (a) histogram (b) and EDS analysis (c) of ruthenium(0) nanoparticles in **3**.

tetrahydrofuran, the catalyst is almost inactive, but alcoholic solvents give high conversion, the best solvent being methanol (optimal volume 18 mL). The catalytic reaction was also studied under various hydrogen pressures (15–30 bar) and at various temperatures (40–60 °C), the best conditions being 40 °C and 20 bar.

The hydrogenation of FA was done by using **3**, obtained by reduction of **2** in methanol (18 mL) under a pressure of hydrogen (50 bar) at 100 °C for 14 h. GC-MS analysis shows complete conversion of FA (100%) into THFA. The commercial production of THFA by the hydrogenation of FA over Ni-based catalysts usually results in the formation of a number of by-products attributable to hydrogenolysis [26] or hydrolytic ring cleavage [27]. In practice, these are separated by fractional distillation, being recovered as a low-boiling fore-run and a high-boiling residue. Formation of by-products such as 2,5-bis(trimethyleneoxy)-1,4-dioxane, is a common problem during catalytic FA hydrogenation [28]. However, these side-reactions do not occur during the catalytic hydrogenation of FA over **3**, and only the traces of 1,2-pentandiol was observed. The overall selectivity of **3** towards THFA was >99% presumably due to mild reaction conditions. The turnover number was determined by adding 0.2 mL of FA after regular intervals (1 h), until the catalyst became almost inactive, the total volume of substrate added being 2 mL (Table 1).

Once the ruthenium nanoparticles became inactive, the ruthenium(0)-hectorite **3** was recycled by washing three times with methanol (18 mL) (Fig. 2). The recycled ruthenium(0)-hectorite **3** regained their activity by transforming FA into THFA selectively (selectivity upto 100%). However, the reaction takes longer using recycled nanoparticles (see Table 2).

Table 1

Furfuryl alcohol hydrogenation using Ru(0)-hectorite **3** in methanol by adding fresh substrate each hour.

Cat. Run	FA Conversion (%)	Time (h)	TON	THFA Selectivity (%)
1	100	1	144	100
2	100	1	142	98.7
3	100	1	143	99.6
4	100	1	144	99.8
5	100	1	144	99.8
6	100	1	144	99.9
7	100	1	142	98.9
8	100	1	142	98.6
9	94.8	1	136	99.3
10	100	2	142	98.7

It was also observed that the presence of air during the catalytic reaction results in a loss of activity and selectivity. But this inactive catalyst can be regenerated by reacting the thoroughly washed suspension of recycled ruthenium(0)-hectorite **3** in a magnetically stirred stainless-steel autoclave (volume 100 mL) with H₂ (50 bar) at 100 °C for

Table 2

Furfuryl alcohol hydrogenation using recycled Ru(0)-hectorite **3**.

Cat. Run	FA Conversion (%)	Time (h)	TON	THFA Selectivity (%)
1	100	2	142	98.7
2	100	2	144	100
3	100	2	144	100

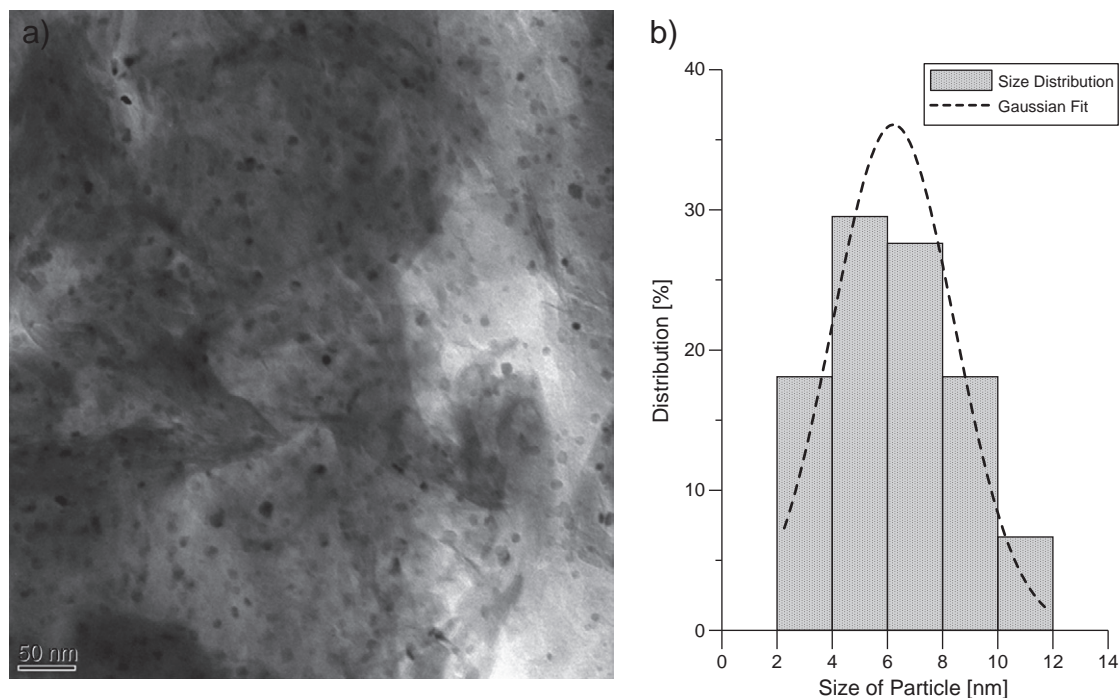


Fig. 2. TEM micrograph (a) histogram (b) of recycled ruthenium(0) nanoparticles in **3**.

14 h in methanol (18 mL). This regenerated ruthenium(0)-containing hectorite **3** was also able to selectively produce THFA with a selectivity upto 100%.

4. Conclusion

Ruthenium nanoparticles intercalated in hectorite are found to efficiently catalyze the hydrogenation of FA at low temperatures. The best results were obtained at 40 °C under a hydrogen pressure of 20 bar (conversion 100%, selectivity >99%, TON = 1423). Hectorite-supported ruthenium nanoparticles can be recycled and regenerated.

Acknowledgements

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