Ruthenium Nanoparticles Intercalated in Montmorillonite (nano-Ru@MMT) Is Highly Efficient Catalyst for the Selective Hydrogenation of 2-Furaldehyde in Benign Aqueous Medium

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Abstract: Chemoselective hydrogenation of 2-furaldehyde to furfuryl alcohol using green solvents is an important research area to get eco-friendly fuels and fine chemicals. Herein, we report ruthenium nanoparticles (~1.8 nm) intercalated in montmorillonite as an efficient catalytic system, which can selectively hydrogenate 2-furaldehyde in a benign aqueous medium. The complete conversion was observed at 40 °C with 1 MPa H₂, the selectivity of furfuryl alcohol being >99%, and turnover number 1165. After a catalytic run, the montmorillonite-supported ruthenium nanoparticles can be recycled and reused without losing their activity and selectivity.

Keywords: 2-furaldehyde; furfural; furfuryl alcohol; biomass valorization; hydrogenation; ruthenium nanoparticles; green solvent; eco-friendly fuels; smectite; montmorillonite

1. Introduction

Hydrogenation of biomass-derived chemicals is considered an important route towards renewable energy resources [1,2]. Among bio-mass derived organics, 2-furaldehyde is a versatile source of many fine chemicals. Its hydrogenated product—furfuryl alcohol—is a key synthetic intermediate and feedstock for the manufacture of lysine, ascorbic acid, lubricants, corrosion-resistant fiberglass, thermostatic resins, acid proof bricks, and it is also being used in the polymer industry [1,3–5]. Thus, selective hydrogenation of 2-furaldehyde to furfuryl alcohol using environment-friendly solvents, such as water, is a fascinating area of research to fulfill the increasing demand for eco-friendly fuels and fine chemicals [6]. Using water as a solvent is also more consistent with “Green Chemistry” objectives. It is therefore important to develop a catalyst capable of converting 2-furaldehyde to furfuryl alcohol under mild conditions in a benign aqueous medium. A brief literature survey...
reveals that metallic ruthenium nanoparticles have the potential to selectively hydrogenate aldehydes and ketones into their respective alcohols [7]. Yuan et al. showed that 2-furaldehyde can be converted into furfuryl alcohol using the ruthenium nanoparticles (conversion 100%, selectivity 95%) [8]. Similarly, Chen et al. achieved this hydrogenation by employing ruthenium nanoparticles under mild conditions (water, 0.5 MPa H₂, 25 °C), although catalyst selectivity was moderate [9]. Graphene oxide supported ruthenium nanoparticles (Ru/rGO) were shown to yield 91% furfuryl alcohol in water (1 MPa H₂, 20 °C) [10]. Likewise, Yuan et al. found 94.9% furfuryl alcohol selectivity over ruthenium nanoparticles supported on a zirconium-based metal-organic framework (water, 0.5 MPa H₂, 20 °C) [8]. However, ruthenium nanoparticles supported on a metal-organic framework having an aromatic linker (Al-MIL-53-BDC) could completely convert 2-furaldehyde to furfuryl alcohol under these conditions [11]. Similarly, G. Bagnato et al. reported a novel ruthenium-polyethersulfone type catalytic membrane (Ru/Ph₂P(CH₂)₄PPh₂), which could selectively produce furfuryl alcohol at 140 °C [12]. To sum up the ruthenium-based catalysts, neutral supports seem preferable for the production of furfuryl alcohol under mild reaction conditions in water. Kyriakou, G. and co-workers developed a platinum-based catalyst involving different oxide supports, such as MgO, Al₂O₃, ZnO, SiO₂, and CeO₂. Furfural hydrogenation was found to be sensitive toward platinum nanoparticle size and solvent choice. Their catalyst showed high activity and selectivity in alcohols. Non-polar solvents offered poor conversions and favored many side products [13]. Trimetallic Cu-Fe-Al-containing catalyst had an overall furfuryl alcohol yield of 97% in isopropyl alcohol at 100 °C and 6.0 MPa hydrogen pressure [14]. Gómez et al. prepared copper containing a heterogeneous catalyst using clay minerals (bentonite and sepiolite). 2-Furaldehyde conversion up to 83% was observed for Cu-Bentonite catalyst [15]. Overall, a number of catalysts have been reported in the literature for selective hydrogenation of 2-furaldehyde including Ni, Pt, Pd, Cu, Ru, Pd-Au, Pt-Sn, Cu-Ca, Cu-Fe-Al on various metallic, bimetallic, and amorphous supports [1,3–5,16–18]. However, commercial production of furfuryl alcohol is mainly achieved with copper chromate catalysts. Nevertheless, drastic temperature conditions (>100 °C) are employed, which results in the formation of bi-products mainly due to hydrogenolysis [19]. Although copper chromate exhibits high selectivity and activity, its application is limited due to high Cr(VI) toxicity and serious environmental concerns [3]. Thus, it is highly desirable to develop an environment-friendly catalyst with high activity and selectivity.

In heterogeneous catalysis, montmorillonite (MMT) is one of the most intensively explored catalytic materials [20]. This clay, as catalyst support, shows great potential in the design of green hydrogenation catalyst. Montmorillonite is dioctahedral smectite with an ideal unit cell formula of Na₀.₄(Al₁₃S₄Mg₀₄)Si₄O₁₀(OH)₂. It’s 2:1 phyllosilicate, in which an octahedral sheet of alumina is sandwiched between two tetrahedral silicate layers [21]. Interlamellar space usually contains exchangeable sodium cations (see Figure 1). Water-soluble organometallic cations, such as arene ruthenium complexes can easily intercalate the interlamellar space of smectite clays by replacing these sodium cations in an aqueous medium.
For hydrogenation reactions, ruthenium is considered a promising catalytic material. However, designing a selective catalyst necessitates a suitable metal precursor, which plays a crucial role in size, morphology, and individual molecular behavior on the surface of nanoparticles [23]. Nanoparticles with controllable chemical and physical properties can conveniently be obtained by employing suitable organometallic precursors [24]. We have previously shown that the selectivity during catalytic hydrogenation reactions can be conveniently controlled with nano ruthenium, which was obtained from arene ruthenium complexes devoid of interfering chloride ions [21,25–31]. In this work, dicationic aqua complex \([\text{Me(C}_6\text{H}_4\text{Pr}^+\text{Ru(H}_2\text{O})_3]^{2+}\) was used as a precursor to avoid the presence of contaminants on the surface of nanoparticles. Herein, we report a highly efficient catalyst (conversion 100%, selectivity >99%, turnover number (TON) 1165) containing montmorillonite-supported ruthenium nanoparticles (~1.8 nm), which can hydrogenate 2-furaldehyde into furfuryl alcohol under mild conditions (1 MPa \(\text{H}_2\), 40 °C) in a benign aqueous medium.

2. Results and Discussion

When dimeric ruthenium complex \([\text{Me(C}_6\text{H}_4\text{Pr}^+\text{RuCl}_2]^{2+}\) is dissolved in water, the solution contains three complexes \([\text{Me(C}_6\text{H}_4\text{Pr}^+\text{RuCl}_2\text{H}_2\text{O}])], [\text{Me(C}_6\text{H}_4\text{Pr}^+\text{Ru(H}_2\text{O})_3]^{2+}, and [\text{Me(C}_6\text{H}_4\text{Pr}^+\text{RuCl(H}_2\text{O})_2]^{+}\) in equilibrium (Scheme 1). However, this equilibrium can be shifted towards dicatonic aqua complex \([\text{Me(C}_6\text{H}_4\text{Pr}^+\text{Ru(H}_2\text{O})_3]^{2+}\) over a pH range of 5–8, just like in the case of dimeric benzene ruthenium complex \([\text{C}_6\text{H}_6\text{Pr}^+\text{RuCl}_2]^{2+}\) [32].

![Figure 1. Structural model of sodium montmorillonite Na0.4(Al1.6Mg0.4)Si4O10(OH)2 showing exchangeable cations and water molecules in the interlamellar space [22].](image)

Scheme 1. Hydrolysis of dimeric ruthenium complex \([\text{Me(C}_6\text{H}_4\text{Pr}^+\text{RuCl}_2]^{2+}\) in water gives a mixture of aqua complexes, the dicatonic tri aqua complex \([\text{Me(C}_6\text{H}_4\text{Pr}^+\text{Ru(H}_2\text{O})_3]^{2+}\) being the major product.
When the yellow aqueous solution of \([\text{Me}(\text{C}_6\text{H}_4)\text{Pr}^+\text{Ru}_2\text{Cl}_4]\), predominantly containing \([\text{Me}(\text{C}_6\text{H}_4)\text{Pr}^+\text{Ru}(\text{H}_2\text{O})_3]^{2+}\) after pH adjustment to 8, is added to sodium montmorillonite (1), the dicationic aqua complex \([\text{Me}(\text{C}_6\text{H}_4)\text{Pr}^+\text{Ru}(\text{H}_2\text{O})_3]^{2+}\) intercalates the lamellae of 1 by ion-exchange with sodium cations giving the yellow Ru(II)-modified montmorillonite 2. Reduction of the dicaticonic aqua complex in 2 with hydrogen (10 bar) at 100 °C in ethanol affords black Ru(0)-modified montmorillonite 3 (Scheme 2).

Scheme 2. Na\(^+\) cations exchange in montmorillonite 1 (white) against \([\text{Me}(\text{C}_6\text{H}_4)\text{Pr}^+\text{Ru}(\text{H}_2\text{O})_3]^{2+}\) cations to give Ru(II)-modified montmorillonite 2 (yellow) and reduction of \([\text{Me}(\text{C}_6\text{H}_4)\text{Pr}^+\text{Ru}(\text{H}_2\text{O})_3]^{2+}\) in 2 by hydrogen gives Ru(0)-containing montmorillonite 3.

BET surface area of 3, determined by low-temperature nitrogen adsorption, was 38.60 m\(^2\) g\(^{-1}\) whereas the average pore diameter was 75 Å (Figure 2). Ruthenium loading in 3 (3.0 wt.%) was calculated from the molar ratio of \([\text{Me}(\text{C}_6\text{H}_4)\text{Pr}^+\text{Ru}(\text{H}_2\text{O})_3]^{2+}\) used, which corresponds to 75 percent CEC of 1. Ruthenium loading determined by ICP-MS was found to be in agreement with the calculated value. A transmission electron microscope (TEM) was used to determine the overall size distribution of nanoparticles in Ru(0)-modified montmorillonite 3. To calculate the particle size in TEM micrographs, 250 particles were chosen. Selected area electron diffraction (SAED) ascertained the crystalline nature of these nanoparticles. TEM micrographs were processed with “ImageJ” software, which revealed the nanoparticles having an average size of 1.8 nm with a standard deviation (σ) being less than 25%. Scanning electron microscope (SEM) was used to study the catalyst morphology and SEM coupled energy-dispersive X-ray spectroscopy (EDXS) confirmed the presence of ruthenium in 3. X-ray powder diffraction (XRD) pattern comparison of Ru(0)-containing montmorillonite 3 with that of unmodified montmorillonite 1 is shown in Figure 2, the high basal spacing value (d001 = 17.1 Å) of 3 can be related to the expansion of interlaminar space due to ethanol.
Montmorillonite intercalated ruthenium nanoparticles 3 demonstrate high selectivity and high activity for the hydrogenation of 2-furaldehyde. However, catalyst activity is highly dependent on the way Ru(0)-montmorillonite 3 is prepared. When the catalyst is prepared by reducing Ru(II)-montmorillonite 2 in water (1 MPa H₂, 100 °C), the resulting catalyst 3 shows poor activity. TEM micrographs revealed the presence of ruthenium nanoparticles with an average size of 12 nm (see Figure 3). Conversely, the reduction of 2 in ethanol (1 MPa H₂, 100 °C) affords 3, which demonstrates high activity and selectivity for the hydrogenation of 2-furaldehyde in water. This catalyst affords furfuryl alcohol selectively under suitable mild conditions while avoiding the formation of side products. Now TEM analysis indicates the existence of smaller-sized (1.8 nm) Ru(0)-nanoparticles in montmorillonite, which leads us to the conclusion that 2-furaldehyde conversion and furfuryl alcohol selectivity is mainly dependent on the size of ruthenium nanoparticles. Moreover, previous literature suggests that an aromatic π cloud can act as an H-bond acceptor [33,34]. A clear manifestation of the H-bond formation with π-electrons was previously reported by Suzuki et al., wherein they observed 1:1 clusters of benzene with water [35]. Therefore, we can safely assume that the high furfuryl alcohol selectivity may be due to H-a bond formation between water molecules and the π-electrons from the furan ring of 2-furaldehyde, which hampers the adsorption of this aromatic ring on the surface of the catalyst. The carbonyl oxygen atom would be likely to coordinate to the ruthenium surface and would thus receive the hydrogen atoms already present at the surface of the nanoparticle, thus yielding furfuryl alcohol almost exclusively in water.

Catalytic hydrogenation of 2-furaldehyde was also studied in other green solvents such as ethanol, methanol, tetrahydrofuran, and acetonitrile. However, furfuryl alcohol selectivity was inferior although Ru(0)-montmorillonite 3 was prepared in ethanol. Catalyst 3 demonstrated optimal performance at 40 °C in water. At lower temperatures, relatively poor conversion of 2-furaldehyde was observed, whereas the catalyst selectivity suffered at higher temperatures. Montmorillonite 1 was also tested on its own (after activation under exactly the same conditions) and found no conversion of furfural into furfuryl alcohol. Similarly, furfural hydrogenation without a catalyst did not proceed at all, since no substrate conversion was observed. Commercial production of furfuryl alcohol is achieved in gas-phase using Cu-based catalysts at higher temperatures (>100 °C), which results in hydrogenolysis reactions leading to the formation of bi-products [3]. However, hydrogenation of 2-furaldehyde with Ru(0)-montmorillonite 3 occurs at a mild temperature (40 °C), which affords furfuryl alcohol selectively (>99%). In order to determine the turnover number, 25 µL of 2-furaldehyde was added at regular intervals (12 h), until the catalyst lost its activity. The total volume of the substrate used was 125 µL (Table 1).
Fig. 3. TEM micrographs with nanoparticle size distribution histograms (inset): Ru(0)-montmorillonite prepared in water (B); and in ethanol (A).

Table 1. Hydrogenation of 2-furaldehyde in water at 40 °C using Ru(0)-containing montmorillonite.

| Cat. Run | 2-Furaldehyde Conversion (%) | Time (h) | TON  | Furfuryl Alcohol Selectivity (%) | Carbon Balance (%) |
|----------|------------------------------|----------|------|----------------------------------|--------------------|
| 1        | 100                          | 12       | 203  | >99                              | 99                 |
| 2        | 100                          | 12       | 203  | >99                              | 99                 |
| 3        | 100                          | 12       | 201  | >98                              | 98                 |
| 4        | 100                          | 12       | 201  | >98                              | 98                 |
| 5        | 100                          | 12       | 203  | >99                              | 99                 |
| 6        | 76                           | 12       | 154  | >99                              | 76                 |

Ru(0)-hectorite was regenerated by ethanol washing (1 mL, 3×) followed by its activation. The regenerated Ru(0)-hectorite could selectively transform 2-furaldehyde into furfuryl alcohol. However, the reaction takes a longer time with recycled nanoparticles. Ruthenium leaching was determined by combining the washings of six consecutive runs followed by their analysis via ICP-MS. No correction was applied since the interfering iron peak was not observed. Overall, less than 1% leaching was observed with respect to original ruthenium loading. Transmission electron microscopy of the catalyst after five runs shows an overall increase in the size of ruthenium nanoparticles (2.4 ± 0.49 nm, Fig. S3). The possible reason for catalyst deactivation can tentatively be attributed to the reduction in surface to volume ratio of nanoparticles. Moreover, slight leaching during each run may also have contributed to the catalyst deactivation.

3. Experimental Section
3.1. Syntheses

Sodium montmorillonite (1) was prepared according to the Reinholdt method [36]. By following the Lagaly method [37], cation exchange capacity (CEC) determined was 1.21 mEq g⁻¹. The dimeric complex [Me(C₆H₄Pr)₃Ru₂Cl₄] was prepared according to a procedure reported by Smith and co-workers [38].
3.1.1. Preparation of the Ru(II)-Containing Montmorillonite \(2\)

A clear yellow solution was obtained by dissolving \([\text{Me}(C_6H_4)Pr^3]_2\text{Ru}_2\text{Cl}_4\) (91 mg, 0.15 mmol) in argon-saturated de-ionized water. After rigorous 1 h stirring, a pH of the solution was adjusted to 8 with sodium hydroxide (0.1 N). The filtered solution was then poured into 1 g of degassed sodium montmorillonite \(1\). For the next 6 h, the suspension was stirred at 20 °C to give Ru(II)-containing montmorillonite \(2\), which was then filtered off and dried in vacuo.

3.1.2. Preparation of the Ru(0)-Containing Montmorillonite \(3\)

In a stainless-steel autoclave, a suspension of the yellow Ru(II)-containing montmorillonite \(2\) (5 mg, 0.00148 mmol Ru) in absolute ethanol (1 mL) was stirred magnetically at 100 °C under 1 MPa hydrogen pressure for 15 h. After cooling and pressure release, Ru(0)-containing montmorillonite \(3\) was obtained as a black material. Standard Schlenk technique was employed to remove ethanol under an inert atmosphere followed by the addition of de-ionized and degassed water (1 mL). The catalyst \(3\) was then activated for 15 h under 1 MPa hydrogen pressure.

3.2. Catalysis

In a stainless-steel autoclave, 2-furaldehyde (25 µL) was introduced to a suspension (1 mL) of Ru(0)-containing montmorillonite \(3\). At 40 °C, a constant hydrogen pressure (1 MPa) was maintained with intensive stirring for 12 h. Then, after releasing pressure, the catalyst activity and product selectivity was analyzed. In order to determine the turnover number, 2-furaldehyde (25 µL) was added at regular intervals until the catalyst lost its activity. For the recycled and regenerated Ru(0)-containing montmorillonite \(3\), this same catalytic procedure was followed.

3.3. Analysis

An Agilent 1260 series Ultra Performance LC system with the column ZORBAX SB-C18 (4.6 × 150 mm, 5 µm), both obtained from Agilent (Santa Clara, CA, USA), was used for the analysis of samples. The mobile phase comprised MeOH (A) and water (B), by using the following general solvent gradient system: 5–95% A from 0 to 20 min, 95% A from 20 min to 25 min, followed by 5% A from 25.1 min to 30 min. The flow rate was set at 1.0 mL min\(^{-1}\), and the column temperature was maintained at 25 °C. Quantitative ruthenium analysis in \(3\) and the catalyst leaching was determined by using Agilent 7700x type inductively coupled plasma mass spectrometry (ICP-MS).

4. Conclusions

Montmorillonite supported ruthenium nanoparticles were found to efficiently catalyze the hydrogenation of 2-furaldehyde in a benign aqueous medium. The best results were achieved under 1 MPa hydrogen pressure at 40 °C (conversion 100%, selectivity >99%, TON = 1165). These nanoparticles are recyclable and reusable.

Supplementary Materials: The following are available online at https://www.mdpi.com/2073-4344/11/1/66/s1, Figure S1: SEM micrographs showing the morphology of Ru(0)-montmorillonite \(3\) prepared in ethanol, Figure S2: SEM micrographs showing the morphology of Ru(0)-montmorillonite \(3\) prepared in water, Figure S3: TEM micrographs of Ru(0)-montmorillonite \(3\) after the deactivation, Table S1: Amount of ruthenium confirmed by ICP-MS.

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