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Cellulose nanocrystals as non-innocent support to the synthesis of ruthenium nanoparticles and their application to arene hydrogenation

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Ru nanoparticles were synthesized from $RuCl_3$ under mild H_2 pressure within a suspension of cellulose nanocrystals. X-ray photoelectron spectroscopy and transmission electron microscopy revealed that the small Ru(0) nanoparticles (3.3 ± 1 nm) were deposited onto their cellulosic support. This hybrid proved to be a highliy efficient arene hydrogenation catalyst operational at 4 bars and room temperature.

The development of more sustainable synthetic methods to access nanoparticles is an active research field, stimulated by both the interest in the discovery of novel and functional nanomaterials and the ever growing impact of mankind on its environment.[1-4] In this context, biomass derived nanomaterials constitute an opportunity to reduce nanosynthesis footprint, but also to discover unexpected properties and enhanced applications.[5, 6] Cellulose Nanocrystals (CNCs) are easily obtained by strong acid hydrolysis of cellulose from plant or bacterial origin.[7-9] An industrial process provide access of this material at the ton scale from wood pulp. This material is renewable, biodegradable and non-toxic. [10] CNCs from wood pulp, used in this study, present themselves as high aspect ratio whiskers with well-defined size and morphology – 5 nm in width from 150 to 250 nm in length. They possess high specific surface area,[11] high crystalline order and chirality, superior mechanical strength, and controllable surface chemistry.[7-9] CNCs have thus been applied to a variety of fields, including the production of iridescent and birefringent films,[7] chiral templating of silica[12] and carbon [13] materials, reinforcing fillers in plastics and polymers,[7, 14 15-17] flocculants,[18] aerogels, [19] hydrogels,[20] and supercapacitors. [21]As CNCs form stable colloidal suspensions in water and feature a high specific surface area, they are attractive supports for various catalytically active nanoparticles (NPs)[22] including Pd,[23-26] Au,[27] and Ag.[28] Importantly, CNCs are non-innocent supports for metal NPs, as they act as reducers and control metal seeding. Additionally, they were recently shown to act as chiral inducers in the enantionselective Pd-catalyzed hydrogenation reaction of ketones.[6] With these ideas in mind, we envisaged to apply CNCs for the design of catalysts towards the challenging arene hydrogenation reaction.[29] Arene hydrogenation is of prime industrial importance. [30] For instance, benzene hydrogenation to dipic acid is an intermediate step in the production of nylon. Lately, the increased regulation[31, 32] on the aromatic content of fossil fuels has also triggered interest in more efficient catalytic hydrogenation of aromatics. Conventionally, arene hydrogenations are carried out at high temperatures (~120°C) and high H_2 pressures (~100 bars).[33, 34] Supported nanoparticles of Rh(0), Ir(0), Ru(0) and Pt(0) have opened avenues to achieve heterogeneous arene hydrogenations under milder conditions.[30, 35-39] The more prohibitive price of Rh, Ir and Pt has made Ru NPs a very appealing candidate for this reaction. Recently, ionic liquid stabilised Ru NPs have demonstrated their ability to hydrogenate arenes under conditions as mild as 4 bars of H_2 pressure and 75°C. [37, 40] Zahmakiran *et al.* and Favier *et al.* have achieved these hydrogenations at room temperatures and 3 bars H_2 pressure, where they use Ru nanoclusters stabilised by nanozeolite framework and 4-(3-phenylpropyl)pyridine respectively.[41, 42] Beyond the study of the catalytic properties of Ru NPs, novel and sustainable synthetic methods to access them have also been an active research field. To replace ruthenium chloride ($RuCl_3$),[41, 43-45] bis(methylallyl)(1,5-cyclooctadiene) ruthenium(II) [46-48] and Ru(1,5-cyclooctadiene)(cyclooctatriene) [45] have been used as precursors, as they do not lead to the generation of salt by-products upon reduction, and also they can be reduced under mild H_2 pressures. [49] They are however expensive, require synthetic skills to prepare and careful handling. RuO_2 was also used as a precursor compatible with H as a reductant. [37, 50] On the other end, typical $RuCl_3$ reduction relies on the use of $NaBH_4$ to afford the desired nanomaterial.[41, 43] $NaBH_4$ is a hazardous substance implying regulated handling and the boron species generated during this reaction may affect the Ru catalytic surface.[51] Recently our group showed that $RuCl_3$ could be effectively reduced and supported by Fe NPs to afford a magnetically recoverable transfer hydrogenation catalysts.[52]

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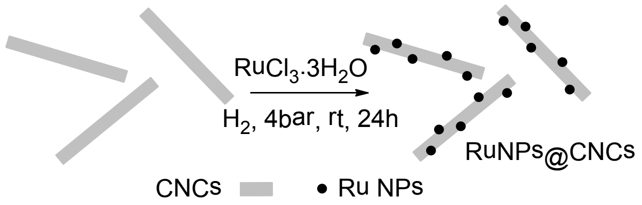
Interestingly, very few examples exist where $RuCl_3$ is effectively reduced by mild H_2 pressure. For instance, when cyclodextrins are used as stabilizers, this reactivity is enabled.[53, 54] We present herein a novel approach where CNCs promote the generation of Ru NPs from $RuCl_3$ using mild H_2 pressure as the reducing agens and effectively support the resulting NPs to afford RuNPs@CNCs composite. Subsequently, RuNPs@CNCs were shown to act as powerful arene hydrogenations catalysts under 4 bars H_2 pressure, at room temperature.



Scheme 1: Synthesis of RuNPs@CNCs

The synthesis of RuNPs@CNCs proceeded very easily by the addition of $RuCl_3$ to 20 ml 0.5% CNC (w/w) suspension in water. The resulting mixture, dark brown in colour, was subjected to 4 bars H_2 at room temperature for 24 hours (Scheme 1).

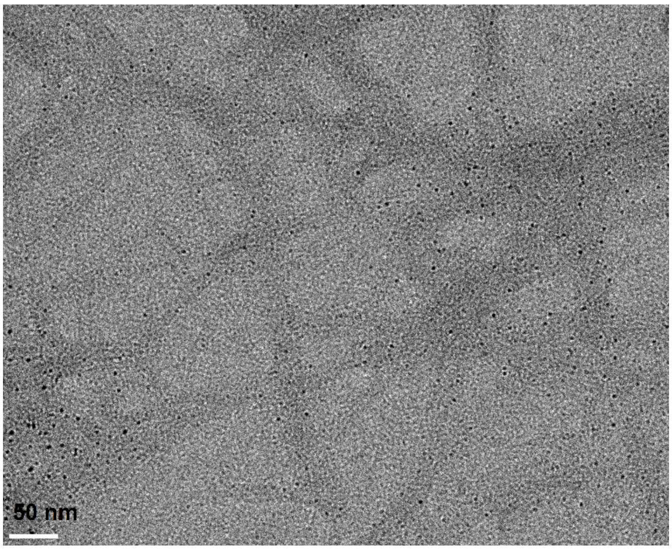
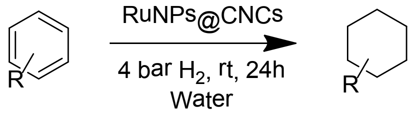


Fig. 1: TEM of unstained sample of RuNPs@CNCs. The inset shows the EDS confirming the presence of Ru.

In 24 hours, the complete reduction to Ru (0) was confirmed by both the black colour of the suspension and the XPS $3p_{3/2}$ peak at 461.27 eV (Figure S1 and S3). This suspension has a Ru content of 63 ppm. If stopped after 2 hours, the reduction was not complete and a light brown coloured solution was obtained, corresponding to Ru(II) species[55-57] (Figure S1). For comparison, this experiment was performed using $NaBH_4$ instead of H_2 as reducer, which also resulted in the reduction of Ru (III) to Ru (0) in 24 hours. The suspension colour was monitored over time and the following colours were observed in sequence: dark brown, light brown, light green and finally black, corresponding respectively to Ru (III), Ru (II), Ru (I) and Ru (0) (Figure S1). [55-57] When the reaction mixture was stirred at room temperature for over 72 hours, without the use of any external reducing agent, the colour of the suspension changed to light brown. This confirmed that the CNCs have the ability to reduce the Ru (III) partially to Ru (II) but no further.

Transmission electron microscopy (TEM) was performed to characterize the material. The imaging of CNC/metal hybrid material is a challenge, requiring conditions where both the organic CNCs and the denser metal are seen with good contrast.[58, 59] With RuNPs@CNCs, good images were acquired. CNCs were observed as low contrast whiskers, as reported before.[7-9, 58] The Ru NPs were present in conjunction with CNCs, revealing that they were deposited onto the CNC surface (Figure 1, S4). The Ru NPs, seen as darker spots onto the less dense CNCs, featured an average size of 3.3 ± 1 nm, a size where Ru is known to be catalytically active (Figure S5).[37] The TEM also concluded that the CNCs did not aggregate in the catalyst suspension and retain their high surface area and rod-like form. These results show that the CNCs are capable of facilitating the reduction of Ru (III) to Ru (0) in presence of H_2, as a mild reducing agent, at 4 bars and room temperature in water. Additionally this reaction affords a Ru NP-hybrid composite of CNC useful to sustain the catalytically active Ru under a reactive environment.



Scheme 2: Arene hydrogenation at 4 bars H_2 pressure, rt, 24h, in water, using RuNPs@CNCs as catalyst

Table 1: Optimisation of reaction conditions for toluene hydrogenation with RuNPs@CNCs (3mol% in Ru)

S. No.	Time (h)	Pressure (bars)	Temperature	Yield (%)
1.	2	20	100°C	100
2.	2	20	rt	16
3.	4	20	rt	40
4.	8	20	rt	91
5.	24	20	rt	100
6.	24	10	rt	100
7.	24	4	rt	100
8.	24	2	rt	11

RuNPs@CNCs, was thus tested for the catalytic hydrogenation of arenes (Scheme 2, Table 1). At first, we started with hydrogenation conditions used by Schwab *et al* at 20 bars H_2 pressure and 100°C.[40] After 2h, 100% conversion of toluene to methylcyclohexane was achieved (entry 1). The reaction was carried out in the water suspension of the catalyst, with no addition of any other solvent, allowing biphasic extraction for workup. In an attempt for using milder conditions, the same reaction was carried out at room temperature, instead of 100°C and only afforded a mere 16% conversion to methylcyclohexane (entry 2). At room temperature, 20 bars of H_2 pressure, the time of reaction was increased from 2 hours to 24 hours. After reaction, the products could be easily extracted out of the catalyst aqueous suspension. Aliquots of the reaction mixture were taken out at times 2h, 4h and 8h and analysed by GC-MS. Conversions ramped up to 91% at 8 hours and

24h afforded 100% conversions (entries 2-5). Next, H_2 pressure was reduced, at 24h and room temperature, to 10 bars, 4 bars and 2 bars, giving conversions of 100%, 100% and 11% respectively (entries 6-8). Therefore, the mildest reaction conditions providing complete conversion are 4 bars H_2, 24 h at room temperature in water. These reaction conditions are milder than the ones usually reported for the arene hydrogenations including ones based on Ru NPs stabilised by ionic liquids.[40, 47] Hence, CNCs are a powerful catalyst support for Ru NPs to achieve both easy synthesis and reactivity

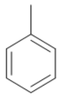
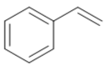
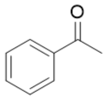
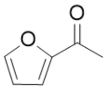
Substrate	 (1)	 (2)	 (3)	 (4)
Yield (%)	100	96	76	90

Table 2: Arene hydrogenations of different substrates using RuNPs@CNCs

In order to check the scope of the reaction, other aromatic substrates with varied substitutions were also hydrogenated at the optimised conditions (Table 2). Styrene (2) hydrogenation provided a 96% yield for completely hydrogenated product, ethylcyclohexane and 4% yield for partially hydrogenated product, ethylbenzene. Acetophenone (3) gave 76% of ethylcyclohexane, and the rest were a mixture of partially hydrogenated product (see ESI). Excellent results for a heterocyclic aromatic (4) were also observed, giving 90% yield for the completely hydrogenated product. After reaction, potential ruthenium leaching in the product was measured to be negligible (0.6 ppb) by inductively coupled plasma – mass spectroscopy (ICP-MS). The catalyst was checked for recyclability, and it was recyclable *via* biphasic separation for six cycles. After that the conversion rates dropped significantly (Figure S2). In addition, as a control experiment, when using just $RuCl_3.3H_2O$ for the reaction, no conversion was observed. To determine whether the catalysis was truly heterogeneous, a poisoning experiment using CS_2 was also performed. The addition of 0.5 equivalents of CS_2 to the reaction mixture made the catalyst totally ineffective under the reaction conditions used.

Conclusions

These results conclusively show that the role of CNCs as a non-innocent support for catalytically active NPs. In the synthesis of Ru NPs, the CNCs and H_2 gas synergistically achieve the reduction of Ru (III) to Ru (0) at just 4 bars and room temperature. Furthermore, the catalyst, RuNPs@CNCs was successfully applied to arene hydrogenations under mild conditions of 4 bars H_2, room temperature in water. The product is easily extracted in a biphasic system, and the catalysts can be recycled up to 6 times with no loss of activity. These reaction conditions are competitive with the best results in the field.

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