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ORIGINAL REPORT



Magnetically separable Ru-based nano-catalyst for the hydrogenation/hydro-deoxygenation of lignin-derived platform chemicals

S. Gyergyek^a, A. Kocjan^b, A. Bjelić^c, M. Grilc^c, B. Likozar^c and D. Makovec^a

^aDepartment for Materials Synthesis, Jožef Stefan Institute, Ljubljana, Slovenia; ^bDepartment for Nanostructured Materials, Jožef Stefan Institute, Ljubljana, Slovenia; ^cDepartment of Catalysis and Chemical Reaction Engineering, National Institute of Chemistry, Ljubljana, Slovenia

ABSTRACT

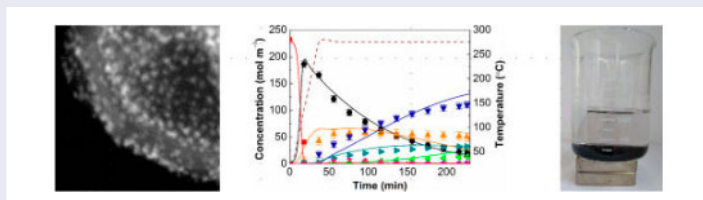
A facile and replicable stepwise chemical method was explored to synthesise magnetically separable Ru-based nanocatalyst. Structural investigation revealed that nanocatalyst is a hierarchical multi-phase nanocomposite, consisting of highly magnetic Fe₃C (and Fe) nanoparticles, distributed within a high-surface-area graphitic carbonaceous matrix, uniformly decorated with superiorly active catalytic ruthenium nanoparticles and clusters. The nanocatalyst showed an improved catalytic activity and selectivity for the hydro-deoxygenation of bio-resource-related compound eugenol when compared to the commercial Ru/C. In combination with ultrafast magnetic separation, it holds a good emerging potential in the valorisation of renewable resources and recycling of noble metals.

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Catalyst; ruthenium; biomass; microkinetic; magnetic separation



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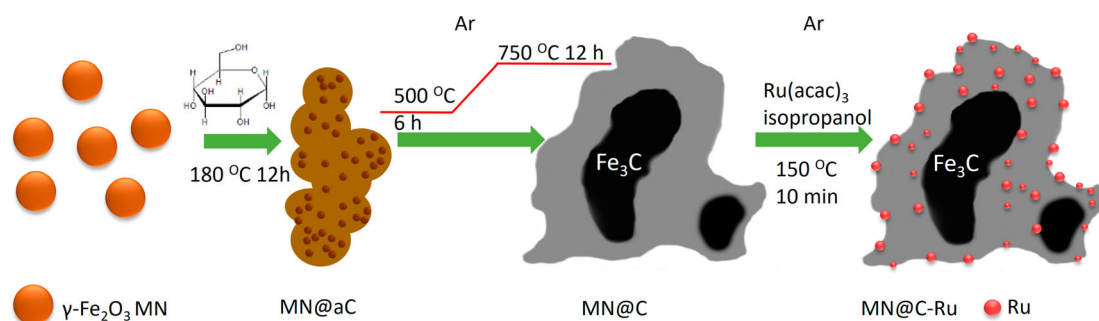
The well-designed magnetically separable Ru based nanocatalyst is synthesised using simple and scalable chemical method without using surfactants and toxic reagents, which demonstrate high catalytic activity and ultrafast magnetic separation.

The production of fuels and other valuable chemicals from biomass using a simple and energy-efficient process is a global challenge and an important objective being pursued by many. At the heart of the process is an efficient catalyst. Noble metal nanoparticles such as ruthenium (Ru) are widely used catalysts in numerous chemical processes. Metallic Ru is an especially efficient catalyst for the hydrogenation and transfer hydrogenation reactions involved in converting biomass or CO to important chemicals, such as liquid fuels, for example [1–6]. Among other factors, such as the catalyst particles' morphology and size, the nature of the support can have a significant influence on the catalyst's activity and selectivity. Many studies revealed that carbonaceous materials are a suitable support due to their non-reducibility and the electronic interactions between the support and the catalyst [7–12]. Usefully, carbon materials can be prepared from

various natural products, such as biomass and sugars [7,13,14]. Magnetic nanoparticles incorporated within the catalyst offer a major advantage over conventional catalytic materials because of their rapid and efficient separation. So-called magnetically recyclable or magnetically separable catalysts significantly shorten the tedious separation and offer the selective heating of the catalyst using AC-fields [4,15,16]. The most often used magnetic nanoparticles are iron-oxide nanoparticles. They are easily synthesised in large quantities and their properties can be tuned relatively easily [17–20]. However, their magnetisation is rather low. Elemental Fe nanoparticles display much larger magnetisation and were efficiently used in magnetic separation; however, they are prone to degradation through oxidation [21]. Fe carbides also exhibit a high magnetisation and are known to be much more stable against oxidation [22,23].

CONTACT S. Gyergyek ✉ saso.gyergyek@ijs.si Department for Materials Synthesis, Jožef Stefan Institute, Jamova 39, Ljubljana SI-1000, Slovenia.

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Scheme 1. Schematic illustration for the preparation of the nanocatalyst.

Herein, we present a simple and versatile synthetic chemical route for the preparation of a magnetically separable nanocatalyst that is remarkably active for the hydro-deoxygenation (HDO) of a representative lignin monomer model compound eugenol.

The nanocatalyst was synthesised in a three-step method, shown in Scheme 1 and described in detail in the ESM. In the first step, the precursor particles MN@aC were synthesised using the hydrothermal carbonisation of glucose dissolved in an aqueous colloidal suspension of citric-acid-coated magnetic iron-oxide nanoparticles. The 100–300 nm-sized MN@aC particles contained the iron-oxide nanoparticles (~ 10 nm in size), homogeneously dispersed in an amorphous carbonaceous matrix (TEM image Figure S1 in the ESM). Raman and DRIFT spectroscopies (Figures S2 in the ESM) showed that the carbonaceous matter contained predominantly sp^3 hybridised C species and was rich in O-bearing functional groups, respectively. In the second step, the nanocatalyst support MN@C was prepared by annealing the MN@aC precursor particles in an Ar atmosphere (Scheme 1). The DRIFT and Raman spectroscopies (Figures S2 and S3 in the ESM) suggested that the organic part transformed to carbonaceous matter, predominantly composed of nanocrystalline graphite with a high content of defects; however, elucidating the detailed chemical structure is not part of the present work.

During annealing in an inert atmosphere the iron-oxide nanoparticles were reduced. A quantitative phase analysis based on a Rietveld refinement of the XRD pattern (Figure S4 in the ESM) showed that the MN@C is composed of cohenite Fe_3C (50.7 wt.%) and graphite (30.3 wt.%) as the main phases, and BCC Fe (10.7 wt.%) and cubic spinel iron oxide (8.3 wt.%) as the minor phases (See ESM). The in-situ formed C and CO, the high temperature, and the inert atmosphere reduced the iron oxide to the metallic Fe, which reacted with the C to form the cohenite phase. The SEM analysis showed that the MN@C is in the form of irregularly shaped particle agglomerates of several microns in size

(Figure 1(a)). An individual agglomerate is composed of interconnected, sub-micron-sized, rough particles, full of edges, steps and bulges (Figures 1(b)). The STEM analysis (Figure 1(c,d)) further revealed a highly irregular shape that is reflected in a relatively large BET surface area of $74 \text{ m}^2 \text{ g}^{-1}$ (see the ESM and Figure S5 in the ESM). The nitrogen-sorption analysis showed that the nanocatalyst support is porous, with a mesopore volume of $0.236 \text{ cm}^3 \text{ g}^{-1}$ and a monomodal pore size distribution centred at 3.9 nm. The homogeneous distribution of the magnetic nanoparticles (20–100 nm in size) within the carbonaceous matrix is clearly visible in the HAADF STEM images (Figure 1(d) and Figure 2(b)) and in the corresponding EDXS elemental mappings (Figure 2(c,d)). The EELS spectroscopy of the carbonaceous matrix in the STEM further supports the graphitic nature of the carbonaceous matrix (See ESM and Figure S6 in the ESM). In the final, third step of the MN@C-Ru nanocatalyst synthesis, the Ru nanoparticles were deposited on the MN@C by a simple solvothermal reduction of the Ru^{3+} using isopropanol, which is a nontoxic solvent (5 wt.% Ru basis). Good dispersibility of the MN@C in the isopropanol, its large surface area, combined with the well-tuned reaction conditions, strongly favoured the heterogeneous nucleation of the Ru nanoparticles at the nanocatalyst support surfaces in an exceptionally homogeneous manner (Figures 1(e,f) and 2). The size distribution of Ru nanoparticles was narrow, with an average diameter $d = 1.5 \text{ nm} \pm 0.4 \text{ nm}$ (Figure S7 in the ESM). Free Ru nanoparticles, not attached to the support, were never observed in the sample, indicating that Ru nucleates and grows exclusively on the support. High-resolution HAADF imaging (Figure 1(f)) revealed that besides the well-defined, small Ru nanoparticles, clusters composed of a few Ru atoms are present on the surfaces of the support (marked with an arrow in Figure 1(f)). The EELS analysis of the Ru nanoparticles suggests that Ru is in the metallic, 0-valent state (see the ESM and Figure S6(c) in the ESM).

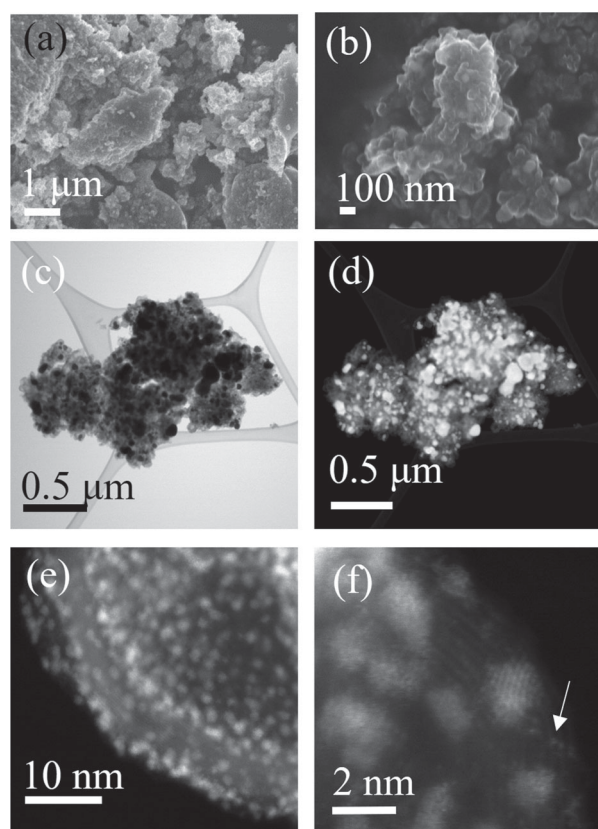


Figure 1. SEM ((a) and (b)), BF (c) and HAADF ((d–f)) STEM images of the nanocatalyst MN@C-Ru.

The MN@C-Ru nanocatalyst exhibited ferromagnetic (Figure S8 in the ESM) behaviour characteristic of Fe_3C and a high saturation magnetisation $M_s = 38 \text{ emu g}^{-1}$,

which, in combination with the relatively large size of the support particles, guarantees rapid magnetic separation of the nanocatalyst from the reaction medium after the catalysis (Figure S9 and Video in the ESM). The saturation magnetisation of the MN@C-Ru remained constant for months in an atmosphere of air at ambient temperatures and during testing of the catalytic activity. To obtain a better insight into the oxidation resistance, the MN@C-Ru was heated for 72 h at 120°C in circulating air. The saturation magnetisation dropped by only 30%, indicating exceptional stability against oxidation. Having this in mind we can conclude that the graphitic matrix provides excellent resistance to oxidation.

To evaluate the catalytic capability of the material, a temperature-programmed desorption (TPD) of CO and NH_3 from the MN@C-Ru was analysed. The TPD of CO showed one peak at the high temperature of 550°C , indicating strong interactions between the CO and the metal active sites (Figure S10(a)). Strong interactions are known to be favourable for the hydrogenation of an aromatic ring [24,25]. The TPD of NH_3 showed the presence of both weak and strong interactions between the NH_3 and the acid active sites (Figure S10(b) in the ESM). According to Jin and Li [26], Lewis acid sites are dominant at lower temperatures ($200\text{--}300^\circ\text{C}$), while Brønsted acid sites are dominant at higher temperatures ($300\text{--}450^\circ\text{C}$). Considering the TPD results, the MN@C-Ru nanocatalyst could be capable of catalysing both the hydrogenation and deoxygenation reactions.

The catalytic activity of the MN@C-Ru nanocatalyst was tested with eugenol, a lignin model compound, in

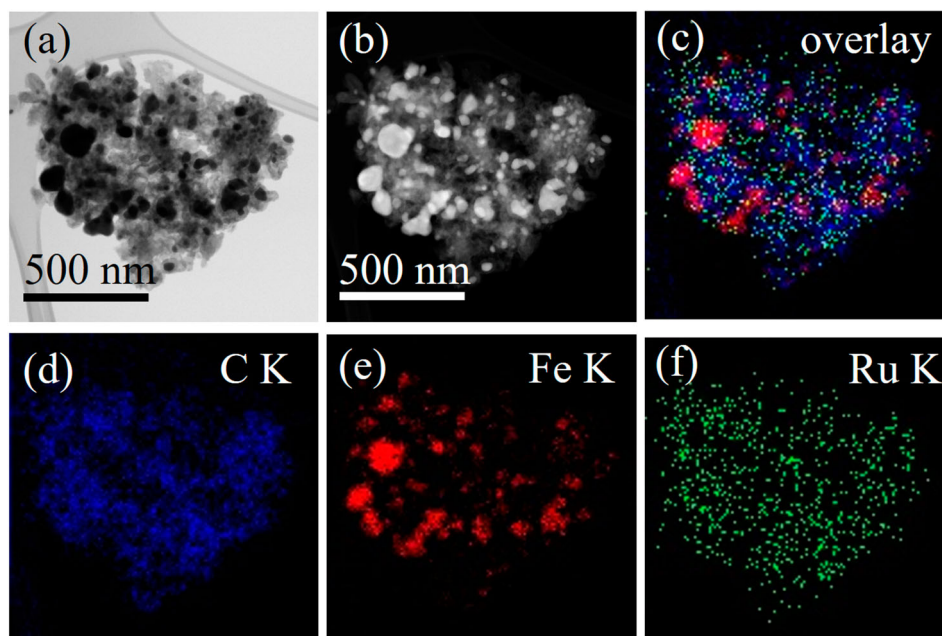
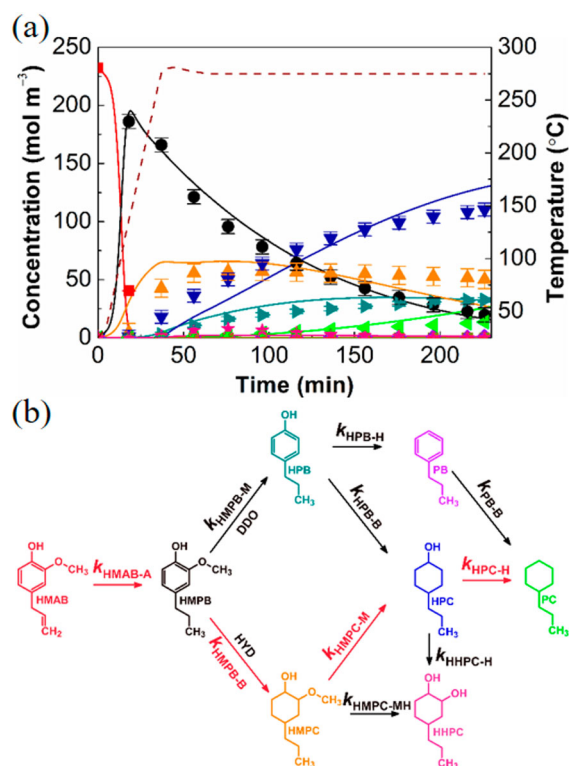


Figure 2. BF (a), HAADF (b) STEM images and the corresponding EDXS elemental mappings of the nanocatalyst MN@C-Ru.

Table 1. Kinetic parameters for eugenol hydrogenation and deoxygenation over a MN@C-Ru catalyst.

Adsorption and desorption constants				
$K_j = \frac{k_{\text{ads}j}}{k_{\text{des}j}}$		$K_H = \frac{k_{\text{ads(H)}}}{k_{\text{des(H)}}}$		
$3.15 \times 10^{-2} \text{ m}^3 \text{ mol}^{-1}$		$3.17 \times 10^{-1} \text{ m}^3 \text{ mol}^{-1}$		
Surface reaction rate constants at 275°C $\text{m}^3 \text{ mol}^{-1} \text{ min}^{-1}$				
$k_{\text{HMAB-A}}$ 1.30×10^7	$k_{\text{HMPB-B}}$ 1.52×10^4	$k_{\text{HMPB-M}}$ 3.19×10^3	$k_{\text{HMPC-M}}$ 9.28×10^3	$k_{\text{HPB-B}}$ 2.82×10^2
$k_{\text{HPB-H}}$ 1.12×10^2	$k_{\text{PB-B}}$ 1.62×10^5	$k_{\text{HMPC-MH}}$ 1.22×10^4	$k_{\text{HHPC-H}}$ 1.41×10^5	$k_{\text{HMPC-C}}$ 2.22×10^1

**Figure 3.** Kinetic plot for HDO of eugenol over MN@C-Ru fitted with model curves. ■ HMAB, • HMPB, ▴ HPB, ▴ HMPC, ▴ HPC, ★ HHPC, ▴ PC, --- temperature profile over the reaction time (a) and reaction pathway (red—dominant, black—less dominant pathway) (b) for a definition of the abbreviations see ESM.

the solvent hexadecane. The eugenol molecule has two types of double bonds and two types of O functional groups, and is well suited for the simultaneous testing of the hydrogenation and deoxygenation for lignin-derived platform chemicals. Based on the product's evolution and distribution presented in Figure 3(a), an eugenol reaction pathway is depicted in Figure 3(b). The in-depth analysis and modelling [27] of the hydrogenation and deoxygenation processes are presented in the ESM. The essential findings are that approximately 70% of the oxygen was removed, which is 9% more than commercial Ru/C

(Sigma Aldrich 5 wt.% Ru basis) [27]. Our nanocatalyst exhibited a 13-times-lower hydrogenation activity than the Ru/C, providing a higher yield of the desirable aromatic product HPB [27]. Over the MN@C-Ru, 14 mol% of HPB, a valuable -OH aromatic compound, was formed as a consequence of the over-8-times-slower disappearance. This component was only detected in trace amounts over the Ru/C due to the 2-fold-faster conversion relative to the formation. Additionally, our catalyst exhibited a 5-times-higher activity in the removal of the methoxy group from saturated species in comparison to the Ru/C [27]. According to the TPD CO results the total number of metal active sites was very similar for both allowing us a direct comparison of the observed activities although the significantly higher mass of the MN@C-Ru was used. Detailed comparison with the Ru/C and other relevant studies are provided in ESM. The favoured oxygen removal can be assigned to the support's acidity. The positive influence of the Fe-containing catalyst on the promotion of deoxygenation reactions has been shown in many studies [28,29]. The kinetic parameters determined by the regression analysis are shown in Table 1. It is clear that the hydrogenation is nearly 5-times more favoured than the deoxygenation. Among the deoxygenation reactions, the removal of the methoxy group from the HMPB is 28-times faster than that of the hydroxyl group from the HPB (and negligible from the HMPB), while the deoxygenation of saturated rings is an order of magnitude faster than that of the unsaturated products. Here, it should be mentioned that the suspension of the nanocatalyst in hexadecane resulted in superparamagnetic behaviour, despite the ferromagnetic nature of the MN@C-Ru (Figure S4 in the ESM). The magnetic interactions in the suspension are clearly insufficient to cause substantial aggregation of the MN@C-Ru and a decrease of the catalytic surface in contact with the reactants.

The MN@C-Ru nanocatalyst after the catalytic test was observed using the TEM (Figure S12 in the ESM). The Ru nanoparticles at the support surfaces remained homogeneously distributed and their size distribution

practically unaffected, indicating that aggregation and growth did not occur (Figure S13 in the ESM).

Conclusions

In conclusion, we have demonstrated a facile and robust method for the preparation of a novel, magnetically separable, Ru-based nanocatalyst. First, precursor particles containing iron-oxide nanoparticles dispersed in an amorphous carbonaceous matrix were synthesised by the hydrothermal carbonisation of glucose in a nanoparticle suspension. Subsequent annealing of the precursor particles at 750°C in an inert atmosphere caused the reduction of iron-oxide nanoparticles to Fe, which reacted with the carbon to form Fe₃C. At the same time, the organic matter transformed to nanocrystalline graphite, which encloses Fe and Fe₃C nanoparticles and strongly suppresses their oxidation, retaining the high magnetisation of the nanocatalyst. Finally, catalytic Ru is homogeneously deposited on the magnetic carbon support with the solvothermal reduction of Ru³⁺ at 150°C in the isopropanol suspension. Besides 0-valent Ru nanoparticles of 1.5 nm in diameter, clusters composed of a few Ru atoms also deposited on the surfaces of the support. The combined results of the TPD of CO and NH₃ suggest the nanocatalyst's potency for the hydrogenation and deoxygenation of aliphatic and aromatic compounds. The hydrogenation of eugenol, a lignin monomer model compound, proved the high catalytic activity for both the hydrogenation and deoxygenation reactions. The determined kinetic parameters showed that hydrogenation dominates over deoxygenation. Our nanocatalyst was 9% more efficient at oxygen removal than commercial non-magnetic Ru/C. More importantly, our nanocatalyst showed a higher yield of the valuable aromatic compound, in comparison to Ru/C. This clearly demonstrates its potency in the catalytic valorisation of lignocellulosic biomass into value-added chemicals. This is particularly attractive from the standpoint of the economical use of hydrogen. The improved efficiency is ascribed to the presence of Fe. Future work will be devoted to improving the yield of the aromatic compounds and studying recycling of the nanocatalyst.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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ORCID

S. Gyergyek  <http://orcid.org/0000-0002-7325-2984>

D. Makovec  <http://orcid.org/0000-0002-0190-6758>

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