

# Ruthenium nanoparticles supported on nanohydroxalcalcite: Efficient heterogeneous catalyst for the oxidation of lignin model compounds

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Nanohydroxalcalcite decorated ruthenium nanoparticles (Ru/n-HT) were prepared by following a two-steps procedure: n-HT was first added to the aqueous solution of potassium aquapentachlororuthenate(III) in an amount depending on the degree of ion-exchange, and the suspension was stirred for 12 hours at room temperature. At the end of 12 hours the opaque supernatant solution became colorless, indicating the completion of ion-exchange. The isolated and vacuum dried  $K_2RuCl_5(H_2O)$ -exchanged n-HT sample was reduced by sodium borohydride in aqueous medium at room temperature. After filtering, copious washing with water, and drying at 373 K, Ru/n-HT sample was bottled as black powder. The amount of ruthenium loading in terms of % wt Ru was determined by considering ICP-OES analyses (with a detection limit of 24 ppb for Ru). The effect of the preparation procedure on the integrity and crystallinity of the host material n-HT was investigated by P-XRD analysis. Fig. 1 shows P-XRD patterns of materials used and formed through the preparation of Ru/n-HT. The main Bragg peaks at  $2\theta$  values of 11.5, 23.1, 34.6, 60.5 and 61.9° can be assigned to crystal faces of HT (003), (006), (009), (110) and (013), respectively which agrees with the JCPDS no: 22-700.

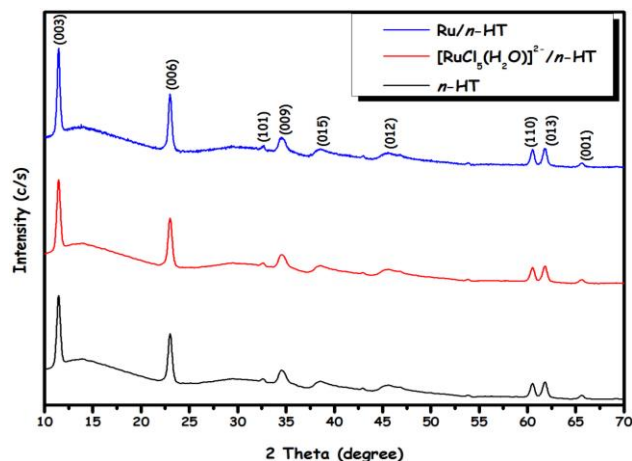


Fig. 1 P-XRD patterns of n-HT,  $[RuCl_5(H_2O)]^{2-}/n-HT$  and Ru/n-HT samples in the range of  $2\theta = 10-70^\circ$ .

Owing to the low ruthenium loading (1.2 wt % Ru), there is no Bragg peak was observed in P-XRD patterns of  $[RuCl_5(H_2O)]^{2-}/n-HT$  and Ru/n-HT samples. A comparison of the P-XRD patterns clearly shows that the incorporation of  $[RuCl_5(H_2O)]^{2-}$  ions into n-HT framework and the formation of Ru/n-HT cause no observable alteration in the lattice and no loss in the crystallinity of nanohydroxalcalcite, since the peak positions and intensities are almost the same in all the patterns. The morphology, structure and size of the resulting Ru/n-HT sample were investigated by BFTEM, TEM-EDX and HRTEM analyses. BFTEM images of Ru/n-HT in different magnifications were given in Fig. 2, which reveal that the existence of well-dispersed ruthenium(0) nanoparticles on the surface of n-HT. These

BFTEM images also indicated that the resulting ruthenium(0) nanoparticles were not agglomerated or clumped on the surface of *n*-HT support. Their mean particle size was found to be ca.  $3.2 \pm 0.9$  nm by using the NIH image program [1] which included the particle size analysis for >100 non-touching particles. TEM-EDX analysis (Fig. 2(c)) during the BFTEM observation from many different areas confirmed that the presence of Ru as judged by  $L_{\alpha 1}$  and  $L_{\beta 1}$  lines of Ru at 2.9 and 19.7 keV [2] respectively as well as support material elements (Mg, Al, O and Cu from BFTEM grid). The crystallinity of the resulting ruthenium(0) nanoparticles in Ru/*n*-HT sample was analyzed by HRTEM investigation. Fig. 2(d) shows HRTEM image of Ru/*n*-HT and inspection of this image revealed that the highly crystalline feature of the ruthenium(0) nanoparticles. The crystalline spacing was measured to be 0.209 nm, which agrees with (101) lattice spacing of ruthenium [3].

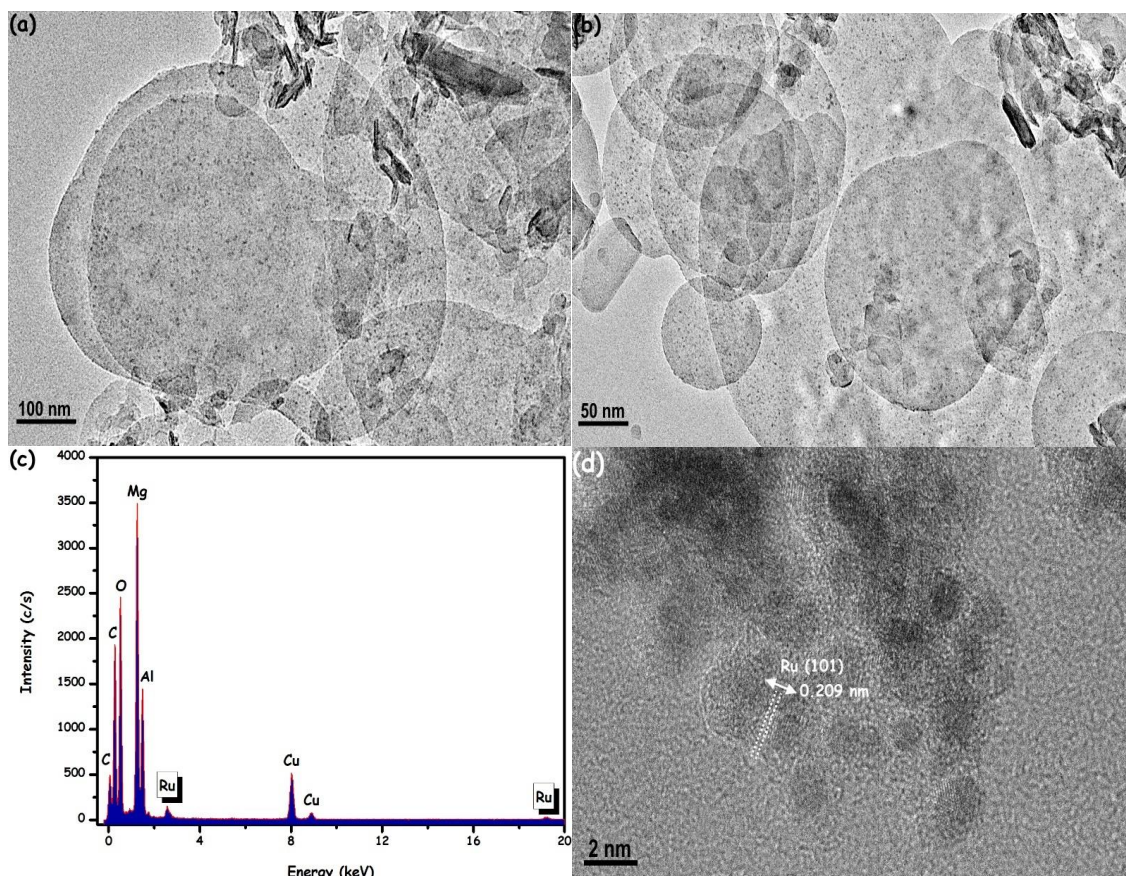


Fig. 2 (a) and (b) BFTEM images of Ru/*n*-HT sample in different magnifications, (c) TEM-EDX spectrum of Ru/*n*-HT, (d) HRTEM image of Ru/*n*-HT.

Under optimized conditions the catalytic activity of Ru/*n*-HT in the aerobic oxidation of cinnamyl (1), vanillyl (2) and veratryl (3) alcohols to corresponding aldehydes; cinnamaldehyde, vanillin and veratraldehyde were investigated (Fig. 3). Fig.4 shows conversion/selectivity (%) values with respect to time obtained in the Ru/*n*-HT catalyzed aerobic oxidation of cinnamyl, vanillyl and veratryl alcohols, we found that Ru/*n*-HT provided turnover frequency (TOF;  $\text{TOF} = \text{mol of product/mol of catalyst} \times \text{time}$  and all TOF values given here are not corrected to for the number of exposed surface atoms; that is, the values given are lower limits) values of 13.2, 5.1 and 11.4  $\text{h}^{-1}$  for the aerobic oxidation of cinnamyl, vanillyl and veratryl alcohols, respectively. These TOF values are notably higher than those of obtained by Bi-Pt/ $\text{Al}_2\text{O}_3$  (2.1  $\text{h}^{-1}$  for (1)) [4], Pd/SWCNT (0.7  $\text{h}^{-1}$  for (1)) [5],  $\text{MnFe}_{1.5}\text{Ru}_{0.35}\text{Cu}_{0.15}\text{O}_4$  (7.9  $\text{h}^{-1}$  for (1)) [6], Au/ $\text{CeO}_2$  (1.2  $\text{h}^{-1}$  for (1)) [7],  $\text{CoMn}_2\text{O}_4$  (3.1  $\text{h}^{-1}$  for (2)) [8],  $\text{Co}_3\text{O}_4$  (2.8  $\text{h}^{-1}$  for (2))

[9], Ru/Al<sub>2</sub>O<sub>3</sub> (1.8 h<sup>-1</sup> for (3)) [10], Ru/SiO<sub>2</sub> (1.6 h<sup>-1</sup> for (3)) [10] and Ru/ZIF-8 (1.9 h<sup>-1</sup> for (3)) [11] catalysts tested in the aerobic oxidation of same substrates.

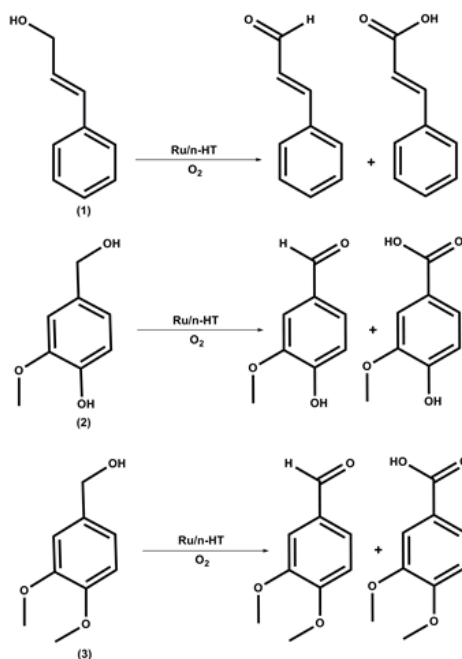


Fig. 3 Ru/n-HT catalyzed aerobic oxidation of cinnamyl alcohol (1), vanillyl alcohol (2) and veratryl alcohol (3).

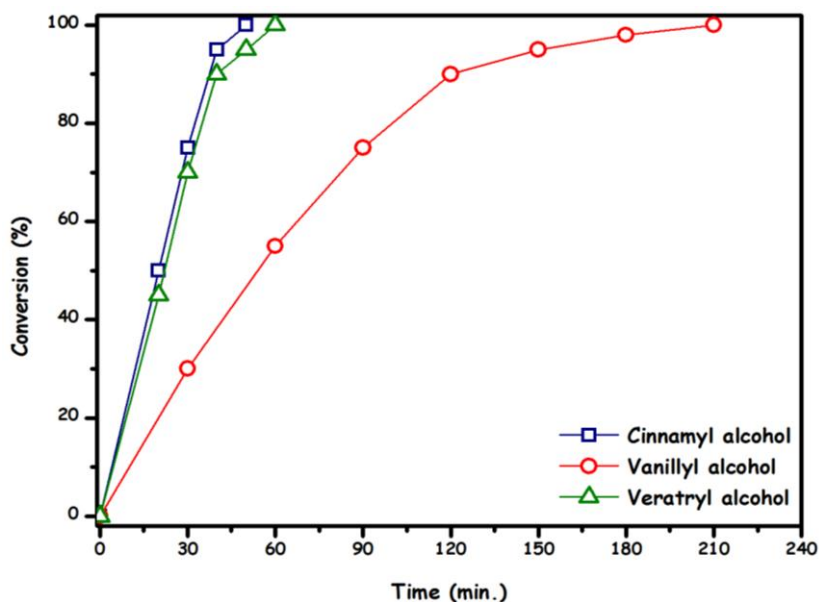


Fig. 4 The conversion (%) versus time graph for Ru/n-HT (100 mg; 1.2 wt % Ru loading) catalyzed aerobic oxidation of cinnamyl, vanillyl and veratryl alcohols (0.1 mmol) in toluene at 353 K under 3 bar initial O<sub>2</sub> pressure. In all substrates corresponding aldehyde formation selectivity was found to be > 99 %.

The isolability and reusability of Ru/n-HT were also investigated in the aerobic oxidation of cinnamyl, vanillyl and veratryl alcohols. After the first catalytic run, Ru/n-HT catalyst was isolated as powder by high-speed centrifugation, purified and dried under

vacuum at room temperature. When the isolated sample of Ru/*n*-HT reused in toluene, Ru/*n*-HT still acts as an active catalyst in the oxidation of cinnamyl, vanillyl and veratryl alcohols by retaining minimum > 85 % of the activity and > 90 % of both conversion and selectivity even at the third reuse. The possibility of leaching throughout the reusability experiments was checked by ICP-OES and no Ru was detected in the filtrate solutions (with a detection limit of 24 ppb for Ru) confirms that no leaching of ruthenium(0) nanoparticles from *n*-HT matrix to reaction solution. Additionally, a control experiment showed that the aerobic oxidation of veratryl alcohol is wholly stopped by removing of Ru/*n*-HT from the reaction solution.

In conclusion, the high catalytic activity-selectivity, easy preparation and reusability of Ru/*n*-HT nanocatalyst raise the prospect of using this type of simply prepared nanomaterial for the oxidative valorization of lignin or lignin model compounds in industrial applications as well as in small scale organic synthesis.

## References

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