RSC Advances

This article can be cited before page numbers have been issued, to do this please use: V. Srivastava, *RSC Adv.*, 2014, DOI: 10.1039/C4RA12324G.

ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/advances

View Article Online
DOI: 10.1039/C4RA12324G

Ruthenium nanoparticles intercalated montmorillonite clay for solvent free alkene hydrogenation reaction

Vivek Srivastava

Applied Sciences: Chemistry, NITT University, NH-8 Jaipur/Delhi Highway, Neemrana
(Rajasthan) Pin Code: 301705

Contact Number: 0+911494302423, email id: vivek.shrivastava@niituniversity.in

Abstract

Well characterized ruthenium nanoparticles intercalated montmorillonite clay was used as a catalyst for solvent free alkene hydrogenation reaction and the corresponding products were obtained in good yield. The catalytic activity of ruthenium nanoparticles intercalated montmorillonite clay was successfully tested for 16 different functionalized and non-functionalized alkenes. Apart from alkene reduction, the ruthenium nanoparticles intercalated montmorillonite clay was also applied for Wittig-type reaction for obtain dehydrobrittonin A, an important intermediate for the syntheses of brittonin A. Ruthenium nanoparticles intercalated montmorillonite clay was found active for the synthesis of dehydrobrittonin A and brittonin A. 9 times catalyst recycling, low catalyst loading, high catalytic activity and catalytic selectivity were the noteworthy outcomes of the proposed protocol.

Keywords: ruthenium nanoparticles, Montmorillonite clay, hydrogenation reaction, dehydrobrittonin A, brittonin A, solvent free reaction, alkene hydrogenation

1. Introduction

Ru nanoparticles are well known catalyst for a wide range of organic reactions such as hydrogenation, hydrogenolysis, nitrile hydration, epoxidation, Fischer-Tropsh synthesis etc. [1,2] Various organic-inorganic supports such as activated carbon [3], SiO_2 [4, 5], Al_2O_3 [6, 7], zeolite [8, 9], ionic liquids [10, 11] and polymers [12] have been reported to support the Ru nanoparticles to utilize them as an effective heterogeneous catalyst. Montmorillonite clay (MMT) is one of the important materials for supporting the catalysts due to its unique phytochemical properties like high cation exchange capacity and good swelling properties. [13-15] Furthermore, reactions that are catalyzed by MMT are extremely easy to "work-up" since the clay does not dissolve in the reaction medium (solvent), it can simply be filtered away when the reaction is complete. MMT has been the most frequently used support to intercalate different metal ions and is further tested as catalyst in various organic transformations such as oxidation, reduction, transesterification, coupling reactions, etc. [15] Metal intercalated MMTs are well documented catalyst for the selective hydrogenation reaction of different organic compounds. Rh^{3+}, Ru^{3+} or Pd^{3+} ions are still difficult to exchange completely by the interlayer cations of MMT clay. [16] Few reports are available for exchanging the Ru3+ ions within the interlayer spacing of MMT clay. Recently, Liu *et al* reported the synthetic protocol for Ru nanoparticle immobilized MMT clay using task specific ionic liquid [IL]. [17] In this report, the firstly ionic liquid was exchanged with exchangeable ions of MMT and then Ru3+ ions were loaded onto the IL-exchanged MMT clay. This catalytic system was successfully tested as a catalyst for the benzene hydrogenation reaction.

Hydrogenation of alkenes is an important synthetic tool for achieving the different biologically important molecules with good yield. [16-21] Several hydrogenating reagents such as $NiCl_2$-$NaBH_4$, $PdCl_2$-$NaBH_4$ polyethylene glycol (PEG)-CH_2Cl_2, $CoCl_2$-$NaBH_4$ etc., have been tested as hydrogenation systems. [22] Along with toxicity, these systems also suffered with long reaction time, high catalyst loading, costly starting materials and tedious reaction protocol of these hydrogenating reagents.

In this paper, we are offering the controlled synthesis of Ru metal nanoparticles (Ru MNPs) by exchanging $[Ru\ (NH_3)\ _6]^{+3}$ ions for interlayer Na^+, K^+ or Ca^{2+} ions. The exchanged Ru3+ ions were successively reduced by sodium boron hydride to Ru MNPs which were intercalated into MMT clay which were successively reduced sodium boron hydride to Ru MNPs intercalated into MMT clay. High dispersion of Ru^{3+} ions were successively reduced by sodium boron hydride to Ru MNPs which were intercalated into MMT clay followed by ion exchange process. Ruthenium nanoparticles intercalated montmorillonite clay Ru MMT was used to hydrogenate cyclic as well as acyclic olefins under different reaction conditions such as different temperature, pressure, solvent systems, etc., to obtain the corresponding reaction products with good yield.

2. Experimental

Reagent Plus® grade ruthenium(III) chloride hydrate was purchased from Aldrich. ReagentPlus® and extra pure grade alkenes were purchased from Aldrich and Acros chemicals. Lindlar catalysts, 5% Pt on carbon and Renney nickel were supplied Vinneth chemicals, India as free samples. Nuclear Magnetic Resonance (NMR) spectra were recorded on a standard Bruker 300WB spectrometer with an Avance console at 400 and 100 MHz for ^1H and ^{13}C NMR, respectively. *Z/E* ratio determined from the crude product ^1H NMR spectroscopy. The commercial sodium montmorillonite clay (Cloisite®Na) used in the present study was supplied by Southern Clay Products, Gonzales, Texas (USA). The cation exchange capacity (CEC) of sodium montmorillonite (Na-MMT) is 92.6 meq/100 g as reported by suppliers. All the hydrogenation reactions were carried out in a 100 mL stainless steel autoclave (Amar Equipment, India). The Ru MMT catalyst material was characterized by TEM (Hitachi S-3700N) and Energy-dispersive X-ray spectroscopy (EDX) (Perkin Elmer, PHI 1600 spectrometer). The specific surface area (BET) of the catalyst was determined on a Micrometrics Flowsorb III 2310 instrument. The catalyst was pre-treated at 120^oC under vacuum for over 2h to desorb contaminating molecules (mainly water) from the catalyst surface for the determination of BET.

2.1 Catalysts Preparation

The $[Ru\ (NH_3)\ _6]\ Cl_3$ solution was prepared by reacting a solution containing equimolar amounts of water and ammonia with $RuCl_3.\ 3H_2O$.[23, 24] The solvent was evaporated under mild reduced pressure on the steam bath until only a faint odor of ammonia gas was noticeable. The resulting pale yellow solution was filtered and allowed to cool in ice bath (5-10^oC). The neat MMT clay (without any treatment or modification) was dispersed in 250mL deionized water and stirred to facilitate complete dispersion for 2 hours at room temperature. Then, 40 mL hexamine ruthenium (III) solution (0.92 meq/g of MMT) were added under constant stirring at room temperature (303K) with an addition rate of 0.5 mL/min to obtain obtain $[Ru\ (NH_3)_6]$-MMT, which was subsequently reduced by NaBH4 at room temperature. A grayish black dispersion was formed. Ru MMT was filtered, washed, dried at 313 K for the next 3 hours in a vacuum oven and grounded to fine powders using a pestle and a mortar.

DOI: 10.1039/C4RA12324G

2.2 Hydrogenation of alkenes and catalyst recycling

The autoclave (1mL) was charged with alkenes (2mL) and catalyst (0.1g). Solvent, additive and hydrogen source (except hydrogen gas) was added as required. After closing the autoclave, the air was replaced with hydrogen gas (10 bar), then the reactants were allowed to react at 80^oC for 1 hour. After that, the autoclave was cooled by supplying cold water ($2-5^oC$). The reaction product was isolated with diethyl ether (5 x2mL). The isolated product was further purified by a column chromatography using ethyl acetate/hexane solvent system (15:85). The catalytic system was further dried under reduced pressure at 50^oC for 30 minutes and recycled for the next run.

2.3 One pot Wittig olefination reaction

50 mL round bottom flask was charged with 1.6 M *n*-BuLi (6.25 µL,1.0 mmol) which was added dropwise to a suspension of corresponding methoxylated benzyltriphenylphosphonium halide (1.5 mmol) in dry THF (2 mL), at 0^oC under argon atmosphere to obtain the corresponding ylide. After 20 minutes, Ru MMT (0.1g) was added to the combined reaction mass of the (3,4,5-trimethoxyphenyl) methanol (1 mmol) and the initially prepared ylide suspension. The reaction mixture was allowed to stir for next 1 hour at 80^oC. The resulting reaction product was isolated by diethyl ether washing (5 x2mL) and the reaction product was further purified with a column column chromatography using ethyl acetate/hexane solvent system (10:90) to obtain product dehydrobrittonin A.

3. Result and Discussion

A small to medium angle X-ray scattering (SAXS) analysis was carried out to study the change between the basal spacing of Ru MMT with respect to neat MMT (Figure 1). The basal spacing of neat MMT was d_{001}=12.95Å, while after the exchange of Ru ions within the interlayer spacing of MMT, a significant increase was observed and the Ru MMT was enlarged to d_{001}=14.96Å. Such increase between the basal spacing of MMT represents the presence of Ru ions between the basal spacing of MMT. It is worth noting here, the small characteristic peak for Ru nanoparticles in the XRD data, represents the existence of Ru MNPs (either very small or amorphous) (Figure 2).

<u>Insert figure 1 here</u>

The average TEM particle size of Ru is 20.5±2 nm in Ru-MMT. The TEM image clearly reveals the agglomeration of Ru MNPs on MMT (Figure 3 a & b). The presence of Ru species within the interlayer spacing of MMT clay was also confirmed by using high resolution transmission electron microscopy (HRTEM) analysis (Figure 4). We embedded Ru MMT in epoxy resin in order to get a uniform solid specimen and cut the specimen using ultra- microtome to achieve an ultra-thin section of Ru MMT. Ruthenium wt% in catalyst was calculated using inductively coupled plasma atomic emission spectrometer (ICP-AES, ARCOS from M/s. Spectro, Germany). 0.1 g of sample was digested in a minimum amount of conc. HNO_3 with heating, and volume made up to 10 ml. Theoretical (cation exchange capacity) and an experimental (ICP-AES) method was used to calculate the amount of Ru species in MMT. Both theoretical and experimental values were found to be in good agreement, and 2.5 wt% Ru MMT. [22] This protocol also minimizes the loss of Ru nanoparticles during the synthesis of Ru MMT.

<u>Insert figure 2 here</u>

View Article Online
DOI: 10.1039/C4RA12324G

The specific surface area of Ru MMT was measured by nitrogen adsorption using the BET method. This is an important characteristic of heterogeneous catalyst and liable to change during preparation, conditioning, in use and particularly if exposed to excessive temperatures. The specific surface area of neat MMT (82 m^2/ g) was increased up to 85 m^2/ g for Ru MMT clay.

A primary study to check the catalytic activity of Ru MMT was carried out using hydrogenation of allylbenzene as a model test reaction to optimize the reaction conditions and all the corresponding results were summarized in table 1, entries 1-19. The best test result was obtained while stirring the allybenzene and Ru MMT without solvent at 80^{o}C for 1 hour under hydrogen atmosphere (Table 1, Entries 1).

Three different hydrogen sources were screened to replace the hydrogen gas, but as per the corresponding results the high yield only obtained with hydrogen gas (Table 1, Entries 1, 15 and 16). On the basis of experimental results (Table 1, Entries 1-19), Ru MMT catalyzed alkene hydrogenation reaction was totally dependent on temperature, reaction time and the pressure of the hydrogen gas because once any one of the factor deviated, the lower catalytic response of Ru MMT was observed on the corresponding product yield (Table 1, Entries 1-14). We also checked the catalytic behavior of Ru MMT in the presence of additives and the results were documented in Table 1, entries 18-19. Raney nickel and other catalysts were also evaluated under optimized reaction condition, but no noteworthy results (Table 1, Entries 20-22) were obtained.

Insert Table 1 here

Ru MMT was further evaluated for the hydrogenation of 13 different functionalized and non-functionalized alkenes (Table 2, Entries 1-13). Terminal alkenes were easily reduced to the corresponding alkanes in quantitative yield (Table 2, Entry 1). The same behavior was observed with t*rans*-stilbene as well as for α-methylstyrene and we easily isolated their corresponding products in good yield (Table 2, entries 2-3). Further, we studied hydrogenation of functionalized olefins (entries 4-13). Ru MMT was found catalytically sound for both terminals as well as for internal unsaturated esters and offers their corresponding product in high yield. Interestingly, no transesterification was detected while performing the hydrogenation reaction of ethyl 6-heptenoate (Table 2, entries 4). In the presence of Ru MMT, not only electron-rich aromatic 3,4-dimethoxystyrene and isosafrole were also nicely reduced in high isolated yields (entries 7 and 8) but also allylic alcohols, with either a monosubstituted or geminal C=C bond were nicely reduced without any isomerization of corresponding reaction products, (Table 2, Entries 9 and 10). It is significant to write here that transition-metal catalysts, during catalytic hydrogenation, encourage such type of type of isomerization. Monoterpene (±)-linalool [25], which holds both a mono- as well as tri-substituted C=C bond, was easily altered into the saturated tertiary alcohol 3,7-dimethyloctan-3-ol (tetrahydrolinalool) in moderate yield (Table 2, Entries 11). The reduction of allyl benzyl ether and N-allylcyclohexylamine were easily taken care by Ru-MMT, for both substrates the desired products were obtained in quantitative yield (Table 2, entries 12 and 13).

Insert table 2 here

The flexibility of Ru MMT was also checked for the synthesis of two unique biologically important products. First, we performed the synthesis of brittonin A, which was isolated from *Frullania brittoniae* subsp. *truncatifolia* (F. *F. muscicola*). [26] The brittonin A obtained as a hydrogenated product of dehydrobrittonin A in high yield. [27] To the best of our knowledge, this is the first solvent free Ru

View Article Online
DOI: 10.1039/C4RA12324G

MMT catalyzed Wittig-type reaction of properly substituted benzyl alcohols and phosphorus ylides, in which there is no standard redox step was used and we synthesized dehydrobrittonin A with moderate yield and the process also displayed low diastereoselectivity, mainly in favor of the *E* diastereoisomer. [28] In our study, a maximum ca. 1:4 *Z/E* ratio of diastereomeric dehydrobrittonin A was obtained while Nickel nanoparticles offered the same reaction product with comparatively low diastereomeric *Z/E* ratio (46:54) (Scheme 1).

Insert scheme 1 here

After getting delightful results of Ru MMT catalyzed hydrogenation of different alkenes, we also tested the stability of Ru MMT in catalyst recycling experiment for our model test reaction (hydrogenation of allylbenzene) and recycled Ru MMT up to 9 runs without any significant loss of yield (Figure 3). Potential Ru leaching into the reaction mixture was also analyzed with ICP/OES analysis. For this purpose, samples were taken through a syringe filter (Whatman Puradisc 4, 4 mm diameter, 0.45 μm, PTFE) during our model test reaction (hydrogenation of allylbenzene). Volatile impurities were evaporated, and the residue was dissolved in HNO_3. The analysis of these samples with ICP- AES showed that the Ru concentration in the reaction solution was less than the detection limit (i.e., 50 ppb). The same result was obtained when the complete reaction mixture of model test reaction was filtered, the solvent was evaporated, and the residue was dissolved in HNO_3. Both findings indicate that virtually no Ru leaches from the Ru MMT into the solution.

Insert figure 3 here

4. Conclusion

The synthetic protocol for Ru nanoparticles intercalated into MMT is represented in this manuscript using different analytical techniques for Ru MMT. Physiochemical parameters were investigated using different sophisticated analytical techniques for Ru MMT. TEM image showed agglomeration of Ru nanoparticles in MMT and subjugated that the average particle size of Ru nanoparticle was 20.5±2 nm. Catalytic activity of well characterized Ru MMT was tested for 13 types of functionalized and non-functionalized alkenes. All the alkenes were nicely hydrogenated under solvent free condition with good yield of corresponding reaction products in good yield. The catalytic activity of Ru MMT was also exploited for the synthesis of natural product brittonin A as well as for Wittig-type reaction to obtain dehydrobrittonin A. Both products were obtained in quantitative yield. Apart from that low catalyst loading, no use of additives, wide substrate scope, solvent free approach, easy product isolation and catalyst recycling up to 9 times are the major outcomes of this proposed protocol.

References

1. P. Lara, K. Philippot and B. Chaudret, *ChemCatChem* 2013, **5**, 28–45.
2. J. Gavnholt and J. Schiøtz, *Phys. Rev. B* 2008, **77**, 1-10.
3. E. J. García-Suárez, P. Lara, A. B. García and K. Philippot, *Recent Pat Nanotechnol.* 2013, 2- 247-264.
4. A. I. Carrillo, L. C. Schmidt, M. L. Marínab and J. C. *Scaiano Catal. Sci. Technol.* 2014,**4**, 435-440.
5. R. B. N. Baig and R. S. Varma, *ACS Sustainable Chem. Eng.* 2013, **1**, 805–809.

View Article Online
DOI: 10.1039/C4RA12324G

6. I. Balinta, A. Miyazakib and K.-i. Aika, *Journal of Catalysis* 2002, **207**, 66-75.
7. I. Balint, A. Miyazakib and K.-i. Aikab, *Chem. Commun.* 2002, 630-631.
8. J. Sun, X. Li, A. Taguchi, T. Abe, W. Niu, P. Lu, Y. Yoneyama and N. Tsubaki, *ACS Catal.* 2014, **4**, 1–8.
9. D. K. Mishra, A. A. Dabbawala and J.-S. Hwang, *Journal of Molecular Catalysis A: Chemical* 2013, **376**, 63-70.
10. L. M. Rossi, J. DupontI, G. MachadoI, P. F. P. Fichtner, C. Radtke, I. J. R. Baumvol and S. R. Teixeira, *J. Braz. Chem. Soc.* 2004, **15**, 904-910.
11. G. Salas, P. S. Campbell, C. C. Santini, K. Philippot, M. F. C. Gomesd and A. A. H. Pádua, *Dalton Trans.* 2012,**41**, 13919-13926.
12. D. K. Mishra and A. A. Dabbawala, J.- S. Hwang, *Catalysis Communications* 2013, **41**, 52-55.
13. A. Jhaa, A.C. Garadea, M. Shiraib, C.V. Rode, *Applied Clay Science* 2013, **74**, 141-146.
14. J. M. Adams, T. V. Clapp and D. E. Clement, *Clay* 1983, **18**, 411–421.
15. V. Srivastava, *Bulletin of the Catalysis Society of India* 2012, **11**, 56-77.
16. A.B. Boricha, H.M. Mody, H.C. Bajaj and Raksh V. Jasra, *Applied Clay Science* 2006, **31**, 120-125.
17. H. Xu, K. Wang, H. Zhang, L. Hao, J. Xua and Z. Liu, *Catal. Sci. Technol.* 2014, **4**, 2658-2663.
18. C. Morina, D. Simonb and P. Sautet, *Surface Science* 2006, **600**, 1339-1350.
19. M. Guerrero, N. T. T. Chau, S. Noël, A. Denicourt-Nowicki, F. Hapiot, A. Roucoux, E. Monflier, and K. Philippot, *Current Organic Chemistry* 2013, **17**, 364-399.
20. M. Cano, A. M. Benito, W. K. Masera and E. P. Urriolabeitia, *New J. Chem.* 2013,**37**, 1968-1972.
21. C. P. Ruas, D. K. Fischer and M. A. Gelesky, *Journal of Nanotechnology* 2013, **2013**, 1-6.
22. P. K. Sharma, S. Kumar, P. Kumar and Poul Nielsen, *Tetrahedron Letters* 2007, **48**, 8204-8708.
23. K. B. Sidhpuria, H. A. Patel, P. A. Parikh, P. Bahadur, H. C Bajaj and R. V. Jasra, *Applied Clay Science* 2009, **42**, 386-390.
24. L. Jiao and J. R. Regalbuto, *Journal of Catalysis* 2008, **260**, 329–341.
25. V.R. Coelhoa, J. Gianesinia, R. Von Borowskia, L. Mazzardo-Martinsb, D.F. Martinsb, J.N. Picadaa, A.R.S. Santosb, L.F.S. Bruma and P. Pereira, *Phytomedicine* 2011, 896-901.
26. Y. Asakawaa, K. Tanikawaa and T. Aratanib, *Phytochemistry* 1976, **15**, 1057–1059.
27. F. Alonso, , P. Riente and M. Yus, Tetrahedron 2009, 65, 10637–10643.
28. F.Alonso, P. Riente and M. Yus, European Journal of Organic Chemistry 2009, 2009, 6034–6042.

View Article Online
DOI: 10.1039/C4RA12324G

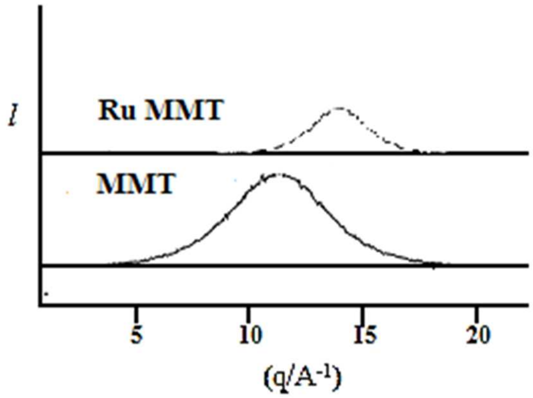


Figure 1 Small to medium angle X-ray scattering (SAXS) data for MMT and Ru MMT

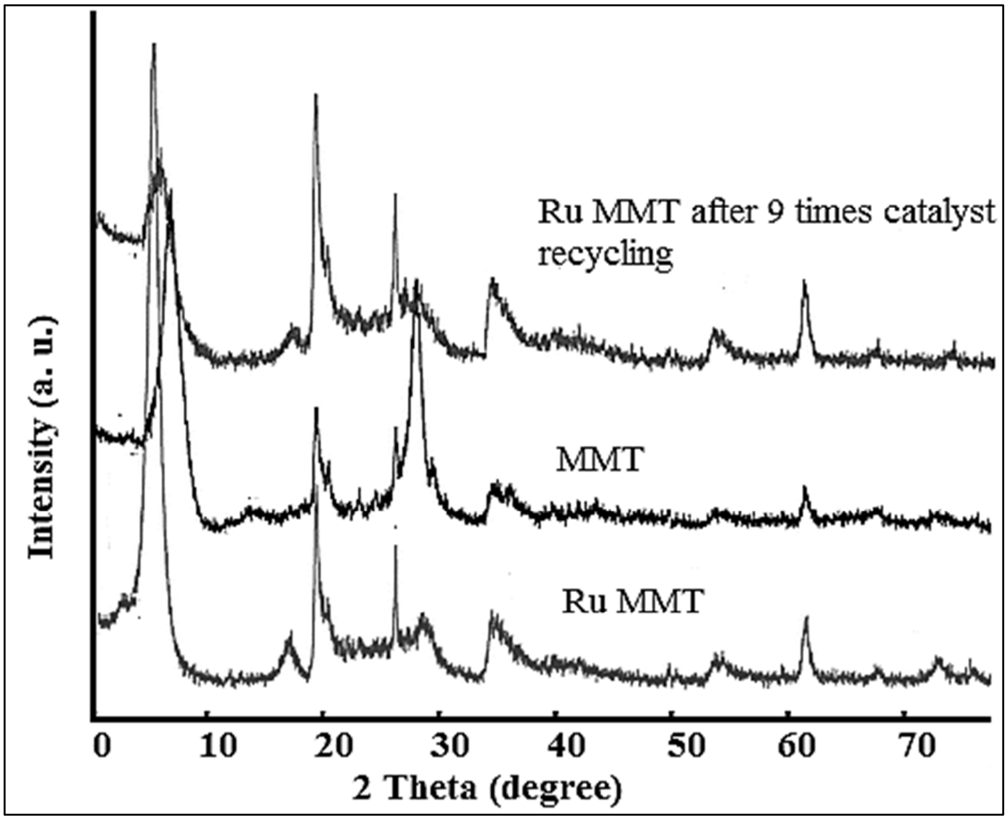
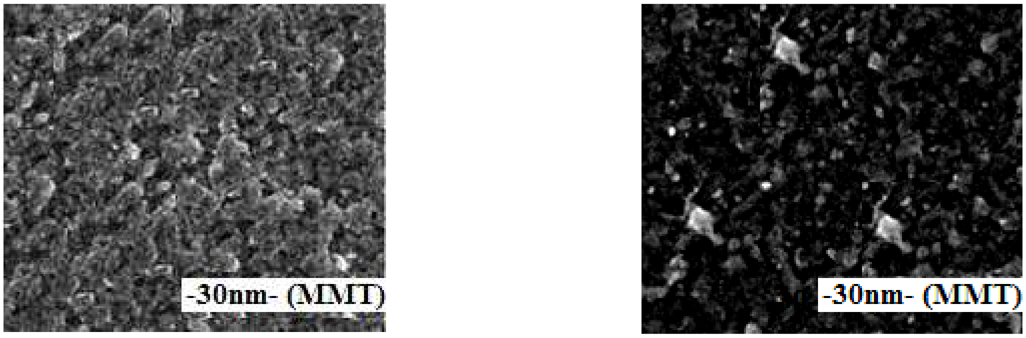


Figure 2 XRD patterns of the MMT, Ru MMT (fresh), Ru MMT (used)

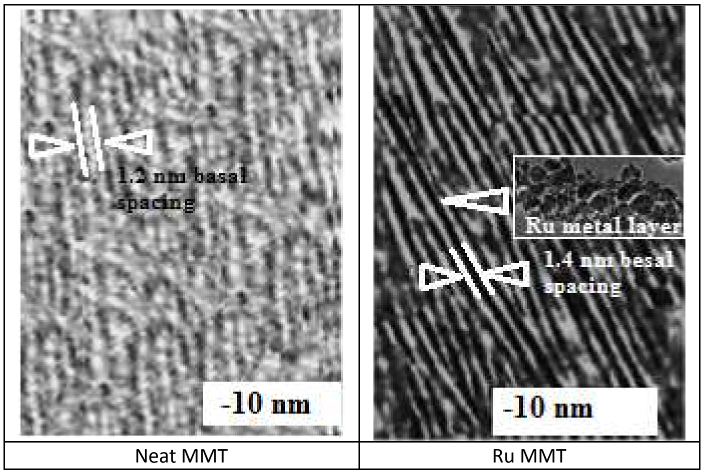
View Article Online
DOI: 10.1039/C4RA12324G



a. TEM image of MMT

b. TEM image of Ru MMT

Figure 3 TEM images of MMT and RU MMT

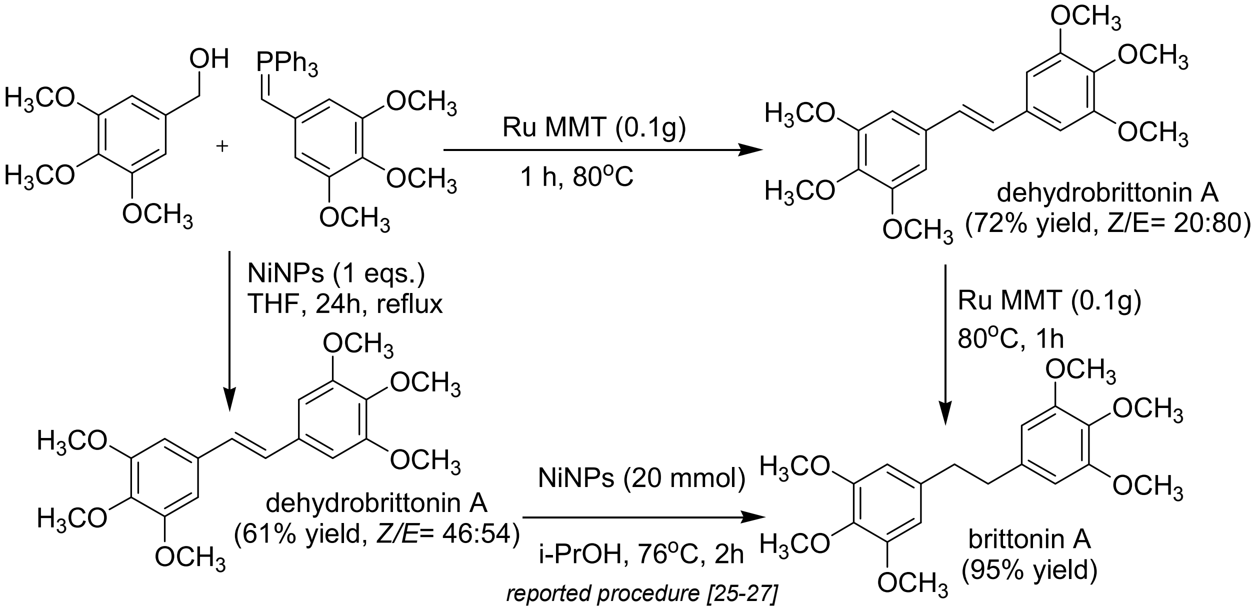


Neat MMT

Ru MMT

Figure 4 HRTEM analysis

View Article Online
DOI: 10.1039/C4RA12324G



Scheme 1 Synthesis of brittonin A

View Article Online
DOI: 10.1039/C4RA12324G

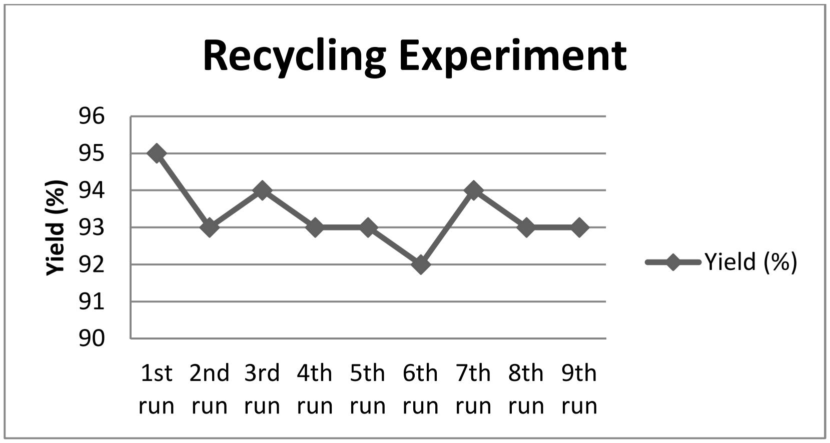


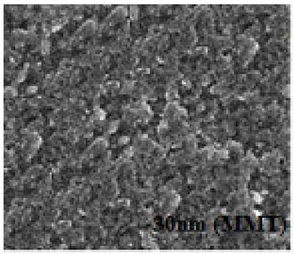
Figure 3 Recycling test of Ru MMT for allylbenzene hydrogenation reaction

View Article Online
DOI: 10.1039/C4RA12324G

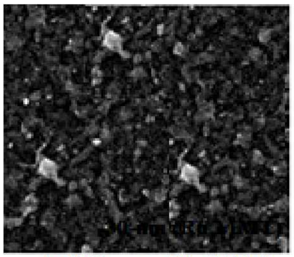
Ruthenium nanoparticles intercalated montmorillonite clay for solvent free alkene hydrogenation reaction

Vivek Srivastava

Applied Sciences: Chemistry, NITT University, NH-8 Jaipur/Delhi Highway, Neemrana
(Rajasthan) Pin Code: 301705



TEM image of MMT



TEM image of Ru MMT