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Journal Name

ARTICLE

Aromatic ring hydrogenation catalysed by nanoporous montmorillonite supported Ir(0)-nanoparticles composite under solvent free condition

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Prabin Das, Podma Pollov Sarmah, Bibek Jyoti Borah, Lakshi Saikia and Dipak Kumar Dutta

Ir(0)-nanoparticles (Ir-NPs) were synthesized into the nanopores of modified montmorillonite clay by incipient wetness impregnation of the IrCl_3 followed by reduction with ethylene glycol. Activation of the montmorillonite clay was carried out by treating with HCl under controlled condition to increase the surface area by generating nanopores which act as host for the metal nanoparticles. The synthesized Ir-NPs-montmorillonite composites were characterized by N_2 -sorption, powder XRD, SEM, EDS, TEM, XPS etc. exhibiting high surface area of $327 \text{ m}^2/\text{g}$ and size around 4 nm uniformly distributed on the support. The Ir-NPs show efficient catalytic activity in aromatic ring hydrogenation under solvent free condition with maximum conversion up to 100% and Turn Over Frequency (TOF) upto 79 h^{-1} . The catalyst can be easily separated by simple filtration and remained active for several runs without significant loss of catalytic efficiency.

Introduction

Over the past several decades, nanostructured materials are the most intensive area of research due to their potential applications in diverse fields¹⁻⁵. The high surface to volume ratio and high density of active sites in nanomaterials lead to the development of sustainable catalysis⁶. Various industrially important organic reactions like oxidation, hydrogenation, hydroformylation, carbonylation, C-C bond formation reactions are catalyzed by a wide variety of nanomaterials⁶⁻¹¹. However, the metal nanoparticles are very reactive and tend to agglomerate during synthesis, if no stabilizing agents are used. Therefore, a large numbers of stabilizing agents or supports such as, natural and activated montmorillonite clay, zeolites, activated carbon, polymers, organic ligands, metal oxides etc.¹²⁻²⁵ are employed which prevent the agglomeration of metal nanoparticles and controls the particle size¹¹⁻²¹. Among these, montmorillonite clay, one of the environmentally benign, cheap, easily available and robust supports, is used for the synthesis of different metal nanoparticles to make heterogeneous catalysts having several advantages over homogeneous process, like easily separable from reaction mixture²⁶⁻³⁵. Acid activated montmorillonite clay is partially delaminated and exhibits higher surface area containing both micro and mesopores, and can be utilized as a host for synthesis of metal nanoparticles³⁶. Hydrogenation of aromatic compounds is one of the important

reactions to produce the desired products in the fine chemicals and pharmaceutical industries³⁷. Moreover, aromatic ring hydrogenation by efficient heterogeneous catalyst may pave the way for more efficient process for liquefaction of coal³⁸⁻⁴⁰. A large number of homogeneous and heterogeneous catalysts prepared from various metals like Ni, Fe, Ru, Rh etc. have been reported for hydrogenation reactions. However, applications of Ir-metal for such reactions are less exploited and therefore, needs to be addressed⁴¹⁻⁴⁷.

In the present manuscript, we report the synthesis of Ir-NPs of less than 4 nm size into the nanopores of modified montmorillonite clay. The catalyst can be easily separated by simple filtration technique. The montmorillonite clay is modified by acid activation to achieve high surface area and nano-porosity which act as a support and restrict the size in the nano-particle range. The synthesized Ir-NPs are characterized by powder XRD, TEM, XPS and N_2 -sorption analysis etc. and evaluated as catalyst for the hydrogenation of some aromatic compounds.

Experimental

Materials and methods

Purification of the naturally occurring Bentonite clay (procured from Gujarat, India) was carried out by sedimentation technique by following Stokes' law to remove impurities like quartz, iron oxide etc. to produce pure montmorillonite clay (mont.) of size less than $2 \mu\text{m}$. The basal spacing (d_{001}) of the air dried samples, determined by powder XRD, was about 12.5 Å. The surface area (BET) of the mont. as determined by N_2 sorption technique was $101 \text{ m}^2/\text{g}$. The analytical oxide composition of Bentonite determined was SiO_2 : 48.62%; Al_2O_3 :

Materials Science Division, CSIR-North East Institute of Science and Technology, Jorhat 785006, Assam, India, Fax: (+)91 376 2370011, E-mail: dipakkrdutta@yahoo.com.
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20.02%; Fe₂O₃: 7.49%; MgO: 2.82%; CaO: 0.69%; loss on ignition (LOI): 17.51%; and others (Na₂O, K₂O and TiO₂): 2.95%. Mont was converted to the homoionic Na-exchanged form by stirring in 2 M NaCl solution for about 48 h, washed and dialysed using deionized distilled water until the conductivity of the water approached that of distilled water. The cation exchange capacity (CEC) was 126 milliequivalent (meq) per 100 g of clay (sample dried at 120 °C).

IrCl₃, ethylene glycol, ethanol, methanol and all the substrates were purchased from Sigma-Aldrich, USA and Acros Organics. All reagents were used as supplied. IR spectra were recorded on KBr discs in a Shimadzu IR Affinity-1 spectrophotometer. Specific surface area, pore volume, average pore diameter were measured with the Autosorb-1 (Quantachrome, USA). Specific surface area of the samples was measured by adsorption of nitrogen gas at 77 K and applying the Brunauer–Emmett–Teller (BET) calculation. Prior to adsorption, the samples were degassed at 250 °C for 3 h. Pore size distributions were derived from desorption isotherms using the Barrett-Joyner-Halenda (BJH) method. Powder XRD were recorded on a Rigaku Ultima IV diffractometer using a CuK α source (λ = 1.54 Å). The products were analyzed by Gas Chromatography (Thermo Scientific TRACE 1300, FID detector). Scanning Electron Microscopy (SEM) images and energy dispersive X-ray spectroscopy (EDS) patterns were obtained from the samples by using Carl Zeiss SIGMA FE-SEM operated at 5 and 20 KV and Oxford X-Max 20 EDS detector. Transmission electron microscopy (TEM) images were recorded on a JEOL JEM-2011 electron microscope; the specimens were prepared by dispersing powdered samples in isopropyl alcohol and placing them on a carbon coated copper grid followed by drying. X-ray Photoelectron Spectra were recorded on Kratos ESCA model Axis 165 spectrophotometer.

Synthesis

Preparation of Support. The purified mont. (7.0 g) was dispersed in 350 mL 4 M hydrochloric acid and refluxed for 1 h. After cooling, the supernatant liquid was discarded and the acid activated mont. was repeatedly redispersed in deionized water until no Cl[−] ions could be detected by the AgNO₃ test. The modified mont. was recovered, dried in air at 50 ± 5 °C overnight to obtain the solid product. The acid activated mont. was designated as AT-mont. The analytical oxide composition of Bentonite determined was SiO₂: 72.59%; Al₂O₃: 8.13%; Fe₂O₃: 2.39%; MgO: 0.19%; CaO: 0.56% loss on ignition (LOI): 13.74%; and others (Na₂O, K₂O and TiO₂): 2.40%.

Synthesis of Ir-NPs. 1 g AT-mont. was impregnated with 0.50 mmol IrCl₃ in aqueous medium (15 mL) under vigorous stirring condition for about 24 h. and thereafter evaporated to dryness in a rotavapour. 0.5 g of the composite was dispersed in 20 mL ethylene glycol and refluxed at 197 °C for 5–6 h to ensure complete reduction of the Ir salt. The colour of the solid mass changed from reddish purple to black. The solid was allowed to settle and washed repeatedly with distilled water for several times and finally filtered through a sintered crucible

and washed with methanol followed by distilled water. The composite was dried under vacuum and stored in airtight bottle. The sample thus prepared was designated as Ir-NPs.

Aromatic hydrogenation reaction. All the reactions were carried out in a high pressure reactor of 50 ml capacity (Parr Instrument Co.) taking 10 mmol of substrate and 50 mg of catalyst (Ir-NPs) and pressurized with H₂ gas to 5 bar at 25 °C. The reactions were performed at 75 °C under stirring at 500 rpm for different reaction time (1, 2, 3, 4, 5, and 6 h). The products of the reactions were analyzed using Gas Chromatography. The catalyst (Ir-NPs) was recovered by simple filtration, washed and dried for further recycling. The effects of catalyst amount on the substrate conversion were also carried out by varying the catalyst amounts (10, 20, 30, 40 and 50 mg).

Results and discussion

Ir-NPs were synthesized into the nanopores of modified mont. by incipient wetness impregnation of the IrCl₃ followed by reduction with ethylene glycol and tested as catalyst in the hydrogenation of aromatic ring. Modification of the mont. was carried out by treating with HCl under controlled condition. Powder XRD analysis of the mont. shows the intense 2 θ reflection at 7.06°, with corresponding basal spacing (d_{001}) of 12.5 Å, but upon acid activation it diminishes indicating partial delamination of the clay layered structure. The CEC of the AT-mont. was found 40.8 meq/100 g, which is much lower compared to mont. (126 meq/100 g), also indicating the delamination upon activation. IR spectrum of the mont. and AT-mont. have shown a shifting of Si–O stretching vibration from 1034 to 1083 cm^{−1}, which is due to change in the clay framework during acid activation. AT-mont. shows surface area of about 418 m²/g with high pore volume (0.60 cm³/g) compared to mont. (Surface area: 101 m²/g, pore volume 0.15 cm³/g), which is due to the leaching of Al³⁺ from the clay structure. The presence of type-IV isotherm with H3 type hysteresis loop at P/P₀ ~ 0.4–0.9 (Figure 1)

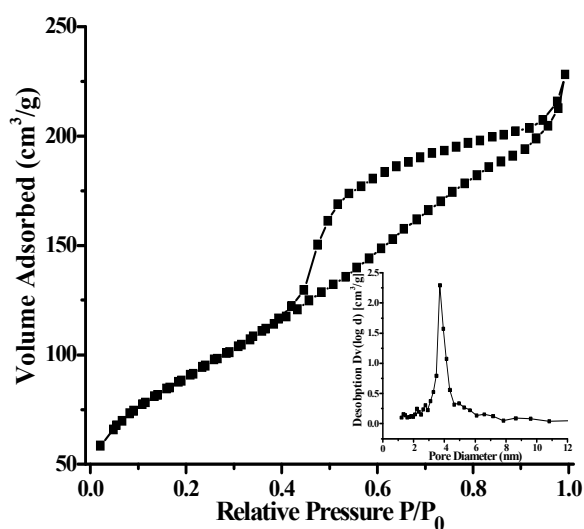


Figure 1. N₂-sorption isotherm and BJH pore size distribution curve of AT-mont.

clearly indicates the mesoporous nature of the activated clay. A narrow pore size distribution with a peak pore diameter centered at 4 nm was observed from the BJH pore size distribution plot, which can act as host for supporting and stabilizing metal nanoparticles. The typical SEM images of mont. and AT-mont. (ESI) indicate the formation of porous surface on mont. upon acid activation. The EDS patterns (ESI) clearly show a decrease in Al content upon acid activation substantiating the leaching of Al^{3+} .

Characterization of supported Ir-NPs

The formation of Ir-NPs was substantiated from the powder XRD analysis (Figure 2) wherein, a broad peak centered at $2\theta = 40.9^\circ$ can be assigned to the (111) reflections of Ir-NPs (JCPDS 01-1212) along with other characteristic peaks of Ir metal³⁵. To confirm the complete reduction of the impregnated iridium salt into the pores of the AT-mont., XPS analysis was carried out and the binding energies (Figure 3) of the supported Ir-NPs show spectrum bands at 60.8 eV and 63.4 eV due to Ir(0) $4f_{7/2}$ and Ir(0) $4f_{5/2}$ respectively, which are marginally higher than that of iridium metal and therefore indicating the formation of metallic particles⁴⁶. These marginally higher values may be attributed to the interaction of Ir-

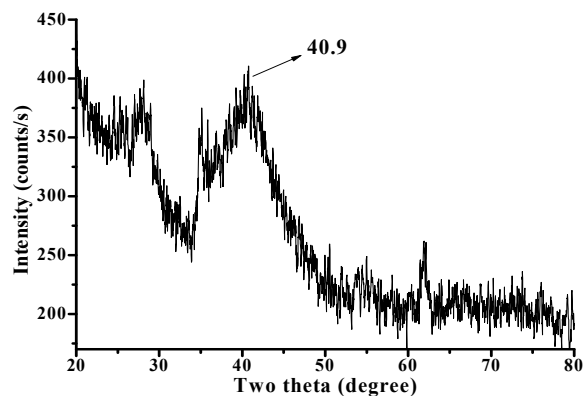


Figure 2. Powder X-ray diffraction pattern of Ir-NPs supported on AT-mont.

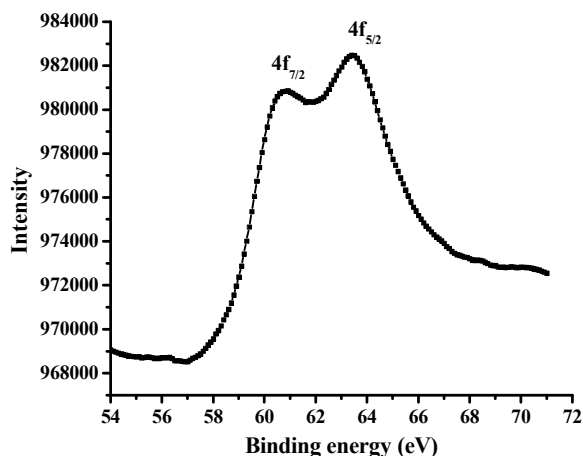


Figure 3. XPS spectra of Ir-NPs supported on AT-mont.

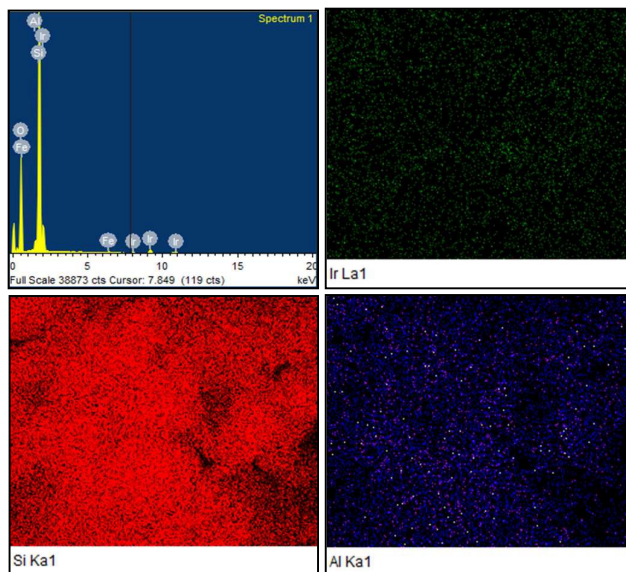
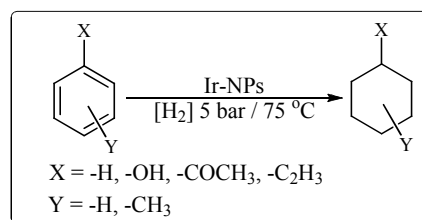


Figure 4. (a) EDS (b) EDS dot mapping of Ir (c) EDS dot mapping of Si (d) EDS dot mapping of Al of Ir-NPs surface

NPs with the framework oxygen of the clay matrix which is expected to induce a positive charge on the metal surface and thereby increasing the binding energies of Ir-NPs¹⁹. The EDS spectra and EDS dot mapping (Figure 4) of Ir-NPs clearly indicates the presence of homogeneously distributed Ir on the AT-mont. The morphology of the supported Ir-NPs was investigated by TEM analysis (Figure 5) and the sizes of Ir-NPs were found to be around 4 nm (with average size of 4.41 nm and standard deviation of less than $\pm 15\%$ calculated from analysis of 100 particles in the TEM image) which is almost equal to pore sizes of the acid activated mont. and evenly distributed in the support matrix. The particle size histogram shows the distribution of the sizes of Ir-NPs nanoparticles in the range 2-8 nm. The N_2 -sorption analysis of the Ir-NPs supported on AT-mont. reveals that the surface area value remarkably decreases to $327 \text{ m}^2/\text{g}$ from $418 \text{ m}^2/\text{g}$, which indicates the generation of the Ir-NPs inside the pores of the clay matrix resulting in decrease of surface area. From ICP-AES, the actual Ir content in AT-mont. was determined and found to be 0.42 mmol of Ir per 1 g of the AT-mont.

Catalytic application

The synthesized Ir-NPs composite was evaluated as a catalyst in the hydrogenation of some aromatic compounds under mild condition (Scheme 1). All these reactions were carried out in a



Scheme 1. Aromatic hydrogenation reaction catalyzed by Ir-NPs supported on AT-mont.

solvent free condition at 75 °C under initial 5 bar H₂ pressure (25 °C), stirring at 500 rpm and the results are shown in Table-1. The effect of catalyst amount on reaction was also studied by varying the catalyst to substrate ratio in the hydrogenation of toluene. The rate of conversion increases with the increase of catalyst amount. The total time required for complete reduction of toluene was also carried out by performing the reaction with a fixed amount of catalyst. It was confirmed that the total conversion of toluene takes place in 6 h of reaction time (ESI). It has been observed that the conversion to hydrogenated product for ortho, meta and para substituted xylene was in the order of 90, 97 and 100% respectively. This can be explained from the electronic effect on the aromatic ring which hinders the hydrogenation process^{49,50}. Additionally, the steric effect also plays an important role for the low conversion in the ortho position of the methyl group in comparison to the meta and para position. The same trend was also observed for ortho and meta cresol with conversion of 43% and 65% respectively. It has been found that the mono-alkyl substituted aromatic rings are more easily hydrogenated in comparison to multi substituted aromatic compounds, which is due to the ease of adsorption of mono-alkyl substrate aromatic ring on the catalyst surface⁴⁹. The recovery of the catalyst was carried out by simple filtration followed by vacuum dry at 150 °C and was used in the hydrogenation of toluene up to three runs by maintaining the stoichiometric ratio of the substrates and catalysts. The powder XRD pattern of the recovered catalyst shows that there is no significant

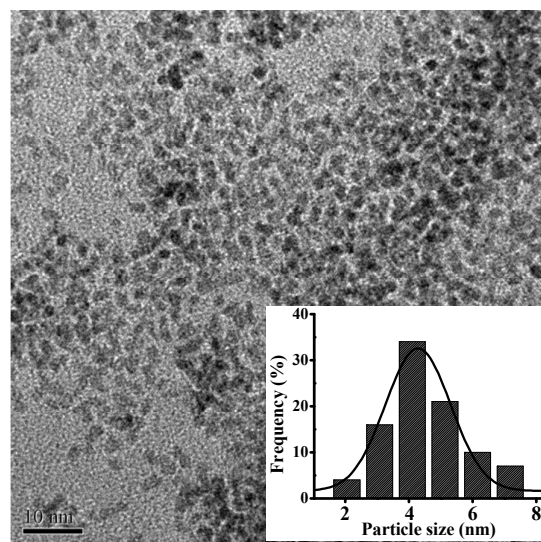


Figure 5. TEM image and particles size histograms with a Gaussian curve fitting of Ir-NPs on AT-mont.

change in the catalyst (ESI). The N₂ sorption isotherm shows that the pore diameter of recovered (third run) Ir-NPs is increased marginally compared to that of fresh catalyst (ESI). The marginal change is may be due to the rupture of the pore walls of some pores leading to larger pores. Ir-NPs have been seen in good morphology with minimum aggregation of few nanoparticles from the TEM images (ESI) of the recovered

Table 1. Tablehydrogenation of arenes by Ir-NPs under solvent free condition.^[a]

Entry	Arene	Product	Conversion ^[b] (%)	TOF ^[c] [h ⁻¹]
1			100 ^[1st] 96 ^[2nd] 95 ^[3rd]	79 76 75
2			90	71
3			97	77
4			100	79
5			43	34
6			65	51
7			45	35
8			73	57

[a] Conditions: catalyst 50 mg, H₂ pressure :5 bars, temperature: 75 °C, time: 6 hours, stirring: 500 rpm.[b] Determined by GC analysis. [c] TOF with respect to product.

catalyst (third run) and the particles are supported into the pores of the mont. having average particle size of 4.67 nm with a standard deviation of 1.27 nm based on the measurement of 100 particles. XPS analysis shows two peaks centered at 60.6 eV and 63.3 eV (ESI) corresponding to Ir(0) 4f_{7/2} and Ir(0) 4f_{5/2} respectively for the recovered catalyst indicating no change in the oxidation state of the Ir metal after the third run of reaction. This indicates that the catalyst is very robust, active with long life time and recyclable for many catalytic runs. To check the heterogeneity of the catalyst, hot filtration test was performed. During the test, a hydrogenation reaction of toluene was carried out and the catalyst was separated from the reaction mixture by filtration after 3 h of reaction and the products were analyzed using GC. The filtrate was further allowed for 3 h reaction time under the same reaction condition, but no increase in the reaction products were observed which indicates that the Ir nanoparticles were intact in the porous clay matrix without any leaching. A number of catalysts with different stabilizing agents/supports have already been reported for hydrogenation of aromatic compounds from which, it is observed that, the Ir-NPs show good catalytic activity under milder reaction condition and remain active for several runs without loss of its activity and morphology^{37,51-57}.

Conclusions

In conclusion, highly stable Ir-nanoparticles can be synthesized by simple incipient wetness impregnation of IrCl₃ into the nanopores of activated montmorillonite matrix followed by reduction using ethylene glycol. The synthesized Ir-nanoparticles were of nearly 4nm in size and distributed homogeneously on the support and are fully characterized using PXRD, XPS, SEM-EDS, TEM and N₂-sorption analysis. Ir-nanoparticles were evaluated as a catalyst in the hydrogenation of aromatic ring and found very active with high turnover frequency up to 79 h⁻¹. The used catalyst can be easily separated by simple filtration. The recyclability test with recovered catalyst was carried and found almost active as fresh catalyst. Recovered catalyst was also fully characterized and found very robust without any remarkable change.

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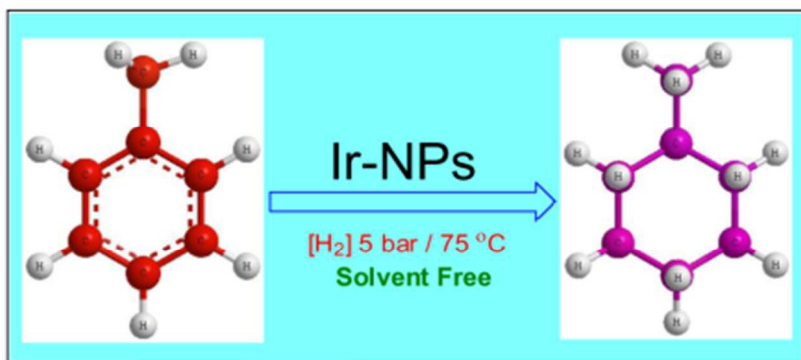
Notes and references

- Chen, H. Qiu and P. N. Prasad, X. Chen, *Chem. Rev.*, 2014, **114**, 5161.
- V. Biju, *Chem. Soc. Rev.*, 2014, **43**, 744.
- A. R. Adini, M. Redlichb and R. Tenne, *J. Mater. Chem.* 2011, **21**, 15121.
- R. G. Chaudhuri and S. Paria, *Chem. Rev.*, 2012, **112**, 2373.
- Q. Zhang, E. Uchaker, S. L. Candelariaza and G. Cao, *Chem. Soc. Rev.*, 2013, **42**, 3127.
- B. Zhou, S. Hermans and G. A. Somorjai (Eds.), *Nanostructure science and technology*, Springer, New York, 2004, Vol. 1-3.
- U. Schmid et. al., *Nanotechnology assessment and prospective*, Springer Berlin Heidelberg, 2006.
- D. L. Feldheim and C. A. Foss (Eds.), *Metal nanoparticles: Synthesis, characterization and application*, CRC Press, New York, 2002.
- C. N. R. Rao, G. U. Kulkarni, P. J. Thomas and P. P. Edwards, *Chem. Soc. Rev.*, 2000, **29**, 27.
- J. M. Campelo, D. Luna, R. Luque, J. M. Marinas and A. A. Romero, *ChemSusChem*, 2009, **2**, 18.
- H. Bönemann, W. Brijoux, R. Brinkmann, M. Feyer, W. Hofstadt, G. Khelashvili, N. Matoussevitch and K. Nagabhushana, *The Strem Chemiker*, 2004, XXI No. 1.
- A. Phukan, J. N. Ganguli and D. K. Dutta, *J. Mol. Catal. A: Chem.*, 2003, **202**, 279.
- O. S. Ahmed and D. K. Dutta, *Langmuir*, 2003, **19**, 5540.
- O. S. Ahmed and D. K. Dutta, *Thermochim. Acta*, 2003, **395**, 209.
- P. B. Malla, P. Ravindranathan, S. Komarneni and R. Roy, *Nature*, 1991, **351**, 555.
- B. J. Borah, D. Dutta, P. P. Saikia, N. C. Barua and D. K. Dutta, *Green Chem.*, 2011, **13**, 3453.
- D. Manikandan, D. Divakar, A. R. Valentine, S. Revathi, M. E. L. Peethi and T. Sivakumar, *Appl. Clay Sci.*, 2007, **37**, 193.
- S. K. Bhorodwaj and D. K. Dutta, *Appl. Clay Sci.*, 2011, **53**, 347.
- P. P. Sarmah and D. K. Dutta, *Green Chem.*, 2012, **14**, 1086.
- B. J. Borah, S. J. Borah, L. Saikia and D. K. Dutta, *Catal. Sci. Technol.*, 2014, **4**, 1047.
- B. J. Borah, S. J. Borah, K. Saikia and D. K. Dutta, *Catal. Sci. Technol.* 2014, **4**, 4001.
- E. Bayram, J. Lu, C. Aydin, A. Uzun, N. D. Browning, B. C. Gates and R. G. Finke, *ACS Catal.*, 2012, **2**, 1947.
- Y. Zhang, H. Jiang, Y. Wang and M. Zhang, *Ind. Eng. Chem. Res.*, 2014, **53**, 6380.
- A. Buonerba, A. Noschese and A. Grass, *Chem. - Eur. J.*, 2014, **20**, 5478.
- M. Fang and R. A. Sanchez-Delgado, *J. Catal.*, 2014, **311**, 357.
- M. Bora, J. N. Ganguli and D. K. Dutta, *Thermochim. Acta*, 2000, **346**, 169.
- D. K. Dutta, B. J. Borah and P. P. Sarmah, *Catal. Rev.*, 2015, **57**, 257.
- C. J. Jia and F. Schuth, *Phys. Chem. Chem. Phys.*, 2011, **13**, 2457.
- W. W. Weare, S. M. Reed, M. G. Warner and J. E. Hutchison, *J. Am. Chem. Soc.*, 2000, **122**, 12890.
- R. Tatumi, T. Akita and H. Fujihara, *Chem. Commun.*, 2006, 3349.
- M. Tamura and H. Fujihara, *J. Am. Chem. Soc.*, 2003, **125**, 15742.
- L. O. Brown and J. E. Hutchison, *J. Am. Chem. Soc.*, 1999, **121**, 882.
- M. Brust, M. Walker, D. Bethell, J. D. Schiffrin and R. Whyman, *J. Chem. Soc. Chem. Commun.*, 1994, 801.
- K. R. Gopidas, J. K. Whitesell and M. A. Fox, *J. Am. Chem. Soc.*, 2003, **125**, 6491.
- M. Choi, Z. Wu and E. Iglesia, *J. Am. Chem. Soc.*, 2010, **132**, 9129.
- F. Bergaya, B. K. G. Theng and G. Lagaly (Eds.), *Handbook of clay science: Developments in clay science*, Elsevier, 2006, Vol. 1, 263.

ARTICLE

Journal Name

- 37 Y. Tonbula, M. Zahmakiran and S. Özkar, *Appl. Catal. B- Environ.*, 2014, **148-149**, 466.
- 38 C. Higman and S. Tam, *Chem. Rev.* 2014, **114**, 1673.
- 39 I. Mochida, O. Okuma and S. -Ho Yoon, *Chem. Rev.*, 2014, **114**, 1637.
- 40 Y. Li, F. Ma, X. Su, L. Shi, B. Pan, Z. Sun and Y. Hou, *Ind. Eng. Chem. Res.*, 2014, **53**, 6718.
- 41 E. Bayram, M. Zahmakiran, S. Özkar and R. G. Finke, *Langmuir*, 2010, **26**, 12455.
- 42 M. Zahmakiran, Y. Tonbulz and S. Özkar, *Chem. Commun.*, 2010, **46**, 4788.
- 43 M. Zahmakiran, Y. Roman-Leshkov and Y. Zhang, *Langmuir*, 2012, **28**, 60.
- 44 L. Zhu, L. Zheng, K. Du, H. Fu, Y. Li, G. You and B. H. Chen, *RSC Adv.*, 2013, **3**, 713.
- 45 M. Zahmakiran, Y. Tonbul and S. Özkar, *J. Am. Chem. Soc.*, 2010, **132**, 6541.
- 46 H. B. Pan and C. M. Wai, *J. Phys. Chem. C*, 2009, **113**, 19782.
- 47 J. Huang, T. Jiang, B. Han, W. Wu, Z. Liu, Z. Xie and J. Zhang, *Catal. Lett.*, 2005, **103**, 59.
- 48 J. D. Rogers, V. S. Sundaram, G. G. Kleiman, S. G. C. de Castro, R. A. Douglas and A. C. Peterlevitz, *J. Phys. F: Met. Phys.*, 1982, **12**, 2097.
- 49 M. V. Bahaman and M. A. Vannice, *J. Catal.*, 1991, **127**, 251.
- 50 G. S. Fonseca, E. T. Silveira, M. A. Gelesky and J. Dupont, *Adv. Synth. Catal.*, 2005, **347**, 847.
- 51 G. S. Fonseca, A. P. Umpierre, P. F. P. Fichtner, S. R. Teixeira and J. Dupont, *Chem. Eur. J.*, 2003, **9**, 3263.
- 52 V. Mevellec, A. Roucoux, E. Ramirez, K. Philippot and B. Chaudret, *Adv. Synth. Catal.*, 2004, **346**, 72.
- 53 I. S. Park, M. S. Kwon, K. Y. Kang, J. S. Lee and J. Park, *Adv. Synth. Catal.*, 2007, **349**, 2039.
- 54 B. Yoon and C. M. Wai, *J. Am. Chem. Soc.*, 2005, **127**, 17174.
- 55 H. Gao and R. J. Angelici, *J. Am. Chem. Soc.*, 1997, **119**, 6937.
- 56 J. Pellegatta, C. Blandy, V. Colliere, R. Choukroun, B. Chadret, P. Cheng and K. Philippot, *J. Mol. Catal. A: Chem.*, 2002, **178**, 55.
- 57 K. S. Weddle, J. D. Aiken III and R. G. Finke, *J. Am. Chem. Soc.*, 1998, **120**, 5653.

Graphical Abstract

Ir nanoparticles supported on nanoporous montmorillonite clay showing efficient catalytic activity for hydrogenation of aromatic compounds.