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# Journal Name

## COMMUNICATION

# Efficient alkene hydrogenation over magnetically recoverable and recyclable Fe₃O₄@GO nanocatalyst using hydrazine hydrate as the hydrogen source†

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**Magnetic Fe₃O₄ nanoparticles embedded on Graphene Oxide (Fe₃O₄@GO) behaves as highly efficient and reusable heterogeneous nanocatalyst for alkene hydrogenation in the EtOH at 80 °C temperature using hydrazine hydrate as hydrogen source to deliver corresponding alkanes in good to excellent yields together with high TOF (>4500 h⁻¹) within 4-20 h reaction time.**

Alkene hydrogenation catalyzed by expensive metal catalysts including Pd, Pt and Rh using hydrogen as reducing agent has emerged as an efficient protocol for petrochemical conversions and pharmaceuticals synthesis.[1] But the problems traditionally associated with these catalytic pathways are high cost of these precious metal catalysts, use of flammable hydrogen gas at high pressure and elevated temperatures. Considerable progress has been achieved with the first row transition-metal catalysts for catalytic alkene hydrogenation. Owing to high surface-to-volume ratio, transition-metal or metal oxide nanoparticles used as nanocatalysts nicely link the gap between ordinary homogeneous and heterogeneous metal based catalytic systems. Moores *et.al* have utilized polystyrene supported Fe(0) nanoparticles for alkene hydrogenation at 40 bar H₂ pressure.[2] New cobalt complexes have been designed by Chirik group for catalytic asymmetric alkene hydrogenation.[3] Wangelin and co-workers have developed complex Co and Fe catalysts for hydrogenation of alkene at 1 bar H₂ pressure.[4] Fe nanoparticles supported on functionalized graphene have been employed as catalyst by Breit group for catalytic alkene hydrogenation at 20 bar H₂ pressure requiring 24 h reaction time.[5] Almost 100% conversion has been achieved for alkene hydrogenation at 10 bar H₂ pressure using Pd@Co/C catalyst.[6] But all of these alkene hydrogenation catalysts involve use of H₂ at high pressure. So an alternative strategy for efficient alkene hydrogenation over a heterogeneous catalyst is highly desirable, which avoids highly flammable H₂ at high temperature.

Use of hydrazine hydrate as hydrogen source unlike H₂ (requiring high pressure) has gained a considerable importance as it facilitates easy handling and generation of only environmentally benign N₂ as a byproduct.[7] Limitations regarding the hydrazine hydrate are storage and disposal in terms of atom economy. Upon contact with the strong oxidizing agents some exothermic reactions and evolution of gases may result and also this hydrogen source relies ultimately on ammonia synthesis which itself requires extreme high pressure of H₂. Alkene hydrogenation using hydrazine was carried out by different catalysts including guanidine,[8] metal-organic framework[9] and copper nanoparticles supported on diamond nanoparticles.[10] Long reaction times and high catalyst loading (40 mol% catalyst loading) are major drawbacks.[11] Recently graphene and metal oxide nanoparticles are hugely recognized as reusable heterogeneous catalyst for conducting different types of organic transformations owing to their large surface area, high mechanical and hydrothermal stability.[12]

In this study, we have prepared magnetic Fe₃O₄ nanoparticles (5 nm and 15 nm) embedded on graphene oxide and carried out alkene hydrogenation over these magnetic Fe₃O₄@GO nanocatalyst using hydrazine hydrate as hydrogen source



**Scheme 1** Synthesis of Fe₃O₄@GO nanocatalyst and catalytic alkene hydrogenation reaction with this nanocatalyst using N₂H₄.H₂O as hydrogen source.

source. Magnetic separation of the catalyst, absence of flammable $H_2$ gas, high product selectivity, low catalyst loading and high recycling efficiency are the major advantages of $Fe_3O_4$@GO nanocatalyst. As shown in Scheme 1, magnetically recoverable nanocatalysts $Fe_3O_4$@GO bearing 5 and 15 nm $Fe_3O_4$ particle sizes have been synthesized by one step hydrothermal process using graphene oxide and anhydrous $FeCl_3$ at 200 °C for 4 and 10 h reaction time, respectively. Detailed experimental procedure for catalyst synthesis and comparison with existing, comparable materials is given is given in the ESI (S2). $Fe_3O_4$@GO samples have been thoroughly characterized by wide angle powder XRD, TEM, XPS, Raman, FT-IR and AFM spectroscopic tools. The two nanocatalysts with the $Fe_3O_4$ sizes of 5 and 15 nm particle sizes are designated as $Fe_3O_4$@GO-1 and $Fe_3O_4$@GO-2, respectively.
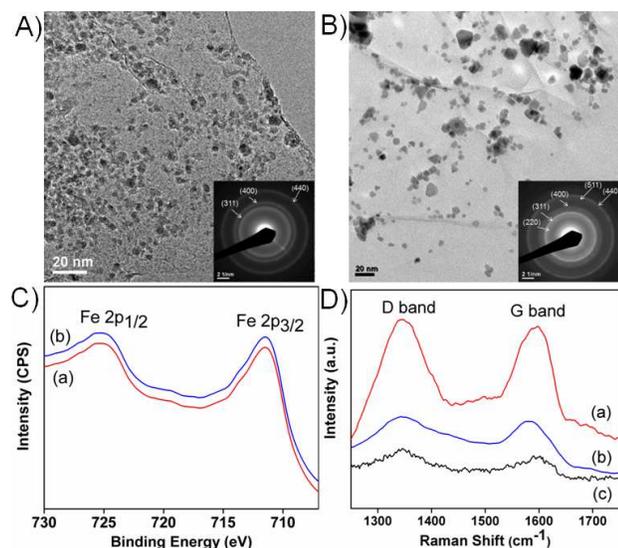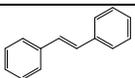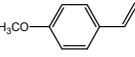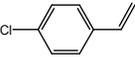


**Fig. 1** (A and B) TEM images of $Fe_3O_4$@GO-1 and $Fe_3O_4$@GO-2 nanocatalysts, C) High resolution XPS spectra and D) Raman spectra of (a) $Fe_3O_4$@GO-1, (b) $Fe_3O_4$@GO-2 nanocatalysts and (c) GO respectively. Corresponding SAED patterns are given in the inset of (A) and (B).
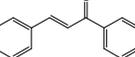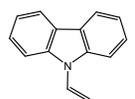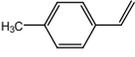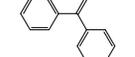
TEM images (Fig. 1A and 1B) suggest that the $Fe_3O_4$ nanoparticles (black in color) with the size 5 nm and 15 nm are homogenously dispersed throughout the graphene oxide surface of $Fe_3O_4$@GO-1 and $Fe_3O_4$@GO-2 nanocatalysts, respectively. Selected area electron diffraction (SAED) patterns (inset of Fig. 1A and 1B) confirm crystalline feature of $Fe_3O_4$ nanoparticles.[13] In the Xray photoelectron spectroscopy (XPS) spectra (Fig. 1C) the binding energy peaks centered at 711.5 eV and 725.2 eV, attributed to the $Fe2p_{3/2}$ and $Fe2p_{1/2}$ for $Fe_3O_4$, respectively.[14] The presence of graphene layer was confirmed by Raman spectroscopy which showed D band at 1348 $cm^{-1}$ and G band at 1583 $cm^{-1}$ (Fig. 1D).[15] The $I_D/I_G$ for $Fe_3O_4$@GO-1, $Fe_3O_4$@GO-2 and as synthesized GO are 1.06, 1.04 and 0.9, respectively, revealing molecular defects and reduction of GO in hydrothermal process. EDX pattern and elemental mapping (Figures S3 and S4, ESI) prove the presence of C, O and Fe elements in the $Fe_3O_4$@GO materials. Wide angle powder XRD and FT-IR data are provided in Figures S5 and S8, ESI. AFM

topography images signify the cross sectional features of the $Fe_3O_4$@GO nanocatalysts (Figure S10, ESI). The catalytic activity of $Fe_3O_4$@GO nanocatalyst has been investigated in the alkene hydrogenation in EtOH solvent using hydrazine hydrate as reducing agent at 80 °C (Scheme 1). All the products have been confirmed by GC-MS analysis. Detail catalytic procedure is provided in the section S2 of ESI. 4-chlorostyrene was chosen as model compound for this hydrogenation reaction (Table S1). With the gradual increase of $N_2H_4.H_2O$ (from 3.0 equivalents to 10.0 equivalents) catalytic reactions proceed faster (Table S1, entries 3-7). 10.0 equivalents $N_2H_4.H_2O$ is optimum to complete the reduction of without leaving any trace of incomplete reduction products (Table S1, entry 8). From the Table S1 it is quite evident that in EtOH at 80 °C temperature is most suitable condition for hydrogenation reaction. $Fe_3O_4$@GO-1 nanocatalyst has been employed to achieve conversion 70% keeping other parameters same (Table S1, Entry 9). Under the same reaction conditions $Fe_3O_4$@GO-2 nanocatalyst resulted 99% conversion (Entry 8). This result indicates that large $Fe_3O_4$ nanoparticles (15 nm size) with high crystalline feature embedded on graphene oxide support are beneficial for the catalytic transfer hydrogenation reaction from hydrazine hydrate in EtOH medium. The Fe content in the $Fe_3O_4$@GO-1 and $Fe_3O_4$@GO-2 catalysts are 0.05298 μmol/g and 0.1232 μmol/g, respectively determined by ICP-MS analysis, indicating that the reactions were carried out with $3.17×10^{-4}$ mol% and $7.39×10^{-4}$ mol% loading of iron. Catalytic reaction with bare $Fe_3O_4$ nanoparticles (Table S2, Entry 1) gives 45% conversion of 4-chlorostyrene, suggesting that graphene oxide has a promising role. Strong adsorption of organic molecules onto graphene oxide sheet is attributed to the π stacking and hydrophobic interactions that renders enhancement of catalytic conversion of $Fe_3O_4$@GO nanocatalyst. Effect of catalyst dose on catalytic performance was evaluated by considering reaction with $Fe_3O_4$@GO-2 nanocatalyst with different mol% loading of $Fe_3O_4$ (Table S2).

Substrate scope was examined by carrying out alkene hydrogenation reaction with various alkenes over $Fe_3O_4$@GO-2. Electron donating styrenes (Table 1, entries 2 and 4) required long reaction times to yield corresponding substituted ethylbenzenes. 4-chlorostyrene and norbornene (Table 1, entries 3 and 7) showed 98-99% conversions in 4-6 h. Vinyl substituted polycyclic aromatic hydrocarbon (Table 1, entry 5) was reduced to corresponding ethyl derivative with 99% conversion at 18 h. Cyclic alkene cyclohexene underwent 86% conversion (Table 1, entry 6) but surprisingly very poor conversion was achieved for *cis*-cyclooctene (Table 1, entry 8) could be due to the presence of almost orthogonal allylic C-H bonds. Chemoselective reduction of C=C has been achieved for α,β-unsaturated ketone, chalcone (Table 1, entry 9) with 90% conversion. Successful hydrogenation was conducted for mono- and di-substituted alkenes (Table 1, entries 1 and 12). 9-vinylcarbazole (Table 1, entry 10) exhibited moderate conversion of alkene hydrogenation reaction. $Fe_3O_4$@GO is also effective for the larger scale reaction with the consistent conversion (Table 1, entry 11). The TOF values range from

4650-33482 h⁻¹ and these are impressively high, suggesting

| Entry | Alkene | Time (h) | Conversion[b] (%) | TOF×10² (h⁻¹) |
|---|---|---|---|---|
| 1 | | 20 | 80 | 54.1 |
| 2 | | 20 | 94 | 63.5 |
| 3 | | 4 | 99 | 334.8 |
| 4 | | 12 | 85 | 95.8 |
| 5 | | 18 | 99 | 74.4 |
| 6 | | 10 | 86 | 116.3 |
| 7 | | 6 | 98 | 221 |
| 8 | | 16 | 55 | 46.5 |
| 9 | | 12 | 90 | 102 |
| 10 | | 20 | 70 | 47.3 |
| 11[c] | | 12 | 87 | 127.5 |
| 12 | | 18 | 99 | 74.4 |
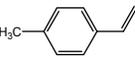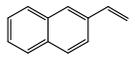
huge future potential of the $Fe_3O_4$@GO nanocatalyst.

**Table 1** Hydrogenation of alkenes catalyzed by $Fe_3O_4$@GO-2[a]

[a]Reaction conditions: Alkene (0.25 mmol), catalyst (15 mg), $N_2H_4.H_2O$ (10 equivalent, 2.5 mmol, 125 mg), EtOH (3 mL), 80°C. [b] Determined by GC analysis. TOF= Turn over frequency (moles of substrate converted per mole of active sites per hour). All the products were confirmed by GC-MS analysis. [c]Reaction was conducted with 10 mmol of 4-methylstyrene.

To confirm that the alkene hydrogenation catalytic reaction is indeed heterogeneous in nature, we have performed hot filtration test and leaching test by considering 4-methylstyrene as model substrate (See ESI, section S15). In order to check mechanical stability of $Fe_3O_4$@GO catalyst we have carried out TEM (Figure S13) and XPS (Figure S14A) analyses, which suggest that our catalyst is stable under reaction conditions. The efficacy of a $Fe_3O_4$@GO-2 nanocatalyst is also evident from its recyclability and stability (for example, no metal leaching). The catalyst can be efficiently recycled and reused for ten successive catalytic cycles for hydrogenation of 4-methylstyrene under optimized conditions (Figure S12, ESI). No leaching of Fe from $Fe_3O_4$@GO-2 catalyst is observed (AAS analysis, section S15, ESI), suggesting GO as an excellent support for the liquid phase catalytic reactions.[16]

In summary, $Fe_3O_4$ nanoparticles embedded on GO behaves as magnetically recoverable heterogeneous nanocatalyst for alkene hydrogenation with low catalyst loading using hydrazine hydrate as hydrogen source in EtOH at 80°C together with high

TOF of >4500 h⁻¹. This newly developed protocol avoids use of highly flammable $H_2$ gas at high pressure and temperature.

### Notes and references

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† Electronic Supplementary Information (ESI) available: synthesis, characterizations and catalysis details. See DOI: 10.1039/c000000x/

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