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Pd on Amine-Terminated Ferrite Nanoparticles: A Complete Magnetically Recoverable Facile Catalyst for Hydrogenation Reactions[†]

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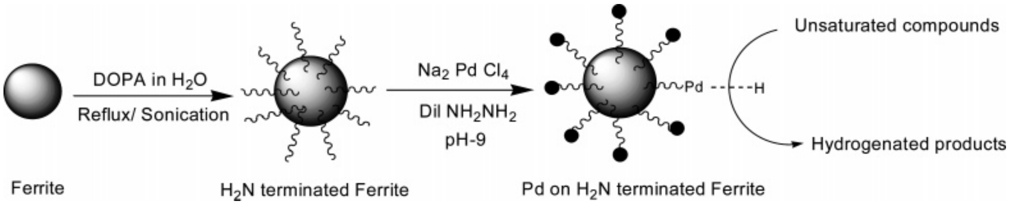
ABSTRACT



The present communication reports a facile route for Pd(0) immobilization on the surface of amine-terminated Fe_3O_4 and $NiFe_2O_4$ nanoparticles for a series of hydrogenation reactions. The catalysts are completely recoverable with the simple application of an external magnetic field, and the efficiency of the catalyst remains unaltered even after 10 repeated cycles for each of the reactions.

Conventionally, heterogeneous catalysis is favored over homogeneous catalysis for a large number of applications in both fundamental research and industrial applications due to its ease of handling, simple workup, and regenerability.[1] Despite their synthetic simplicity, heterogenized catalysts are typically less effective than their homogeneous counterparts.[2] To overcome this limitation, nanosized catalysts have been introduced,[1] as they are endowed with larger surface area when compared to their bulk counterparts. Recently, nanocrystalline metals and metal oxides have been efficiently used as environmentally friendly solid catalysts and also as solid supports for organic transformation reactions such as epoxidation,[1] benzylation,[3] coupling[4] reactions, etc. Although a higher surface area affords nanomaterials with more active sites, an associated higher surface energy unfavorably increases the particles' tendency to agglomerate and hence nullifies the high surface area advantage. Thus, to derive maximum benefit, surface-modified catalysts have been designed.[5]

Surface modification with appropriate capping agents offers better dispersion of the catalyst in appropriate solvents, and thus better performance can be anticipated in their various applications. Surface-modified nanoparticles can be used as noble metal supports to prepare heterogeneous catalysts that are more accessible to the reactants. Tamura et al.[6] have shown that BINAP- capped Pd nanoparticles possess the ability to catalyze asymmetric hydrosilylation

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of styrene to give chiral alcohols. The primary formidable task in using such nanoparticles for heterogeneous catalysis is the problem associated with the separation of the catalyst after the reaction. It is here that nanoparticles, especially superparamagnetic particles amenable for magnetic separation, come as a redeemer.[7] Magnetic separation is an attractive alternative to filtration or centrifugation as it prevents loss of the catalyst and the reusability increases. This makes the catalyst cost-effective and promising for industrial applications. Recently, Hu et al. reported a Fe_3O_4-immobilized chiral Ru catalyst for the asymmetric hydrogenation of aromatic alcohols.[8] Yi et al. reported[9] the synthesis of nano Pd on SiO_2-coated Fe_2O_3 and their application in the hydrogenation of nitrobenzene.

The present communication reports a facile route for Pd(0) immobilization on the surface of amine-terminated Fe_3O_4 and $NiFe_2O_4$ nanoparticles for a series of hydrogenation reactions. These include aromatic nitro and azide compounds to their respective amine derivatives with better efficiency than earlier reports[10] and saturation reaction of double- and triple-bond compounds. To the best of our knowledge, this is a first report for the use of these catalysts for the named reactions with high efficiency. The catalysts are completely recoverable with the simple application of an external magnetic field and remain active even after 10 repeated cycles for each of the reactions.

The synthesis and characterization of the nanosized $NiFe_2O_4$ and Fe_3O_4 have been reported previously.[11,12] Anchoring of dopamine molecules on the surface of $NiFe_2O_4$ and Fe_3O_4 has been achieved by refluxing and sonication, respectively. The procedure for the synthesis of the materials is provided as Supporting Information. Hereafter, the two catalysts will be referred to as $NiFe_2O_4$-DA-Pd and Fe_3O_4-DA-Pd.

The FTIR spectra of surface-functionalized nanoparticles and pure dopamine are given in the Supporting Information. In the FTIR spectrum, the peak at 3410 cm^{-1} has been assigned to the surface-adsorbed water and peaks at 2924 and 2848 cm^{-1} are assigned to the C−H stretching vibrations of aromatic groups. The peak at 1616 cm^{-1} is due to the N−H bending. The peak at 1486 cm^{-1} is due to C−H bending of aromatic groups, whereas peaks at 1263 and 1121 cm^{-1} are due to C−O stretching and aliphatic C−H bending, respectively. The sharp peak at 594 cm^{-1} is the IR signature for ferrite particles.

The concentration of Pd in $NiFe_2O_4$-DA-Pd and Fe_3O_4-DA-Pd as estimated by inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis is 8.54 and 5.87 wt %, respectively. To monitor the changes in the composition, Pd concentration was estimated after five cycles in both the catalysts and found to be 8.49 and 5.84, respectively. This proves that there is no loss of Pd due to leaching during the reaction. This explains the unaltered efficiency of the catalyst even after 10 cycles.

X-ray photoelectron spectroscopy studies were carried out to establish the oxidation state of Pd in the catalyst. Figure 1 is the Pd 3d5/2 binding energy spectrum that consists of a single peak at 334.42 eV with a full width at half-maximum (fwhm) of 1.6 attributed to the Pd in the zero oxidation state. This unambiguously establishes that Pd exists as Pd(0), a primary requirement for the Pd-catalyzed hydrogenation reactions.

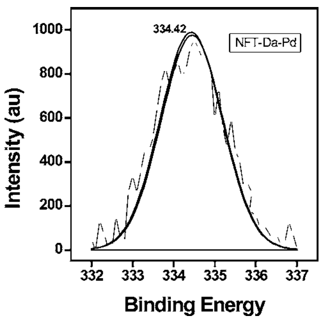

Figure 1. Binding energy spectra of Pd 3d5/2 in the as synthesized catalysts showing the presence of only Pd(0) in them.

The magnetization Vs applied field plot shows that the particles are superparamagnetic at room temperature. The magnetization does not saturate up to 8000 and 20 000 G for $NiFe_2O_4$ and Fe_3O_4, respectively, and the coercivity is almost negligible. The magnetizations for the as synthesized $NiFe_2O_4$ and Fe_3O_4 nanoparticles at the highest applied fields are 43.3 and 57.10 emu/g, respectively. The magnetization results indicate the suitability of nanosized $NiFe_2O_4$ and Fe_3O_4 as catalyst supports for the magnetic separation.

Figure 2a,b shows the TEM micrographs of the $NiFe_2O_4$-DA-Pd and Fe_3O_4-DA-Pd catalysts before reaction. Figure 2c,d shows the micrographs of the $NiFe_2O_4$-DA-Pd catalyst after three and five reactions. It is observed that the synthesized particles are spherical, about 10−12 nm in size, and nearly monodisperse.

The morphology and size of the particles do not change considerably even after five reactions. This result again supports the unaltered efficiency of the catalyst. The figure also shows the photograph of the catalyst being pulled magnetically.

In a typical reaction, 2 mmol of the reagent is dissolved in 10 mL of ethyl acetate or ethanol with 0.025 g of catalyst under 1 atm of hydrogen pressure. Completion of the reaction is monitored by thin-layer chromatography (TLC). After

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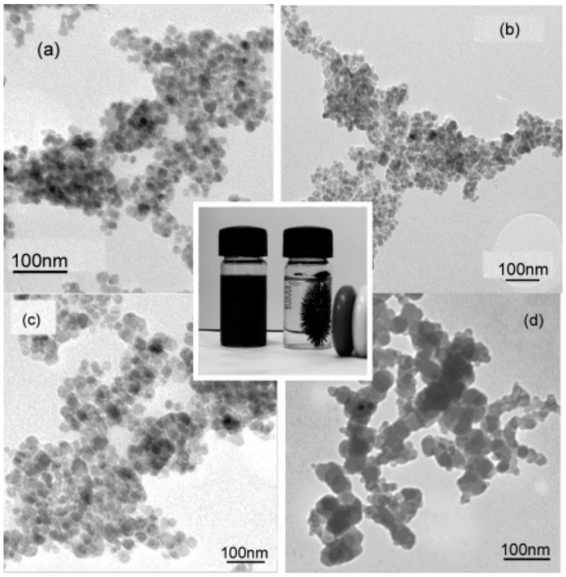
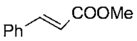
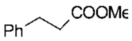
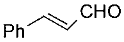
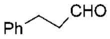
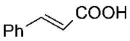
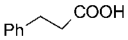
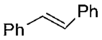
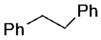
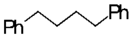
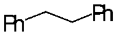
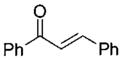
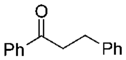
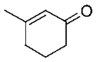
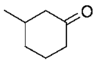
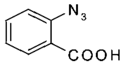
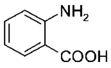


Figure 2. TEM micrographs of the $NiFe_2O_4$-DA-Pd (a) and Fe_3O_4-DA−Pd (b) catalyst before reaction. $NiFe_2O_4$-DA-Pd catalyst after 3 (c) and 5 reactions (d), respectively.

completion, the catalyst is separated by a small magnet placed at the bottom of the reaction vessel. Thereafter, the catalyst is washed with ethyl acetate and used for the next reaction. The catalytic reactions have been repeated, and even after 10 cycles there is no deterioration in the catalytic efficiency. The time required for the completion of the reactions using ethanol as a solvent was less than that using ethyl acetate. This is because of the complete heterogeneous behavior of the catalyst in ethyl acetate, whereas in the case of ethanol, the catalyst is readily dispersible thereby providing more active sites. This latter phenomenon may therefore be termed as "solubilized heterogeneous catalysis".[13] The detailed observations of all the reactions are given in Table 1. The unaltered efficiency of the catalyst even after 10 cycles is obvious from our TEM micrographs and AES studies where no significant change in the catalyst is observed even after five reactions. All the above reactions have also been repeated using the Fe_3O_4-DA-Pd catalyst, and except for the extended time period, no other difference is observed. The lower Pd concentration as determined from ICP-AES in the latter catalyst explains the longer reaction period.

Table 1. Summary of the Observations from the Different Reactions Carried Out on the $NiFe_2O_4$-DA-Pd Catalyst[a]

substrate	product	conversion (%)	isolated yield[a] (%)	time (min)	
				etoh	etoac
		100	97	20	45
		100	75	20	45
		100	98	25	55
$Ph-NO_2$	$Ph-NH_2$	100	98	15	30
		100	98	20	40
$Ph-C\equiv C-C\equiv C-Ph$		100	98	30	60
$Ph-C\equiv C-Ph$		100	99	25	55
		100	85	35	60
		100	95	15	35
		100	98	15	30

[a] Reactant amount, 2 mmol; catalyst amount, 0.025 g; and solvent amount, 10 mL; respectively, in each case. [a] Yield after 5 reactions.

In summary, we have synthesized an efficient Pd(0) catalyst immobilized on amine-modified $NiFe_2O_4$ and Fe_3O_4 nanoparticles highly suitable for the hydrogenation of aromatic nitro and azide compounds to their respective amines as well as saturation of different kinds of unsaturated compounds. The catalyst is completely magnetically recoverable because of the superparamagnetic behavior of $NiFe_2O_4$ and Fe_3O_4 nanoparticles. The efficiency of the catalysts remains unaltered even after 10 cycles making them remarkable catalysts for industrial applications because of their efficiency, ease of handling, and cost effectiveness.

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Supporting Information Available: Experimental methods, FTIR spectra, VSM plots, GCMS spectra,[1] H and [13] C spectra, and table for the Fe_3O_4-DA-Pd catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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