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Tetrahedron Letters 49 (2008) 1818–1823

Tetrahedron Letters

Clay entrapped nickel nanoparticles as efficient and recyclable catalysts for hydrogenation of olefins

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Received 24 October 2007; revised 3 January 2008; accepted 10 January 2008
Available online 15 January 2008

Abstract

Nickel nanoparticles are prepared in the interlamellar spaces of K10-Montmorillonite clay by chemical reduction at moderate temperatures. These clay entrapped nickel nanoparticles are characterized by UV–vis, powder XRD, EDX and HRTEM studies. The resultant ecofriendly supramolecular assembly with nickel content (2.84 wt %) has good catalytic efficiency in hydrogenation of alkenes and alkynes with hydrazine as a reducing agent in ethanol medium. Advantages of the present study include absence of an external hydrogen source, catalyst reusability and a green medium.

Keywords: Nickel; Nanoparticles; K10-Montmorillonite; Hydrogenation; Olefins

Recent advances in organic synthesis in which smectite clays are used as catalysts or catalyst supports have led to a rational approach to the design of new heterogeneous catalysts.[1] Amongst the advantages of pillared smectite clays, the most significant is their large size and hence they can accommodate a greater number of reagents for better catalytic activity under controlled conditions.[2] A number of methods have been used to prepare nickel nanoparticles both in solution as well as in heterogeneous media. In a seminal approach, Rao et al. prepared nickel nanoparticles in Montmorillonite clays via in situ reduction of Ni(II) with boiling ethylene glycol.[3] In subsequent studies, nickel nanoparticles were also prepared via various approaches such as in water-in-oil microemulsions,[4] aqueous hydrazine,[5] ethylene glycol,[6] *N*,*N*-dimethylformamide[7] as well as on heterogeneous media like carbon nanotubes,[8] silica,[9] surfactant,[10] activated carbon,[11] and on protein.[12]

Recently, catalytic applications of nickel nanoparticles have gained significance and they have been used effectively for chemoselective oxidative coupling of thiols,[13a] reduction of ketones,[13b] aldehydes[13c] and semihydrogenation (ethanol as hydrogen source) of alkynes.[13d] Surprisingly, until now there has been no report of hydrogenation of olefins and enones. Also, a general problem of metal nanoparticles is their tendency to undergo agglomeration, which increases their particle size, and therefore, dramatically reduces the catalytic activity.[14] Two general strategies have been developed to stabilize the particle size of the metal, namely, supporting the metal nanoparticles on suitable solid surfaces or by using suitable ligands.[15] New possibilities for nickel catalysis can be developed when the nickel nanoparticles could be stabilized by encapsulating them in a structured host to combine the unique catalytic properties of nickel nanoparticles with reaction shape-selectivity effects.

This prompted us to develop nickel(0) entrapped in a clay matrix from cheap precursors (Scheme 1) in a simple experimental protocol, using hydrazine as a reducing agent. This selective and active hydrogenation catalyst can replace Raney nickel[16] and other common heterogeneous hydrogenation catalysts such as Pt and Pd, and also reduce costs since these catalysts are normally used in excess and generate poisonous waste end-products after

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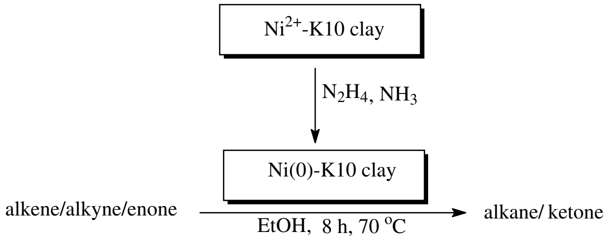
doi:10.1016/j.tetlet.2008.01.061



Scheme 1. Hydrogenation of unsaturated substrates with clay entrapped nickel nanoparticles.

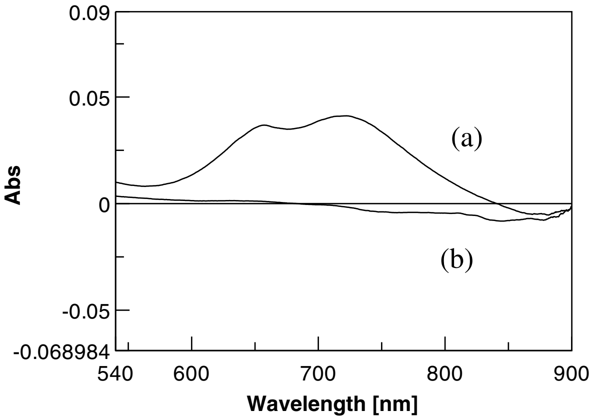


Fig. 2. (a) UV–vis spectrum (in ethanol) of the $NiCl_2$ solution from nickel supported on K10-Montmorillonite and (b) UV–vis spectrum (in ethanol) of the reduced nickel.

the reaction is complete. Our method is also expected to result in the following advantages: (a) Ni^{2+}-exchanged K10-Montmorillonite acts a source for metallic nickel, (b) hydrazine not only acts as a reducing agent but also generates an inert atmosphere by releasing nitrogen, (c) ethanol or water can be used as a solvent, (d) one of the most significant advantages of this methodology is that it avoids the risk of handling external molecular hydrogen.

We report here the preparation, characterization and hydrogenating properties of nickel nanoparticles entrapped in K10-Montmorillonite clay. The catalyst was prepared by reduction with hydrazine in an aqueous alkaline medium using Ni^{2+}-exchanged K10-Montmorillonite clay as a precursor. The black suspension after centrifugation was washed with deionized water and dried at 100 °C for 6 h. The Ni content of these clay entrapped nanoparticles was found to be 2.84 wt %, by using energy dispersive X-ray analysis (EDX, a technique used in conjunction with SEM). Importantly, EDX analysis also indicated that, within the detection limits, nickel was the only element present in these particles. The recovered catalyst (after the third cycle) was also subjected to EDX analysis and the nickel content was only marginally decreased (2.82 wt %). Though a change in shape and size of the nanoparticles may have occurred, this, however, does not affect the catalytic activity. It is relevant to note here that El-Sayed[17] has established that changes in the size and shape of the nanoparticles could occur during the course of their catalytic function. The absence of chlorine in the sample, showed that the entrapped nickel is zerovalent (Fig. 1). The catalyst was characterized by UV–vis, powder XRD and also by high resolution transmission electron microscopy. The reduction of Ni^{2+} was considered complete after the disappearance of a broad band at 630–680 nm (Fig. 2). A powder XRD study was undertaken for the estimation of phases present in the prepared materials (Fig. 3).

All the reflection peaks can be indexed as face centered cubic Ni. Three characteristic peaks for nickel ($2\theta = 44.5$, 51.8 and 76.4), marked by their indices, [(1 1 1), (2 0 0) and (2 2 2)] were observed. In accordance with the above two analyses, it can be concluded that the nanoparticles prepared in this method are pure nickel of fcc structure. No oxides or hydroxides of nickel were observed, as was evident from the phase analysis by XRD. This may be explained by the nitrogen gas which is produced continuously during the reaction, which in turn created an inert atmosphere. A typical high-resolution transmission electron micrograph (HRTEM) and the size distribution of the nickel nanoparticles obtained in a layer of the clay matrix are shown in Figure 4. The particles are essentially mono-dispersed with an average diameter of 15–20 nm (Fig. 4a–d). The corresponding electron diffraction patterns for the particles (Fig. 4e) revealed that the

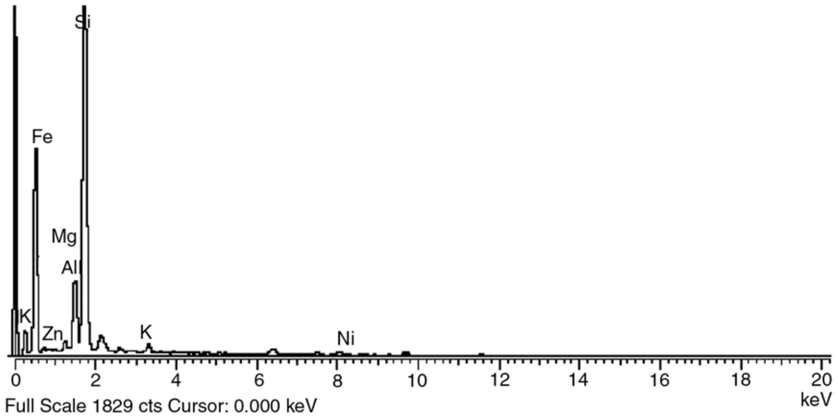


Fig. 1. EDX spectra of clay entrapped nickel nanoparticles.

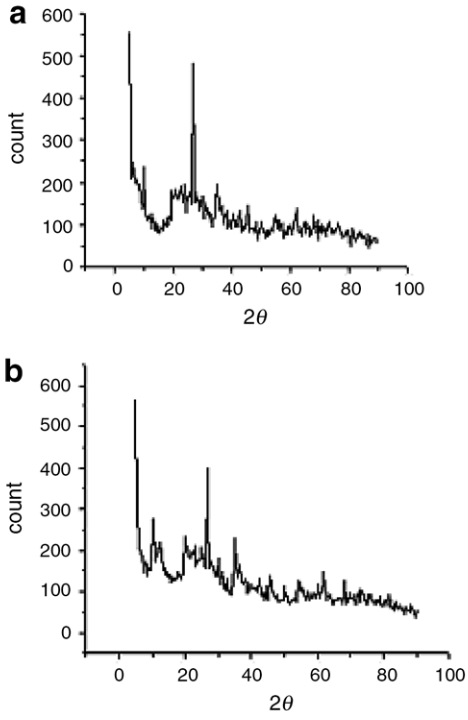
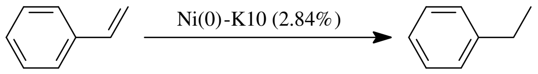


Fig. 3. (a) Powder XRD pattern of K10-Montmorillonite clay. (b) Powder XRD pattern of nickel nanoparticles entrapped on K10-Montmorillonite clay matrix.

Table 1
Optimization of the reaction conditions for the hydrogenation of styrene using clay entrapped nickel nanoparticles as catalyst[a]



Run	Catalyst (mg)	Hydrazine (mL)	Solvent	Time (h)	Yield[b] (%)
1	None	None	ACN	8	—
2	100[c]	0.1	ACN	8	—
3	100[d]	0.2	EtOH	8	—
4	50	0.1	ACN	24[e]	—
5	50	None	ACN	8	—
6	None	0.1	ACN	8	—
7	100	0.1	ACN	3	39
8	100	0.1	ACN	8	91
9	50	0.2	ACN	8	78
10	100	0.2	ACN	8	100
11	100	0.1	EtOH	8	62
12	100	0.2	EtOH	8	100
13	100	0.2	ACN/H_2O[f]	8	100
14	100	0.2	Hexane	8	91

[a] Reagents and reaction conditions: styrene (0.45 mmol), solvent (3 mL), at 70 °C.

[b] Yield determined by GC.

[c] K10-Montmorillonite clay used as catalyst.

[d] Ni^{2+}–K10 clay used as catalyst.

[e] Reaction carried out in rt.

[f] Acetonitrile–water (1:1) mixture.

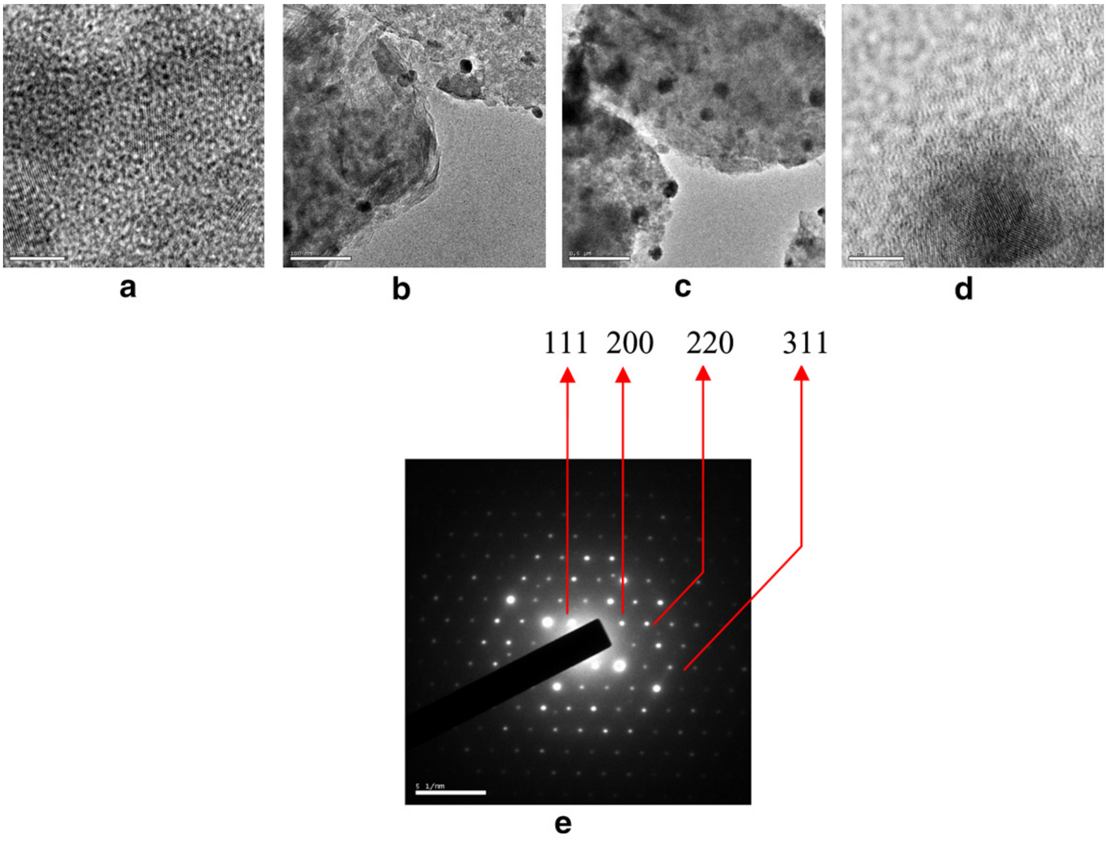
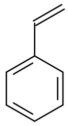
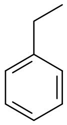
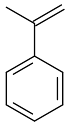
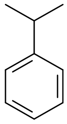
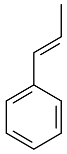
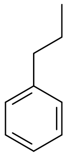
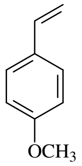
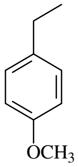
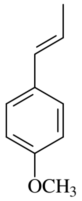
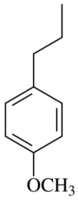
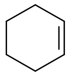
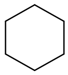
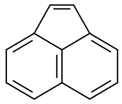
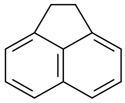
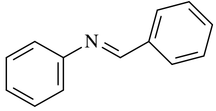
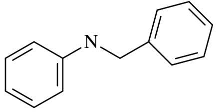
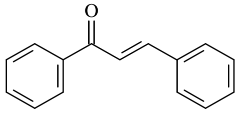
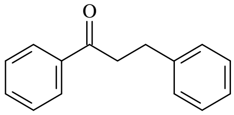
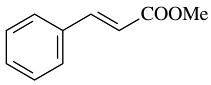
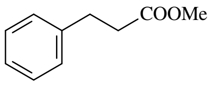
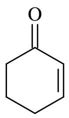
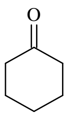
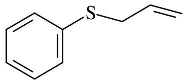
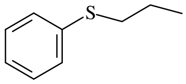


Fig. 4. (a–c) HRTEM images of highly dispersed nickel nanoparticles embedded in clay matrix. (d) A HRTEM image of a selected portion of nickel nanoparticles on clay matrix. (e) Selected area electron diffraction pattern for the nanoparticles shown in (a) and also the electron intensity profile expected for fcc nickel nanocrystallites.

Table 2
Catalytic reduction of various unsaturated substrates with nickel nanoparticles embedded in clay matrix[a]

Entry	Substrate	Product	Yield[b] (%)
1			82 (84)[c]
2			74
3			68
4			88
5			79 (81)[c]
6			52[d]
7			91
8			84
9			74
10			81
11			48[d]
12	Ph—C≡C—H	Ph—CH_2CH_3	78
13			79

[a] Reaction conditions: Substrate (0.9 mmol), hydrazine hydrate (0.4 mL), ethanol (3 mL), Ni–K10 (100 mg), 8 h, 70 °C.
[b] Yield of isolated product characterized by ^{1}H NMR.
[c] Yield after third cycle.
[d] Yield determined by GC.

composition of the nickel nanoparticles was fcc[18] and the diffraction line width is consistent with a mean crystallite size of 4 nm. The high intensity spot clearly indicates the nanocrystalline nickel nanoparticles (Fig. 4e).

Hydrogenation of styrene as a model system was used to study the efficiency of the material as a catalyst. Without any catalyst and hydrazine, with hydrazine alone and catalyst alone, no reduction occurred at room temperature or at reflux (Table 1, entries 1, 5–6). Furthermore, experiments performed on native clay as well as Ni^{2+} exchanged K10 clay did not yield any reduced product, highlighting the key role of the nickel nanoparticles (Table 1, entries 2–3). On the other hand, with clay-entrapped nickel nanoparticles, hydrogenation was successful at reflux temperature in the presence of hydrazine (Table 1, entries 7–10). However, lowering the amount of hydrazine caused an increase in the reaction time and hence an excess quantity of hydrazine was used in all the cases. Good to high yields were obtained in refluxing ethanol, acetonitrile (ACN) or an acetonitrile/water mixture (Table 1, entries 11–13), thus this catalytic system works efficiently in polar protic, polar aprotic and non-polar solvents without the detectable formation of byproducts. Ethanol proved to be the best solvent in this study.

To extend the scope, various other olefins (Table 2, entries 1–4) were examined. Simple olefins such as styrene and its derivatives reacted very efficiently. Surprisingly, α,β-unsaturated carbonyl compounds, except cyclohexenone, were also selectively reduced to the corresponding ketone in good yields. Furthermore, an ester also underwent selective hydrogenation. Phenylacetylene was reduced completely to ethylbenzene. Allyl phenyl sulfide was also efficiently reduced without loss in catalytic activity. Other functional groups such as nitro, carbonyl and aromatic rings were not reduced.

The recyclability of the clay entrapped nickel nanoparticles was also surveyed. After the reaction, the solution was filtered, washed with CH_2Cl_2 (2×5 mL) and dried at 60 °C. The catalyst could be reused directly without further purification and was used for three consecutive runs without the loss of activity (Table 2).

We suggest that the efficient catalytic activity of the present system can be attributed to the very homogeneous dispersion of nickel nanoparticles (as evidenced from HRTEM) inside the clay matrix due to stabilization of the particles, thus avoiding their aggregation and allowing control of the particle size. Moreover, the substrate diffusion rate to the active sites of the nickel nanoparticles may also be increased due to the large size of the clay matrix.

Preparation of Ni^{2+}-exchanged clay: K10-Montmorillonite clay (Fluka) was used as received. The nickel ions were exchanged into the K10-Montmorillonite clay (10 g) by stirring with nickel chloride (1 M in 25 mL of water for 1 g of clay) solution at room temperature for 72 h. The clay was filtered, washed thoroughly with distilled water and then dried.

Preparation of nickel nanoparticles entrapped on K10-Montmorillonite clay: Ni^{2+}-supported on K10-clay (500 mg) was suspended in 1 mL of 25% aqueous ammonia. Then, 2 mL of hydrazine hydrate was added to the solution and the mixture was stirred at 60 °C for 5 h, cooled and centrifuged with continuous washing with distilled water until the mother liquor was neutral. The solid was then dried and stored.

General procedure for the hydrogenation of alkene, alkyne or enone: The catalyst (100 mg) was suspended in 3 mL of ethanol followed by the addition of substrate (0.1 mL, 0.9 mmol). To this heterogenous solution, hydrazine hydrate (0.4 mL) was added slowly and the resulting mixture was heated with stirring for about 8 h at 70 °C. The reaction was monitored by gas chromatography. The cooled solution was filtered, dried with anhydrous sodium sulfate and the solvent was removed to give the pure product. In some cases, the product was purified by column chromatography (silica gel 60–120 mesh size). The structure of the product was confirmed from ^{1}H NMR and GC analyses.

In conclusion, we have shown that nickel nanoparticles entrapped in a clay matrix can be easily prepared and were found to exhibit good catalytic activity for the reduction of a wide range of substrates. This catalytic system is economic and ecofriendly as it requires neither high temperature nor harsh acids or bases, and produces high yields with excellent chemoselectivity. The work-up and product isolation from the catalyst is easy. Catalyst poisoning, a common problem with heterogeneous catalysts, is significantly reduced (the catalytic efficiency remaining unaltered even after the third run).

Acknowledgements

K.P. thanks the University Grants Commission (for sanctioning UPE programme to Madurai Kamaraj University) and the Department of Science and Technology, New Delhi for financial assistance. A.D.M. thanks the Council of Scientific and Industrial Research, New Delhi for the award of Senior Research Fellowship.

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