Selective and efficient hydrogenation of halonitrobenzene catalyzed by clay supported Niº-nanoparticles

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ABSTRACT

Niº-nanoparticles of approximately 5 nm were generated by incipient wetness impregnation of $NiCl_2 \cdot 6H_2O$ into the nanopores of the acid activated montmorillonite (AT-Mont) followed by reduction with hydrazine hydrate. The modification of montmorillonite was carried out by activating with H_2SO_4 under controlled conditions for generating nanopores up to about 10 nm size on the surface, which act as a "Host" for Niº-nanoparticles. Powder-XRD, SEM-EDX, HR-TEM, N_2 adsorption, XPS, etc. analyses were carried out to characterize the stabilized nanoparticles as well as the supports. TEM study reveals that Niº-nanoparticles of size below 5 nm were evenly distributed over the support and exhibit face centred cubic (fcc) lattice. The supported Niº-nanoparticles serve as efficient and selective heterogeneous catalyst for hydrogenation of halonitrobenzene (HNB) to corresponding haloaniline (HAN) with conversion 78–100% and selectivity 96–99.4%. The metal nanocatalysts could be recycled and reused several times without significant loss of their catalytic activities.

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1. Introduction

Nickel nanoparticles attract significant attention in many fields including catalysis, permanent magnets, magnetic fluids, magnetic recording media, solar energy absorption, fuel cell electrodes, drug delivery, etc. owing to their unique size and shape dependent structure and properties [1,2]. Recently, attempts were made to stabilize Niº-nanoparticles into 1D or 2D supporting materials such as carbon nanotube, carbon nanofibres, graphene, silica, TiO_2, indium tin oxide and inorganic clay in order to construct new composite materials [3–6]. Although fabrication of these nanocomposites was successful, most of it involves complicated modifications using organic surfactants [7], organic ligands [8,9], alkylammonium salts [10], polymer or ionic liquid stabilizers [11,12] with negative consequences such as reduced activity or unwanted organic residues during various applications. On the other hand, clay is low cost inorganic mineral with layered structure which finds enormous interest as functional materials due to their incredible properties such as appreciable surface area, ordered structure, intercalation abilities and high exchange capacities. Datta et al. used organically modified aminoclay [i.e. $CH_2CH_2NH_2Si_8Mg_6O_{16}(OH)$] to prepare composites with various nanoparticles [13]. Zhang et al. synthesized clay-3-aminopropyltriethoxyilane (APTES)-gold nanocomposites in which the APTES act as a linkage [14]. Platinum and gold nanoparticles embedded in clay or layered double hydroxides have been used for catalytic applications [15–17]. The majority of these protocols involve intricate multistep synthesis, elevated temperature or stabilizer such as polymer or organic ligands to inhibit agglomeration of particles. Therefore, with growing environmental regulations, chemical industry needs the development of eco-friendly and sustainable synthetic methods without any organic modification. Keeping in view of the above, we used environmentally benign, cheap, easily available and robust montmorillonite for generation of Niº-nanoparticles. Herein, we report a procedure for the in situ synthesizing Niº-nanoparticles using environmentally benign montmorillonite as a support. The virgin montmorillonite was purified and activated with mineral acid by controlling the acid concentration, activation time or temperature to generate a matrix having high surface area and contain micro- and mesopores with diameter in the range 0–10 nm on the surface [18–24]. These nanopores act as a host for generation of Niº-nanoparticles and limit the growth of the particles up to the desired range [25–29]. Furthermore, the potential applications of these Niº-nanoparticles were confirmed by investigating their catalytic activity.

Aromatic haloamines are important class of industrial intermediate for the synthesis of organic fine chemicals, such as dyes, analgesic, herbicides, pesticides and antipyretic drugs [30–33]. The main routes of synthesis of the haloamines involved reduction of corresponding nitrocompounds catalyzed by either metal–acid

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systems or with noble metal. Processes involving later route are favoured now a days due to environmental issues associated with the use of hydrochloric acid in the former route. Control of selectivity is the critical problem while carrying out hydrogenation of halonitroaromatics with noble metal. For this type of hydrogenation reaction, various precious catalysts (Pt, Pd, Ru and Rh) have been well-studied [30–36]. However, it has been found that the hydrogenation process is accompanied by hydrogenolysis of the carbon–halogen bond over most of catalysts and that hydrogen halide (e.g. hydrogen chloride) produced from this process is corrosive to the reactor in addition to their higher cost. Therefore, much effort have been made to overcome this problem over the past decades, including introducing special additives (promoters and inhibitors), modifying the active metal with a second metal component and tuning the particle sizes of the catalysts.

There are several reports that dechlorination can be suppressed during hydrogenation of chloronitrobenzene (CNB) by using noble metal catalyst such as Ag/SiO$_2$ [37], Au/SiO$_2$ [38], Au/ZrO$_2$ [39], AuPd/Al$_2$O$_3$ [40], Au/Fe(OH)x [41], Pt/γ-Fe$_2$O$_3$ [42,43], Pt/γ-ZrP [44], decorated Pt/TiO$_2$ [45,46], and Ru/SnO$_2$ [33]. The hydrogenation of CNB was usually carried out at 90–150 °C with Au and Ag nanoparticles and at 30–60 °C with Pt catalysts and the selectivity to the undesired aniline was less than 1% [47]. However, the use of these noble and platinum metal catalysts (Au, Ag, Pd, Ru and Pt) in large scale production should be expensive. Therefore, from both economic and environmental point of view, there has recently been increasing interest in hydrogenation of chloronitrobenzene with different chlorine substituent sites (*o*-, *m*-, or *p*-CNB) to corresponding chloroaniline (CAN) catalyzed by less costly metal like nickel. Mahata et al. reported that when the hydrogenation of CNB was performed at 120 °C over filamentous carbon-stabilized Ni catalyst in methanol, the specific activity was ∼50 mmol h^{-1} g^{-1} Ni and there was no intermediate detected at any level of CNB conversion [48]. The catalyst was prepared by methane decomposition over Raney Ni, which is expensive for industrial catalyst preparation. Hence, none of these methods have been completely satisfactory and is still a lot of scope to enhance the catalytic performance by improving the reaction time, catalyst quantity, selectivity keeping in mind both the economic and environmental issues. Herein, we report a procedure for synthesizing Ni^o-nanoparticles using environmentally benign modified montmorillonite as a support and their catalytic performance in hydrogenation of halonitrobenzene.

2. Results and discussion

2.1. Characterization of Support

The characterization of modified montmorillonite was carried out thoroughly with the help of different analytical instruments like Powder-XRD, ^{29}Si and ^{27}Al MAS-NMR, FTIR, SEM studies, N$_2$ adsorption–desorption and are well documented in our earlier reports [25–29]. The powder XRD of the parent montmorillonite shows an intense band at 2θ = 7.06 corresponding to basal spacing (d_{001}) of 12.5 Å while in acid activated montmorillonite (AT-Mont-I and AT-Mont-II), the band almost disappear indicating depletion of the lamellar structure [18,19] (supporting information, Fig. S1). The CEC of the modified montmorillonite decreased from 126 to 40.8 and 21.0 meq/100 g of clay upon acid activation for 1 and 2 h, respectively. The parent montmorillonite showed an intense Si peak at about −93 ppm [Q^3(OAl)], attributed to tetrahedral (3Si, Al) units (supporting information, Fig. S2). With increasing acid activation time, the intensity of the peak at −93 ppm decreases and a new peak appeared at −111 ppm due to Q^4 Si after 2 h acid activation [20]. The ^{27}Al MAS-NMR spectra of parent montmorillonite exhibited an intense peak at 3.48 ppm and a weak peak at
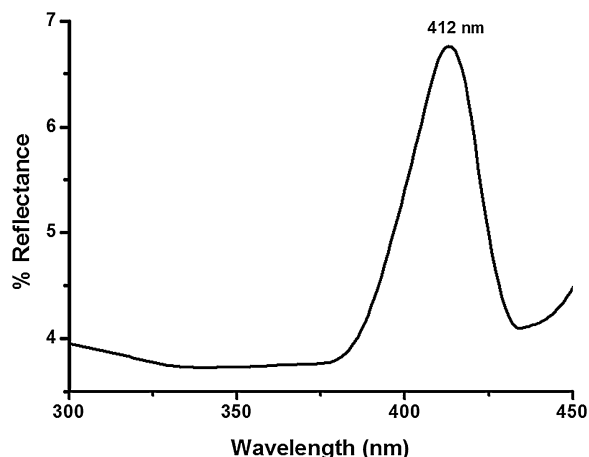

Fig. 1. Solid state UV of Ni^o-AT-Mont.

67.39 ppm for octahedral and tetrahedral Al, respectively (supporting information, Fig. S2). During acid activation, the intensity of the octahedral Al peak decreased and shifted to 2.03 ppm after 2 h, while the tetrahedral Al peak remained unchanged. IR study reveals that the parent montmorillonite exhibits an intense absorption band at ∼1034 cm^{-1} for Si–O stretching vibrations of tetrahedral sheet and also shows broad absorption band at 3633 cm^{-1} due to stretching vibrations of –OH groups of Al–OH (supporting information, Fig. S3). The bands at 522 and 460 cm^{-1} were due to Si–O–Al and Si–O–Si bending vibrations, respectively. Acid activation shifted the band from ∼1034 to ∼1083 cm^{-1} indicating the change in bonding environment surrounding the tetrahedral sheet [21,22]. Upon acid activation, the surface area 417 m^2 g^{-1} (AT-Mont-I) and 362 m^2 g^{-1} (AT-Mont-II) and the pore volume ∼0.57 cm^3 g^{-1} (AT-Mont-I) and ∼0.70 cm^3 g^{-1} (AT-Mont-II) were observed for 1 and 2 h acid treatment, respectively. Acid activation leads to modification of layered structure of montmorillonite by leaching out Al from their tetrahedral and octahedral sites, which also introduced permanent porosity on the clay surface. The clay matrix contained micro- (<2 nm) and mesopores (2–50 nm) with average pore diameters ∼4.45 nm (AT-Mont-I) and ∼6.70 nm (AT-Mont-II), respectively. The plot of differential volumes against pore diameter, i.e. BJH plot indicated relatively narrow pore size distributions for AT-Mont-I than AT-Mont-II (supporting information, Fig. S4). The initial increase in surface area for AT-Mont-I may be due to the formation of micro- and mesopores by leaching out aluminium from octahedral sites but it decreases on prolonging acid activation time (2 h) because of destruction of the pore walls, there by forming bigger pores resulting in wider pore size distribution. The shape of N$_2$ adsorption–desorption isotherm (supporting information, Fig. S4) was of the type-IV with an H3 hysteresis loop at $P/P_0 \sim 0.4$–0.8, indicating mesoporous solids [23,24]. Considering higher surface area and narrow pore size distribution, AT-Mont-I is advantageously utilized for generation of Ni^o-nanoparticles.

2.2. Characterization of supported Ni^o-AT-Mont

The preliminary investigation on the formation of Ni^o-nanoparticles into the pores of modified montmorillonite was carried out by UV–Visible spectroscopy (Fig. 1). The surface plasmon resonance band at 412 nm indicates the formation of Ni^o-nanoparticles [6]. The crystalline natures of the Ni^o-nanoparticles were confirmed by their corresponding powder XRD pattern (Fig. 2). The three characteristic peaks at 2θ values 44.5, 51.8 and 76.4 degrees can be assigned to the corresponding (111), (200) and (222) indices of fcc Ni, which are in good agreement with