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Original Research Paper

Mechanistic aspects of formation of MgO nanoparticles under microwave irradiation and its catalytic application

Aravind L. Gajengi [a], Takehiko Sasaki [b], Bhalchandra M. Bhanage [a,*]

[a] Department of Chemistry, Institute of Chemical Technology, Matunga, Mumbai 400 019, India
[b] Department of Complexity Science and Engineering, Graduate School of Frontier Sciences, The University of Tokyo, 5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8561, Japan

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ABSTRACT

This work reports a preparation of $Mg(OH)_2$ and MgO nanoparticles (NPs) using magnesium acetate in benzylamine and mechanistic study of its formation. The benzylamine acts as a solvent, base, promoter and capping agent in this reaction. The structure and morphology of particles were analyzed by X-ray diffraction pattern (XRD), transmission electron microscopy (TEM), high resolution TEM (HRTEM), selected area energy dispersion (SAED), energy-dispersive X-ray spectroscopy (EDAX), thermogravimetric analysis (TGA), FT-IR, CO_2–temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS) and Brunauer–Emmett–Teller (BET) surface area analysis techniques. The application of as prepared MgO NPs was used in catalysis as a catalyst for the formylation of amines with recyclability studies of nanocatalyst.

1. Introduction

Recently, developing novel methods for the synthesis of nanomaterials is gaining considerable attention in material science [1]. Magnesium oxide (MgO) is an important material which is widely used in catalysis [2,3], dye removing agents [4], defluorination [5], sensors [6] and CO_2 storage materials [7]. The MgO NPs shows excellent catalytic activity due to small particle size and availability of high surface area. As the particle size decreases, the relative number of surface atoms increases, and thus the activity increases. The materials having a high surface area are of interest in catalysis as a catalyst or support of catalyst. Some of the organic reaction in which MgO or metal supported MgO used as catalyst for Claisen–Schmidt condensation reaction [2], *N*-methylation of indole and *o*-methylation of phenol [7], Suzuki–Miyaura cross-coupling reaction [8] etc. There are several methods of synthesis of MgO NPs with different size and morphology such vapour ablation method [9], wet chemical method [10], hydrothermal method [11], sol-gel [12], thermal decomposition [13], ultrasound synthesis [14].

Nowadays, microwave-assisted synthesis of metal and metal oxide NPs has attracted great attention because of several advantages such as it is simple, require less time and energy efficient [15]. Recently we showed the importance of microwave assisted method for synthesis of various nanoparticles [16–20]. The microwave synthesis have some advantages over conventional methods as it improves the kinetics of reactions by one or two orders of magnitude due to rapid initial heating and generation of the localized high pressure zone at reaction sites. The efficiency of microwave power (P) dissipated per unit volume is given by following equation:

$$P = cE^2 f \varepsilon''$$

where c, E, f and ε'' are radiation velocity, electric field in the material, radiation frequency and dielectric loss constant respectively. These are most vital parameters which decide the ability of heating material in the microwave field.

We herein report a rapid, template/capping agent and additive free method for synthesis of $Mg(OH)_2$ and MgO NPs using benzylamine as solvent. The detailed mechanism for the formation of MgO NPs investigated. This synthesized MgO NPs shows high catalytic activity towards the formylation of amines with formic acid under microwave irradiation method with recyclability of the catalyst.

2. Experimental details

2.1. Materials

All commercial reagents, $Mg(CH_3COO)_2{\cdot}4H_2O$ and benzylamine were purchased from M/S Merck Chemicals Pvt. Ltd. India and were used directly without further purification.

* Corresponding author. Fax: +91 3361 1020.
E-mail addresses: bm.bhanage@gmail.com, bm.bhanage@ictmumbai.edu.in (B.M. Bhanage).

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2.2. Preparation of MgO NPs

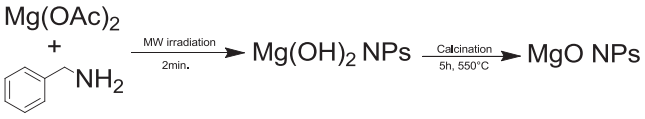
In a typical procedure, the mixture of 1.0 g of $Mg(CH_3COO)_2 \cdot 4H_2O$ and 10 mL benzylamine was transferred to a 30 mL teflon lined tube and kept in a microwave oven for 2 min at 360 watts (W) using on/off mode with a time interval of 30 s. After microwave heating, the white turbid precipitate was formed which indicates the formation of $Mg(OH)_2$ NPs. These particles were separated by centrifugation and then washed twice with distilled water followed by ethanol. The $Mg(OH)_2$ NPs was calcinationed in oven at 550 °C for 5 h which gave MgO NPs (Scheme 1).

2.3. Characterization of prepared MgO NPs

The prepared MgO NPs were characterized by using various analytical techniques such as TEM and SAED (Philips, CM 200, operating voltage of 200 kV model CM 200), HRTEM (JOEL, JEM-2100F operating voltage of 200 kV with a probe size under 0.5 nm), TGA (PerkinElmer STA 6000), XPS (PHI 5000 Versa Probe Scanning ESCA Microprobe) and EDAX (Oxford instrument, model 51-ADD0007). The FT-IR spectra were recorded using Perkin Elmer-100 Spectrometer, XRD analysis done by using Shimadzu XRD-6100, BET surface area and CO_2-TPD by using TPDRO 1100 thermo scientific model.

2.4. General procedure for N-formylation of amines

In a 25 mL sealed tube, amine (1 mmol), formic acid (3 mmol) and MgO NPs (20 mg) were added and kept for microwave irradiation at 480 W for 2 min. The reaction progress was monitored by GC equipped with a flame ionization detector (FID) and a capillary column (Perkin–Elmer, Clarus 400, 30 m × 0.32 mm × 0.25 m). After completion, the reaction mixture was filtered to separate catalyst. The filtrate containing desired product was quenched in water and were extracted using ethyl acetate (5 ml × 3). The organic layer was washed with saturated $NaHCO_3$ to remove excess of formic acid. The combined organic layer was then dried over Na_2SO_4 and evaporated under vacuum. The obtained crude product was purified by column chromatography using silica gel (100–200 mesh size) with petroleum ether/ethyl acetate (PE-EtOAc, 95:05) as eluent to afford the pure product. The products are well known in the literature and were confirmed by GC–MS analysis of the comparison with literature data.



Scheme 1. Synthesis of MgO NPs by microwave irradiation method.

3. Results and discussion

3.1. Characterization of $Mg(OH)_2$ and MgO NPs

The morphology of prepared $Mg(OH)_2$ and MgO NPs was observed by transmission electron microscopy (TEM). The TEM images show $Mg(OH)_2$ are in the nano range and having flake like morphology (Fig. 1a and b) and its SAED pattern as shown in Fig. 1a inset which indicates its crystalline nature. The HRTEM images of $Mg(OH)_2$ are shown in Fig. 1c and d.

The images in Fig. 2a and b show flake like morphology of MgO which are lacunal and loose connection of particles and its SAED pattern as shown in Fig. 2a inset which indicates the crystalline nature of MgO NPs. The HRTEM of MgO NPs as shown in Fig. 2c and d. The HRTEM images of $Mg(OH)_2$ (Fig. 1c and d) and MgO NPs (Fig. 2c and d) having a particle size approximately ~6 nm and ~16 nm which is complying with average crystallite size obtained by XRD using Scherrer's equation. The energy-dispersive X-ray spectroscopy of MgO NPs (Fig. 2e), which indicates magnesium and oxygen elements only, suggesting MgO NPs were in pure form and particle size distribution histogram (Fig. 2f) which shows the most of the particles are in the range of 12–22 nm.

Phase identification was done by using X-ray diffraction technique with an X-ray wavelength of Cu Kα radiation at $\lambda = 1.5405$ Å with a scanning rate of 2°/min from 10° to 80°.

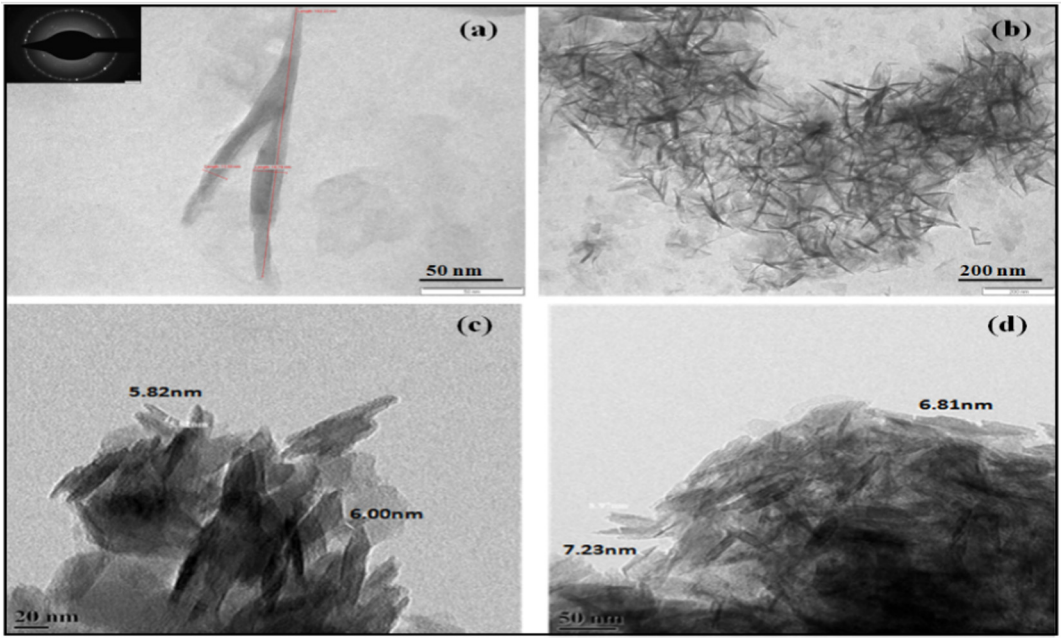


Fig. 1. (a and b) TEM with SAED pattern (inset a) and (c and d) HRTEM images of $Mg(OH)_2$ NPs.

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