



Investigation of nano NiO, supported and metal ion substituted NiO for selective hydration of aromatic nitriles to amides



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ABSTRACT

Freshly prepared nano NiO, NiO supported HAP, TiO₂, ZrO₂ and γ -Al₂O₃ and metal ion substituted nickel oxide (Ni_{1-x}M_xO, M = Co, Cu and Mn) have been tested for hydration of aromatic nitriles. Mn substituted compound of nominal composition, Ni_{0.7}Mn_{0.3}O was found to be the highly active catalyst. The reaction was carried out in autoclave using water as a solvent and the reaction time varied between 2 and 24 h for heterocyclic cyano nitriles to methyl benzonitriles.

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1. Introduction

Amides are potential organic compounds in chemical and biological applications [1]. Conventionally primary amides have been synthesized by treating carboxylic acids with amines at high temperature [2]. Methods involving carboxylic acids activated by functional groups such as acyl chloride, anhydride, acyl azide, N-acylbenzotriazoles [3] have been reported. Such methods are associated with drawbacks such as modest yields, expensive coupling reagents and difficulty in the removal of excess reagents and by-products. Catalytic hydration of nitriles [4] has emerged as an alternative efficient synthetic route that avoids the formation of undesirable side products, use of corrosive acidic or basic media.

Initially, in this approach hydration of nitriles is carried out in the presence of strong acids or bases at high temperature [5]. This method rules out selectivity of the product if the nitrile possesses acid or base sensitive functional groups and associated with the formation of carboxylate salts and polymers in the presence of base and acid respectively [4]. To overcome these difficulties various, homogenous, heterogeneous systems and enzymes have been used as catalysts.

Various metal complexes and organometallic compounds have been studied as homogenous catalysts [6]. The main problem

associated with homogenous systems is catalyst and product separation. Enzyme catalysts such as Nitrile hydratase have been used in nitrile hydration. Under high temperature conditions of the nitrile conversion such enzymatic catalysts are found to be disadvantageous due to their instability or low activity [7]. Heterogeneous catalytic conversion using metal oxides [8], KF/Al₂O₃ [9], Na/HAP [10], and MnO₂/SiO₂ [11] as catalysts has been reported.

Due to their diverse physical and chemical properties transition metal oxides find applications in various fields such as, nonlinear optics, sensors, magnetic materials, conducting materials and catalysis to name a few. Heterogeneous catalysis is one of the most significant fields in which transition metal oxides find potential application. They are used in many organic transformations because of they lead to high level of chemo-selectivity, simplicity of operation and are available in low cost [12].

Controlled hydrolysis of nitriles to amides using catalysts containing active metal centres is one of the striking routes [13]. Garcia-Alvarez et al.'s recent review reports on the various metal based catalysts for amide synthesis in aqueous medium [14]. Various metal oxides have been utilized as heterogeneous catalysts for nitrile hydration [8]. The oxides Fe₂O₃, Co₂O₃, CuO and ZnO are found to be active catalysts at 225 °C in the hydration of benzonitrile. However, in the presence of Fe₂O₃ benzoic acid formed. The cobalt and copper oxides lose their reusability due to the interaction with the reaction product. While in the presence of ZnO, over hydrolysis of benzamide occurs [8]. Zirconium oxide exhibits a weak catalytic activity, while titanium (IV) oxide is almost inactive [8]. Among the other group oxides tested, alumina is found to be a

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weak catalyst [15]. Moderate yield of benzamide (59%) is obtained in the presence of lead (II) oxide. Germanium oxide shows weak catalytic activity, while silicon oxide proves to be inactive [8].

Sugiyama et al. studied hydration of acrylonitrile over various metal oxides such as MnO₂, CuO (source Cu(NO₃)₂), CuO (source CuCO₃·2Cu(OH)₂), Fe₂O₃, WO₃, Ag₂O, ZnO, NiO (source Ni(NO₃)₂), NiO (source NiCO₃·2Ni(OH)₂), PbO, MgO, SiO₂, TiO₂, Al₂O₃, La₂O₃ and Co₃O₄. These metal oxides show low conversion and some of them such as NiO (NiCO₃·2Ni(OH)₂) and CuO (CuCO₃·2Cu(OH)₂) exhibit poor selectivity for acrylamide formation [16]. Tamura et al. reported the catalytic hydration of 2-cyanopyridine in water at 60 °C with various metal oxides such as CeO₂, TiO₂, MnO₂, CaO, Y₂O₃, La₂O₃, ZrO₂, SiO₂, SnO₂, Fe₂O₃, Al₂O₃, MgO, Nb₂O₅, Er₂O₃, Dy₂O₃ and Pr₆O₁₁. Among these metal oxides, CeO₂, MnO₂, TiO₂, CaO, Y₂O₃, La₂O₃, and ZrO₂ produces the amide, and CeO₂ shows more than two orders magnitude of higher activity than the other metal oxides. But this method is limited to nitriles with heteroatom adjacent to 'α' carbon of the CN group [17]. Microwave assisted amide synthesis via hydration of nitrile using silica supported MnO₂ has been reported by Khadiolkar and Madyar [18]. Recent investigations report on the application of nano-Fe@SiO₂Ru [19] under microwave condition, K₂CO₃ [20], amorphous MnO₂ [21] and Hydrotalcite-clay supported nickel nanoparticles [22].

Sakai et al. [23], studied hydration of heteroaromatic nitriles with water in the presence of nickel and copper oxides under reflux condition. In the hydration of 3- and 4-cyanopyridines, corresponding amides are obtained with NiO (90% in 7 h) and CuO (10% in 7 h). On the other hand, 2-cyanopyridine resulted in the formation of metal chelates. Watanabe [24] studied the catalytic activity of Urushibara Ni (U-Ni-A and U-Ni-B), Urushibara (U-Cu), precipitated nickel (ppt.Ni), precipitated copper (ppt.Cu), raney nickel, stabilized nickel and NiO + CuO in the hydration of various nitriles. The mixture of NiO and CuO is used to convert benzonitrile to benzamide in the presence of ethanol under reflux condition where, 5% amide is obtained after 10 h reaction. In the case of hydration of o-nitrobenzonitrile and p-nitrobenzonitrile with nickel containing catalyst (U-Ni-B) corresponding amines and nickel complexes are obtained because of hydrogenation of nitriles.

Even though metal oxides as heterogeneous catalysts are cost effective and simple in processing, their utility in the hydration of nitrile is found to be limited due to the various reasons listed above. The hydration of nitriles in the presence of nickel based catalysts suffers lower activity and poor selectivity. From the point of view of its cost effectiveness and simplicity the present study has focused on the applicability of NiO and explored the possibility of improving its catalytic activity by using nano NiO, NiO supported metal oxides and metal ion substituted NiO.

2. Experimental

2.1. Materials

Nickel oxide (CN) (Thomas Baker, LR and Sigma Aldrich, 99.9%), Nickel acetate (98%, CDH), TiO₂ (98%, Thomas Baker), ZrO₂ (99%, Sigma Aldrich), γ-Al₂O₃ (prepared in the current work-supporting material), Hydroxyapatite (HAP) (prepared in the current work-supporting material), dimethyl glyoxime, DMG (98%, S.d. fine chemicals), acetyl acetone (98%, S.d. fine chemicals) and urea (98%, S.d. fine chemicals).

2.2. Catalyst preparation

2.2.1. Preparation of NiO by combustion method (NA)

Homogenized mixture of nickel nitrate (nickel acetate dissolved in 1:1 HNO₃) and urea was kept in a preheated furnace at 500 °C for 30 min and then cooled to room temperature.

2.2.2. Thermal decomposition of Nickel dimethyl glyoxime (Ni-DMG)

To an alcoholic solution of DMG (25 mL of 6 mmol), Ni(II) sulfate solution (25 mL of 3 mmol) was added in the presence of slight excess of ammonia and stirred gently. The precipitate was digested on water bath for 2 h. After cooling, it was filtered, washed with water and ethanol and dried at 80 °C. The raspberry red powder was heated at 300 °C to obtain the oxide.

2.2.3. Thermal decomposition of nickel acetyl acetonate (Ni-AA)

Ammonia solution was added to a solution of 4 g of NiSO₄ dissolved in 40 ml of water till the formation of deep blue color. Acetyl acetone (4.72 ml) was added dropwise to the solution and stirred for 30 min. Subsequently, the precipitate was filtered, washed with water and ethanol and dried at 90 °C. The mass obtained was heated at 400 °C.

2.2.4. Synthesis of metal substituted nickel oxide (Ni_{1-x}M_xO, M = Co, Cu and Mn) by co-precipitation method

Synthesis of Ni_{1-x}Co_xO (x = 0.1–0.5) was carried out by co-precipitation method. To the mixed metal nitrate solution, 2 M NaOH was added while stirring and the pH of the solution was maintained at ~11. The precipitate formed was filtered, washed with water and dried at 100 °C. The mass obtained was heated at 400 °C for 3 h. Similar procedure was followed for the synthesis of Ni_{1-x}Cu_xO and Ni_{1-x}Mn_xO (x = 0.1, 0.3 and 0.5).

2.3. Catalytic test

Hydration of nitrile was carried out initially under reflux condition using commercial NiO (CN). The reaction mixture of benzonitrile (5 mmol), NiO (0.2 g) and water (15 ml) was heated at 100 °C for 72 h. Stirring rate was kept around 550–600 rpm. Work up procedure included the addition of ethanol followed by filtration to separate the catalyst. The solvent was removed on evaporation. Similar experiment was carried out using autoclave. In the latter procedure, the ingredients were placed in a Teflon vessel with a magnetic stir bar. The Teflon vessel was inserted into a stainless steel vessel (autoclave) and heated at 140 °C (bath temperature) in oil bath with stirring.

2.4. Characterization

The catalytic materials were characterized by powder X-ray diffraction method (Cu Kα, Bruker, D8 Advanced), BET technique for surface area measurements (Micromeritics, ASAP 2020 V3.00H), XPS analysis (XM1000 spectrometer using Al Kα radiation (hν = 1486.6 eV) and SEM-EDAX analysis (FEI Quanta FEG 200 attached with EDS). Elemental analysis was carried out using VARIAN AA240 Atomic Absorption Spectrometer. The organic products were identified based on their melting points, ¹H NMR, (Bruker AVANCE III 400 MHz) and IR (JASCO FT-IR-4100) spectra.

3. Results and discussion

3.1. Catalyst characterization

Catalytic materials such as NiO by combustion method (NA), by complex decomposition (Ni-DMG, Ni-AA), NiO supported on HAP, TiO₂, ZrO₂ and γ-Al₂O₃ (NiO/HAP, NiO/TiO₂, NiO/ZrO₂ and NiO/γ-Al₂O₃-supporting material) and metal ion substituted nickel oxide (Ni_{1-x}M_xO, M = Co, Cu and Mn) are synthesized. Analysis for pure phase formation is carried out by powder X-ray diffraction technique.

Pure NiO phase formation (Fig. 1) in both combustion and thermal decomposition methods is confirmed by indexing the patterns

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