Molecular Catalysis 450 (2018) 112–120

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Silanization of Iron Oxide Magnetic Nanoparticles with ionic liquids based on amino acids and its application as heterogeneous catalysts for Knoevenagel condensation reactions

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ARTICLE INFO

Keywords:
Amino acid
Ionic liquid
Magnetic nanoparticles
Knoevenagel condensation

ABSTRACT

Iron oxide magnetic nanoparticles (MNPs) stabilized with silane ligands, containing choline hydroxide and amino acid ionic liquid functionalities, have been prepared. The appropriate silane ligands have been synthesized; the choline hydroxide propyl silane ligand in a process inspired in the industrial production of choline hydroxide and the amino acid ionic liquids in a straight forward acid-base process using the former compound. The synthesized materials have been fully characterized by elemental analysis, X-ray diffraction (XRD), fourier-transform infrared spectroscopy (FT-IR), UV–vis diffuse reflectance spectroscopy (DRUV-vis), thermogravimetric analysis (TG-DTG), N_2 adsorption-desorption, transmission electron microscopy (TEM) and voltammetry solid state techniques. Ionic liquid stabilized magnetic nanoparticles have been very effective as heterogeneous basic catalysts in Knoevenagel condensation reaction at room temperature. The catalyst containing choline hydroxide ionic liquid (Chol-MNPs) exhibited highest catalytic activity and can easily be recovered under an external magnetic field and subsequently reused several times.

1. Introduction

The synthesis of pharmaceutical and fine chemicals by methods inspired by green chemistry principles is still a challenge. The search of new heterogeneous Brönsted-type basic catalysts able to perform green chemistry condensation reactions with high activity and selectivity values is gaining prominence in order to overcome the drawbacks of their classical homogenous inorganic counterparts, KOH and NaOH [1]. Magnetic nanoparticles have found a broad range of applications as support due to their interesting properties [2,3,4]. Various methods to prepare MNPs are available [5], but the co precipitation technique is probably the easiest and most efficient chemical pathway. The use of surfactants to stabilize these synthesized nanoparticles is critical, as Fe_3O_4 nanoparticles have high surface energies and tend to aggregate. They also have high chemical reactivity and are easily oxidized to Fe_2O_3, causing loss of magnetism. Magnetic particles can be stabilized by electrostatic and steric repulsions by using inorganic supports or polymers as surface coatings [6,7]. Several studies have been published on the synthesis and characterization of magnetite nanoparticles with basic amino groups on the surface. Pinteala and co-workers [8] have synthesized hydrophilic magnetite particles by employing a two-step method: in the first step magnetite particles with hydrophobic shell were formed in presence of oleic acid–oleylamine complex through a synthesis in mass, without solvent; while in the second step the hydrophobic shell was interchanged with an aminosilane monomer. Yamaura et al. [9] have performed a direct silanization procedure in an acidic aqueous to deposit aminopropylalkoxysilane on the surface of the magnetite core. He and co-workers [10] have published a complete kinetic study of this process based on grafting density calculated by TGA studies. Tetramethylammonium hydroxide has also been used to stabilize nanoparticles of magnetite by a direct reduction precipitation method [11]. It is noteworthy that in many cases the protecting outer shells not only stabilize the nanoparticles, but can also be used for further functionalization, for instance, with other nanoparticles or various ligands, depending on the desired application. In this context, the development of solid base catalysts as heterogeneous catalysts and the use of ionic liquids able to act as both basic catalyst and stabilizer of “naked” metal NPs should be a useful strategy [12].

In this study, we have designed and synthesized iron oxide magnetic nanoparticles, stabilized with silane ligands, containing choline hydroxide ionic liquid and choline amino acid ionic liquid. In addition, the surface of these stabilized magnetic nanoparticles has been

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https://doi.org/10.1016/j.mcat.2018.03.008
Received 6 February 2018; Received in revised form 9 March 2018; Accepted 10 March 2018

characterized by XRD, FT-IR, TGA, UV–vis and electrochemical solid-state studies and their morphology determined by TEM microscopy. We have tested these materials as heterogeneous basic catalysts in Knoevenagel condensation of benzaldehyde with malononitrile or ethyl cyanoacetate at room temperature. Different reaction conditions and the effect of choline amino acid have been studied and possible reaction mechanism have been proposed. Reusability tests have also been performed and the stability of recovered catalyst has been demonstrated.

2. Experimental section

2.1. Materials

When required, the reactions were performed using standard Schlenk tube techniques under an atmosphere of dry nitrogen. Sodium hydroxide 97% and hydrochloric acid 35% were purchased from Panreac. Iron(II) sulphate heptahydrate ($FeSO_4{\cdot}7H_2O$) 99.5% and iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$) 95% were purchased from Scharlau. 3-Glycidyloxypropyl)trimethoxysilane, trimethylamine solution 4.2 M in ethanol, glycine, lysine, malononitrile, ethyl cyanoacetate and benzaldehyde were purchased from Sigma Aldrich and used as received. Milli-Q water was used in the experiments when required. Ethanol was purchased from VWR. Toluene and chloroform were purchased from Scharlau and VWR respectively, distilled and dried before use according to conventional literature methods. Water was obtained from a Millipore Milli-Q system (Waters, USA).

2.2. Preparation of catalysts

2.2.1. Synthesis of silane ligand containing choline hydroxide ionic liquid (OH-Chol)

Trimethylamine (4.2 M) in ethanol (1.2 mL, 5.0 mmol) was added by syringe over an aqueous solution of 3-glycidyloxypropyl)trimethoxysilane (1 mL, 4.52 mmol) and the mixture stirred 2 h at room temperature. Finally, water and ethanol were removed under reduced pressure to obtain a pale-yellow oil. ^{1}H NMR (400 MHz, D_2O, 25°C): δ = 0.36 (m, 2H, Si-CH_2-), 1.51 (m, 2H, Si-CH_2−CH_2−), 3.38 (m, 2H, Si-CH_2−CH_2−CH_2−), 3.07 (s, 9H, N-$(CH_3)_3$), 3.39 (m, 2H, −O−CH_2−), 4.26 (m, 1H, −C*H*-OH), 3.34 (m, 2H, −CH_2−N). ^{13}C{H}-NMR (400 MHz, D_2O, 25 °C): δ = 9.7 (Si-*C*H_2-), 23.2 (Si-CH_2-*C*H_2-), 72.0 (Si-CH_2−CH_2-*C*H_2-), 54.2 (N-(*C*H_3)$_3$), 74.3 (-O-*C*H_2-), 68.5 (−*C*H−OH), 64.8 (−CH_2−N). (See Fig. S1)

2.2.2. Synthesis of silane ligands containing choline amino acid ionic liquid (Gly-Chol and Lys-Chol)

In a typical synthesis: an aqueous solution of the silane ligand containing choline hydroxide ionic liquid, freshly prepared, was added over an aqueous solution of the amino acid (glycine or lysine), maintaining an equimolar ratio. The mixture was stirred for 24 h at room temperature and water was removed under reduce pressure, first using a rotary evaporator (60 °C, 15 min), and then in vacuo to yield a sticky pale yellow solid. Ionic liquid with glycine (Gly-Chol); ^{1}H NMR (400 MHz, D_2O, 25°C): δ = 0.44 (m, 2H, Si−CH_2−), 1.50 (m, 2H, SiCH_2−CH_2-), 3.34 (m, 2H, Si-CH_2−CH_2−CH_2-), 3.04 (s, 9H, N−$(CH_3)_3$), 3.35 (m, 2H, −O−CH_2-), 4.22 (m, 1H, −C*H*−OH), 3.28 (m, 2H, −CH_2−N). 3.13 (s, 2H, COO−CH_2−NH_2). ^{13}C{H}-NMR (400 MHz, D_2O, 25 °C): δ = 8.8 (Si-*C*H_2-), 22.6 (SiCH_2-−*C*H_2−), 72.1 (Si-CH_2−CH_2-CH_2-), 54.4 (N-(*C*H_3)$_3$), 73.9 (−O−*C*H_2−), 68.4 (-*C*H−OH), 64.8 (-CH_2−N), 43.4 (COO-*C*H_2−NH_2). 178.1 (*C*OO-*C*H_2−NH_2). Ionic liquid with lysine (Lys-Chol); ^{1}H NMR (400 MHz, D_2O, 25°C): δ = 0.31 (m, 2H, Si-C*H*$_2$-), 1.51 (m, 2H, Si-CH_2−CH_2-), 3.34 (m, 2H, Si-CH_2−CH_2−CH_2−), 3.03 (s, 9H, N-$(CH_3)_3$), 3.34 (m, 2H, −O−CH_2-), 4.20 (m, 1H, −C*H*−OH), 3.26 (m, 2H, −CH_2−N). 3.78 (m, 2H, COO−C*H*R-NH_2); 1.32-1-34, 1.49, 2.57 (m/t, 2H, COO−CH(NH_2)−CH_2−CH_2−CH_2−CH_2−NH_2) ^{13}C{H}-NMR (400 MHz, D_2O, 25 °C): δ = 9.5 (Si-*C*H_2-), 22.3 (Si-CH_2-*C*H_2-), 72.0 (Si-CH_2−CH_2−*C*H_2-), 54.2 (N-(*C*H_3)$_3$), 74.2 (−O−*C*H_2−), 68.5 (−*C*H−OH), 64.8 (−CH_2−N), 57.5 (COO−*C*HR−NH_2), 39.9, 29.6, 34.2, 55.9 (COO−CH(NH_2)-*C*H_2-*C*H_2-*C*H_2-*C*H_2−NH_2), 183.3 (*C*OO−*C*H_2−NH_2). (See Fig. S2 and S3).

2.2.3. Synthesis of iron oxide magnetic nanoparticles (MNPs)

An aqueous solution of NaOH (400 mL, 0.5 M) was deoxygenated by bubbling nitrogen for 30 min. $FeCl_3{\cdot}6H_2O$ (1.89 g, 7 mmol) and $FeSO_4{\cdot}2H_2O$ (1.94 g, 7 mmol) were dissolved in 30 and 45 mL water, respectively. The two solutions were mixed and added into the alkaline solution, previously prepared, dropwise under vigorous stirring. The reaction was heated to 80 °C and stirred for 30 min under nitrogen atmosphere. The black solid obtained was washed with milliQ water (3 × 50 mL) and dried under vacuum.

2.2.4. Stabilization of MNPs with ionic liquids

The MNPs obtained by co-precipitation (0.25 g) were dispersed in water (50 mL) and an aqueous solution of ionic liquid (OH−Chol, Gly-Chol or Lys-Chol) (2 mmol), previously synthesized, was added under mechanical stirring. The reaction was stirred and heated at 80 °C for 2 h and the stabilized magnetic nanoparticles separated by centrifugation or magnetic decantation and washed with ethanol. The samples denoted as Chol-MNPs, Gly-Chol-MNPs and Lys-Chol-MNPs were dried under vacuum and stored.

2.3. Characterization

X-Ray diffraction (XRD) patterns of the silicas were obtained on a Phillips Diffractometer model PW3040/00 X'Pert MPD/MRD at 45 KV and 40 mA, using Cu-Kα radiation (λ = 1.5418 Å). N_2 gas adsorption-desorption isotherms were obtained using a Micromeritics TriStar 3000 analyser, and pore size distributions were calculated using the Barret-Joyner-Halenda (BJH) model on the adsorption branch. Infrared spectra were recorded on a Nicolet-550 FT-IR spectrophotometer (in the region 4000–400 cm^{-1}) as KBr disks. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian Mercury FT-400 spectrometer. The DRUV-vis spectroscopic measurements were carried out on a Varian Cary-500 spectrophotometer equipped with an integrating sphere and polytetrafluoroethylene (PTFE) as reference, with d = 1 g cm^{-3} and thickness of 6 mm. Thermogravimetric analysis was performed using a Setsys 18 A (Setaram) thermogravimetric analyzer. Elemental analyses were carried out by the Microanalytical Service of the Universidad Complutense de Madrid. The C, H and N analysis was accomplished by combustion analysis with elemental microanalyzers LECO CHNS-932.

2.4. Modified carbon paste electrode preparation

The modified carbon paste electrodes (MCPE) used as working electrode were prepared by mixing with a pestle in an agate mortar the iron oxide nanoparticles materials under study with graphite (Metrohm) (10% (w,w) ratio) and mineral oil as agglutinant (Sigma-Aldrich) until a uniform paste was obtained. The material was then packed into the end of a Teflon cylindrical tube equipped with a screwing stainless steel piston providing an inner electrical contact. All the initial electrode activity could always be restored by simply removing the outer layer of paste by treatment with polishing paper.

2.5. Knoevenagel condensation reaction

In a typical experiment, 11 mmol of benzaldehyde, 11 mmol of ethyl cyanoacetate and 50 mg of catalyst (Chol-MNPs, Gly-Chol-MNPs o Lys-Chol-MNPs) in ethanol (5 mL) were mixed in a 50 mL tube and the mixture was stirred at room temperature. After reaction completion 10 mL of dichloromethane were added to dilute and solubilize the organic compounds. The solid catalyst was precipitated by centrifugation or magnetic decantation and separated from the liquid phase. To