



Preparation, characterization and catalyst application of ternary interpenetrating networks of poly 4-methyl vinyl pyridinium hydroxide–SiO₂–Al₂O₃

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ABSTRACT

In this work, Al₂O₃ was mixed with SiO₂ and poly 4-vinylpyridine by the sol-gel method in order to make a composite which is used as a heterogeneous basic catalyst for Knoevenagel condensation reaction. The physical and chemical properties of the composite catalyst were investigated by XRD, FT-IR, TG, BET and SEM techniques. The catalytic performance of each material was determined for the Knoevenagel condensation reaction between carbonyl compound and malononitrile. The reactions were performed in solvent-free conditions and the product was obtained in high yield and purity after a simple work-up. The effects of the amount of catalyst, amount of monomer for the synthesis of composite and recyclability of the heterogeneous composite were investigated. The composite catalyst used for this synthetically useful transformation showed considerable level of reusability besides very good activity.

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1. Introduction

Homogeneous catalysts are soluble species that are usually very active and selective. Their syntheses are guided by molecular design principles, but are often difficult to use in industry. They suffer from high costs associated with separating them from products and consequential difficulties in recycling. The development of heterogeneous catalysts to replace homogeneous systems for the production of a wide range of chemicals is motivated by several potential advantages such as easier separation of the catalyst from the reaction medium, greater catalyst stability, improved regenerability, eco-benignity, and fitting the concepts of “green chemical process”. They can be designed to give higher activity, selectivity and longer catalyst lifetimes [1–4].

Polymer-inorganic hybrid materials obtained by combining organic polymers and inorganic compounds at nano or molecular order are expected to be the original material which exhibit high performance in all properties. Both pure organic polymer and pure inorganic materials have their own advantages and disadvantages. The organic polymer materials exhibit excellent flexibility, toughness, moldability and adhesiveness, but their heat-resistance properties are inferior to those of inorganic materials. On the

other hand, inorganic materials show high elastic modulus, heat resistance, corrosiveness, weather resistance, solvent resistance and mechanical strength. However, they are very brittle and their moldability is very poor. Therefore, the combination of inorganic and organic moieties in a single-phase material can lead us to tailor the mechanical, electrical and optical properties with respect to numerous applications [5–8] such as catalysis, adsorption, separation, drug delivery and sensing [9–17].

Sol-gel technology, which is mainly based on inorganic polymerization reactions, is an important way to synthesize organic-inorganic hybrid materials because of its unique low temperature processing characteristic providing opportunities to let organic and inorganic phases mix well and incorporate with each other at temperatures under which the organic phase can survive. Since the last few decades, the preparation, characterization and application of those organic-inorganic hybrid materials based on the sol-gel process have been the fast growing research field in materials science [5–9,18–20].

Knoevenagel condensation is one of the well-known reactions in organic chemistry right from the syntheses of small molecules to the elegant intermediates of anti-hypertensive drugs and calcium antagonists. It is generally catalyzed by weak bases like primary, secondary, tertiary amines, ammonium or ammonium salts under homogeneous conditions. In the last decade, a wide range of catalysts, such as MgO [21], NbCl₅ [22], MgF₂ [23] Na₂CaP₂O₇ [24] chitosan [25], ionic liquids containing imidazole [26] or guanidinium group [27], have been employed to catalyze

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this reaction. However, the use of such catalysts is associated with environmental pollution. In the recent years, solid basic catalysts have received an increased attention as they facilitate a variety of organic reactions that take place via carbanionic intermediates [28–39].

In this paper, we report the synthesis of poly 4-methyl vinyl pyridinium hydroxide–SiO₂–Al₂O₃ (P4MVPH–SiO₂–Al₂O₃) by the in-situ polymerization of 4-vinylpyridine (4VP) in the presence of aluminum isopropoxide and tetraethyl orthosilicate (TEOS), subsequent quaternization with methyl iodide and ion exchange occurs with NaOH. The novelty of this procedure is at easy preparation together with using inexpensive materials. The basic property of this new polymeric inorganic catalyst was tested for Knoevenagel condensation of various aldehydes with malononitrile in solvent-free conditions. The composite could be easily recovered by simple washing and filtration and reused up to 5 times without significant loss in its catalytic activity.

2. Experimental

2.1. Instruments and characterization

The catalyst was characterized by X-ray diffraction (Bruker D8ADVANCE, Cu K α radiation), FT-IR spectroscopy (Nicolet 400D in KBr matrix in the range of 4000–400 cm⁻¹), BET specific surface areas and BJH pore size distribution (Series BEL SORP 18, at 77 K), thermal analyzer TGA (Setaram Labsys TG (STA) in temperature 30–700 °C and heating rate of 10 °C/min in N₂ atmosphere) and SEM (Philips, XL30, SE detector).

The products were characterized by ¹H and ¹³C NMR spectra (Bruker DRX-500 Avance spectrometer at 500.13 and 125.47 MHz, respectively), GC (Agilent 6820 equipped with a FID detector) and GC-MS (Agilent 6890). Melting points were measured on an Electrothermal 9100 apparatus and they were uncorrected. All the products were known compounds and they were characterized by FTIR, ¹H NMR and ¹³C NMR. All melting points were compared satisfactorily with those reported in the literature.

2.2. Catalyst preparation

2.2.1. Preparation of the 4-methyl vinyl pyridinium hydroxide–SiO₂–Al₂O₃ composite by in-situ polymerization

In the first step, poly 4-vinyl pyridine–SiO₂–Al₂O₃ was prepared by in-situ method. Aluminum isopropoxide (1.84 g, 9 mmol) was dissolved in *n*-butanol. Through this clear solution, acetyl acetone (2.06 mL, 0.02 mol), TEOS (2 mL, 8.9 mmol), 4-vinylpyridine (2 mL, 18.5 mmol) and K₂S₂O₈ (0.5 g, 1.84 mmol) were added under continuous stirring, and the mixture was heated to 60–70 °C. After 1 h, the solution was cooled down to room temperature and deionized water (10 mL) as the hydrolyzing agent was added slowly. The reaction mixture was left overnight to hydrolyze the alkoxides, yielding transparent gel. The obtained gel was dried at 60 °C and gave 4.2 g poly 4-vinyl pyridine–SiO₂–Al₂O₃ (P4VP–SiO₂–Al₂O₃).

In the second step, the obtained P4VP–SiO₂–Al₂O₃ (4.2 g), CH₃I (2 mL, 0.046 mol) and CH₂Cl₂ (20 mL) were added to a 50 mL round-bottomed flask. The solution was stirred with magnetic stirrer and refluxed for 6 h at 40 °C. This mixture was filtered and washed with CH₂Cl₂ (2 × 10 mL) and the precipitate was dried in air to yield poly 4-methyl vinyl pyridinium iodide–SiO₂–Al₂O₃ (P4MVPI–SiO₂–Al₂O₃).

In the third step, the aqueous solution of NaOH (0.027 mol of NaOH in 20 mL H₂O) was added to the obtained P4MVPI–SiO₂–Al₂O₃ at room temperature. The mixture was stirred for 7.5 h. Then, it was filtered and washed sequentially with deionized

water to remove excess NaOH and was dried in room temperature to yield poly 4-methyl vinyl pyridinium hydroxide–SiO₂–Al₂O₃ (P4MVPH–SiO₂–Al₂O₃ (in-situ)) composite.

Hydroxide content of P4MVPH–SiO₂–Al₂O₃ composite was estimated by back titration using NaOH (0.2 N). 10 mL of HCl (0.2 N) was added to 0.05 g of this composite and stirred for 30 min. The catalyst was removed and washed successively with deionized water. The excess amount of HCl was titrated with NaOH (0.2 N) in the presence of phenol phthalein as indicator. Basic sites content of the catalyst was 4.8 mmol g⁻¹.

The procedure for preparing P4MVPH–SiO₂–Al₂O₃ (in-situ) is given in Scheme 1.

2.2.2. General procedure for Knoevenagel condensation reaction

The catalytic activity of P4MVPH–SiO₂–Al₂O₃ was tested for the Knoevenagel condensation. In a typical experiment, 1 mmol of benzaldehyde (0.10 mL), 1 mmol of malononitrile (0.07 mg) and 0.12 g of catalyst (P4MVPH–SiO₂–Al₂O₃) were taken in a round-bottom flask, and were stirred. The reaction was carried out under solvent-free condition at room temperature. (It should be mentioned that in the case solid aldehydes, the mixture was ground at room temperature in a glass mortar and pestle.) The progress and completion of the reaction was monitored by TLC, using *n*-hexane/ethyl acetate (5:1) as eluent. After 3 min of reaction, the mixture was cooled to 10 °C, for the solidification of the product. 10 ml of hot ethanol was added to the reaction mixture and the catalyst was separated from the reaction mixture by filtration. The residual solid was re-crystallized with hot ethanol (5 mL). The product was identified with ¹H NMR, ¹³C NMR and FT-IR spectroscopy techniques and compared with the authentic samples.

3. Results and discussion

3.1. Characterization of the catalyst

3.1.1. X-ray diffraction analysis

Fig. 1 depicts the powder X-ray diffraction patterns of the solids SiO₂–Al₂O₃ (a) and P4MVPH–SiO₂–Al₂O₃ (in-situ) (b). The solid SiO₂–Al₂O₃ displays the characteristic spectral profile of an amorphous aluminosilicate with an amorphous halo present in the 2 θ =23 [40]. This typical halo results from the dispersion of the angles and bond distances between the basic structural units (silicates and aluminates) which destroys the structure periodicity and produces a non-crystalline material. No changes in the diffraction patterns are observed of P4MVPH–SiO₂–Al₂O₃ (Fig. 1b), thus reinforcing the assumption that P4MVPH hybridization occurs on the solid surface without changing the structural form of the SiO₂–Al₂O₃.

3.1.2. FTIR analysis

Fig. 2 presents the FTIR spectra of SiO₂–Al₂O₃ (a), P4VP (b), P4VP–SiO₂–Al₂O₃ (c), P4MVPI–SiO₂–Al₂O₃ (d) and P4MVPH–SiO₂–Al₂O₃ (e). In the case of solid SiO₂–Al₂O₃, the bands expected for the aluminosilicate can be observed in the 1050 cm⁻¹ (Si–O bond stretching) and 460 cm⁻¹ (Al–O bond stretching) regions [41], which are seen in Fig. 1a,c,d,e. The other absorption peak of Al–O stretching vibration in the range of 1000–1200 cm⁻¹ could not be resolved due to its overlap with the absorption peak of Si–O–Si stretching vibration in the range of 1000–1200 cm⁻¹. There is also a band in 3429 and 1632 cm⁻¹ due to the O–H bonds vibration.

In the FT-IR spectrum of P4VP–SiO₂–Al₂O₃ (Fig. 1c), the new bands at 1598, 1558, 1496 and 1406 cm⁻¹ were the characteristic absorptions of pyridine ring. Among them, the band which appeared at 1598 cm⁻¹ was the stretching vibration absorption of C–N bond and the bands at 1558, 1496 and 1406 cm⁻¹ were

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