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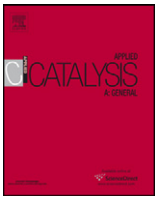

Sulfonic acid functionalized MCM-41 as solid acid catalyst for *tert*-butylation of hydroquinone enhanced by microwave heating

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ABSTRACT

Covalently linked sulfonic acid (—SO_3H) modified MCM-41 mesoporous catalysts was prepared, characterized and its catalytic activity under microwave irradiation was evaluated. The NH_2-MCM-41 was first prepared by anchoring (3-aminopropyl)triethoxysilane (APTES) on Si-MCM-41 and further reacted with 1,4-butane-sultone to yield the desired acid catalyst. The mesophase and porosity of samples were determined by XRD, TEM and N_2 sorption isotherm analyses. The presence of sulfonic acid moiety was confirmed by FT-IR, TG/DTA, sulfur elemental analysis and in situ IR study of pyridine and ammonia adsorptions. The catalyst showed high catalytic activity and high selectivity in *tert*-butylation of hydroquinone under microwave irradiation. No leaching problem was observed after several runs, while the catalyst can be recovered and reused without loss of reactivity under the described reaction conditions.

1. Introduction

New developments in the chemical industries are driven by environmental regulations, safety, energy efficiencies and the need for improved performance. The increasingly environmental regulations require the use of green technology in various areas [1,2]. Particularly, catalysts are attractive in green technology because of their importance in petrochemicals and fine chemicals synthesis. Usually chemical syntheses involve homogeneous catalysts; however, using heterogeneous catalysts such as molecular sieves (e.g. microporous zeolites and mesoporous materials) could be more environment-friendly and cost effective, allowing catalyst separation and reusability [3].

MCM-41 is a structurally well-ordered mesoporous solid, possessing some fascinating properties such as high surface area, uniform pore size (20–100 Å) and relatively hydrophobic nature [4]. It is known that MCM-41 in pure silica form has no substantial acidity and exhibits only weak hydrogen bonding sites [5,6]. The incorporation of metals (Al, Ti, Fe, etc.) in MCM-41 framework structure can be performed to generate acid properties [7–10]. On the other side, functionalizing and supporting some acidic species such as heteropolyacids (HPW) [11–13] and mineral acids (H_3PO_4, H_2SO_4) [14–16] offer another promising solutions to generate the acidity.

Recently, MCM-41 grafted with sulfonic acid (SO_3H-MCM-41) has been prepared to catalyze many organic reactions. The modified catalyst improves the solid acidity and at the same time, high surface areas and tunable pore diameters are retained. For instance, SO_3H-MCM-41 is shown having excellent catalytic activity and selectivity in esterification [17–22], Fischer indole synthesis [23], Claisen–Schmidt condensation [24], Friedel–Crafts alkylation [25,26], Fries and pinacol rearrangements [26], condensation of 2-methylfuran and acetone [27] and transesterification reactions [28]. The results reveal that incorporation of sulfonic acid groups on porous silica supports produces highly convenient solid acid catalysts, exhibiting the advantages of homogeneous catalysts.

Basically, covalent anchoring of the sulfonic acid groups to the mesoporous materials surface can be achieved either by a direct synthesis route or by a post synthetic anchoring of 3-(mercaptopropyl)triethoxysilane (MPTES) followed by an oxidation step to generate the sulfonic acid groups [17–22,28–30]. However, the use of strong oxidation agent in the oxidization of MPTES tends to lower the ordering of the mesopores. In respect to this, chlorosulfonic acid has recently been proposed as another

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promising sulfonating agent to immobilize sulfonic acid groups on mesopore walls [22,26].

Alkylsultones are cyclic sulfate esters. Basically, they are used as main chemical intermediates for the synthesis of dyes, anionic surfactants and secondary lithium ion solution [31]. In this work, the use of alkylsultone was achieved to generate sulfonic acid groups on MCM-41 solid via ring opening approach in an attempt to obtain a heterogeneous acid catalyst. The mesoporous silica was first aminopropylated followed by sulfonation with alkylsultone. The resulting solids were then characterized and their catalytic activity was studied using microwave-assisted Friedel–Crafts *tert*-butylation of hydroquinone as the probe reaction. This reaction was interesting as it can predict the nature of the acidic sites (weak, mild or strong) present in the catalysts [32,33] which will be further confirmed by in situ IR study of pyridine and ammonia adsorptions study. Furthermore, the monosubstituted product of this reaction namely, 2-*tert*-butylhydroquinone, is a highly effective antioxidant and is widely used as a preservative for vegetable oils and edible animal fats [34,35].

2. Experimental

2.1. Preparation of Si-MCM-41 support

The mesoporous MCM-41 powder was synthesized from an alkaline solution containing cetyltrimethylammonium bromide (CTABr, 98%, Aldrich), sodium silicate solution (Na_2O 7.5–8.5%, SiO_2 25.8–28.5%, Merck), sulfuric acid (98%, Merck), and deionized water. CTABr was first dissolved in distilled water under stirring before sodium silicate was introduced into the mixture to give the final composition mole ratio of $1CTABr:1.76Na_2O:6.14SiO_2:335.23H_2O$. After 24 h of hydrothermal treatment at 100 °C, the MCM-41 powder was filtered, washed until pH 7, and dried at 80 °C overnight before it was calcined in a furnace under a flow of air at 550 °C for 4 h with a heating rate of 1 °C/min to remove the organic template.

2.2. Preparation of (3-aminopropyl)triethylsilyl-MCM-41 (NH_2-MCM-41) via aminopropylation

Amine functionalization was achieved by aminopropylating activated Si-MCM-41 (1.5 g, 100 °C, 4 h, Fig. 1a) under vacuum with (3-aminopropyl)triethoxysilane (3.5 g, APTES, 98%, Aldrich) in toluene (10 ml) under reflux for 5 h to form covalent linkages with the mesoporous silica surface (Fig. 1b). The non-reacted amines and the solvent were removed by filtration and the amine modified MCM-41 was washed thoroughly with chloroform and diethyl ether before drying at 80 °C overnight.

2.3. Preparation of SO_3H-MCM-41 via sulfonation

The NH_2-MCM-41 (1.0 g) was preloaded with a solution of toluene (10 ml) containing 1,4-butane-sultone (3 g, Merck) followed by reflux for 5 h. The solid obtained was then purified with chloroform and diethyl ether before drying at 80 °C overnight to give a yellow powder as final product (Fig. 1c).

2.4. Characterization of catalysts

XRD patterns were recorded on a Siemens D5000 Kristalloflex diffractometer. The surface physicochemical properties were analyzed using a Micromeritics ASAP 2010 after degassing overnight at 180 °C. The morphological features of MCM-41 samples were examined by transmission electron microscopy (TEM) using PHILIPS CM-12 microscope. For the quantitative determination of sulfur content or SO_3H density in the samples, the MCM-41 solids were measured with a KZDL-4 Sulfur Analyzer. The organic moieties were determined based on Mettler TGA SDTA851 instrument with a heating rate of 10 °C/min under nitrogen flow. The FTIR spectra were recorded on a PerkinElmer spectrometer (System 2000) using the KBr pellet technique (KBr: sample weight ratio = 150:1).

Pyridine and ammonia FTIR spectra were recorded using a Nicolet 6700 FT-IR spectrometer. The MCM-41 samples were ground and pressed to obtain a wafer (area 2 cm^2, mass of 13 mg) before introduction in the IR cell. The samples were then pre-activated under vacuum (10^{-6} mbar) at 200 °C for 3 h. The reference spectrum was first recorded after cooling and then a 1.33 mbar equilibrium pressure of pyridine (or ammonia) was introduced to the sample for 5 min. The spectrum was recorded with a 4 cm^{-1} resolution and 64 scans accumulation. The sample was then allowed to evacuate at 25 and 100 °C to desorb pyridine (or ammonia) and the spectra were recorded after each evacuation step.

2.5. Catalytic experiments

Friedel–Crafts reactions were performed with microwave irradiation assistance by modifying the synthesis condition [30]. Prior to reaction, hydroquinone (Merck, 2.0 mmol), methyl *tert*-butyl ether (MTBE, Merck, 2.0 mmol) and freshly activated SO_3H-MCM-41 catalyst (0.1 g, 100 °C, 3 h) were loaded into a reactor. The reaction was realized in an Anton Paar Synthos 3000 microwave oven under magnetic stirring and 300 W microwave irradiation, while the reaction temperature was monitored by an infrared pyrometer. The samples were withdrawn after the reaction and the liquid phase was separated and analyzed using a gas chromatograph (Hewlett-Packard 5880) equipped with a Carbowax Equity 1 non-polar capillary column. The identity of the product was confirmed by GC–MS (Perkin-Elmer GC-IR 2000 system).

2.6. Leaching and reusability tests

The leaching and reusability tests were carried out as follows: SO_3H-MCM-41 solid was separated after the first Friedel–Crafts (reaction temperature = 150 °C, HQ:MTBE = 1:1, MW power = 300 W, time = 8 min) run, further washed with diethyl ether and finally activated (100 °C, 3 h) before use for the three subsequent cycles of catalytic reaction. After the reaction, the solution was again separated and analyzed using GC.

3. Results and discussion

3.1. Characterization

Supported sulfonic acid catalysts in this work were prepared in two steps. In the initial step, APTES as a bridging agent was first functionalized on MCM-41, giving (3-aminopropyl)trimethylsilyl-MCM-41 (denoted as NH_2-MCM-41). After this, the nucleophilic attack of the amine group of NH_2-MCM-41 on the cyclic sultone opened the ring of 1,4-butane-sultone, leading to the formation of a linear chain of sulfonic acid solid catalyst (Fig. 1c).

The preparation of SO_3H-MCM-41 was monitored using FT-IR spectroscopy via the KBr salt dilution technique. Fig. 2 shows the infrared spectra of Si-MCM-41, NH_2-MCM-41, and SO_3H-MCM-41 solids. The spectrum shown in Fig. 2a displays several typical IR vibration signals for Si-MCM-41: 3455 and 1642 cm^{-1} (H-bonded hydroxyls ν(OH) stretching and adsorbed water bending vibrations), 1237 and 1085 cm^{-1} (asymmetric stretching vibrations of Si–O–Si), 800 and 584 cm^{-1} (symmetric stretching vibrations of Si–O–Si), 962 cm^{-1} (bending mode of Si–OH) and 464 cm^{-1} (bending vibration of Si–O–Si) [15]. After aminopropylation, the band at 962 cm^{-1} almost completely disappeared and several new vibration bands including those corresponding to C–H groups (2934,