



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 ($-\text{SO}_3\text{H}$) 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.

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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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