



Fe-MCM-41 nanoparticles as versatile catalysts for phenol hydroxylation and for Friedel–Crafts alkylation

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ARTICLE INFO

Article history:

Received 9 May 2012

Received in revised form 10 August 2012

Accepted 14 August 2012

Available online 28 August 2012

Keywords:

Fe-MCM-41 nanoparticles

Shorter mesopore channels

Phenol hydroxylation

Friedel–Crafts alkylation

Higher initial reaction rate

ABSTRACT

Iron-containing MCM-41 nanoparticles (Fe-MCM-41 NPs) were successfully prepared using cetyltrimethylammonium bromide (CTAB) in sodium hydroxide medium at ambient temperature from both direct-hydrothermal and post-synthesis methods. The materials were characterized by X-ray diffraction, nitrogen adsorption/desorption isotherms, SEM, TEM, and UV–vis spectroscopy. The characterization results show the existence of highly ordered hexagonal mesopores in the nanoparticles and tetrahedral Fe species in the framework. In phenol hydroxylation with aqueous H₂O₂, Fe-MCM-41 nanoparticles displayed higher initial reaction rate than Fe-MCM-41 with larger particle size. It is proposed that the diffusion of the reactants is accelerated and the accessibility to the catalytic Fe species is enhanced in the shorter mesopore channels in Fe-MCM-41 nanoparticles. The recyclability potential of the nanoparticles was evaluated in the regeneration by room-temperature washing approach. Fe-MCM-41 NPs also appear to be suitable catalysts for the Friedel–Crafts alkylation of benzene with benzyl chloride.

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1. Introduction

Microporous and mesoporous silicates containing metallic heteroatoms in the open-framework have been greatly explored as heterogeneous catalysts owing to the characteristics of their high surface area and uniform nano-order mesopores [1–12]. Especially, metal-substituted mesoporous silicates have aroused even more extensive interests in the processes of bulky substrates involved because of the enhanced accessibility of active sites given by mesopores [4,5]. Up to now, a wide variety of metal elements including Ti, V, Cr, Fe and Cu have been successfully incorporated in the framework of mesoporous silicates, achieving a series of novel heterogeneous catalysts for various selective oxidations [13–22]. Mesoporous silicates containing titanium, showing outstanding catalytic performances in selective oxidations, are most studied. However, their wider application is rather limited by the complexity of the synthetic procedures, in which the conditions must be strictly controlled to avoid precipitation of TiO₂ as a separate phase. Therefore, metal-substituted mesoporous materials with high

catalytic activity in selective oxidations, that could be easily obtained, have always been sought.

Iron-containing mesoporous MCM-41 (Fe-MCM-41) is of particular interest in heterogeneous selective oxidations due to their comparable catalytic performances to Ti-MCM-41 and the facile and controllable preparation routes [23–28]. As tetravalent titanium element, the incorporation of tetrahedral trivalent iron into mesoporous silicate matrixes can create isolated redox centers [29]. On the other hand, the incorporation of iron generates acid sites and the obtained Fe-MCM-41 materials proved to be active for Friedel–Crafts alkylations that are usually catalyzed by liquid acids [30–32]. In order to get Fe-MCM-41 with highly catalytic activity, many approaches have been developed, such as direct-hydrothermal synthesis, template ion exchange, chemical vapor deposition, and post-synthesis [23–32]. Several structural parameters that could have direct influence on catalytic activities of Fe-MCM-41 have also been widely studied in aspects of pore architecture, loading amount of isolated iron in the framework and coordinated environment of Fe species in Fe-MCM-41 [23–32]. In contrast, much less work focused on the effect of morphology of Fe-MCM-41 on their catalytic performances, which is impending the extensive study and their wide applicability. To date, no attempt to prepare nanoparticles of Fe-MCM-41 has been reported, although nanoparticles of TS-1 and Ti-MCM-41 proved to be more active

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