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Propylsulfonic acid functionalized MCA cubic mesoporous and ZSM-5-MCA composite catalysts for anisole alkylation

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ABSTRACT

Propylsulfonic acid functionalized mesoporous cubic *Ia-3d* amorphous (MCA) silica (MCA-Pr-SO_3H) was synthesized by co-condensation. Different amounts of ZSM-5 seeds were added into the *Ia-3d* mesopore silica gel to yield ZM-x composites (where x is the wt.% loading level of ZSM-5). The structure characterization, morphology and acidity of the synthesized materials were characterized by X-ray diffraction, nitrogen adsorption-desorption, scanning and transmission electron microscopy, X-ray photoelectron spectroscopy and ^{13}C-NMR techniques. The composite materials were found to have properties of both mesoporous (MCA) and ZSM-5, with the ZSM-5 loading level having a major effect on the structure of the *Ia-3d* mesoporous composite. The MCA-Pr-SO_3H catalytic activity in the anisole alkylation reaction with *tert*-butanol was compared to that of Amberlyst-15, ZSM-5 and ZM-30 materials. The highest yield of total *tert*-butylated anisole (TBA) products was obtained with MCA-Pr-SO_3H, with the major products being 4-*tert*-butyl anisole (4-TBA), 2-*tert*-butyl anisole and 2, 4-di-*tert*-butyl anisole. Compared with the other materials, ZM-30 promoted high selectivity of *para*-alkylated anisole (4-TBA) and the yield of TBA products.

1. Introduction

Alkylation of aromatics is an important reaction in the preparation of various chemicals that are used in antioxidants, dye developers and stabilizers for fats, oils, plastic and rubber (amongst other uses). Normally, Friedel-Crafts catalysts, such as $AlCl_3$, $FeCl_3$, $ZnCl_2$ and H_2SO_4 [1], are used for the alkylation of aromatics. However, the use of homogeneous catalysts gives rise to many problems, such as their corrosive and environmentally toxic nature and the presence of several side products that are difficult to separate [2]. In order to avoid these disadvantages of the conventional homogeneous catalysts, it is essential to find suitable heterogeneous solid acid catalysts for alkylation reactions that are more selective and environmentally friendly. Heterogeneous catalysts, such as clays [3,4], zeolites [5,6] and ion exchange resins [7,8], have been used in the alkylation of aromatic compounds.

The ordered mesoporous MCM-41S family, which are very attractive materials because of their high specific surface area, narrow pore size distribution (from 2 to 10 nm) and a high efficiency as a heterogeneous catalyst, have found diverse applications, including as molecular sieves, catalysts, adsorbents, sensors and guest-host chemical supporters. The most well-known representatives of this class include the silica solids, such as MCM-41, SBA-15 [9,10] (with a hexagonal arrangement of the mesopores) and MCM-48 [11] (with a cubic arrangement of the mesopores). To develop the application of these mesoporous silica materials they are frequently surface modified by incorporating a wide range of different organic-inorganic functional groups, including thiol, amine, epoxide, imidazole, nitrile, alkyl, allyl and phenyl groups [12–16]. However, the small pore size (>4 nm) of these mesoporous materials limits their application as catalysts when the organic-inorganic functional groups are incorporated into the pore. Thus, the synthesis of cubic *Ia-3d* mesoporous silica with pores larger than 5 nm has attracted a lot of recent attention for medium and large molecular applications. The large-pore mesoporous molecular sieve (cubic *Ia-3d*) [17,18] has a three-dimensional (3D) structure that is similar to the MCM-48 structure, but the cubic *Ia-3d* has a larger pore diameter. The advantage of this 3D structure and large pores is that it can increase the

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diffusion speed of reactants into the pore and can work with large molecules, and so it is of interest as a potential catalyst in alkylation reactions [3]. However, cubic mesoporous *Ia-3d* has very few acid active sites compared to that of microporous zeolite, and so acid-functional groups are added onto its surface for applications requiring an acidic catalyst. To this end, alkylsulfonic-functionalized silica materials have generally been prepared via post-grafting [19] or co-condensation [12,16,20].

Recently, porous materials have been developed by combining materials of a different porosity to form new generation composite materials that are a combination of microporous and mesoporous materials. The microporous (pore size < 2 nm) zeolites, such as ZSM-5, Beta and zeolite Y, have been used in several applications [21,22], due to their good stability, selectivity and activity. However, the pore size of zeolites is too small to be used as a catalyst for reactions involving large molecules. The mesoporous materials (pore size in range of 2–50 nm), such as MCM-41, SBA-15 and MCM-48, contain larger pores that allow a higher diffusion rate of reactants compared to zeolites, but have a low hydrothermal stability and acidity. Therefore, several studies have reported on the combination of both microporous and mesoporous materials to form composites for application as catalysts in order to overcome the respective disadvantages of the microporous and mesoporous materials [2,23–25]. Basically, three methodologies have been reported for the preparation of composite materials that combine crystalline zeolite and a mesoporous material. The first approach is to prepare mesoporous molecular sieves and then to recrystallize the original amorphous walls into the crystalline zeolitic walls using an appropriate structure directing agent [26–28]. The second approach is based on using zeolite seeds as framework building units, where these seeds are organized into the mesoporous structure [29,30]. The third approach is a dual template method through a process of two-step crystallization [28,31].

Anisole is a by-product from the dimethyl carbonate to diphenyl carbonate (DPC) process [32]. Since DPC is in high demand as a precursor in the production of polycarbonate through trans-esterification with bisphenol A, then this process provides a large amount of anisole. Therefore, anisole alkylation is an important process for increasing the value of anisole. Amongst these, alkylation of anisole with *tert*-butanol has been used to produce 4-*tert*-butyl anisole (4-TBA), 2-*tert*-butyl anisole (2-TBA) and 2, 4-di-*tert*-butyl anisole (2, 4-DTBA) [33], which are intermediates in the chemistry industry. In addition, several mesoporous materials have been synthesized to improve the catalytic activity in alkylation reactions. For example, the alkylation of anisole with *tert*-butanol has been catalyzed by AlMCM-41 [33,34], which has a highly-ordered mesoporous structure. The alkylation of anisole to yield 4-TBA has been performed in the presence of $ZrCl_4$ [35] and over solid catalysts, such as Filtrol-24 clay, K-10 clay and heteropolyacids supported on K-10 catalysts, with methyl *tert*-butyl ether (MTBE) [36]. In this work, an organic-functionalized cubic mesoporous material and a composite material were prepared using a modification of the method of Kubota et al. [16], where the microporous material ZSM-5 was incorporated into the cubic *I*a-3d (MCA) mesoporous material for the synthesis of a composite micro/mesoporous material. The choice of ZSM-5 as a microporous material was because of the well-established methods for pore modification of ZSM-5 to enhance the *para*-selectivity of products [37]. However, there has been no report on the synthesis of ZSM-5/propylsulfonic acid functionalized cubic *Ia-3d* mesoporous cubic amorphous silica (MCA-Pr-SO_3H) as bi-porous material with different loading amounts of ZSM-5 seeds. The prepared materials were tested as acid catalysts in the anisole alkylation with *tert*-butanol to produce *tert*-butylated methoxy benzene.

2. Experimental

2.1. Chemicals

Triblock copolymer pluronic P123 (PEO_{20}-PPO_{70}-PEO_{20}, molecular weight = 5800; Aldrich), tetraethyl orthosilicate (TEOS, 98%; Fluka), 3-(mercaptopropyl) trimethoxysilane (MPTMS, 95%; Aldrich), commercial ZSM-5 (ZEOCHEM, Si/Al = 28), hydrochloric acid (HCl, 37%; Merck), hydrogen peroxide (H_2O_2, 30%; Merck), sulfuric acid (H_2SO_4, 95–97%; Merck), anisole (99%; Merck), *tert*-butanol (99%; Fluka), *n*-octane (95%; Merck), tetrahydrofuran (99%; Fluka), toluene (99.5%; Aldrich) and deionized water.

2.2. Synthesis of MCA-Pr-SO_3H

The MCA-Pr-SO_3H was prepared by a modification of the method of [16], using the co-condensation of TEOS (8.19 g) and MPTMS (0.69 g) in the presence of P123 (4.0 g), conc. HCl (7.8 g) and deionized water (100 mL), and then aged at 40 °C for 24 h with stirring. Thus, the gel composition (mole ratio) was 1 TEOS: 0.089 MPTMS: 0.018 P123: 2.0 HCl: 148 H_2O. After aging, the milky reaction mixture was transferred into a Teflon-lined stainless steel autoclave and crystallized in an oven at 100 °C for 48 h. The white product was filtered, washed in deionized water and dried at 60 °C overnight to yield as-syn MCA. The P123 surfactant was then removed from the as-syn MCA by extracting with 0.37 M HCl in EtOH and then dried at 70 °C for 24 h to give MCAex. The thiol groups (-SH) in the MCAex sample were converted to sulfonic groups (-SO_3H) by oxidation with 30 wt% H_2O_2 aqueous solution (10 g of H_2O_2 solution per 3.0 g of MCAex) at 60 °C for 24 h [19], and then further stirred with 50 mL of 0.2 M H_2SO_4 at room temperature for 2 h, filtered and dried overnight to give the MCA-Pr-SO_3H.

2.3. Synthesis of SBA-Pr-SO_3H

SBA-15 was synthesized using a gel mole composition of 1.0 TEOS: 0.0165 P123: 6.95 HCl: 140 H_2O, as reported by Zhao et al. [10]. In a typical procedure, P123 (4.0 g) was homogenized in 1.9 M HCl (100 mL) solution with stirring at room temperature. Subsequently, TEOS (8.5 g) was added drop wise and the mixture was aged at 40 °C for 24 h with stirring. The milky reaction mixture was then transferred to a Teflon-lined autoclave for hydrothermal crystallization at 100 °C for 48 h. As-synthesized SBA-15 was harvested by filtration and washed with deionized water several times, and then dried overnight. The template was removed by calcination at 550 °C for 5 h. The calcined SBA-15 (3.0 g) was suspended with MPTMS (5.3 g) in dry toluene (50 mL) and refluxed at 60 °C for 6 h. After that, the thiol groups were oxidized to sulfonic acid groups by 30% H_2O_2 [19]. Finally, the functionalized material was filtered and dried overnight at 60 °C.

2.4. Synthesis of micro/mesoporous composite material

The method of synthesis of the propylsulfonic functionalized ZSM-5(x)/MCA composite materials was modified from that described previously [16] by adding different amounts of commercial ZSM-5 (Si/Al = 28) in the seeding method [23]. The ZSM-5 powder was added in the homogeneous P123 surfactant solution at 40 °C, stirred for 2 h and then (8.19 g) TEOS and (0.69 g) MPTMS were added into the mixture. The mixture was continuously stirred for 24 h and then transferred into an autoclave and crystallized in an oven at 100 °C for 48 h. The white product was filtered, washed with deionized water and dried at 60 °C overnight. The product was removed from the template by extracting with 0.37 M HCl in EtOH and dried at 70 °C overnight to leave the ZM-x composite material,