



Tuning the acidic and textural properties of ordered mesoporous silicas for their application as catalysts in the etherification of glycerol with isobutene



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ABSTRACT

Several silicas (MCM-41, SBA-15 and HMS) were acid-modified by incorporating aluminium or by introducing phosphorus species or sulfonic groups. The modified silicas maintained mesostructural ordering and a narrow pore size distribution. However, Their surface area and pore volume was lower than that of unmodified samples. The incorporation of aluminum in the structure of MCM-41 and SBA-15 increased the amount of Brønsted acid sites, leading to greater catalytic activity (i.e., higher conversion values) for glycerol etherification with isobutene than pure silicas, but their relatively weak acid strength resulted in low selectivity to di- and tri-tertiary butyl ethers of glycerol (h-GTBE). The introduction of phosphoric groups, with higher acidity strength, improved the selectivity to h-GTBE, and glycerol triether was detected in low amounts. Interestingly, HMS synthesized with dodecylamine and later sulfonated exhibited total conversion and 84% of selectivity to h-GTBE (26% to glycerol triether) after 24 h of reaction. The presence of textural mesoporosity in HMS reduced diffusion limitations, and consequently increased the incorporation of sulfonic groups and their accessibility, leading to higher catalytic activity.

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1. Introduction

In the last few years, the catalytic etherification of glycerol (glycerine or 1,2,3-propanetriol), in the presence of *tert*-butanol or isobutene, to obtain di- and tri- tertiary butyl ethers of glycerol (h-GTBE) has been extensively studied [1–19]. h-GTBE can be used as oxygenated fuel in place of the environmentally highly toxic methyl tertiary butyl ether (MTBE), and to remarkably reduce emissions of particulate matter [20]. Additionally, this reaction is a challenging option for glycerol revalorization.

To date, the best catalytic results for etherification of glycerol have been achieved with strong acid ion exchange resins (Amberlyst type) as catalysts [1–4]. The incorporation of organosulfonic acid groups in mesoporous materials can generate effective solid acid catalysts with enhanced catalytic properties. Mesoporous silica SBA-15 functionalized with organosulfonic acid groups, introduced by conventional heating, resulted in high conversion and moderate selectivity values to h-GTBE for glycerol etherification with isobutene [5,6]. In a previous study, we prepared an organosulfonic acid functionalized SBA-15 by direct synthesis in

one step microwave process. The resulting catalyst achieved total conversion and 91% to selectivity to h-GTBE (with 36% of selectivity to the glycerol triether) after 4 h of reaction for the etherification of glycerol with isobutene [16]. Apart from these studies of organosulfonic acid-functionalized SBA-15, there are no reports on the use of other mesoporous silicas such as MCM-41 or HMS modified by incorporation of Al, phosphorus species or sulfonic groups, as catalysts for glycerol etherification.

The incorporation of Al into the walls of MCM-41 or SBA-15 can generate active sites for adsorption, ion exchange and catalysis, which may function in aqueous media in a manner similar to that of aluminosilicate zeolites [21,22]. Zeolites are extensively used as acid catalysts, adsorbents and ion exchangers but their microporosity limits their applications to small molecules, and processes involving larger organic or biological molecules are excluded. Mesoporous molecular sieves have attracted much interest because of their potential application in reactions or separations involving bulky molecules. Aluminium is usually introduced into MCM-41 and SBA-15 by direct synthesis [23,24] or by post-synthesis grafting methods [25,26].

Another alternative to improve acidity in mesoporous materials and zeolites is to introduce phosphorus species. Kawi and co-workers proposed incorporation of phosphorous moieties onto MCM-41 via impregnation in H₃PO₄ solution [27]. More recently,

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McKeen and co-workers incorporated organic sulfonic, carboxylic and phosphoric acid groups into zeolite Beta, MCM-41 and MCM-48 [28] and observed that the order of proton conductivities in the functionalized materials was sulfonic acid groups > phosphoric acid groups > carboxylic acid groups.

HMS is a hexagonal mesoporous silica which shows significant differences compared to MCM-41 in that it exhibits complementary extra-framework (i.e., textural) mesopores in addition to framework pores. Textural mesopores are important because they greatly facilitate mass transport to the framework. For this reason the catalytic reactivity of HMS is usually superior to MCM-41, especially for reactions involving large substrates in a liquid reaction medium where the reaction rates are limited by diffusion [29,30]. It is now known that the degree of textural mesoporosity is quite sensitive to both the solvent and the nature of the surfactant used in the synthesis of HMS [31].

The aim of this work was to generate several mesoporous silicas with varying amount and strength of Brønsted acid sites and test their catalytic activity for glycerol etherification with isobutene. The acidic properties of the mesoporous silicas were varied via a number of routes, namely; (a) incorporation of aluminium via post-synthesis alumination of MCM-41 and SBA-15, (b) introduction of phosphorus species in MCM-41 and SBA-15, (c) sulfonation of MCM-41 via direct synthesis, and (d) post-synthesis sulfonation of several HMS samples synthesized with surfactants of varying length.

2. Experimental

2.1. Catalyst preparation

2.1.1. Synthesis of mesoporous silicas: MCM-41 and SBA-15

MCM-41: Tetramethylammonium hydroxide (TMAOH) and cetyltrimethylammonium bromide (CTAB) were dissolved in distilled water by stirring at 308 K to generate a template solution. Fumed silica was added to the template solution under stirring for 1 h to have a molar composition of 1 Si:0.25 CTAB:0.2 TMAOH:40 H₂O. After further stirring for 1 h the resulting gel was aged at room temperature for 20 h and then transferred to a Teflon-lined autoclave and heated at 423 K for 48 h. The solid was recovered by filtration, washed, dried in air at room temperature, and calcined at 823 K for 8 h.

SBA-15: An amount of 4.0 g triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EO₂₀PO₂₀EO₂₀) was added to a solution of 25 g HCl (35% wt%) and 125 g water under stirring. After stirring for 2 h, the copolymer was completely dissolved after which 8.6 g tetraethyl orthosilicate (TEOS) was added. Following continuous stirring at 313 K for 20 h, the reaction mixture was transferred to a Teflon-lined autoclave and heated at 373 K for 24 h. The resulting product was obtained by filtration, washed repeatedly with a large amount of water, air dried at room temperature and calcined at 773 K for 6 h to remove the surfactant.

2.1.2. Synthesis of mesoporous aluminosilicates: Al-MCM-41 and Al-SBA-15

For the alumination process, 1.0 g of calcined pure silica (MCM-41 or SBA-15) was added to 50 ml hexane (dry) containing the required amount of aluminium isopropoxide (Si/Al ratio = 5) and stirred at room temperature (Al-MCM-41) or 343 K (Al-SBA-15) for 24 h. The resulting powders were obtained by filtration, washed with dry hexane, dried at room temperature and calcined at 823 K for 4 h.

2.1.3. Synthesis of phosphoric acid-functionalized MCM-41, SBA-15

Phosphorus species were introduced onto the surface of the calcined silica samples by impregnating 1 g of mesoporous silica (MCM-41 or SBA-15) with 4.5 ml of H₃PO₄ solution (Si/P = 25), according to the method reported by Kawi et al. [27]. In order to prevent the framework from being destroyed in the strong acid solution, the phosphoric acid impregnated samples were rapidly dried under stirring. Finally, the sample was dried in the oven at 373 K for 8 h and calcined at 673 K for 3 h. Samples were designated as MCM-41-P and SBA-15-P.

2.1.4. Synthesis of ethylphosphoric acid-functionalized SBA-15

SBA-15-P2: Another phosphoric acid-functionalized SBA-15 sample was prepared by direct synthesis as follows; 4.0 g triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (EO₂₀PO₂₀EO₂₀) was added to 125 ml of 2 M HCl at room temperature under stirring. Then, the solution was heated to 313 K and 9 g of TEOS was added dropwise. After 45 min, 2.8 g of diethylphosphatoethyltriethoxy silane (DEPTES, Gelest) was added dropwise (to prevent phase separation). The sample was then heated under continuous stirring at 313 K for 2 h by refluxing under microwave heating. The reaction mixture was then transferred to a Teflon-lined autoclave and heated in a conventional oven at 373 K for 24 h. The resulting product was filtered, washed repeatedly with a large amount of water, and dried in air overnight. The surfactant template was removed by extraction with ethanol under reflux for 24 h. Finally, diethylphosphatoethyl groups were cleaved and converted to phosphoric acid groups by refluxing 1 g of diethylphosphatoethyl functionalized SBA-15 in 21 ml of concentrated HCl at 313 K for 24 h.

2.1.5. Synthesis of propylsulfonic acid-functionalized MCM-41

MCM-41-S: A template solution was prepared by dissolving tetramethylammonium hydroxide (TMAOH) and cetyltrimethylammonium bromide (CTAB) in distilled water at 308 K. The silica source, fumed silica, and (3-mercaptopropyl)trimethoxysilane (MPTMS) were then added to the template solution under stirring for 1 h. After further stirring for 1 h the resulting synthesis gel of composition 1 Si: 0.1 MPTMS: 0.25 CTAB: 0.2 TMAOH: 40 H₂O was aged at room temperature for 20 h. Then, the gel was transferred to a Teflon-lined autoclave and heated at 423 K for 48 h. The solid was recovered by filtration, washed, dried in air at room temperature, and refluxed in ethanol for 24 h. Material with immobilized mercaptopropyl groups was oxidized with H₂O₂ in a methanol-water mixture. Typically, 2.04 g of aqueous 35% H₂O₂ dissolved in three parts of methanol was used per g of material. After 24 h, the suspension was filtered and washed with water and EtOH. The wet material was resuspended (1 wt%) in acidified H₂O (0.1 M H₂SO₄) for another 4 h. Finally, the solid was extensively rinsed with H₂O, dried at 333 K, and stored in a desiccator.

2.1.6. Synthesis of arenesulfonic acid-functionalized HMS

HMS was synthesized at 338 K from a gel containing 0.02 TEOS, 0.005 amine, 0.088 EtOH and 2.56 H₂O. The amine (dodecylamine (dda), hexadecylamine (hda) or octadecylamine (oda)) was first dissolved in an alcohol-water mixture. TEOS was then added and the mixture was stirred at 338 K for 24 h. The amine template was removed by calcining at 873 K for 4 h to generate HMS samples designated as HMS(dda), HMS(hda) and HMS(oda) for templating via dodecylamine (dda), hexadecylamine (hda) or octadecylamine (oda), respectively. Then, the HMS samples were treated with 1.5 g of (2-(4-chlorosulfonylphenyl)ethyl)triethoxysilane (CSPTMS) by refluxing at 313 K for 2 h to introduce the organosulfonic groups.

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