Available online at www.sciencedirect.com
ScienceDirect
Journal of Molecular Catalysis A: Chemical 256 (2006) 29–36
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Etherification of benzyl alcohols with 1-hexanol over organosulfonic acid mesostructured materials

Rafael van Grieken *, Juan Antonio Melero, Gabriel Morales

Department of Chemical and Environmental Technology, ESCET, Rey Juan Carlos University, C/Tulipán s/n, 28933 Móstoles, Madrid, Spain

Received 9 March 2006; received in revised form 10 April 2006; accepted 12 April 2006
Available online 23 May 2006

Abstract

Etherification of benzyl alcohols with 1-hexanol was performed in liquid-phase over propyl- and arene-SO_3H-modified mesostructured SBA-15 silica. H_2O TPD measurements indicate a stronger interaction of arene-sulfonic acid sites with water molecules than that occurring in propyl-sulfonic groups. Hence, the higher catalytic activity of propyl-sulfonic-modified SBA-15 material is related to the more hydrophobic microenvironment of $-SO_3H$ sites which reduces the acid site deactivation associated with adsorption of water generated during the reaction. Moreover, propyl- and arene-sulfonic functionalized SBA-15 materials show a clear improvement of the catalytic performances as compared to other commercial homogeneous and heterogeneous acid catalysts in this particular reaction.

Keywords: Etherification; Benzyl alcohol; Sulfonic acid; SBA-15

1. Introduction

Conventional homogeneous acid catalysts, such as H_2SO_4, HF or $AlCl_3$ are widely used in the industrial chemical processes to synthesize bulk and fine chemicals, but they have serious drawbacks concerning hazards in handling, corrosiveness, difficult separation, and production of toxic waste. Restrictions in environmental legislation are driving the chemical industries to consider alternative processes to avoid the use of these conventional homogenous mineral acids as catalysts [1,2]. The heterogenisation of homogeneous catalysts and their use in the production of fine chemical synthesis has become a major research area, since the potential advantages of these materials (simplified recovery and reusability) over homogeneous systems can introduce positive environmental consequences [3,4]. Most of the novel acid-solid catalysts are based on silica supports, primarily because silica displays some advantageous properties, such as excellent stability (chemical and thermal), good accessibility due to high surface areas, and the fact that organic moieties can be robustly anchored to the surface to provide heterogeneous catalytic acid sites. However, a suitable system must not only give environmentally more benign processes, but also should exhibit activities and selectivities comparable or superior to the existing homogeneous route.

In the present work the etherification of benzyl alcohols, such as the vanillyl alcohol (4-hydroxy-3-methoxybenzyl alcohol) which is a derivative of vanilline, with a middle length-chain linear alcohol such as the 1-hexanol, has been studied. The selection of benzyl alcohols as etherification substrates has two major reasons: on the one hand due to their interest in some fine chemistry applications for the production of fragrances and flavourings and on the other hand because they are relatively bulky molecules which are not readily worked up over microporous catalysts such as conventional acid-zeolites. In the etherification of benzyl alcohols, the most used homogeneous catalyst is H_2SO_4, and when heterogeneous catalyst has been proposed as alternative, acid-zeolites and sulfonic acid functionalized resins have been the predominant materials. A German patent application DE-4434823 [5] discloses the preparation of ethers from benzyl alcohols reacting a hydroxybenzyl alcohol with an aliphatic one in the presence of a SO_3H-functionalized polystyrene resin (Amberlyst$^{®}$ A21). This kind of resin is hardly regenerable and the reaction yields are not too high. These drawbacks limit the feasibility of an industrial application. U.S. Patent No. 6362378 [6] shows a complete study including several etherifications with different benzyl alcohols employing a solid-acid catalyst

---

* Corresponding author. Tel.: +34 91 488 70 07; fax: +34 91 488 70 68.
E-mail address: rafael.vangrieken@urjc.es (R. van Grieken).

1381-1169/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2006.04.040

comprising certain amounts of acid-zeolites (Beta, Y, X, mordenite, ZSM family, etc.). Catalytic results obtained over these catalysts are acceptable for the majority of substrates.

New kind of acid-solids have emerged in the last years based on sulfonic acid groups contained in mesostructured MCM-41, HMS and SBA-15 materials [7–12]. Likewise, the increasing of acid strength by close attachment of different electron-withdrawing moieties to the sulfonic site (arene-sulfonic [12] and perfluorosulfonic groups [13,14]) as well as the hydrophobicity control of the microenvironment surrounding sulfonic acid sites [15] have opened up definitively the catalytic application of these materials. These sulfonated mesoporous silicas have been already tested in a broad variety of acid catalyzed reactions (esterifications [10,16,17], condensations and additions [8,18,19], etherifications [20], rearrangements [21–23], Friedel–Crafts acylations [24] and alkylations [23], ...) and in most of the cases showing better catalytic performance than conventional homogenous and heterogeneous catalysts.

Herein, a detailed study of the catalytic performance of these sulfonic acid-modified SBA-15 materials on the liquid-phase etherification of benzyl alcohols with 1-hexanol, never reported before, is carried out. Attention was brought on the comparison of their catalytic properties with other acid catalysts and on the effect of water production during the reaction, since these materials are expected to be hydrophilic and hence poisoning by water might occur [25].

2. Experimental

2.1. Catalysts preparation

Propyl-sulfonic acid functionalized mesostructured silicas (*Samples 1 and 2*) were synthesised as follows: 4 g of Pluronic 123 (Aldrich) were dissolved under gentle stirring in 125 g of 1.9 M HCl at room temperature. The solutions were heated to 40 °C and then tetraethylorthosilicate (TEOS, Aldrich) was added. A prehydrolysis time for TEOS species of 45 min was considered. Following this TEOS initial hydrolysis stage, mercaptopropyltrimethoxysilane (MPTMS, Aldrich) and an aqueous solution of H_2O_2 (30 wt%, Merck) were added at once. The resulting mixtures were stirred at 40 °C for 20 h and aged at 100 °C for an additional time of 24 h under static conditions. After synthesis, the solid products were recovered by filtration and air-dried overnight. Template molecules were removed from as-synthesised materials by washing with ethanol under reflux for 24 h (2 g of as-synthesised material per 200 mL of ethanol). The molar composition of the mixture, relative to 4 g of copolymer, was: $(0.0369-X)$ TEOS:$(0.0041+X)$ MPTMS:$(0.0369+9X)$ H_2O_2:0.24 HCl:≈6.67 H_2O. The amount of sulfur precursor (MPTMS) was fixed to provide 10% or 20% of total silicon atoms functionalized with sulfonic groups ($X=0$ and 0.0041 for Samples 1 and 2, respectively).

Arene-sulfonic acid functionalized mesostructured silicas (*Samples 3 and 4*) were synthesised as described for the functionalized mesostructured solid above. Following TEOS prehydrolysis, chlorosulfonyl-propyl-trimethoxysilane (CSPTMS, Gelest) was added and the resulting mixtures were stirred at 40 °C for 20 h, and aged at 100 °C for an additional period of 24 h under static conditions. The solid products were recovered and the template removed as previously described. The molar composition of the mixtures for 4 g of polymer was: $(0.0369-X)$ TEOS:$(0.0041+X)$ CSPTMS:0.24 HCl:≈6.67 H_2O. The amount of the precursor for arene-sulfonic acid groups (CSPTMS) was fixed at 10% or 20% of total silicon atoms ($X=0$ and 0.0041 for Samples 3 and 4, respectively).

Other commercial acid catalysts. Methanesulfonic acid (CH_3SO_3H), *p*-toluenesulfonic acid ($C_7H_7SO_3H$), Nafion-SiO_2 composite (SAC-13) and Amberlyst-15 were supplied by Sigma–Aldrich. Arene-sulfonic acid and propyl-sulfonic acid functionalized non-ordered silica materials were acquired from Silicycle. Zeolite Al-beta (Si/Al molar ratio = 41) was synthesized in our research group following standard fluoride-mediated procedures [26].

2.2. Catalyst characterization

Nitrogen adsorption and desorption isotherms at 77 K were measured using a Micromeritics TRISTAR 3000 system. The data were analysed using the BJH model and the pore volume (V_p) was taken at $P/P_o = 0.975$ single point. X-ray powder diffraction (XRD) patterns were acquired on a PHILIPS X'PERT diffractometer using Cu Kα radiation. The data were recorded from 0.6 to 5° (2θ) with a resolution of 0.02°. Cation-exchange capacities corresponding to the sulfonic acid mesostructured materials were determined using aqueous solutions of sodium chloride (NaCl, 2 M) as cationic-exchange agent. In a typical experiment, 0.05 g of solid was added to 15 g of aqueous solution containing the sodium salt. The resulting suspension was allowed to equilibrate and thereafter was titrated potentiometrically by dropwise addition of 0.01 M NaOH (aq). Sulfur and organic content were determined by means of Elemental Analysis (HCN) in a Vario EL III apparatus, and by means of thermogravimetry analysis (SDT 2960 Simultaneous DSC-TGA, from TA Instruments). Aluminum content in the zeolitic catalyst was determined by atomic emission spectroscopy with induced coupled plasma (ICP-AES) collected with a Varian Vista AX system. Table 1 summarizes the most relevant physicochemical properties for sulfonic acid-modified mesostructured material, and Table 2 incorporates characterization data (textural properties and acid capacities) corresponding to the commercial acid catalysts.

Temperature programmed desorption (TPD) experiments were carried out in a Micromeritics AutoChem 2910 equipment provided with thermal conductivity detector (TCD) using helium as carrier gas. Previously to the TPD experiment, the adsorbent sample was introduced in a quartz tube and outgassed in 30 $cm^3\,min^{-1}$ He flow by thermal treatment at 150 °C for 15 min, heating at 50 °C min^{-1} from room temperature. After cooling to 40 °C, the material was contacted with the gas-phase water until saturation by successive injections of adsorbate pulse, in amounts ranging from 0.1 to 2 μL under He flow. The reversibly adsorbed water was then removed in He flow for 2 h at 40 °C. The completion of this physidesorption process was confirmed