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MCM-48 as a support for sulfonic acid catalysts

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ABSTRACT

The ordered mesoporous silica, MCM-48, has been functionalised with sulfonic acid. Its physico-chemical properties have been compared with those of sulfonated MCM-41 and SBA-15. A higher catalytic activity for the functionalised MCM-48 in the alkylation of toluene with benzyl alcohol suggests that MCM-48 behaves as a better sulfonic acid support than MCM-41 and SBA-15. Ammonia adsorption calorimetric data shows that acid site strengths on the three supports are similar so the higher activity of MCM-48 sulfonic acid is probably due to better accessibility of its acid sites in the three-dimensional pore structure.

1. Introduction

Since the discovery of the family of inorganic mesoporous molecular sieves these materials have attracted much attention [1–5]. Several strategies have been proposed to impart specific properties to these materials for their use in applications such as catalysis, adsorption and chemical sensing [6–10]. Surface functionalisation permits the introduction of a number of groups to the internal pore surfaces through co-condensation or post-synthesis treatments [10–19]. One of the more widely studied systems involves tethered sulfonic acid groups, usually via a propyl linkage to a silane which is condensed with surface silanol groups. For ordered mesoporous solids, they offer an alternative, and generally superior, way of developing surface acidity to those methods that rely on isomorphous lattice substitution (as in zeolites) to generate intrinsic acidity [20,21], and mesoporous materials functionalised with sulfonic acid have been shown to be active acid catalysts in various reactions [22,23].

A so-far relatively unexploited mesoporous siliceous molecular sieve, MCM-48, has been investigated in this work as a support for sulfonic acid catalyst. The structure of this mesoporous molecular sieve contrasts with that of the more commonly used MCM-41 and SBA-15 in that it has an interconnected three-dimensional pore network whereas the latter two materials have one dimensional pore structures in which pores extend in one direction only. The shorter diffusion distances in MCM-48 arising from the pore structure might be expected to influence both the way sulfonic acid groups are distributed through the lattice during the functionalisation process (concentrated near external surfaces or evenly spread through the pore network), and the facility with which reactants can diffuse to active sites inside the pores of the support. It is not clear how these differences, which might act in opposite directions, would affect catalytic activity. Cheng compared sulfonic acid functionalised MCM-48 with similarly functionalised MCM-41 for bisphenol-A synthesis from phenol and acetone [24], and found that the specific activity per sulfonic acid group was slightly higher using MCM-41 as a support than when using MCM-48. Whether this difference is related to active site accessibility, or some other factor such as differing sulfonic acid group strengths on the two supports, has not so far been established.

The objective of this work has been to compare sulfonic acid functionalised MCM-48, MCM-41 and SBA-15 catalysts, in terms of the concentration and strength of supported sulfonic acid groups, and to relate these properties to the catalytic activities of the supported acid groups. In this way we hoped to identify the factors in these three support materials that are important in conferring optimised catalytic properties to tethered acid groups. The approach has been to prepare the siliceous supports and then, in each case, functionalise with 3-mercaptopropyltrimethoxysilane, and oxidise the thiol group to the sulfonic acid [25–27]. Acidity has been characterised by titration and by ammonia adsorption microcalorimetry [28], and catalytic activity using the Friedel–Crafts alkylation of toluene with benzyl alcohol [29].

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2. Experimental

2.1. Synthesis of MCM-48

In a typical procedure [30], 14 ml of NaOH solution (1 M) was mixed with 29 ml cetyltrimethylammonium chloride (CTACl) solution (Fluka, 25% solution) over a water bath at 50 °C with stirring, followed by the addition of 6.9 ml tetraethoxysilane (TEOS) (Merck). The final gel molar composition was 1.0TEOS:0.7CTACl:0.5NaOH:64H_2O. The gel was poured into a Teflon bottle and kept at 100 °C for 4 days. The product was filtered off, washed thoroughly with water and then dried at room temperature. The surfactant inside the as-synthesized material was removed by calcination at 540 °C for 5 h.

2.2. Synthesis of MCM-41

Cetyltrimethylammonium bromide (CTMABr) (Aldrich) (0.8 g) was dissolved in 43 ml of a solution of NaOH (0.1 M) at 40 °C. After dissolution, TEOS (3.8 g) was added to the mixture. The mixture was stirred for 2 h and poured into a Teflon bottle. The gel was kept at 100 °C for 24 h. The product was filtered off, washed thoroughly with water and dried at room temperature. The surfactant template was removed by calcination at 540 °C for 5 h [31].

2.3. Synthesis of SBA-15

The poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide) block co-polymer Pluronic 123 (BASF) was used as a template. First 2 g of copolymer was mixed with 15 g of H_2O and stirred for 3 h until a clear solution was obtained. 60 ml HCl solution (2 M) was added and stirring continued for another 2 h. Finally 4.5 g of TEOS was added and stirred at room temperature for 24 h. The solution was poured into a polypropylene bottle and kept at 80 °C for 48 h. After two days the product was filtered off, washed thoroughly with water and dried at room temperature. The material was calcined in air at 540 °C for 5 h [32].

2.4. Sulfonic acid functionalisation

In each case 1.5 g of catalyst support was dispersed in 50 ml of toluene. 3.6 g (0.018 mol) of 3-mercaptopropyltrimethoxysilane (Alfa Aesar) was added and the mixture refluxed for 12 h at 110 °C. The solid was collected by filtration, washed with toluene and air-dried. The resulting solid was stirred at room temperature for 24 h with an excess of 30% H_2O_2 solution, filtered and washed with water. All samples were dispersed in excess 0.2 M H_2SO_4 solution and stirred overnight. The resultant solids were filtered, washed with water and dried at 60 °C [28].

2.5. Catalytic activity measurement

Catalyst (100 mg) was activated at 100 °C for 1 h. For the reaction 10 ml of toluene was mixed with 0.6 ml of benzyl alcohol (20:1 mol) and 0.2 ml of tetradecane was used as an internal standard. The pre-heated reaction mixture was added to the catalyst and the reaction carried out with stirring at 85 °C. Samples were taken periodically and analysed by GC. The reaction was monitored through the conversion of benzyl alcohol.

2.6. Catalyst characterisation

MCM-48, MCM-41 and SBA-15 were characterised by powder X-ray diffraction using Cu K_α radiation (Bruker AXS D8 advance) and nitrogen adsorption at −196 °C (Micromeritics ASAP 2020). The functionalised materials were also characterised by nitrogen adsorption. Ammonia adsorption calorimetry under flow conditions was performed using a system based on a flow-through Setaram 111 differential scanning calorimeter (DSC) and an automated gas flow and switching system, with down-stream mass spectrometer detector (Hiden HPR20) connected via a heated capillary [28]. In a typical experiment, the sample (5–15 mg) was activated under dried helium (5 ml min^{-1}) for two hours at 100 °C. Small pulses (typically 1 ml but from 0.2 to 10 ml) of the probe gas (1% ammonia in helium) were then injected at regular intervals into the carrier gas stream from a gas sampling valve, also at 100 °C. The concentration of ammonia downstream of the sample was monitored with the mass spectrometer (*m/z* 15), and heat evolution with the calorimeter.

The net amount of ammonia irreversibly adsorbed from each pulse was determined by comparing the mass spectrometer signal during each pulse with a signal recorded during a control experiment through a blank sample tube. Net heat released for each pulse was calculated from the DSC thermal curve. From this the molar enthalpy of ammonia adsorption (ΔH^o_{ads}) was obtained for the ammonia adsorbed from each pulse. Because calorimetric measurements are sensitive to small, sometimes, unnoticed, variations in experimental conditions, each sample was analysed in duplicate to ensure reproducibility. Data is plotted as a profile of (ΔH^o_{ads})(NH_3) vs. amount of ammonia irreversibly adsorbed.

3. Results and discussion

Powder XRD patterns are shown in Fig. 1 for the ordered mesoporous materials on synthesis and after calcination. The siliceous MCM-48 sample shows characteristic reflections from the 211, 220, 420, 332 planes. On calcination all reflections show increased intensity due to increased diffraction contrast between channel pore and wall after the removal of the surfactant template, and they move to higher angles due to the condensation of silanol groups [30]. The diffraction patterns for MCM-41 and SBA-15 are also characteristic and well resolved, indicating good long range order.

Nitrogen sorption isotherms (Fig. 2) are of type IV with a sharp capillary condensation steps between partial pressures of 0.1 and 0.8, characteristic of typical mesoporous materials with uniform pore size distributions. Surface areas and porosity data taken from adsorption–desorption isotherms measured before and after the functionalisation are shown in Table 1. On sulfonation significant decreases in surface area, pore volume and pore size are observed. This is expected as tethered sulfonic acid groups extend into the pores, reducing their diameter and volume. These reductions are less in the case of SBA-15 than the other two, consistent with the lower concentration of acid sites on SBA-15 (see later).

The calorimetric adsorption experimental results are shown in the form of (ΔH^o_{ads})(NH_3) versus the amount of ammonia adsorbed profiles for the catalysts in Fig. 3. In the materials studied here, in which sulfonic acid is supported on siliceous supports, comparison reflects the abundance and strengths of essentially similar Bronsted acid sites, with differences dependent on the supports and the way they influence the tethered acid groups. The profiles have been interpreted as follows. It is assumed that each acid site adsorbs one ammonia molecule, and that the molar enthalpy of adsorption is an indicator of the strength of the acid site. On the basis that the progressive adsorption process is under thermodynamic control so that adsorbed ammonia molecules occupy acid sites in order of decreasing acid strength (but still subject to adsorption energy spreads governed by the Boltzmann distribution) the profiles can be interpreted as an acid site strength distribution profiles. A simple way of quantifying the catalyst acidity