Sulfonic acid functionalized mesoporous MCM-41 silica as a convenient catalyst for Bisphenol-A synthesis

Debasish Das,[a] **Jyh-Fu Lee**[b] **and Soofin Cheng***[a]

[a] *Department of Chemistry, National Taiwan University, Taipei 106, Taiwan.*
   E-mail: chem1031@ccms.ntu.edu.tw
[b] *Research Division, Synchrotron Radiation Research Center, Hsinchu 300, Taiwan*

Sulfonic acid groups anchored to the surface of mesoporous MCM-41 silica have been identified with S K-edge XANES spectra and the material is an efficient catalyst for the liquid phase condensation of phenol with acetone to form Bisphenol-A with high selectivity.

We report here that sulfonic acid functionalized mesoporous MCM-41 silica can be an efficient catalyst for the condensation of phenol and acetone at relatively low temperature to synthesize Bisphenol-A with a very high selectivity. Bisphenol-A is an important raw material for polymer and resin production, and it is produced industrially using ion-exchange resins such as Amberlyst.[1] However, thermal stability and fouling of the resins are major problems for these catalysts and the search for thermally stable and regenerable solid acid catalysts are continuing.

Zeolites have been increasingly used in the synthesis of fine chemicals due to their high surface area and confined domains.[2] However, the suitability of zeolites for the conversion of larger substrates has been severely limited by the available dimensions of their pores, which are in the micropore region with pore mouth diameter usually less than 1 nm.[3] For reactions to occur within the pores, the reaction substrates and products must be allowed to diffuse smoothly through the zeolite pores. The discovery of surfactant–templated mesoporous silica materials such as MCM-41 (hexagonal *P6m* symmetry) and MCM-48 (cubic *Ia*3*d* symmetry) with controlled pore diameters (2–10 nm) and topologies has extended the suitability of these materials for the conversion of larger substrates.[4] They are very promising for the application as catalysts and/or catalyst supports and are likely to offer potential improvements in reaction selectivity in the conversion of larger substrate molecules in their well-defined channels with narrow pore size distributions. However, in spite of these favorable pore dimensions, the acidity of Al-substituted mesoporous materials such as Al-MCM-41, is much weaker than that of microporous zeolites.[5] To overcome this drawback, the synthesis of inorganic–organic hybrid mesoporous materials with alkylsulfonic acid groups has been reported recently.[6–9] These hybrid materials can be synthesized either by direct one-step synthesis or *via* secondary silylation. Thus, MCM-SO₃H prepared by direct synthesis and secondary silylation is reported to be highly efficient in the synthesis of bisfurylalkanes[6] and also in the esterification of glycerol with fatty acids.[7,9] However, as the organic functional groups may be damaged or destroyed during the template removal process, the secondary silylation technique seems to offer a better alternative for preparing mesoporous acid catalysts.

Pure silica MCM-41 was synthesized according to the method described earlier.[10] Surface functionalization with sulfonic acid groups was carried out according to the method described in the literature.[7,8] Typically, 3.0 g of the freshly calcined MCM-41 sample was evacuated at 150 °C and then an excess of 3-mercaptopropyltrimethoxysilane (MPTS) in dry toluene was introduced. The mixture was refluxed for 6 h and the solid was filtered off, washed with dry toluene and air-dried.

The –SH groups were converted into –SO₃H groups by mild oxidation with H₂O₂ (stirring for 24 h at 60 °C with excess oxidant). The solid was filtered off, washed with water and ethanol, followed by acidification with 0.1 M H₂SO₄ followed by thorough washing with water to remove all traces of liquid acid. The solid material was finally dried at 60 °C overnight.

Sulfur loading of the solid material was determined by elemental analysis (Heraeus) and was typically in the range 0.9–1.8 meq. g⁻¹ of solid. Thermogravimetric analysis (Du Pont 950) shows the material to be more hydrophobic than MCM-41. While calcined pure silica MCM-41 shows *ca.* 5% weight loss in the range 30–100 due to water removal, sulfonic acid functionalized MCM-41 (denoted MCM-SO₃H) showed only <1% weight loss in this region. Loss of sulfonic acid groups starts at *ca.* 200 °C and is completed by 325 °C. The specific surface area and pore volume of the pure silica MCM-41 material was reduced from 1035 m² g⁻¹ and 0.85 cm³ g⁻¹, respectively, to 690 m² g⁻¹ and 0.42 cm³ g⁻¹ after anchoring the sulfonic acid groups. Although the pore size distribution curve (Fig. 1) becomes somewhat broad after sulfonic acid group introduction and the peak maximum shifts from 27 Å (pure MCM-41) to 22 Å, the pore size distribution still remains very narrow with major fractions of pores lying within the 7 Å region. These results indicate that anchoring sulfonic groups to the channels of MCM-41 reduced the pore diameter and volume of MCM-41 but did not damage the mesoporous structure. This was also affirmed by the retention of sharp diffraction peaks in the corresponding XRD pattern.

To obtain good catalytic activity it is imperative that the thiol groups can be effectively oxidized to active sulfonic acid groups. To monitor this process, the oxidation states of sulfur were examined by studying the S K-edge XANES spectra of the sample before and after oxidation. The XANES experiments were performed at Beam line 15B at the Synchrotron Radiation Research Center facility at Hsinchu, Taiwan. Standard operating conditions were 1.5 GeV and 200 mA beam current and the
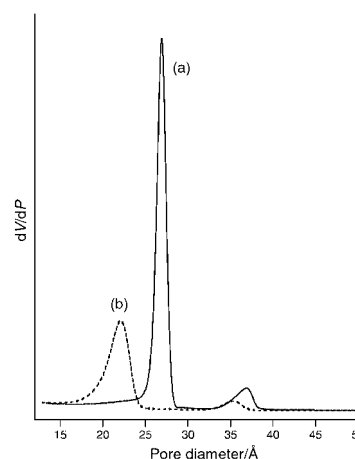

Fig. 1 Pore size distribution of (a) calcined pure silica MCM-41 and (b) MCM-41 functionalized with sulfonic acid groups.

photon energies were calibrated using the L-edge of pure Mo foil. Fig. 2 shows the S K-edge XANES spectra of the thiol functionalized samples before and after H_2O_2 oxidation. It has been reported that both the energy position (E_k) and intensity of the S s→p transition peak (white-line) are sensitively related to the oxidation state of the S atom.[11] Studies with model compounds showed an increase of E_k and amplitude of the white-line with increasing formal oxidation states of S. Thus, for unoxidized sample containing thiol groups the white-line appears at 2472 eV corresponding to sulfur in the reduced state. After H_2O_2 oxidation the white-line shifts to higher energy (2481 eV) which corresponds to sulfonic acid with S in the +5 state.[11,12] It can be seen from Fig. 2 that most of the anchored thiol groups have been oxidized to sulfonic acid groups under the above oxidation conditions.
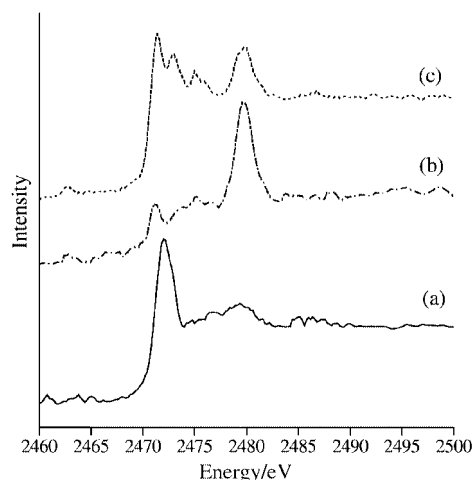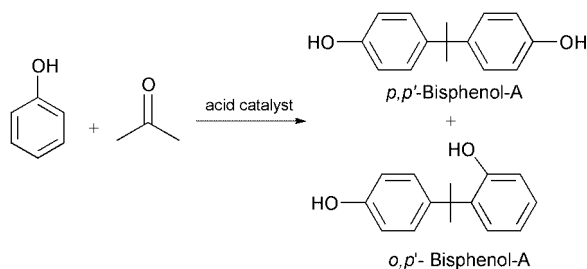

Fig. 2 S K-edge XANES spectra of thiol functionalized MCM-41 materials (a) before oxidation, (b) after oxidation and (c) sample with incomplete oxidation of thiol groups.

Condensation of phenol and acetone to Bisphenol-A (Scheme 1) was carried out at temperatures of 70–125 °C with the sulfonic acid functionalized MCM-41 silicas. Several other acidic zeolites such as H-ZSM-5, H-Y and H-beta have also been used for comparison. The products were analyzed and identified using a Chrompak 9000 gas chromatograph and HP 6890 GC-MS, and the results are given in Table 1. No conversion of phenol was observed in the absence of catalyst. While acidic zeolites like H-ZSM-5, H-Y and H-beta showed negligible activity at 70 °C, MCM-SO₃H showed 30% phenol conversion (*cf.* 40% maximum theoretical conversion at a phenol:acetone molar ratio of 5:1) with >90% selectivity towards *p,p′*-Bisphenol-A; the other product was *o,p′*-Bisphenol-A. The conversion was found to increase with the reaction temperature, but the selectivity remained almost unchanged up to 120 °C. Chroman and trisphenols were not detected at temperature below 125 °C, but small amounts (<1%) of these byproducts were detected at or above 125 °C. Recently, the synthesis of Bisphenol-A over heteropolyacid encapsulated MCM-41 has been reported.[13] However, 12-tungstophosphoric acid encapsulated MCM-41 was found to be catalytically active only at temperatures above 120 °C. Due to this high reaction temperature, several by-products such as alkylated phenols and chroman derivatives were formed, and

Scheme 1

Table 1 Synthesis of Bisphenol-A with sulfonic acid functionalized MCM-41 silicas[a]

Entry	Catalyst	Phenol conversion (%)	Selectivity[b] (%)
1	—	0	—
2	H-beta[c]	5	55
3	HY[d]	7	—
4	HZSM-5[e]	<5	10
5	MCM-SO₃H	30	92
6	MCM-SO₃H[f]	17	90

[a] *Reagents and conditions*: Phenol 4.7 g, acetone 0.58 g, (molar ratio = 5:1), catalyst 50 mg, 70 °C, 24 h. [b] Selectivity to *p,p′*-Bisphenol-A. [c] Si/Al = 50. [d] Si/Al = 10.6. [e] Si/Al = 80. [f] Incomplete oxidation (from XANES).

the selectivity to Bisphenol-A was much lower than that obtained with MCM-SO₃H. Furthermore, leaching of sulfur during the catalytic reaction was found to be negligible with MCM-SO₃H. Elemental analysis of the catalyst before reaction indicated *ca.* 3.4% sulfur and 5.6% carbon content. After reaction at 70 °C, these values were 3.2% S and 9.5% C. The slight decrease in sulfur content is mainly due to the increase in weight from adsorption of organic species. On the other hand, it is noted that optimization of the oxidation process in the preparation of MCM-SO₃H is essential to achieve high catalytic activity. For samples with similar sulfur loadings but with incompletely oxidized thiol groups (dotted line in Fig 2) the activity was found to be much lower (see Table 1). XANES spectra of the samples with incompletely oxidized sulfur species showed a number of peaks around 2472 eV, suggesting the presence of lower valent sulfur species such as sulfides and disulfides.[11,12] It has also been observed that at higher sulfur loadings (>1.5 meq. g⁻¹ solid) part of the sulfur remains in the reduced form even after prolonged oxidation, probably due to formation of sulfides and disulfides.

In conclusion, sulfonic acid anchored MCM-41 has been found to be very effective in the synthesis of *p,p′*-Bisphenol-A with very high selectivity at relatively low reaction temperatures. S K-edge XANES studies can be used as a convenient tool for easy monitoring of the oxidation state of sulfur in the samples.

Notes and references

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