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# Dehydration of xylose into furfural over micro-mesoporous sulfonic acid catalysts

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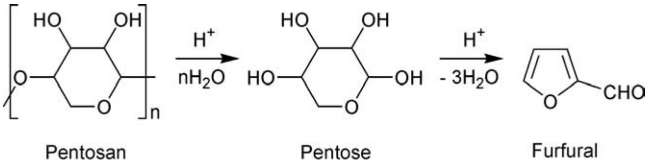
**Abstract**

Surfactant-templated micro-mesoporous silicas possessing sulfonic acid groups (SAGs) have been prepared, characterized, and tested as catalysts in the dehydration of D-xylose to furfural. All of the materials possessed catalytic activity. In general, selectivity to furfural was lower for a poorly ordered microporous hybrid material, prepared via the co-condensation of (3-mercaptopropyl)trimethoxysilane with bis(trimethoxysilylethyl)benzene, than for mesoporous MCM-41 silica anchored with SAGs via postsynthesis modification. The MCM-41 material with the highest loading of SAGs (0.7 meq $g^{-1}$) displayed fairly high selectivity for furfural (ca. 82% in DMSO or water/toluene mixture) at high xylose conversion ($>$ 90% within 24 h, at 140 °C). Xylose conversion increased significantly with reaction temperature. At 170 °C, more than 85% conversion was achieved within 4 h with any of the sulfonic acid-functionalized catalysts. Furfural yield tended to increase with temperature. Xylose conversion increased with increasing amount of catalyst, and for a xylose/MCM-41-$SO_3H$ ratio of 0.5, 76% conversion was achieved within 4 h, at 140 °C. Catalyst deactivation was observed after long residence times, possibly because of the interaction of reaction products with the acid sites, leading to surface loading.

*Keywords:* Xylose; Furfural; Dehydration; Heterogeneous catalysis; MCM-41; Mesoporous materials; Solid acid; Sulfonic acid

## 1. Introduction

Furfural is a key derivative, readily accessible from renewable biomass and agricultural surpluses, for the production of a wide range of important non-petroleum-derived chemicals, competing with crude oil [1–3]. There is considerable literature on the use of furfural and its increasing demand in different fields, such as oil refining, plastics, and the pharmaceutical and agrochemical industries. Furfural can be produced from agricultural raw (or waste) materials rich in pentosan polymers (e.g., xylan present in corncobs, bagasse, wood chips, etc.) by acidic degradation. The reaction involves hydrolysis of pentosan into pentoses (e.g., xylose) and successive (much slower) dehydration of the latter to form furfural (Scheme 1). These sequential reactions are catalyzed by acids. According to the literature the reaction mechanism for the dehydration of xylose to furfural involves irreversible development of conjugation via the formation of enediol intermediates [1,4].



Scheme 1. Simplified reaction mechanism of acidic degradation of pentosan to furfural.

In most industrial furfural processes, such as that used for Quaker Oats, which is the main source of furfural production, concentrated sulfuric acid is used as the catalyst, which is extremely corrosive and highly toxic and suffers from serious drawbacks concerning homogeneous catalytic processes, such as difficult separation and recycling of the

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mineral acid and product contamination. The same applies for phosphoric acid or superphosphate, which is used as a catalyst in the Petrole-chimie process [1,3]. Alternatively, in the Rosenlew process, no catalyst is added. Other major drawbacks of these processes are extensive side reactions, resulting in loss of furfural yield due to long residence times, and the need for significant waste disposal. Improvement of the chemical technology for the production of furfural therefore remains of great interest for the growth of furan-based chemical industries.

With the aim of finding potential industrial applications, attempts have been made to develop heterogeneous catalytic processes for the transformation of pentosans/pentoses into furfural that offer environmental as well as economic benefits [5]. Unfortunately, the catalytic performances achieved up to now have been unsatisfactory for industrial implementation. Moreau et al. [6,7] reported on the use of microporous materials such as zeolites (faujasites and mordenites) as interesting catalysts for the transformation of xylose into furfural, giving high selectivity (90–95%) as long as conversion is kept at about 30%. Recently, a sulfonic acid resin, Amberlyst-15, was used as a catalyst for the acid-catalyzed dehydration of fructose, with the use of a solvent mixture composed of an ionic liquid and dimethyl sulfoxide (DMSO) [8]. Approximately 87% 5-hydroxymethylfurfural was yielded after 32 h, at 80 °C, for a catalyst/substrate weight ratio of 2.

Commercial sulfonated resins such as Amberlyst-15 have surface areas lower than 1 $m^2\,g^{-1}$, a feature that limits their use as solid acids for liquid-phase reactions. A potentially interesting alternative is to use micelle-templated silicas functionalized with sulfonic acid groups [9]. These mesoporous materials can have surface areas in the range of 400–1000 $m^2\,g^{-1}$ and high pore volumes, in addition to narrow pore size distributions, tunable in the range of 20–100 Å. The active sulfonic group is obtained postsynthetically by sulfonation reactions or by the oxidation of thiol-functionalized silicas previously synthesized by a one-step sol gel or post-modification grafting route. Sulfonic acid-functionalized mesoporous silicas (SAMS) have been shown to be active and selective catalysts for a number of reactions, including the preparation of bisfurylalkanes from 2-methylfuran and acetone [10], esterification of polyols with fatty acids [11,12], and alcohol coupling to form ethers [13]. In the present work, SAMS have been prepared and tested as catalysts for the dehydration of D-xylose to furfural under a broad range of conditions.

## 2. Experimental

### 2.1. Catalyst preparation

#### 2.1.1. Synthesis of MCM-41

Pure silica MCM-41 was synthesized from a gel with the molar composition $SiO_2$:0.29 $Na_2O$:0.50 $C_{16}$TMABr:150 $H_2O$ ($C_{16}$TMABr = cetyltrimethylammonium bromide) [14]. In a standard procedure, sodium silicate solution (8% $Na_2O$, 27% $SiO_2$, 9.9 g, 44.5 mmol $SiO_2$, 12.8 mmol $Na_2O$) was diluted with water (30 ml), and this solution was added slowly to a rapidly stirred solution of $C_{16}$TMABr (8.10 g) in water (80 ml). The immediate formation of a precipitate was observed. Dilute sulfuric acid (2 M) was then added dropwise to bring the pH from 12.0 to 10.0. The suspension was stirred for a further 30 min, and then the pH was readjusted to 10.0 with a few drops of $H_2SO_4$. The mixture was split between four autoclaves (50 ml) and heated at 100 °C for 2 days. The solid was recovered by filtration, washed with hot water, and dried at 30 °C. Calcination was carried out at 560 °C for 6 h to remove the surfactant template.

#### 2.1.2. Anchoring of mercapto groups to the silica surface

"Silylated" and "coated" thiol-functionalized materials were prepared as described previously [11], with (3-mercaptopropyl)trimethoxysilane (MPTS) (Fluka) as the organosulfonic acid precursor.

*2.1.2.1. Silylated MCM-41-SH* Calcined MCM-41 (3.15 g) was evacuated at 145 °C for 2 h ($10^{-2}$ mbar). A solution of MPTS (5.25 ml) in dry toluene (300 ml) was then added, and the mixture was refluxed overnight. The solid was collected by filtration, washed thoroughly with dry dichloromethane, and dried under vacuum at 50 °C.

*2.1.2.2. Coated MCM-41-SH* Calcined MCM-41 (3.50 g) was hydrated by refluxing for 3 h in 500 ml water and removed from the suspension by filtration. The wet filter cake was suspended in toluene (300 ml) in a Dean Stark apparatus, and water/toluene was removed until a translucent suspension was obtained (ca. 150 ml). MPTS (19 ml) was then added, and, after stirring overnight at room temperature, the suspension was refluxed for 3 h. The material was isolated as described above for silylated MCM-41-SH.

#### 2.1.3. Synthesis of hybrid organo-silica

The method used here is adapted from that reported by Inagaki and co-workers for the synthesis of thiol-functionalized periodic mesoporous benzene-silica [15]. In the present work, bis(trimethoxysilylethyl)benzene (BTSEB) (ABCR) was used rather than 1,4-bis(triethoxysilyl)benzene. $C_{16}$TMABr (4.67 g) was dissolved in a solution of NaOH (1.31 g) in water (125 ml). BTSEB (3.15 ml) and MPTS (0.95 ml) were slowly added, and, after stirring overnight at room temperature, the mixture was aged at 90 °C for 24 h. The precipitate was recovered by filtration and washed with ethanol to yield the as-synthesized sample. We removed the surfactant by washing 2 g of as-synthesized material in ethanol (400 ml) with 5% HCl (5 ml) at 55 °C for 6 h. The material was isolated by filtration, washed with ethanol, and dried at 30 °C.

### 2.1.4. *Oxidation of mercapto groups*

Materials with immobilized mercaptopropyl groups were oxidized with a solution of 30% $H_2O_2$ (2.5 ml) dissolved in three parts of methanol per gram of material. After stirring for 24 h, the suspensions were centrifuged and washed with ethanol. The wet materials were resuspended (1 wt%) in 0.1 M $H_2SO_4$ for another 4 h. Finally, the solids were recovered by centrifugation, extensively washed with methanol, and dried at 30 °C.

### 2.2. *Characterization of the catalysts*

Microanalysis for S was carried out at the Instituto de Tecnologia Química e Biológica, Oeiras (C. Almeida). Powder X-ray diffraction (XRD) data were collected at room temperature on a Philips X'pert diffractometer with a curved graphite monochromator (Cu-$K_\alpha$ radiation), in a Bragg–Brentano para-focusing optics configuration. Samples were step-scanned in 0.02° $2\theta$ steps with a counting time of 1 s per step. Thermogravimetric analysis (TGA) was performed with a Shimadzu TGA-50 system at a heating rate of 5 °C $\text{min}^{-1}$ under air. Nitrogen adsorption measurements at 77 K were recorded gravimetrically with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Prior to measurement, the solids were outgassed at 100 °C overnight to give a residual pressure of ca. $10^{-4}$ mbar.

$^{29}$Si and $^{13}$C solid-state NMR spectra were recorded at 79.49 and 100.62 MHz, respectively, on a (9.4 T) Bruker Avance 400P spectrometer. $^{29}$Si MAS NMR spectra were recorded with 40° pulses, a spinning rate of 5.0 kHz, and 60-s recycle delays. $^{29}$Si CP MAS NMR spectra were recorded with 5.5-µs $^1$H 90° pulses, a contact time of 8 ms, a spinning rate of 5 kHz, and 4-s recycle delays. $^{13}$C CP MAS NMR spectra were recorded with a 4.5-µs $^1$H 90° pulse, a contact time of 2 ms, a spinning rate of 5–7 kHz, and 4-s recycle delays. Chemical shifts are quoted in parts per million from TMS.

### 2.3. *Catalytic experiments*

Batch catalytic experiments were performed under nitrogen in a magnetically stirred micro-reactor (mixing speeds $\geqslant 500$ rpm), heated with a thermostated oil bath equipped with a valve for sampling of the liquid phase. In a typical procedure, 30 mg D-xylose, 20 mg powdered catalyst, and 1 ml solvent (in the case of solvent mixtures, 0.3 ml $H_2O$ and 0.7 ml organic solvent) were poured into the reactor. Time zero was taken to be the instant the micro-reactor was immersed in the oil bath.

For the experiments carried out with DMSO or water as solvent, D-xylose and furfural were quantitatively determined with a Knauer K-1001 HPLC pump and a PL Hi-Plex H 300 × 7.7 (i.d.) mm ion-exchange column (Polymer Laboratories Ltd., UK) coupled to a Knauer K-2401 differential refractive index detector (for xylose) and a Knauer K-2600 UV detector (280 nm, for furfural). The mobile phase was 0.01 M $H_2SO_4$. The analysis conditions were a flow rate of 0.6 ml $\text{min}^{-1}$ and a column temperature of 65 °C. Authentic samples of D-xylose and furfural were used as standards, and calibration curves were used for quantification. When isobutylmethylketone (IBMK) or toluene was used as a co-solvent, the furfural present in the organic phase was quantified with a Gilson 306 HPLC pump and a Spherisorb ODS S10 C18 column, coupled to a Gilson 118 UV/Vis detector (280 nm). The mobile phase consisted of 40% v/v methanol in water (flow rate 0.7 ml $\text{min}^{-1}$).

## 3. Results and discussion

### 3.1. *Characterization*

The mesoporous silica MCM-41 was modified with 3-mercaptopropyl groups, with (3-mercaptopropyl)trimethoxysilane (MPTS) as the organosulfonic acid precursor. Immobilization of MPTS in toluene onto MCM-41 with controlled water content resulted in a "coated" material (MCM-41-SHc) with a monolayer of MPTS moieties (7.1 wt% S), and a less covered "silylated" material (MCM-41-SHs) was obtained in dry conditions (4.5 wt% S). The oxidation of the mercaptopropyl groups by hydrogen peroxide in a water–methanol solution was complete but resulted in a reduction of the sulfur contents and in the formation of disulfide and partially oxidized disulfide species (NMR evidence, see below). The oxidized coated material was obtained with a sulfur load of 3.9 wt% (1.2 mmol $\text{g}^{-1}$) and an acid content of 0.7 meq $\text{g}^{-1}$ (determined by titration), and the oxidized silylated material was obtained with a sulfur load of 2.7 wt% (0.8 mmol $\text{g}^{-1}$) and an acid content of 0.4 meq $\text{g}^{-1}$. In this work, a hybrid thiol-functionalized organo-silica with a sulfur content of 4.7 wt% was also prepared via the co-condensation of MPTS with bis(trimethoxysilylethyl)benzene. However, the acid content in the final oxidized material was only 0.1 meq $\text{g}^{-1}$.

The powder XRD pattern of the pristine calcined MCM-41 support exhibited five reflections in the $2\theta$ range 2–8° (Fig. 1), indexed for a hexagonal cell as (100), (110), (200), (210), and (300). The $d$ value of the (100) reflection was 37.3 Å, giving a lattice constant of $a = 43.1$ Å ($a = 2d_{100}/\sqrt{3}$). Modification of MCM-41 resulted in a slight reduction of the XRD peak intensities. However, the first three Bragg peaks were still observed for the oxidized coated and silylated materials, indicating that the hexagonal symmetry of the support was preserved. The attenuation of the XRD peaks is probably due to a reduction in the X-ray scattering contrast between the silica walls and pore-filling material [16,17] rather than a loss of structural order. Nitrogen adsorption–desorption measurements for the modified MCM materials showed a type IV isotherm typical of mesoporous solids (pore width between 2 and 50 nm, according to the IUPAC [18]). A decrease in the BET specific surface

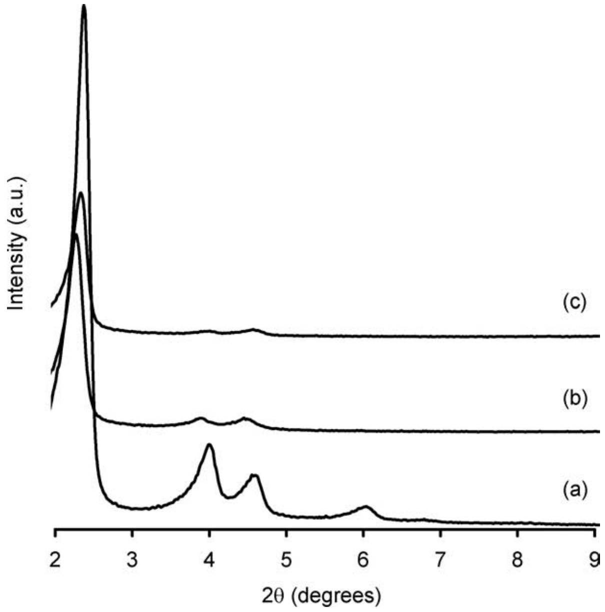


Fig. 1. Powder XRD patterns of (a) pristine calcined MCM-41, (b) silylated MCM-41-$SO_3H$, and (c) coated MCM-41-$SO_3H$.

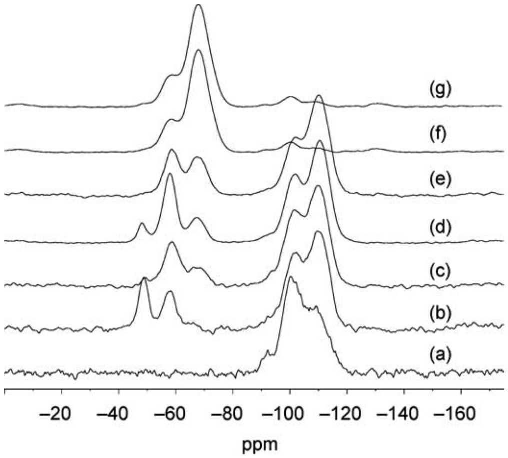


Fig. 2. $^{29}$Si CP MAS NMR spectra (5 kHz) of (a) pristine calcined MCM-41, (b) silylated MCM-41-SH, (c) silylated MCM-41-$SO_3H$, (d) coated MCM-41-SH, (e) coated MCM-41-$SO_3H$, (f) hybrid-SH, and (g) hybrid-$SO_3H$.

area ($S_{\mathrm{BET}}$) and total pore volume ($V_{\mathrm{p}}$) between pristine calcined MCM-41 and the modified materials was observed and attributed to the presence of organic groups in the channels (Table 1). In the case of hybrid-$SO_3H$, the values of $S_{\mathrm{BET}}$ and $V_{\mathrm{p}}$ were much lower than those for the MCM materials. The adsorption isotherm was of type I, characteristic of microporous materials (pore width < 2 nm, according to the IUPAC). Powder XRD showed that the sample was amorphous. The thiol-functionalized precursor exhibited similar characteristics, in contrast to the corresponding material prepared with 1,4-bis(triethoxysilyl)benzene, which was shown to be a highly ordered mesoporous organosilica [15].

All materials were further characterized by $^{13}$C and $^{29}$Si (CP) MAS NMR spectroscopy. Unmodified MCM-41 displays two broad overlapping resonances in the $^{29}$Si CP MAS NMR spectrum at −108.7 and −101.0 ppm, assigned to $Q^4$ and $Q^3$ species of the silica framework, respectively [$Q^n = \underline{\mathrm{Si}}(\mathrm{OSi})_n(\mathrm{OH})_{4-n}$] (Fig. 2). A weak shoulder is also observed at −91.0 ppm for the $Q^2$ species. Grafting of MPTS onto MCM-41 to give the coated and silylated materials resulted in a reduction of the $Q^3$ and $Q^2$ resonances and a concomitant increase in the $Q^4$ resonance (Fig. 2). The peaks observed in the spectral region associated with tertiary silicon atoms, from −45 to −80 ppm, provide direct evidence for the incorporation of the covalently anchored organic system. Broad signals at about −49, −58, and −66 ppm are assigned to $T^1$, $T^2$, and $T^3$ organosilica species, respectively [$T^m = \mathrm{R}\underline{\mathrm{Si}}(\mathrm{OSi})_m(\mathrm{OMe})_{3-m}$]. The silylated material exhibits principally $T^1$ and $T^2$ sites, that is, an anchoring of the organic species via one or two Si–O–Si bonds. For the coated material there are evidently fewer $T^1$ sites and more $T^3$ sites. The reaction of the thiol-functionalized MCMs with $H_2O_2$ resulted in significant decreases in the $T^1$ signals and increases in the $T^2$ and $T^3$ signals. Thus, the oxidation conditions appear to facilitate further reaction between unreacted $SiOCH_3$ of the organosiloxane and the silica surface.

The $^{13}$C CP MAS NMR spectra of coated and silylated MCM-41-SH confirmed the presence of mercaptopropyl groups (Fig. 3). The $\alpha$- and $\beta$-methylene carbon

Table 1
Catalytic performance of sulfonic acid-functionalized materials in the dehydration of D-xylose[a]

| Catalyst | $S_{\mathrm{BET}}$ ($m^2\,g^{-1}$) | $V_{\mathrm{p}}$ ($cm^3\,g^{-1}$) | $H^+$ [b] (meq $g^{-1}$) | TOF[c] (mmol $g_{\mathrm{cat}}^{-1}\,h^{-1}$) | Conversion[d] (%) | Selectivity[e] (%) |
|---|---|---|---|---|---|---|
| None | – | – | – | – | 34/84 | 2/27 |
| MCM-41 | 833 | 0.59 | – | 0.8 | 30/86 | 4/52 |
| MCM-41-$SO_3$Hs | 493 | 0.28 | 0.4 | 2.0 (5) | 81/90 | 49/77 |
| MCM-41-$SO_3$Hc | 438 | 0.24 | 0.7 | 2.1 (3) | 84/91 | 65/82 |
| Hybrid-$SO_3H$ | 278 | 0.13 | 0.1 | 1.4 (14) | 57/88 | 11/61 |
| Amberlyst-15 | – | – | 4.6 | 2.2 (0.5) | 87/90 | 68/70 |

[a] Reaction conditions: 1 ml DMSO, 30 mg xylose, 20 mg catalyst, 140 °C.
[b] Measured by titrating the solid with NaOH.
[c] Turnover frequency calculated after 4 h. In brackets the TOF values are expressed as mmol (meq $H^+)^{-1}\,h^{-1}$.
[d] Conversion after 4/24 h.
[e] Selectivity to furfural after 4/24 h.

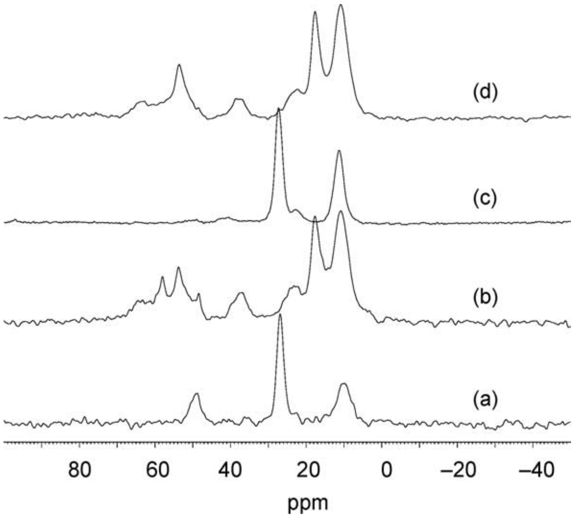


Fig. 3. $^{13}C$ CP MAS NMR spectra (5 kHz) of (a) silylated MCM-41-SH, (b) silylated MCM-41-$SO_3H$, (c) coated MCM-41-SH, and (d) coated MCM-41-$SO_3H$.

atoms gave rise to one peak at around 27 ppm, and the carbon attached directly to the silicon atom resonated at about 10 ppm. A weak signal at 49 ppm is attributed to residual methoxy groups. After oxidation, the spectra show the complete disappearance of the resonance at 27 ppm, consistent with the loss of the thiol group, and the appearance of new peaks at 18 and 54 ppm, typical of *n*-alkyl sulfonic acids. The two peaks are thus assigned to $–\underline{C}H_2CH_2SO_3H$ and $–CH_2\underline{C}H_2SO_3H$, respectively. Weak signals are also observed at around 23, 38, and 60 ppm and are assigned to disulfide and partially oxidized disulfide species [10,19]. The formation of nonacidic sulfur-containing side products could explain the difference between the sulfur loadings and the acid capacity titrations for these materials.

The $^{29}Si$ CP MAS NMR spectrum of the hybrid-SH material shows the presence of $T^2$ ($-59$ ppm) and $T^3$ ($-68$ ppm) resonances for the silicon atoms attached to $CH_2CH_2R$ groups ($R = CH_2SH$ or $C_6H_4R'$) (Fig. 2). A very weak broad peak at around $-100$ ppm may be due to a $Q^3$ site, indicating that some carbon–silicon bonds were disrupted during the synthesis. No changes in the spectrum were observed after treatment of the material with $H_2O_2$. The $^{13}C$ CP MAS NMR spectrum of the thiol-functionalized hybrid (not shown) contained peaks for the aromatic carbons at 127 and 143 ppm and signals at 14 and 29 ppm for the methylene groups. After oxidation, a very weak signal appeared at 58 ppm that was assigned to $–CH_2CH_2SO_3H$ species.

## 3.2. Catalysis

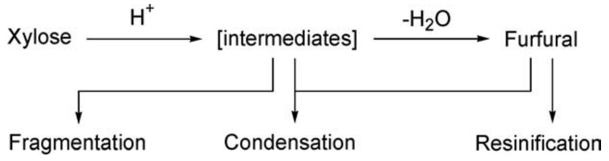
### 3.2.1. General considerations

All sulfonic acid catalysts (without prior activation) were employed in batch experiments for the dehydration of D-xylose to furfural; and the results obtained with DMSO as a solvent, at 140 °C, are summarized in Table 1. According to the literature, furfural can be formed via an autocatalytic mechanism involving organic acid products resulting from furfural decomposition, such as formic acid [4]. Hence, control experiments were conducted under the same process conditions but with no solid catalyst added. Based on conversion at 4 h, the reaction was slower without additional catalyst than in the presence of any of the sulfonic acid catalysts studied in this work. Xylose conversion with the use of pristine unmodified MCM-41 was roughly the same as that obtained in the homogeneous phase without additional catalyst, indicating that the silica support is essentially inert (Table 1). Given that the DMSO used could have a maximum sulfuric acid impurity of 0.001%, the influence of this amount of acid on the reaction was checked with an experiment with no solid catalyst in which an extra 0.001% $H_2SO_4$ was added. This resulted in 2.5% furfural yield at 4 h compared with 1% obtained without the addition of $H_2SO_4$. The influence on the reaction of acid impurities in DMSO can therefore be neglected.

After 24 h, conversions with or without sulfonic acid catalyst added were roughly the same, but selectivity for the target product, furfural, without catalyst was much lower (27%) than that observed in the presence of the sulfonic acid catalysts ($>$ 61% at 88% conversion). These results indicate that the solid-acid catalysts promote the dehydration of xylose into furfural. The coated sample MCM-41-$SO_3$Hc was slightly less active than the silylated one (based on TOF expressed as $mmol\,(meq\ H^+)^{-1}\,h^{-1}$), possibly because of some less accessible acid sites in the former material. Selectivity for furfural was slightly higher for MCM-41-$SO_3$Hc than for MCM-41-$SO_3$Hs, giving, respectively, 82 and 77% selectivity at ca. 90% conversion.

The final step in the preparation of the sulfonic acid catalysts involves the treatment of the oxidized materials with dilute sulfuric acid. As a result, the subsequent washing step has to be carried out rigorously to avoid retention of sulfuric acid in the solids. The efficiency of the washing procedure was checked by application of the same procedure to a sample of unmodified MCM-41 that had been treated with $H_2SO_4$ (under identical conditions). No significant differences were found between the acid contents for this material and pristine MCM-41 (determined by titration with NaOH), and no sulfur was detected in the washed MCM-41 by elemental analysis. For comparison, the coated sample MCM-41-$SO_3$Hc was prepared, excluding the treatment with sulfuric acid. This material possessed 0.65 meq $H^+\ g^{-1}$ and gave 78% xylose conversion at 4 h compared with 84% achieved when the acid treatment was applied, but the furfural yield was lower (31% compared with 55% for MCM-41-$SO_3$Hc).

A plausible mechanism for the xylose-to-furfural reaction consists of two 1,2-eliminations and one 1,4-elimination of water through the transformation of hydroxyl groups of the pentose to $H_2O^+$ by the hydrogen ions, similar to that suggested by Zeitsch [1]. During the reaction the colorless solution turned brown. Several side reactions may contribute to the loss of furfural, as shown in Scheme 2, such as condensation reactions between furfural and intermediates of the



Scheme 2. Simplified scheme of the possible reactions in the xylose-to-furfural process.

xylose-to-furfural conversion to give furfural pentose and difurfural xylose [1,20]. Other compounds, such as glyceraldehydes, pyruvaldehyde, glycolaldehyde, acetol, and lactic acid, may be formed in fragmentation reactions of (acyclic) xylose [4]. Given the ethereal nature of the furan ring, furfural may be destroyed by acids to give formic acid and black resin [3]. Formic acid was identified among the products of xylose conversion under the applied experimental conditions, by retention time (as a small product peak) in the UV at 214 nm and comparison with an authentic sample.

In the case of the hybrid-$SO_3H$ material, TOF expressed on a weight basis is lower than that observed for the MCM-41-$SO_3H$ catalysts. However, if TOF is expressed per unit acid content, the hybrid organosilica catalyst, which possesses the lowest concentration of sulfonic acid groups, shows the highest (specific) activity. Selectivity for furfural (at 88–91% conversion) is lower for hybrid-$SO_3H$ than for the MCM-41-$SO_3H$ materials. The differences in catalytic performance may be due to the hydrophobicity of the surface (compared with the hydrophilic MCM support) and differences in textural properties (amorphous, microporous compared with hexagonally ordered, mesoporous materials). The more hydrophobic surface of hybrid-$SO_3H$ may enhance the adsorption of furfural at the surface, where it reacts with intermediates on the accessible acid sites, increasing the extent of furfural loss reactions. When the macroporous Amberlyst-15 sulfonic acid resin was used as a catalyst, fairly good performances were obtained (Table 1). Although this resin possesses a higher acid density than the synthesized silica-based catalysts, it gives the lowest TOF expressed on the basis of the acid content, which may be due in part to partial catalyst degradation, since its thermal stability is 120–140 °C. After 24 h, the furfural yield in the presence of Amberlyst-15 was lower than that achieved with the MCM-41-$SO_3H$ samples.

### 3.2.2. *Solvent effect*

The influence of the solvent on the reaction was studied at 140 °C, in an aqueous, an anhydrous organic, or a biphasic water-co-solvent mixture (Table 2). The stability of isobutylmethylketone (IBMK) and toluene under the reaction conditions was checked by analyzing the organic phase after the reaction was carried out in the presence of the coated catalyst MCM-41-$SO_3$Hc at 140 °C. Analyses by HPLC with a UV–vis diode array detector and by GC with a FID detector did not reveal any peaks associated with solvent decomposition. Water dissolves the substrate very well and can act as an amphoteric substance capable of donating and accepting protons. However, with no catalyst added, the reaction in water gave less than 8% conversion after 24 h (cf. 84% in DMSO). In the presence of a silica-based material, catalytic activity (based on conversion at 24 h) in DMSO is higher than in water (compare entries 1/2, 5/6, and 9/10 in Table 2). The lower activity in water for the MCM-41-$SO_3H$ materials may be due to the strong adsorption of the polar solvent molecules on the hydrophilic surface, affecting the accessibility of the active sites to the substrate molecules. The low affinity between the hydrophobic surface of the hybrid-$SO_3H$ catalyst and the aqueous medium, which contains the substrate, may explain its lower catalytic activity in water.

Table 2
Influence of the solvent on the catalytic performance of sulfonic acid-functionalized materials in the dehydration of D-xylose[a]

| | Catalyst | Solvent | Time (h) | Conversion[b] (%) | Selectivity[c] (%) | Yield[d] (%) |
|---|---|---|---|---|---|---|
| 1 | MCM-41-$SO_3$Hs | DMSO | 24 | 90 | 77 | 69 |
| 2 | | Water | 24 | 53 | 47 | 25 |
| 3 | | IBMK/water | 24 | 68 | 59 | 40 |
| 4 | | Toluene/water | 24 | 72 | 96 | 69 |
| 5 | MCM-41-$SO_3$Hc | DMSO | 24 | 91 | 82 | 75 |
| 6 | | Water | 24 | 27 | 50 | 14 |
| 7 | | IBMK/water | 24 | 84 | 61 | 51 |
| 8 | | Toluene/water | 24 | 91 | 83 | 76 |
| 9 | Hybrid-$SO_3H$ | DMSO | 24 | 88 | 61 | 54 |
| 10 | | Water | 24 | 53 | 50 | 27 |
| 11 | | Water | 18 | 28 | 73 | 20 |
| 12 | | IBMK/water | 24 | 25 | 48 | 12 |
| 13 | | Toluene/water | 24 | 30 | 16 | 5 |

[a] Reaction conditions: 140 °C, 30 mg xylose, 20 mg catalyst.
[b] Conversion of D-xylose.
[c] Selectivity to furfural.
[d] Furfural yield.

In the case of the biphasic water/organic solvent systems (30/70 vol/vol), furfural has a greater affinity for the organic phase than for the aqueous phase [6]. For a given catalyst, conversion after 24 h was roughly the same with either toluene or IBMK as the co-solvent, suggesting that the main reaction takes place in the aqueous phase, an observation similar to that reported previously for the same catalytic reaction over zeolites [6]. These systems are therefore potentially interesting for simultaneous reaction/product separation processes. A suspension of the catalyst in the aqueous phase was always obtained, with the exception of hybrid-$SO_3H$. When water/toluene was used, the hybrid material “preferred” the organic phase, owing to the hydrophobic nature of its surface. Possibly, as furfural is accumulated in the organic phase, it reacts more easily with itself and/or with intermediates of the xylose-to-furfural conversion (on the catalyst surface), thus leading to by-products. This would explain why the hybrid-$SO_3H$ exhibits a lower selectivity for furfural in the water/toluene mixture than, for example, MCM-41-$SO_3$Hc (see Section 3.2.5). For the hybrid, a selectivity of 50% was measured at 53% conversion with water as the solvent (Table 2), compared with only 11 at 57% conversion in DMSO (Table 1).

In the presence of water the formation of hydronium ion species within the mesopores could increase local acidity and cause the further degradation of furfural [21]. However, in the case of MCM-41-$SO_3$Hc, for example, selectivity at 91% conversion is the same for DMSO and $H_2O$/toluene. For the MCM-41-based catalysts, when IBMK was used as a co-solvent instead of toluene, selectivity for furfural at roughly the same conversions was lower, suggesting that toluene is a more efficient extracting agent than IBMK (compare entries 3/4 and 7/8 in Table 2). Despite the better affinity of furfural for IBMK than for toluene, the former is more soluble in water, which may enhance degradation of furfural at the water–IBMK interface, decreasing selectivity for furfural. The opposite is observed for the less hydrophilic hybrid catalyst, that is, selectivity for furfural at 25–30% conversion is higher when IBMK is used instead of toluene (compare entries 12/13). Furfural yields and selectivities at 25–30% conversion for the hybrid-$SO_3H$ catalyst follow the order $H_2O > H_2O$/IBMK $> H_2O$/toluene (entries 11, 12, and 13 in Table 2). The opposite trend was observed for the MCM-41-based materials: furfural yield at 24 h increased in the order $H_2O$ (14–25%) < $H_2O$/IBMK (40–51%) < $H_2O$/toluene (69–76%). When furfural yields are compared at 24 h, the results are always better for DMSO than for water. In the case of the MCM-41-$SO_3H$ catalysts the yield of furfural after 24 h was similar whether DMSO or $H_2O$/toluene was used as a solvent (69 and 76% for the silylated and coated materials, respectively).

### 3.2.3. *Influence of reaction temperature*

The influence of the temperature on the catalytic performance of the sulfonic acid catalysts was studied in the range 110–170 °C, with DMSO or water/toluene as a solvent (Table 3). An exponential temperature dependence of the rate of xylose disappearance in the homogeneous phase, following the Arrhenius equation, has been proposed in the literature [22,23]. Control experiments carried out in DMSO for the same temperature range showed that the reaction is always much slower without catalyst than with catalyst, at a given temperature. Xylose conversion rate increased with reaction temperature, and in the presence of any of the sulfonic acid-functionalized catalysts, at least 88% conversion was achieved within 4 h at 170 °C. In all experiments, furfural yield increased with reaction temperature. For the synthesized materials, the highest furfural yield was obtained with MCM-41-$SO_3$Hc as a catalyst (70%). Under similar reaction conditions, Amberlyst-15 yielded 78% furfural. It is known that furfural molecules in the vapor phase cannot undergo loss reactions by reaction with intermediates of the pentose-to-furfural conversion, since these and the acid catalyst are nonvolatile, explaining the high yields observed in boiling processes [24]. In a nonboiling liquid process (the boiling points of DMSO and furfural are 189 and 162 °C, respectively), furfural yield tends to increase strongly with increasing temperature because of the "entropy effect" [24]. The furfural loss reactions (condensation and resinification) create larger, nonvolatile molecules, which represents a decrease in entropy, leading to a less negative free energy change [the term $(-T\Delta S)$ in equation $\Delta G = \Delta H - T\Delta S$ becomes positive and the free energy change becomes less negative], and thus furfural loss reactions diminish (e.g., resins are formed in minor amounts at 250 °C [4,6]). Increasing temperature could be even more beneficial than continuous removal of furfural from the reaction mixture, as carried out in the industry by steam stripping [24]. It is also worth mentioning that in the presence of a heterogeneous catalyst, coke may be formed and deposited on the outer surface of the particle or within the pores, leading to a decrease in catalyst acidity, as reported previously for microporous zeolites [25]. After the catalytic experiments the mesoporous catalysts have a brownish color, which may be due to coke deposits, but this does not seem to have a significant detrimental effect on activity and selectivity during the first 4 h of reaction.

The MCM-41-$SO_3$Hc catalyst was used to study the influence of temperature when water/toluene was used instead of DMSO. Similar trends were observed for the two solvent systems, that is, conversion and furfural yield tend to increase with temperature (Table 3). At 170 °C, selectivity for furfural (78 at 85% conversion) was higher than that reported for sulfuric acid in the homogeneous phase at 200–250 °C, which gives less than 70% selectivity [4]. When H-mordenites are used as heterogeneous catalysts (at 170 °C, in water/toluene solvent mixture) selectivity can be as high as 90–95%, as long as conversion is kept relatively low (30–40%) [6]. A similar limitation was reported for fructose dehydration in the presence of acidic zeolites or niobium-based heterogeneous catalysts in batch experiments [21,26]. The high selectivities reported for H-mordenites were correlated with the shape-selective properties of the catalyst and particularly with the low mesoporous volume, which could allow further rearrangement of furfural into by-products. Lourvanij and Rorrer reported that for the dehydration of glucose over Y-zeolite catalyst, 5-(hydroxymethyl)furfural (HMF) was formed both within the Y-zeolite cages and in the bulk phase [25]. Considering that the glucose molecule is too large to diffuse directly into the pore matrix of the zeolite, the authors proposed that glucose molecules were cleaved to a linear 1,2-enediol by Brönsted acid sites on the outer surface of a particle, and that the 1,2-enediol could then either dehydrate to HMF or diffuse into the Y-zeolite matrix for further reaction. The authors suggested the use of molecular sieve catalysts with larger pores to achieve higher yields of the target product. In the case of MCM-41-$SO_3$Hc the fairly high furfural selectivity observed at high conversions may be explained by the presence of the larger unidimensional mesopores in MCM-41 materials that promote the reaction of xylose to furfural by allowing fast diffusion of furfural out of the catalyst once formed, thus avoiding extensive consecutive degradation reactions. The fairly good performance that MCM-41-$SO_3$Hc displays at high conversion constitutes an important im-

Table 3
Influence of the temperature and catalyst amount on the catalytic performance of sulfonic acid-functionalized materials in the dehydration of D-xylose[a]

| Catalyst | Temperature (°C) | Xylose/catalyst (wt) | Conversion[b] (%) | TOF[c] (mmol $g_{cat}^{-1}$ $h^{-1}$) | Selectivity[d] (%) |
|---|---|---|---|---|---|
| None | 110 | 1.5 | 3 | – | 1 |
| | 140 | 1.5 | 34 | – | 2 |
| | 170 | 1.5 | 59 | – | 15 |
| MCM-41-$SO_3$Hs | 110 | 1.5 | 19 | 0.5 | 8 |
| | 140 | 1.5 | 81 | 2.0 | 49 |
| | 170 | 1.5 | 92 | 2.3 | 70 |
| MCM-41-$SO_3$Hc | 110 | 1.5 | 30 | 0.8 | 20 |
| | 110 | 1.5[e] | 34 | 0.9 | 2 |
| | 140 | 1.5 | 84 | 2.1 | 65 |
| | 140 | 1.5[e] | 52 | 1.3 | 82 |
| | | 0.8[e] | 62 | 0.8 | 80 |
| | | 0.8[e,f] | 54 | 0.7 | 34 |
| | | 0.8[e,g] | 37 | 0.5 | 34 |
| | | 0.5[e] | 76 | 0.6 | 80 |
| | 170 | 1.5 | 92 | 2.3 | 76 |
| | 170 | 1.5[e] | 85 | 2.1 | 78 |
| Hybrid-$SO_3$H | 110 | 1.5 | 9 | 0.2 | 1 |
| | 140 | 1.5 | 57 | 1.4 | 11 |
| | 170 | 1.5 | 88 | 2.2 | 41 |
| Amberlyst-15 | 110 | 1.5 | 28 | 0.7 | 16 |
| | 140 | 1.5 | 87 | 2.2 | 68 |
| | 170 | 1.5 | 100 | 2.5 | 78 |

[a] Reaction conditions: 1 ml DMSO, 30 mg xylose.
[b] Conversion calculated after 4 h.
[c] Turnover frequency calculated after 4 h.
[d] Selectivity to furfural after 4 h xylose conversion.
[e] Water/toluene co-solvent mixture used instead of DMSO.
[f,g] MCM-41-$SO_3$Hc reused once[f] or twice[g].

provement with respect to the results obtainable with zeolites.

### 3.2.4. *Influence of catalyst charge*

The influence of the catalyst concentration on the catalytic reaction was studied by varying the amount of MCM-41-$SO_3$Hc from 20 to 60 mg (30 mg substrate), with $H_2O$/toluene as a solvent, at 140 °C. Furfural yield increases with the concentration of catalyst, and selectivity at 4 h was always ca. 81% (Table 3). Conversion increased with increasing amount of catalyst, and for a xylose/catalyst weight ratio of 0.5, enough acid sites are available to accomplish 76% conversion within 4 h. Since coking during catalysis cannot be ruled out, as discussed below, one would expect the extent of coking on the catalyst to increase with increasing xylose/catalyst ratio, accounting for lower xylose conversions. The rate of xylose conversion (based on TOF at 4 h) decreases with increasing catalyst concentration, probably because of the low dispersion of catalyst particles in the aqueous phase at high catalyst charges (e.g., xylose/catalyst = 0.5 corresponds to 60 mg solid in 0.3 ml water), accounting for diffusion effects on the heterogeneous reaction.

### 3.2.5. *Effect of residence time*

Xylose conversion and selectivity for furfural were studied as a function of the reaction time for MCM-41-$SO_3$Hc and hybrid-$SO_3$H, with water/toluene as solvent, at 140 °C (Fig. 4). In the presence of the MCM-based catalyst, selectivity for furfural is initially low but then increases to 81% after 9 h, at which point the conversion is 65%. The low selectivity observed at short reaction time (1 h) may be due partly to loss reactions that are more significant during the initial heating period. On the other hand, it is also possible

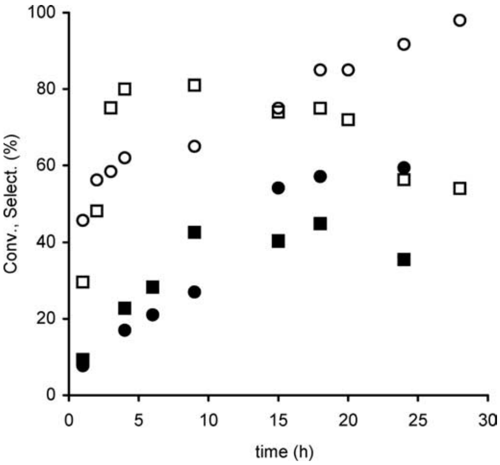


Fig. 4. Conversion of D-xylose (○,●) and selectivity to furfural formation (□, ■) in the presence of MCM-41-$SO_3$Hc (open symbols) and hybrid-$SO_3$H (solid symbols), as a function of reaction time. Reaction conditions: water/toluene, xylose/catalyst wt ratio was 0.8 (140 °C).

that adsorption of xylose on the hydrophilic catalyst surface is relatively fast compared with the surface reaction, accounting for high initial xylose adsorption, thus leading to apparently low initial furfural selectivity. According to the literature, xylose–lyxose isomerization may occur, where lyxose appears to form rapidly from open-chain xylose, after which it disappears more slowly than xylose to produce furfural [4]. However, the formation of lyxose was not detected under the applied reaction conditions. After a reaction time of ca. 9 h, selectivity for furfural started to decrease (to 54 at 98% conversion and a residence time of 28 h), and the reaction solution became darker. The long residence time of furfural on the acid surface of the catalyst leads to degradation of furfural by the aforementioned secondary loss reactions. The condensation loss reactions cease only when all of the pentose is consumed. The initial conversion rate (2.3 $\text{mmol}\,g_{\text{cat}}^{-1}\,h^{-1}$, calculated for a 1-h reaction) is high but then decreases with time. Furfural loss reactions lead to larger molecules, which may act as precursors of coke formation, similar to the observation reported for the dehydration of glucose, which yields 5-(hydroxymethyl)furfural polymers [21,25,27–29]. The accumulation of by-products on the catalyst surface with increasing residence time may cause loading and subsequent partial deactivation by catalyst surface passivation.

In the case of the hybrid-$SO_3H$ catalyst, the trends for conversion and selectivity versus time are similar to those for the MCM-based catalyst, for example, selectivity reaches a maximum after about 9 h and then starts to decrease.

### 3.2.6. *Catalyst stability*

We studied the catalyst stability for MCM-41-$SO_3$Hc with water/toluene as a solvent, by recycling the recovered catalyst twice at 140 °C. After cooling, the solid was separated from the liquid by centrifugation, washed with methanol, and treated with $H_2SO_4$ as described in the Experimental section for the catalyst preparation. Finally, the recovered solid was reused in a catalytic cycle of 4 h. D-Xylose conversion decreased with recycling runs (Table 3). The initially colorless catalyst became brown during the reaction and did not lose this color after the applied regeneration treatment. The observed progressive catalyst deactivation might be connected with the inefficient removal of adsorbed by-products between recycling runs, which load the catalyst surface, leading to increased active site passivation, decreasing the amount of accessible $H^+$ groups for the acid-catalyzed reaction. The NaOH titration of the recovered solid revealed an acid content that was 70% lower than that present in the fresh catalyst. DSC analyses (in air) of both fresh and used catalysts showed an exothermic band centered at 300–370 °C, which coincides with a mass loss observed by TGA (in air). Above 300 °C, the percentage mass loss of the used sample was significantly greater than that observed for the fresh sample, most likely because of the simultaneous decomposition of coke that had appeared on the catalyst during catalysis. This hypothesis is further supported by the fact that $S_{\text{BET}}$ and $V_{\text{p}}$ of MCM-41-$SO_3$Hc decreased by ca. 50–60% after three reaction runs. Despite these changes, the characteristic reflections of the mesoporous phase were still present in the powder XRD pattern of the recovered solid.

Selectivity for furfural also decreased in consecutive recycling runs. Progressive accumulation of (heavy) byproducts on the catalyst surface may lead to slower diffusion of the reactant/products through the porous structure, allowing a longer residence time for secondary reactions, thus affecting the distribution of products. As the concentration of the acid sites decreases, one would expect the chemistry to resemble that of the uncatalyzed situation. A more efficient regeneration of the catalyst could improve the catalytic results for recycling runs. The removal of the accumulated organic matter by thermal processes is not possible, since it requires heating above the thermal stability limit of the surface-bound SAGs (ca. 250 °C). This constitutes a major disadvantage with respect to zeolites as catalysts. More efficient catalyst regeneration might be accomplished by Soxhlet extractions with adequate solvents. Alternatively, catalytic performance might be improved by batch experiments with shorter residence times, followed by extraction of the products with IBMK and recycling of the aqueous solution containing the unreacted substrate and solid catalyst for a subsequent catalytic cycle. According to the literature, these combined experiments allow significant improvements in activity, selectivity, and stability for metal phosphate heterogeneous catalysts in the dehydration of saccharides, in comparison with longer batch experiments [26,30]. Work in this direction is currently in progress.

## 4. Concluding remarks

Sulfonic acid-anchored MCM-41 has been found to be an effective catalyst for the dehydration of D-xylose to furfural. The fairly high selectivities observed at high conversions may be explained by the presence of the large unidimensional mesopores, which promote the reaction of xylose to furfural by allowing fast diffusion of furfural out of the catalyst once formed, thus avoiding extensive consecutive degradation reactions. Selectivity for furfural may be further improved by fine-tuning of the median pore size of MCM-41 with the use of surfactants of different sizes as templates. The hydrophobicity of the catalyst is also an important factor. Thus far it has not been possible to recycle the mesoporous solid acids and maintain the high selectivities and conversions observed in the first runs. The development of efficient regeneration methods will therefore be necessary if these materials are to be considered for practical applications. Furthermore, the transformation of pentosans into xylose and the concomitant conversion to furfural should be carried out in a one-pot reaction design with higher xylose/catalyst molar ratios and preferably without organic solvents.

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## References

[1] K.J. Zeitsch, The Chemistry and Technology of Furfural and Its Many By-Products, first ed., in: Sugar Series, vol. 13, Elsevier, The Netherlands, 2000.
[2] F.W. Lichtenthaler, Carbohydr. Res. 313 (1998) 69.
[3] B. Sain, A. Chaudhuri, J.N. Borgohain, B.P. Baruah, J.L. Ghose, J. Sci. Ind. Res. 41 (1982) 431.
[4] M.J. Antal Jr., T. Leesomboon, W.S. Mok, G.N. Rochards, Carbohydr. Res. 217 (1991) 71.
[5] C. Moreau, M.N. Belgacem, A. Gandini, Top. Catal. 27 (2004) 11.
[6] C. Moreau, R. Durand, D. Peyron, J. Duhamet, P. Rivalier, Ind. Crops Prod. 7 (1998) 95.
[7] C. Moreau, Agro-Food-Industry Hi-Tech. (2002) 17.
[8] C. Lansalot-Matras, C. Moreau, Catal. Commun. 4 (2003) 517.
[9] K. Wilson, J.H. Clark, Pure Appl. Chem. 72 (2000) 1313.
[10] W.M. Van Rhijn, D.E. De Vos, B.F. Sels, W.D. Bossaert, P.A. Jacobs, Chem. Commun. (1998) 317.
[11] W.D. Bossaert, D.E. De Vos, W.M. Van Rhijn, J. Bullen, P.J. Grobet, P.A. Jacobs, J. Catal. 182 (1999) 156.
[12] I. Díaz, C. Márquez-Alvarez, F. Mohino, J. Pérez-Pariente, E. Sastre, J. Catal. 193 (2000) 295.
[13] J.G.C. Shen, R.G. Herman, K. Klier, J. Phys. Chem. B 106 (2002) 9975.
[14] C.D. Nunes, A.A. Valente, M. Pillinger, A.C. Fernandes, C.C. Romão, J. Rocha, I.S. Gonçalves, J. Mater. Chem. 12 (2002) 1735.
[15] Q. Yang, M.P. Kapoor, S. Inagaki, J. Am. Chem. Soc. 124 (2002) 9694.
[16] B. Marler, U. Oberhagemann, S. Vortmann, H. Gies, Microporous Mater. 6 (1996) 375.
[17] W. Hammond, E. Prouzet, S.D. Mahanti, T.J. Pinnavaia, Micropor. Mesopor. Mater. 27 (1999) 19.
[18] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, second ed., Academic Press, London, 1982.
[19] V. Dufaud, M.E. Davis, J. Am. Chem. Soc. 125 (2003) 9403.
[20] A.P. Dunlop, Ind. Eng. Chem. 40 (1948) 204.
[21] C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros, G. Avignon, Appl. Catal. A: Gen. 145 (1996) 211.
[22] C. Bryner, L.M. Christensenm, E.I. Fulmer, Ind. Eng. Chem. 28 (1936) 206.
[23] W. Dunning, E.C. Lathrop, Ind. Eng. Chem. 37 (1945) 24.
[24] K.J. Zeitsch, Chem. Innovat. (2000) 29.
[25] K. Lourvanij, G.L. Rorrer, Ind. Eng. Chem. Res. 32 (1993) 11.
[26] C. Carlini, M. Giutarri, A.M.R. Galletti, G. Sbrana, T. Armaroli, G. Busca, Appl. Catal. A: Gen. 183 (1999) 295.
[27] B.F.M. Kuster, Carbohydr. Res. 54 (1977) 165.
[28] B.F.M. Kuster, Carbohydr. Res. 54 (1977) 177.
[29] B.F.M. Kuster, Carbohydr. Res. 54 (1977) 185.
[30] F. Benvenuti, C. Carlini, P. Patrono, A.M.R. Galletti, G. Sbrana, M.A. Massucci, P. Galli, Appl. Catal. A: Gen. 193 (2000) 147.