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Liquid-phase dehydration of D-xylose over microporous and mesoporous niobium silicates

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Microporous AM-11 crystalline niobium silicates were studied as solid acid catalysts for the dehydration of xylose in a water-toluene solvent mixture at 140–180 °C. After 6 h at 160 °C, xylose conversions of up to 90% and furfural yields of up to 50% were achieved, and the catalysts could be reused without loss of activity or selectivity. The calcined AM-11 catalysts gave higher furfural yields than HY zeolite and mordenite, under identical reaction conditions. Ordered mesoporous MCM-41-type niobium silicates with Si/Nb molar ratios of either 25 or 50 were also found to be recyclable catalysts for xylose dehydration, and gave furfural yields consistently in the range of 34–39% (after 6 h reaction at 160 °C).

KEY WORDS: xylose; furfural; dehydration; acid catalysis; niobium silicates; microporous; mesoporous.

1. Introduction

As non-renewable fossil fuel resources become scarcer, the requirement for reliable and economic alternatives grows. Carbohydrates are among the most abundant organic compounds on earth and represent the major portion of the world's annually renewable biomass, of which less than 5% is used by mankind [1]. The bulk of the renewable carbohydrate-biomass comprises polysaccharides which are composed of numerous monosaccharides that may be used as basic, inexpensive and ton-scale accessible raw materials for the chemical industry. In acidic media, pentosans such as xylan may be hydrolysed to xylose, which can subsequently cyclodehydrate to furfural. Furfural has a broad industrial application profile, including the production of plastic, pharmaceutical and agrochemical products, and so its manufacture constitutes a primary process for generating a variety of non-petroleum derived chemicals from saccharides. In conventional furfural production processes sulphuric acid is used as a catalyst, which is toxic, corrosive and suffers from several drawbacks common to homogeneous catalysts [2,3]. Running a reaction under heterogeneous catalytic conditions has several advantages over a homogeneous process, including easier separation and reuse of the catalyst, longer catalytic lifetimes, toleration of a wide range of temperatures and pressures, and easier/safer catalyst handling, storage and disposal. Hence, the use of solid acid catalysts for the transformation of carbohydrates into furfural may be a promising alternative to the use of mineral acids.

Some of the most recent results reported in the literature show that D-xylose and D-glucose can be catalytically converted to furfural and 5-hydroxymethylfurfural, respectively, by molecular-sieving zeolites, with high selectivity ($>90\%$ selectivity) at ketose conversion lower than 30–40% [4]. The dehydration of fructose to 5-hydroxymethylfurfural was studied by Carlini et al. using niobium, titanium, zirconium and vanadyl phosphates as catalysts, with one of the best results observed for cubic zirconium pyrophosphate that gave 99.8% furfural selectivity at ca. 44% fructose conversion, in aqueous solution at 100 °C [5–7]. Recently, some of us reported that sulphonic acid-functionalised ordered mesoporous silicas are also effective catalysts for the dehydration of D-xylose to furfural [8].

Niobium-containing materials such as hydrated niobium oxide and niobium phosphate exhibit unique activity, selectivity and stability for many different catalytic reactions [9,10]. In the last few years there has been interest in the synthesis of porous niobium silicates, as the presence of niobium in molecular sieves has the potential of generating catalysts with size/shape selective properties and acidic or redox characteristics [11–16]. A novel microporous niobium silicate denoted as AM-11 was reported in 1998 and is a promising catalyst for gas-phase dehydration reactions, such as the conversion of tert-butanol to isobutene [11,17, 18]. Although the structure of this solid has not been solved yet, characterisation studies show that it contains octahedral niobium(V) and tetrahedral silicon, and the charge associated with framework niobium is balanced by Na^+ and NH_4^+ cations. Calcined AM-11 possesses a substantial amount of Brönsted and Lewis acidity [17]. Mesoporous niobium silicates have also been prepared

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by the doping of niobium in the micelle-templated silica MCM-41. These materials have been tested as catalysts for several reactions, such as the oxidative dehydrogenation of ethane and propane [19], the epoxidation of cyclooctene [20], and the hydrosulphurisation of methanol [14]. Herein, we report on the cyclodehydration of xylose to furfural in the presence of microporous AM-11 and mesoporous Nb-MCM-41 niobium silicates. The synthesis of AM-11 in the NH_4-form (without sodium) is attempted for the first time. The catalytic results are compared to those obtained with conventional zeolites.

2. Experimental

2.1. Preparation of AM-11 materials

AM-11 materials were synthesised in teflon-lined stainless steel autoclaves under static hydrothermal conditions. Na,NH_4-AM-11 was prepared from a gel with the molar composition $11.5Na_2O{:}8.2SiO_2{:}Nb_2O_5{:}418.6H_2O$. In a typical procedure, an alkaline solution comprising sodium silicate solution (2.55 g; 8 wt% Na_2O, 27 wt% SiO_2; Merck), H_2O (7.00 g) and NaOH (1.28 g) was mixed with a second solution containing $NbCl_5$ (0.74 g) and HCl (5.07 g). After stirring thoroughly, the pH (after a 1:100 water dilution) was adjusted to 10.3 by adding 25% ammonia solution. The resulting gel was autoclaved for 7 days at 200 °C. The NH_4-AM-11 form was prepared from a gel with the molar composition $5.7SiO_2{:}Nb_2O_5{:}292.4H_2O$. The synthesis procedure was similar to that described above except that the first solution comprised tetraethyl orthosilicate (1.57 g) and H_2O (7.00 g). Prior to catalytic experiments the Na,NH_4-AM-11 and NH_4-AM-11 materials were calcined at 400 °C for 4 h, to give Na,H-AM-11 and H-AM-11, respectively. Complete elimination of ammonia was confirmed by microanalysis for nitrogen. The proton form of AM-11, denoted exH-AM-11, was also prepared by conventional ion-exchange, stirring Na,NH_4-AM-11 (1.0 g) with 0.25 M NH_4NO_3 solution (100 mL) at 60 °C for 24 h (twice), followed by calcination.

2.2. Preparation of Nb-containing MCM-41 materials

Niobium silicate MCM-41-type mesoporous molecular sieves were synthesised from a gel with the molar composition $1SiO_2{:}xNb{:}0.48C_{16}TMABr{:}0.28Na_2O{:}3.7TMAOH{:}222H_2O$ ($x = 0.02$ for Nb50-MCM-41 or 0.04 for Nb25-MCM-41, $C_{16}TMABr$ = cetyltrimethylammonium bromide, TMAOH = tetramethylammonium hydroxide). Based on the procedure described by Parvulescu et al. [21], sodium silicate solution (3.81 g; 8 wt% Na_2O, 27 wt% SiO_2) was added to a solution of $C_{16}TMABr$ (2.81 g) in distilled water (20 mL), and the mixture was stirred for 2 h. A $NbCl_5$/oxalic acid solution was prepared by adding a solution of $NbCl_5$ (0.17 g for Nb25-MCM-41 and 0.087 g for Nb50-MCM-41) in 2-propanol (8 mL) to a solution of oxalic acid (0.24 g for Nb25-MCM-41 and 0.12 g for Nb50-MCM-41) in water (10 mL). The $NbCl_5$/oxalic acid solution was added slowly to the silicate/surfactant solution, and the resultant gel was stirred for ca. 2 h. 25% aqueous TMAOH (21.25 mL) was then added, and the pH was adjusted to 11 with 2 M H_2SO_4. The gels were sealed into Teflon-lined stainless steel autoclaves and heated for 5 days at 100 °C. The products were filtered, washed with water and dried overnight at 60 °C. Calcination was carried out under air at 560 °C for 6 h. The Nb25-MCM-41 and Nb50-MCM-41 materials were finally converted to the ammonium forms by four repeated treatments of Nb25/50-MCM-41 (0.5 g) with 0.1 M NH_4Cl (75 mL) for 4 h. After washing with water, the solids were dried at 65 °C and calcined at 400 °C for 4 h, originating exNb25-MCM-41 and exNb50-MCM-41.

2.3. Catalyst characterisation

ICP-AES measurements were carried out at the Central Laboratory for Analysis, University of Aveiro (by E. Soares), and microanalysis for N was carried out on a Leco CHNS-932 instrument. Powder X-ray diffraction (XRD) data were collected at room temperature on a Philips X'pert diffractometer with a curved graphite monochromator (Cu-K_α radiation), in a Bragg-Brentano para-focusing optics configuration. AM-11 samples were step-scanned in $0.05° 2\theta$ steps with a counting time of 6 s per step. MCM-41 samples were step-scanned in $0.02° 2\theta$ steps with a counting time of 1 s per step. DSC analysis was performed using a Shimadzu DSC-50 system at a heating rate of 5 °C min^{-1} under nitrogen or air. Nitrogen adsorption measurements at −196 °C were carried out gravimetrically with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Prior to measurement, the solids were out-gassed at 200 °C overnight to give a residual pressure of ca. 10^{-4} mbar. ^{29}Si solid-state NMR spectra were recorded at 79.49 MHz on a 9.4 T Bruker Avance 400 spectrometer. ^{29}Si MAS spectra were recorded with 40 ° pulses, a spinning rate of 5.0 kHz, and 35 s or 60 s recycle delays (for AM-11 or Nb25/50-MCM-41 materials, respectively). ^{29}Si CP MAS spectra were recorded with $5.5 \mu s$ ^1H 90 ° pulses, a contact time of 8 ms, a spinning rate of 5.0 kHz, and a 4 s recycle delay (only for Nb25/50-MCM-41 materials). Chemical shifts are quoted in parts per million from tetramethylsilane.

2.4. Catalytic studies

Batch catalytic experiments were performed under nitrogen in a magnetically stirred micro-reactor (mixing speeds ≥500 rpm), heated with a thermostated oil bath, and equipped with a valve for sampling the liquid phase.

In a typical procedure, D-xylose (30 mg), powdered catalyst (30 mg), water (0.3 mL) and toluene (0.7 mL) were poured into the reactor. Zero time was taken to be the instant the micro-reactor was immersed in the oil bath.

The D-xylose present in the aqueous phase was determined quantitatively using 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. Analysis conditions: flow rate 0.6 mL min^{-1}, column temperature 65 °C. The furfural present in the organic phase was quantified using 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 min^{-1}). Authentic samples of D-xylose and furfural were used as standards and calibration curves were used for quantification.

3. Results and discussion

3.1. *Characterisation of the AM-11 materials*

The powder XRD pattern of the as-synthesised Na,NH_4-AM-11 sample was in agreement with that published earlier [11], where the reflections were indexed for an orthorhombic unit cell symmetry with $a = 7.488$ Å, $b = 13.647$ Å and $c = 23.582$ Å [17]. After ammonium exchange and calcination, the powder XRD pattern of exH-AM-11 indicated some loss of crystallinity. An AM-11 structure was also confirmed by powder XRD for the as-synthesised NH_4-AM-11 sample, albeit with slightly lower crystallinity as compared with Na,NH_4-AM-11. The AM-11 materials exhibit reversible type I nitrogen adsorption isotherms, characteristic of microporous solids, with a slight upward distortion above relative pressures of ca. 0.9, suggesting the presence of some mesoporosity. The specific surface areas of the AM-11 materials vary between 320 and 490 $m^2\ g^{-1}$ (Table 1). The lower S_{BET} and V_p values for H-AM-11 are probably related with reduced structural

Table 1
Catalytic results of xylose conversion at 160°C in the presence of microporous and mesoporous niobium silicates as catalysts

Sample/run	S_{BET}[a] ($m^2\ g^{-1}$)	V_p[b] ($cm^3\ g^{-1}$)	Si/Nb[c]	Conv.[d](%)	Select.[e] (%)	TOF[f] (mmol $g_{cat}^{-1}\ h^{-1}$)
Na,H-AM-11	489	0.22	4.3 (19.5)			
run 1				34 (77)	12 (40)	4.6
run 2				37 (88)	12 (52)	5.0
run 3				40 (91)	11 (55)	5.3
exH-AM-11	395	0.22	3.7 (19.5)			
run 1				39 (85)	24 (46)	5.2
run 2				41 (86)	23 (43)	5.4
run 3				39 (90)	25 (45)	5.2
H-AM-11	328	0.17	2.3 (29.2)			
run 1				43 (85)	36 (54)	5.7
run 2				44 (88)	36 (49)	5.8
run 3				46 (89)	35 (56)	6.2
Nb50-MCM-41	1040	0.99 (4.0)	51 (2.4)			
run 1				50 (99)	19 (39)	6.6
run 2				33 (86)	18 (41)	4.4
run 3				22 (79)	17 (43)	3.0
exNb50-MCM-41	1017	0.95 (4.0)	51 (2.3)			
run 1				50 (92)	23 (42)	6.6
run 2				38 (82)	24 (45)	5.0
run 3				38 (78)	24 (46)	5.0
Nb25-MCM-41	962	0.95 (4.0)	24 (4.8)			
run 1				60 (97)	31 (38)	8.0
run 2				46 (92)	23 (41)	6.1
run 3				33 (89)	19 (42)	4.4
exNb25-MCM-41	827	0.66 (3.5)	23 (4.5)			
run 1				51 (94)	31 (42)	6.8
run 2				47 (84)	27 (44)	6.2
run 3				38 (81)	27 (44)	5.1

[a] BET specific surface area calculated in the relative pressure range 0.03–0.12.

[b] Total pore volume calculated using the Gurvitsch equation for $p/p_0 \approx 0.96$. Values in brackets for the MCM-41 materials are the median pore widths in nm, calculated from the adsorption branches using the BJH method with the corrected Kelvin equation.

[c] Si/Nb molar ratio determined by ICP-AES. Values in brackets are the wt% Nb.

[d] Xylose conversion calculated at 30 min; values in brackets were calculated for 6 h reaction.

[e] Furfural selectivity at 30 min (6 h).

[f] Turnover frequency calculated for 30 min reaction.

ordering. The ICP-AES results gave a Si/Nb molar ratio of 4.3 for Na,NH_4-AM-11 and Na,H-AM-11 (Table 1). After ion-exchange of Na,NH_4-AM-11 with ammonium ions, the Si/Nb molar ratio decreased to 3.7. The ammonium-form AM-11 was synthesised with a Si/Nb molar ratio of 2.3. Raman spectroscopy and powder XRD of these samples did not reveal any traces of Nb_2O_5 species. The ^{29}Si MAS NMR spectrum of as-synthesised Na,NH_4-AM-11 was similar to that reported in the literature [11,17], showing one resonance at δ−95 ppm attributed to Si(3Si,1Nb) or Si(2Si,2Nb) environments, three overlapping peaks in the range δ−108 to −105 tentatively assigned to Si(4Si,0Nb) or Si(3Si,1Nb) environments, and a sharp signal atδ − 112 ppm assigned to a Si(4Si,0Nb) environment. After calcination of Na,NH_4-AM-11, the relative intensity of the signal at −112 ppm decreased. In agreement with powder XRD, the ^{29}Si MAS NMR spectrum of exH-AM-11 showed broader peaks, pointing to a crystallinity loss [17]. A similar effect was also observed for the material synthesised in the ammonium form.

3.2. Characterisation of the Nb-containing MCM-41 materials

ICP-AES results for the Nb25-MCM-41 and Nb50-MCM-41 materials confirmed that the initial Si/Nb ratios of 25 and 50 were maintained in the final isolated solids. Furthermore, the ratios were practically unaffected by the post-synthesis treatments. The powder XRD patterns of the calcined niobium silicate materials were characteristic of MCM-41-type materials and, in the high-angle range, did not indicate the formation of crystalline niobium(V) oxide species [19]. With the exception of exNb25-MCM-41, the materials exhibit three Bragg peaks in the low-angle range assigned to (100), (110) and (200) reflections for a hexagonal unit cell (figure 1). The d-value of the (100) reflection is 36.21 Å for Nb25-MCM-41 and 38.20 Å for Nb50-MCM-41, giving lattice constants of $a = 41.8$ and 44.1 Å, respectively ($a = 2d_{100}/\surd 3$). Treatment of Nb50-MCM-41 with aqueous NH_4Cl followed by calcination did not have a substantial effect on the overall appearance of the powder XRD pattern. Conversely, for exNb25-MCM-41, the intensity of the (100) peak is greatly reduced and the other two reflections have disappeared. MCM-41 with higher niobium contents is therefore probably less stable, resulting in a significant loss of structural order and the formation of extra-framework Nb species upon ammonium exchange and thermal treatment. This was also evident in the nitrogen adsorption measurements. All four materials exhibited type IV isotherms, typical of mesoporous solids (not shown). Capillary condensation inside primary mesopores took place at relative pressures above 0.2. The specific surface areas, total pore volumes and median pore widths were in the range 820–1040 $m^2\,g^{-1}$, 0.6–1 $cm^3\,g^{-1}$ and 3.5–4 nm, respectively (Table 1). Unlike the materials with Si/Nb = 50, for which the texture parameters are not significantly affected by ammonium exchange and calcination, the pore volume and width for the material with Si/Nb = 25 decrease by 31% and 13%, respectively. The ^{29}Si MAS NMR spectra for all of the Nb-containing samples were similar (not shown), showing the usual three broad overlapping resonances at −108, −99 and −89 ppm, which are assigned to Q^4, Q^3 and Q^2 species, respectively, of the silica framework [$Q^n = \mathrm{Si(OSi/ONb)_n(OH)_{\{4-n\}}}$].

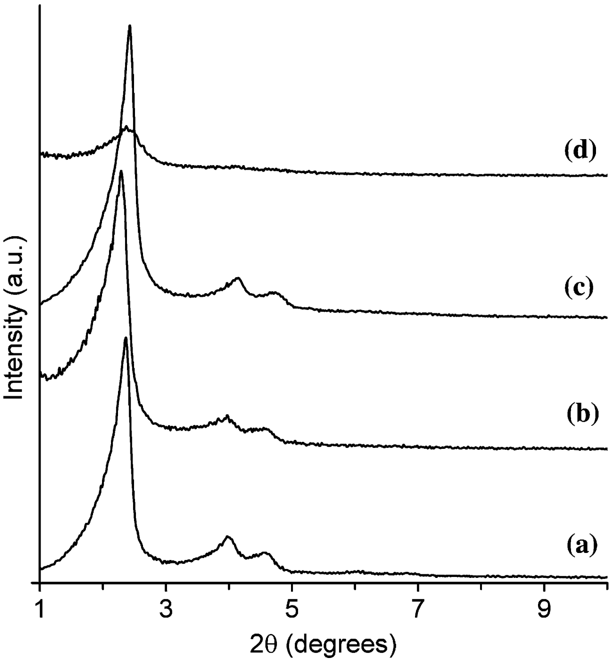

Figure 1. Powder XRD patterns of Nb50-MCM-41 (a), exNb50-MCM-41 (b), Nb25-MCM-41 (c) and exNb25-MCM-41 (d).

3.3. Catalytic studies

The microporous and mesoporous niobium silicates were tested as catalysts for the dehydration of xylose in batch operation, using a water-toluene solvent mixture for simultaneous reaction in the aqueous phase (where xylose is dissolved and the catalyst is suspended) and separation (of furfural, which dissolves preferably in the organic phase) at 160 °C. Under the applied experimental conditions, all of the calcined materials exhibit catalytic activity and after 6 h the xylose conversions are in the range of 77–97% and the furfural yields are between 30 and 46% (Table 1). The non-catalytic reaction at 30 min is negligible, and after 6 h gave 26% conversion and 6% furfural yield. Throughout the discussion the results have not been corrected for this non-catalytic contribution.

The as-synthesised material Na,NH_4-AM-11 gave 47% xylose conversion and 17% furfural yield after 6 h reaction. Calcination of Na,NH_4-AM-11 seems to improve the acid properties, since the conversion and furfural yield for Na,H-AM-11 rise to 77% and 31%, respectively (for a reaction time of 6 h). ^{1}H MAS NMR spectra of Na,H-AM-11, coupled with FTIR studies of pyridine and ammonia adsorption-desorption, have shown that the external surface of Na,H-AM-11 accommodates, predominantly, Lewis acid sites, whereas strong Brönsted acidity is associated with the internal surface [17]. The catalytic dehydration of xylose could involve either of these acid sites [4, 22], assuming that xylose is able to access the internal surface of AM-11. Figure 2a shows that the reaction is somewhat faster still in the presence of H-AM-11 (produced by calcination of the as-synthesised NH_4-form) and exH-AM-11 (produced by ammonium exchange of the as-synthesised Na,NH_4-form, followed by calcination). The turnover frequencies (TOF), expressed as mmol g_{cat}^{-1} h^{-1} and calculated after 30 min reaction, decrease in the order H-AM-11 (5.7) > exH-AM-11 (5.2) > Na,H-AM-11 (4.6) (Table 1). Spectroscopic studies of Na,H-AM-11 and exH-AM-11 indicate that the Lewis acid/Brönsted site ratio increases dramatically upon ammonium exchange and calcination, whereas the Brönsted acid strength is reduced [17]. The Lewis acid sites were suggested to relate mainly to Na^+ cation sites for Na,H-AM-11 and to extra-framework niobium for exH-AM-11. The higher activities observed for H-AM-11 and exH-AM-11 may therefore be due to partial removal of niobium from the frameworks and an increase in the number of Lewis acid sites. The slightly higher activity of H-AM-11 is consistent with this explanation since the ammonium-form precursor was synthesised with a higher niobium content than Na,NH_4-AM-11.

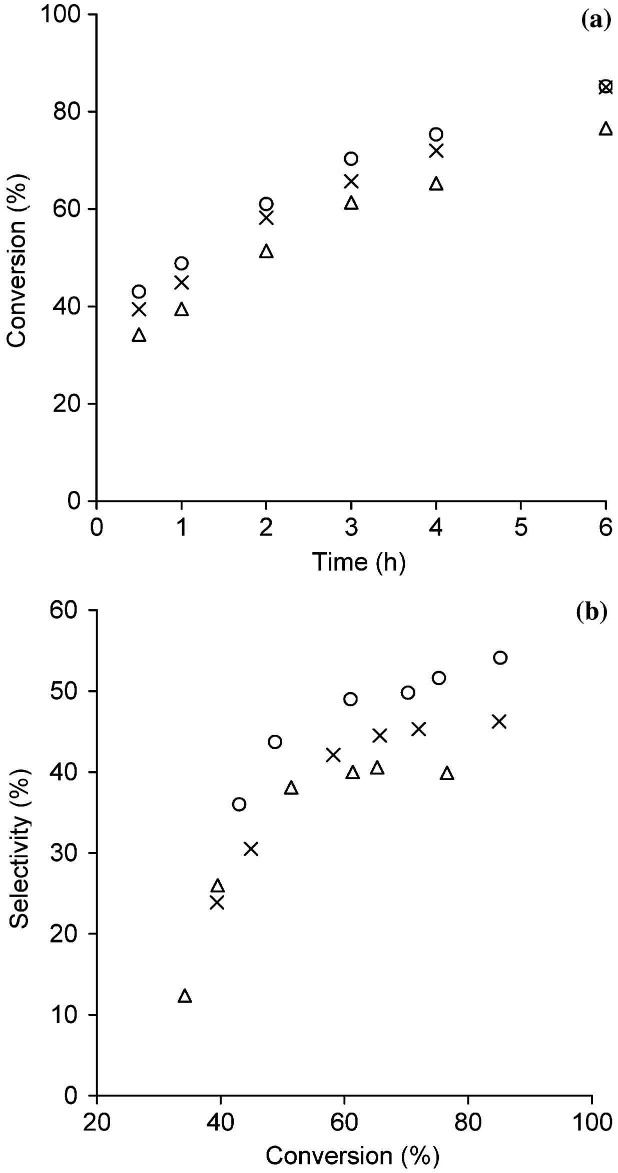

Figure 2. Kinetic profiles of xylose conversion (a) and dependence of furfural selectivity on xylose conversion (b) At 160 °C, in the presence of Na,H-AM-11 (Δ), exH-AM-11 (×) and H-AM-11 (○).

Selectivity to furfural at ca. 77% conversion decreases in the order H-AM-11 (52) > exH-AM-11 (45) > Na,H-AM-11 (40) (figure 2b). The mechanism of xylose dehydration to furfural consists of an acid-catalysed sequence of elementary steps that involves the liberation of three water molecules per molecule of xylose [23]. Generally, by-products are formed in condensation reactions occurring between furfural and intermediates of the xylose-to-furfural conversion [3]. As-synthesised AM-11 reportedly has a high surface polarity, which accounts for negligible adsorption of small hydrocarbon molecules such as propane, but quite significant uptake of ethanol, *n*-propanol and 2-methylpropan-1-ol [17]. The adsorption of xylose and polar intermediates on the catalyst surface may therefore be relatively strong, thereby enhancing consecutive condensation reactions with furfural, and lowering selectivity. This could partly explain why the selectivities observed for the AM-11 catalysts are not very high. Another important factor may be the structure of AM-11. Adsorption measurements of molecules with different sizes have indicated a cage-like framework with narrow windows [11]. The microporous zeolites H-mordenite and HY faujasite have also been tested for this reaction by Moreau et al. at 170 °C in toluene-water, and it was concluded that the absence of cavities within the structure of mordenite avoids the formation of heavy, bulky by-products, resulting in higher selectivity [24]. In the present work, the dehydration of xylose was also carried out in the presence of HY5 (the protonic form of Y-zeolite, with Si/Al = 5; Aldrich) and mordenite (Si/Al = 6). Furfural yields at 6 h followed the order H-AM-11 (46% at 85% conversion) > exH-AM-11 (39% at 85% conversion) ≈ HY5 (39% at 94% conversion) > Na,H-AM-11 (31% at 77% conversion) > mordenite (28% at 79% conversion).

The stability of the AM-11 materials was studied by reusing the catalysts twice, at 160 °C. After reaction the solids were separated by centrifugation and washed thoroughly with methanol at room temperature. The recovered solids did not regain their original white appearance, but instead remained light brown, suggesting that the washing procedure did not completely remove the organic matter from the catalyst's surface. After reaction, the nitrogen uptake at −196 °C of the recovered materials (washed and dried at 60 °C) decreased by at least 16%. DSC analysis (at 10 °C min^{-1} up to 500 °C, under 20 mL min^{-1} air) showed a broad exothermic band with an onset at 250–300 °C that does not appear for the fresh catalyst, and is therefore assigned to coke combustion. These results suggest that organic matter is entrapped inside the pore structure or strongly adsorbed at the pore-entrances. Soxhlet extractions with different solvents (acetone, methanol and toluene) did not enhance desorption of the organic matter. However, when the washing steps were followed by calcination the catalysts regained their white appearance. Therefore, the optimum catalyst regeneration procedure involved centrifugation, washing with methanol and calcination at 350 °C for 3 h (with a heating rate of 1 °C min^{-1}). Under these conditions, the AM-11 catalysts do not loose catalytic activity between the first and third runs, and selectivity to furfural remains roughly the same (Table 1). The conversions after 6 h actually increase with recycling runs. No loss of niobium during the reaction was detected by ICP-AES, and the powder XRD patterns of the fresh and used materials were similar. These results suggest that the AM-11 zeo-type materials are quite stable catalysts under the applied reaction conditions.

Figure 3 shows the kinetic profiles of xylose conversion and the dependence of furfural selectivity on xylose conversion in the presence of the niobium-containing MCM-41 materials. The Nb-MCM-41 samples are more active for xylose conversion than the microporous AM-11 materials, with the highest TOF being observed for Nb25-MCM-41 (8.0 mmol g_{cat}^{-1} h^{-1}, Table 1). After 6 h, 92–99% conversion is achieved in the presence of the Nb-MCM-41 catalysts, compared to 77–85% in the presence of the calcined AM-11 materials. On the other hand, for a given conversion, the Nb-MCM-41 catalysts exhibit slightly lower selectivities to furfural. For example, at ca. 80% conversion, the selectivities in the presence of the Nb-MCM-41 catalysts are between 37 and 44%, while H-AM-11 gives 53% selectivity. The first-run results shown in figure 3 and Table 1 demonstrate that ammonium exchange followed by calcination does not improve the catalytic activities of the Nb-MCM-41 materials. In fact, the activity between 1 and 6 h of reaction is higher for Nb50-MCM-41 than for exNb50-MCM-41 (figure 3a). Conversely, the furfural selectivity (after a given reaction time or conversion) is higher for exNb50-MCM-41 than for Nb50-MCM-41 (figure 3b). These results may be related with the lower structural order of the samples exNb25/50-MCM-41 (as evidenced by powder XRD and N_2 adsorption, especially for exNb25-MCM-41), and the possible formation of extra-framework Nb species. The recyclability of the Nb-MCM-41 catalysts was assessed using the same regeneration procedure used for the AM-11 materials. As Table 1 shows, the conversions after 30 min or 6 h generally decrease with recycling runs. This is probably due to a loss of structural order during the reactions, as evidenced by powder XRD (not shown). Moreover, some leaching of niobium species takes place during the first run, amounting to a 25% decrease in the Nb content for Nb25/50-MCM-41, 13% for exNb50-MCM and 6% for exNb25-MCM. In contrast to xylose conversion,

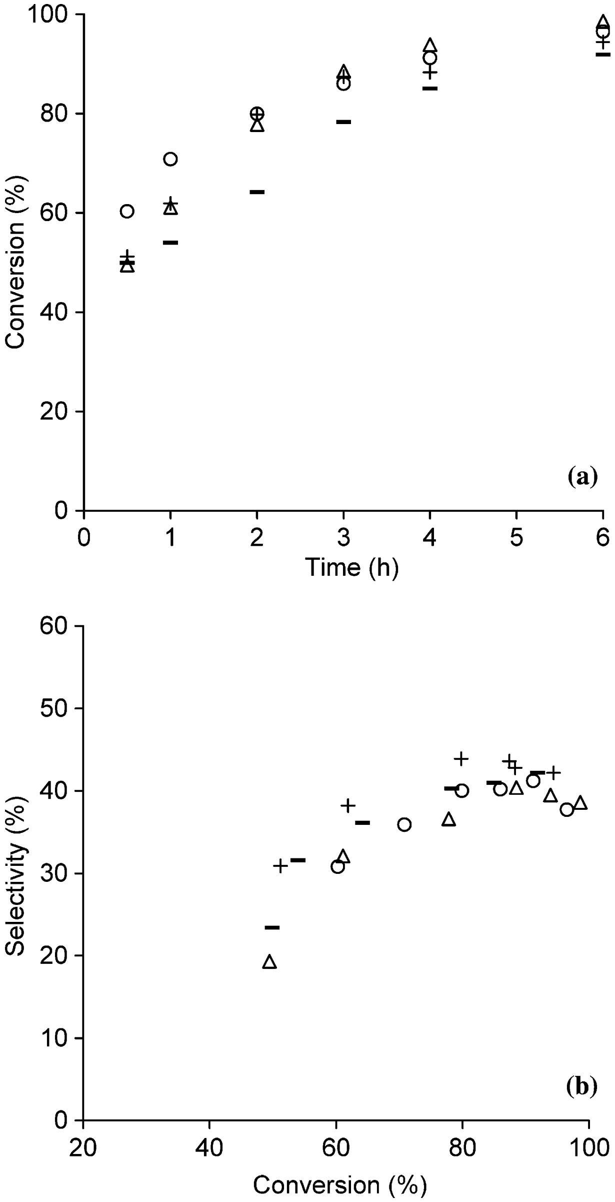

Figure 3. Kinetic profiles of xylose conversion (a) and dependence of furfural selectivity on xylose conversion (b) At 160 °C, in the presence of Nb25-MCM-41 (○), exNb25-MCM-41 (+), Nb50-MCM-41 (Δ) and exNb50-MCM-41 (–).

furfural selectivities after 6 h increase slightly with recycling runs. As a result, the furfural yields after 6 h are in the range 34–39% for all four materials and all catalytic runs.

Since the AM-11 materials exhibited higher catalyst stability, the effect of the reaction temperature on the catalytic performance was investigated for these materials, in the temperature range of 140–180 °C. The results are given in figure 4 and show that the catalytic results are significantly improved by increasing the reaction temperature. The reaction rates more than double when the temperature rises from 140 to 180 °C. Furfural yield increases significantly with temperature, and the best results are observed for H-AM-11, for which the furfural yield at 1 h increases from 6% at 140 °C to 44% at 180 °C.

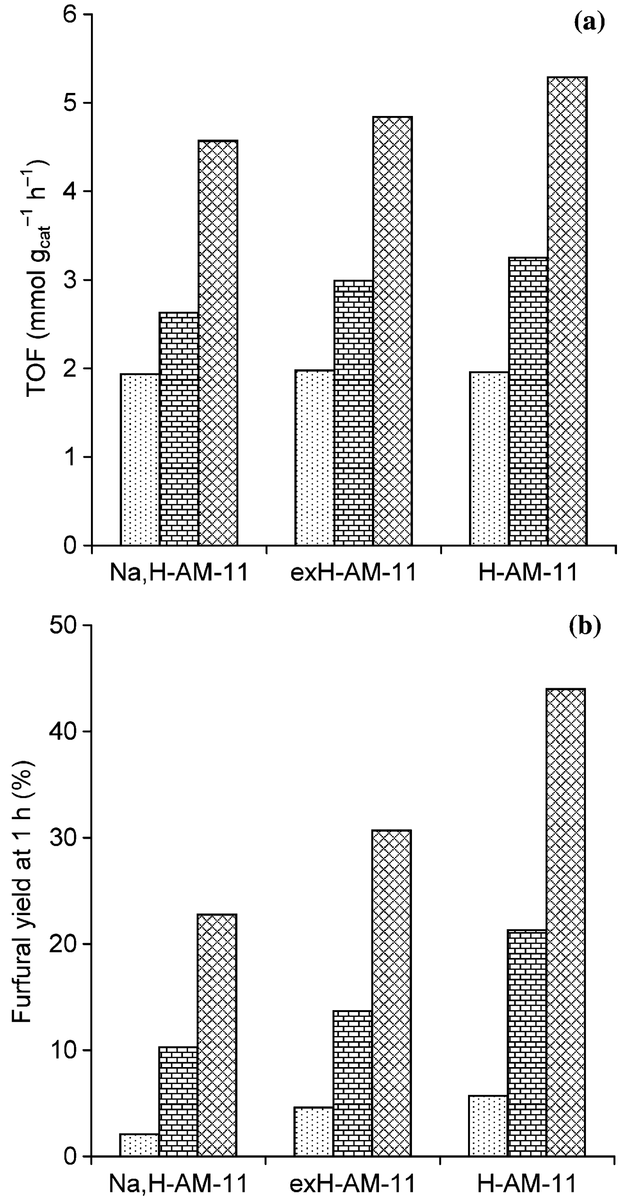

Figure 4. TOFs (1 h) and furfural yields in the presence of the AM-11 materials at 140 °C (dots), 160 °C (bricks) and 180 °C (diamonds).

4. Conclusions

The microporous and mesoporous niobium silicates studied in the present work are active catalysts for the liquid-phase conversion of xylose to furfural. The crystalline AM-11 materials exhibit lower activities than the niobium-containing mesoporous MCM-41-type catalysts (for the first catalytic runs), but are more selective to furfural and are also more stable in recycling runs. The best material was H-AM-11, obtained by the calcination of AM-11 synthesised in the ammonium form. After 6 h at 160 °C, H-AM-11 gives furfural yields in the range 43–50% for up to at least three catalytic runs. Comparable yields can be obtained within 1 h by carrying out the reaction at 180 °C. These yields are significantly higher than those achieved under the same conditions with HY zeolite or mordenite. Adjustment of the reaction conditions, such as temperature and residence time, together with reactor design could open up valuable perspectives in the application of AM-11 materials to the conversion of saccharides into furan derivatives.

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