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Catalytic cyclodehydration of xylose to furfural in the presence of zeolite H-Beta and a micro/mesoporous Beta/TUD-1 composite material

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ABSTRACT

The batch-wise and aqueous phase cyclodehydration of D-xylose to furfural (FUR) at 170 °C has been investigated in the presence of a composite material consisting of zeolite Beta nanocrystals (Si/Al = 12) embedded in a purely siliceous TUD-1 mesoporous matrix (BEATUD), characterised by elemental analysis, powder XRD, TEM and N₂ sorption. After 8 h the xylose conversion reached 98% and the FUR yield was 74%. The initial reaction rates for BEATUD and the bulk nanocrystalline zeolite Beta (BEA) were similar when expressed on the basis of the total amount of acid sites (Lewis + Brønsted) determined through FTIR analysis of adsorbed pyridine. However, the FUR yields at high xylose conversions of ca. 98% were higher for BEATUD (74%) than for bulk BEA (54%). TGA and DSC analyses for recovered catalysts showed that BEATUD possessed a lower amount of carbonaceous matter after a catalytic run, suggesting that the improved performance of the composite may be due to favourable competitive adsorption effects caused by the surrounding silica matrix. By thermally removing the carbonaceous matter between consecutive batch runs, BEATUD could be repeatedly reused without loss of catalytic performance.

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1. Introduction

In face of inevitable oil depletion there is a requirement to develop non-petroleum derived energy, fuels and chemicals, and amongst the Earth's renewable resources, plant biomass may play an important role [1–5]. Furfural (FUR) is an excellent example of a major platform chemical that can be produced from biomass: it is used in different sectors of the chemical industry (oil refining, plastics, pharmaceutical, agrochemical), and is produced worldwide (e.g. China, South Africa, Dominican Republic) [6,7]. FUR is obtained by acid-catalysed dehydration of pentoses (mainly xylose), which in turn are obtained by the acid hydrolysis of hemicellulose (the second most common polysaccharide in nature) fractions of biomass (e.g. bagasse, corncobs, wood processing by-products, forest and agricultural wastes). Industrially, water is used as the solvent, the reaction temperature is in the range of 150-200 °C, and the most common catalyst is sulfuric acid. Although H₂SO₄ is effective for converting raw biomass into FUR, it poses risks to human health, the environment (due to difficult catalyst recovery/recycling; sulfur containing by-products are formed, as well as large amounts of neutralisation waste) and equipment (e.g. corrosion hazards). The improvement of the chemical technology for the production of FUR therefore remains of great interest for the growth of furan-based chemical industries.

The use of porous solid acid catalysts (which have served well the petroleum-based industry) instead of H₂SO₄ seems attractive [8], although there are critical requirements to be considered such as thermal stability and water-tolerance. Of the previously investigated water-tolerant porous solid acid catalysts used for FUR production, crystalline inorganic oxides seem to be the most promising, namely the zeolites H-faujasite, H-mordenite [9] and H-ZSM-5 [10], microporous niobium silicates [11,12], microporous silicoaluminophosphates [13], titanoniobate nanosheets [14], and a delaminated zeolite obtained by the swelling and ultrasonication of a layered precursor of Nu-6(2) [15]. The aluminosilicate catalysts may be more attractive in terms of production costs and/or availability in comparison to the transition-metal containing ones. However, an important drawback is the formation of coke, which may lead to drops in FUR selectivity especially at high conversions. Reducing the crystallite size of the catalyst to the nanoscale would increase the surface area to micropore volume ratio and decrease the diffusion path lengths, which may avoid severe coking. On the other hand, the reduction in crystallite size may enhance the Lewis/Brønsted acid sites ratio, which may be beneficial since Lewis acids may stabilise intermediate species and enhance selectivity towards FUR [16]. However, nanosized materials tend

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Fig. 1. Powder XRD patterns of the fresh and recovered catalysts, and TEM images of BEA (a and b) and BEATUD (c and d). The amorphous carbon support film used for BEA (b) appears as the mottled background in the upper and lower right-hand parts of the micrograph; a holey carbon film was used for BEATUD to clearly distinguish the mesoporous silica matrix of the composite from the background of the support.

to pose concerns related to health, environment, and technical issues (e.g. ease of handling, high pressure drops, up-flow clogging of equipment, and demanding separation techniques such as nanofiltration).

Composite materials consisting of zeolite nanocrystals embedded in a mesoporous inorganic oxide matrix may benefit from the catalytic properties associated with the zeolite nanocrystals, while minimising the nanoscale-related drawbacks [17-26]. The composites can be prepared by blending pre-formed zeolite nanocrystals into the synthesis mixture of a mesoporous carrier. Additional advantages of these composites may include the ability to stably maintain the catalyst component on the carrier, improving its lifetime, and its use for catalyst formulations allowing enhanced porosity of extrudates and fairly good control over composition, size and morphology of the catalyst component. The choice of a three-dimensional mesoporous silica matrix of the type TUD-1 [27] is attractive since its preparation is based on a relatively lowcost, non-surfactant templating route, and may be advantageous in relation to a two-dimensional material in terms of internal mass transfer.

In the present work, the cyclodehydration of D-xylose into FUR in the presence of zeolite H-Beta and a micro/mesoporous Beta/TUD-1 composite material has been investigated and the results are compared with those for bulk nanocrystalline zeolite H-Beta.

2. Experimental

2.1. Preparation of BEATUD and TUD-1

A commercial ammonium-form zeolite Beta powder (NH₄BEA, Zeolyst, CP814E) was converted to the proton form (BEA) by calcination at 550 °C for 10 h with a ramp rate of 1 °C min⁻¹ in static air. The composite material (denoted BEATUD) consisting of H-Beta nanocrystallites embedded in a mesoporous silica matrix was prepared by following a procedure similar to that described by Maschmeyer and co-workers for a composite with a zeolite loading of ca. 40 wt.% [17,18]. Tetraethylorthosilicate (Sigma, 99.9%; 5.34 g, 25.6 mmol) was added dropwise with stirring to a suspension of BEA (1.0 g) in a mixture of triethanolamine (Aldrich, 99.9%; 3.85 g, 25.8 mmol) and water (3.0 g). Then, tetraethylammonium hydroxide (Aldrich, 35 wt.% in water; 3.45 g, 8.2 mmol) was added, and stirring was continued for ca. 2 h. The gel was aged at room temperature for 24 h, followed by drying at 100 °C for 24 h. The solid material was then transferred to a Teflon-lined autoclave and heated under static conditions at 180 °C for 8 h. The product was recovered, washed with distilled water, dried overnight at 60 °C, and finally calcined at 600 $^{\circ}$ C for 10 h with a ramp rate of 1 $^{\circ}$ C min⁻¹ in static air. The purely siliceous TUD-1 material was prepared using the same procedure as that described for the composite, but without zeolite. All materials consisted of powders with particles sizes of less than 150 µm width.

2.2. Catalyst characterisation

ICP-OES measurements for Si (error ca. 7.2%) and Al (error ca. 6.0%) were carried out at the Central Laboratory for Analysis, University of Aveiro (by E. Soares and co-workers). Powder XRD data were collected at room temperature on a Philips X'Pert MPD diffractometer, equipped with an X'Celerator detector, a graphite monochromator (Cu-K_{α} X-radiation, $\lambda = 1.54060$ Å) and a flat-plate sample holder, in a Bragg–Brentano para-focusing optics configuration (40 kV, 50 mA). Samples were step-scanned in 0.04° 2 θ steps with a counting time of 6 s per step. TEM was carried out on Hitachi H9000 and JEOL 2200FS instruments. Samples were prepared by spotting continuous (BEA) or holey (BEATUD) carbon film-coated 400-mesh copper grids with a suspension of BEA or BEATUD in ethanol. The following textural parameters were estimated from N₂ adsorption isotherms measured at –196 °C using a Micromeritics ASAP 2010 instrument (samples were outgassed at 350 °C, under

vacuum): microporous volume (V_{micro}; *t*-plot method), external specific surface area (S_{ext} ; *t*-plot method), total pore volume (V_t), BET specific surface area (S_{BET}), and pore width corresponding to the maximum of the BJH pore size distribution curve for the adsorption isotherm (d_p). The ²⁷Al magic-angle spinning (MAS) NMR spectra were measured at 104.26 MHz with a Bruker Avance 400 (9.4 T) spectrometer, using a contact time of 0.6 µs, a recycle delay of 0.8 s, and a spinning rate of 15 kHz. Chemical shifts are quoted in ppm from Al(H₂O)₆³⁺. The liquid-state ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX 300 MHz spectrometer at 20 °C. The ¹³C CP MAS NMR spectrum of the used BEA catalyst (washed with methanol and dried overnight at 65 °C) was recorded on a 9.4 T Bruker Avance 400 spectrometer at 100.613 MHz, with 3.5 µs ¹H 90° pulses, a contact time of 1.5 ms, a spinning rate of 9.0 kHz, and 4s recycle delays. Chemical shifts are quoted in parts per million from TMS.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out under air, with a heating rate of 5 °C min⁻¹, using Shimadzu TGA-50 and DSC-50 systems. IR spectra were obtained using a FTIR Mattson-7000 infrared spectrophotometer. The acid properties were measured using a Nexus-Thermo Nicolet apparatus (64 scans and resolution of 4 cm⁻¹) equipped with a specially designed cell, using selfsupported discs $(5-10 \text{ mg cm}^{-2})$ and pyridine as the basic probe. Pyridine was chosen since its critical dimension of ca. 6.5 Å [28] is comparable with the molecular diameters of xylose (6.8 Å along the longest axis). After in situ outgassing at $450 \,^{\circ}$ C for 3 h (10^{-6} mbar), pyridine (99.99%) was contacted with the sample at 150°C for 10 min and then evacuated at 150 and 350 °C (30 min) under vacuum (10^{-6} mbar). The IR bands at ca. 1540 and 1455 cm⁻¹ are related to pyridine adsorbed on Brønsted (B) and Lewis (L) acid sites, respectively [29].

2.3. Catalytic cyclodehydration of xylose

Batch catalytic experiments were performed under nitrogen in tubular glass micro-reactors with pear-shaped bottoms and equipped with an appropriate PTFE-coated magnetic stirring bar and a valve for gas purging. In a typical procedure, D-xylose (30 mg), powdered catalyst (20 mg BEA or BEATUD) and a solvent mixture comprising H₂O (0.3 mL, denoted W) and toluene (0.7 mL, denoted T) were poured into the reactor. In the case of the physical mixture (denoted BEA0.4/TUD0.6), BEA (8 mg) and TUD-1 (12 mg) were added. The reaction mixtures were heated with a thermostatically controlled oil bath under magnetic stirring at 700 rpm, which was optimised to avoid external mass transfer limitations: xylose conversion at 30 min was similar (within experimental error) for 700-800 rpm and slightly lower for 600 rpm (e.g. 7% decrease in conversion in the case of BEA as catalyst). Zero time was taken to be the instant the micro-reactor was immersed in the oil bath. The catalysts were recycled for use in four consecutive 6 h runs. After each run, the solid was separated from the reaction mixture, washed with methanol, dried at 60 °C overnight and heated at 450 °C for 5 h with a ramp rate of 1 °C min⁻¹ in air (giving white powders).

The products present in the aqueous phase were analysed 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 2300 differential refractive index detector (for xylose) and a Knauer 2600 UV detector (280 nm, for FUR). The mobile phase was 0.01 M H₂SO₄. 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 30% v/v methanol in an aqueous solution with 10% methanol (flow rate 0.7 mL min⁻¹). Authentic samples of D-xylose and FUR were used as standards and calibration curves were used for quantification. FUR yield (%) was calculated using the formula: (number of moles of furfural formed)/(initial number of moles of xylose) \times 100. For each reaction time, at least three replicates of an individual experiment were made; the reported results are the average values, and the maximum average absolute deviation calculated for xylose conversion and FUR yield was 3% and 4%, respectively: good reproducibility of the results requires "real-time" sampling and HPLC analyses. Initial reaction rates are calculated using conversions at 30 min reaction: initially the reaction conditions are not isothermal (set point is 170 °C and as the reaction time tends to zero, the reaction temperature tends to room temperature).

3. Results and discussion

3.1. Characterisation of the catalysts

Based on the Al contents of BEA and BEATUD measured by ICP-OES (Table 1), the estimated amount of zeolite in BEATUD is 40 wt.%, which is the same as that used in the synthesis gel, suggesting that the zeolite was completely incorporated in the final material. The powder XRD patterns of the bulk nanocrystalline zeolite BEA and the composite BEATUD are similar (Fig. 1), showing the characteristic diffraction peaks of zeolite Beta at $2\theta = 7.5 - 8^{\circ}$ and 22.4° [17]. The low angle peak is broadened due to the presence of an intergrowth of different polymorphs (mainly A and B) in the crystals. TEM images of BEA show that the sample consists of small crystallites with a size of about 20-30 nm, which are clustered to give larger particles with dimensions in the range of 100-200 nm (Fig. 1a). The high-resolution (HR) TEM image shown in Fig. 1b clearly shows the lattice fringes characteristic of zeolite Beta. For BEATUD, TEM characterisation showed a three-dimensional sponge- or wormlike mesoporous matrix with some dark gray domains that may be attributed to the embedded zeolite particles (Fig. 1c). HRTEM images (Fig. 1d) confirmed that BEATUD is a composite of nanocrystalline Beta particles and an amorphous mesoporous matrix. The TEM studies generally revealed aggregates (about 50-200 nm) of nanocrystals surrounded by the mesoporous matrix; areas containing isolated Beta nanocrystals (about 20-30 nm) embedded in the matrix were also observed. The presence of small aggregates is in agreement with previous findings for a Beta/TUD-1 composite material with a zeolite loading of 40 wt.% [17], and can be attributed to the combined effect of the synthesis conditions and the high zeolite loading. Despite the presence of these aggregates, the TEM studies indicated that the nanocrystalline beta particles were fairly evenly distributed in the mesoporous matrix, as reported previously [17].

To assess the textural properties of the materials, nitrogen sorption measurements were performed at -196 °C (Fig. 2, Table 2). The sorption isotherm of BEA shows a significant increase in N₂ uptake at $p/p_0 < 0.01$, typically associated with the filling of micropores, followed by a gradual increase in N₂ uptake as relative pressures approach unity, most likely due to multilayer adsorption on the external surface of the nanocrystallites (accounting for a significant S_{ext} of $176 \,\text{m}^2 \,\text{g}^{-1}$) (Fig. 2). The mesopore size distribution (MSD) shows a very broad and weak maximum centred around a pore width of about 7 nm, which probably arises from inter-nanocrystallite voids. BEATUD and purely siliceous TUD-1 exhibit type IV isotherms, typical of mesoporous materials, with a hysteresis loop at $p/p_0 > 0.4$, which is associated with capillary condensation/evaporation in mesopores. The MSDs show maxima at pore widths of about 4.5 nm for BEATUD and 7.0 nm for TUD-1. In contrast to TUD-1, BEATUD possesses microporosity arising from the zeolite component, although the composite is essentially mesoporous.

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Sample	Al (mmol g^{-1}) ^a	Si/Al ^a	L^b (µmol g ⁻¹)	B^c (µmol g ⁻¹)	$L+B(\mu mol g^{-1})$	L/B	L_{350}/L_{150}^{d}	B_{350}/B_{150}^{e}
BEA	0.96	12	199	152	351	1.31	0.82	0.29
BEATUD	0.38	34	114	95	209	1.19	0.81	0.21

^a Determined by ICP-OES.

^b Lewis acid sites.

^c Brønsted acid sites.

^d Molar ratio of moderate + strong to total L sites.

^e Molar ratio of moderate + strong to total B sites.



Fig. 2. N₂ sorption isotherms at -196 °C and pore size distribution curves (inset) for BEA (\triangle), BEATUD (\bigcirc) and TUD-1 (×). The dotted lines are visual guides.



Fig. 3. ²⁷Al MAS NMR spectra of BEA (a) and (b) BEATUD.

Table 2

Textural properties of the studied materials.

Fig. 3 shows the ²⁷Al MAS NMR spectra of BEA and BEATUD. Both spectra exhibit two groups of peaks at about 55 ppm and 0 ppm, which are attributed to aluminium species in tetrahedral (framework) and octahedral coordination, respectively. The spectrum of BEA is very similar to that reported by Beers et al. for a commercial zeolite Beta in the H⁺-form with a bulk Si/Al ratio of 13 (ref. CP 814 E-22) [30]. The broad octahedral peak centred around -18 ppm could be due to extraframework amorphous aluminiumoxide species, while the sharp peak at 0 ppm has been assigned to a framework connected octahedral aluminium, normally seen for acidic zeolite Beta [30].

BEA and BEATUD possess both Brønsted (B) and Lewis (L) acid sites interacting with pyridine after outgassing at 150 °C, giving a total amount of acid sites which is greater for BEA than for BEA-TUD (Table 1). While the B sites are associated with tetrahedral aluminium, the L sites may be due to extraframework species [31]. The acid properties of BEA and BEATUD are somewhat comparable in terms of the L/B molar ratio and acid strengths. At 350 °C, pyridine desorbed more easily from the B sites than from the L sites. The molar ratio of moderate + strong to total B sites (B₃₅₀/B₁₅₀) is in the range of 0.2–0.3, indicating that most of the sites are of a rather weak nature, while the Lewis ratio (L₃₅₀/L₁₅₀) is ca. 0.8.

3.2. Catalytic cyclodehydration of xylose

3.2.1. General considerations

The reaction of xvlose in the presence of BEATUD, under biphasic water-toluene conditions (denoted W-T) at 170 °C, gave 74% furfural (FUR) yield at 98% conversion (reached at 8 h reaction, Table 3). At 6 h the xylose conversion was 94%, compared with 20% for purely siliceous TUD-1, and 23% without a catalyst, indicating that the zeolite component is responsible for accelerating the reaction. During the reaction of xylose in the presence of BEATUD the W and T phases turned yellow. The aqueous phase was extracted with dichloromethane, giving a yellow solution. No by-products were detected by GC-MS of the toluene phase or of the dichloromethane extract, suggesting that the soluble by-products are of low volatility. The HPLC analysis of the aqueous phase showed some minor peaks, which may include formic acid (based on the comparison of peak retention times with that for an authentic sample), which may be formed by fragmentation reactions of xylose [32]. To get some insight into the nature of the soluble/low volatile by-products formed, the reaction of xylose was carried out in the presence of BEA using D₂O as solvent instead of H₂O, at 170 °C during 8 h. After separating the solid catalyst, the reaction solution was analysed by ¹H (Fig. 4) and ¹³C (Fig. S1 in the supporting information) NMR spec-

Sample	$V_{ m micro}$ (cm ³ g ⁻¹)	$V_{\rm t}~({\rm cm}^3{\rm g}^{-1})$	S_{BET} (m ² g ⁻¹)	d _p (nm)	Average size $(\mu m)^a$
BEA	0.18	0.69	643	-	0.02 (crystallites)
BEATUD	0.05	0.70	712	4.5	15 (particles)
TUD-1	-	0.83	617	7.0	>20 (particles)

^a Estimated by electron microscopy.

Table 3

Performance of solid acid catalysts for the conversion of xylose into FUR at 170 °C.

Catalyst ^a	Time (h) ^b	Conv. (%) ^c	Yield (%) ^d	Initial reaction rate (mmol $g_{cat}^{-1} h^{-1}$)	Ref.
BEA1.0	4/6	98/100	54/49	9.3	This work
BEA0.4	6	97	56	9.6	This work
BEA0.4/TUD0.6	6	94	58	-	This work
BEATUD	6/8	94/98	69/74	5.7	This work
SAPO-11	6	85	41	5.6	[13]
del-Nu-6(1)	6	87	46	2.3	[15]

^a The catalyst bulk density was always 20 g_{cat} dm⁻³ except for BEA0.4 (8 g_{cat} dm⁻³).

^b Reaction time.

^c Xylose conversion.

^d FUR yield.



Fig. 4. ¹H NMR spectrum of the reaction solution obtained after the reaction of D-xylose in the presence of BEA using D₂O as solvent. The spectra of FUR and xylose are given for comparison. Reaction conditions: 30 mg D-xylose, 20 mg BEA, 8 h, 170 °C.

troscopy. As expected, the spectra show the characteristic peaks of FUR. Xylose, which is essentially in the pyranose form in D_2O_1 was not detected in the catalytic reaction mixture, indicating that xylose conversion was 100%. According to Antal et al. [32], FUR is probably formed from the cyclic form of xylose, while the openchain form gives FUR and fragmentation products such as organic acids (e.g. lactic and formic) and glyceraldehyde. The absence of a ¹H NMR signal near 1.4 ppm rules out the presence of significant amounts of lactic acid in the reaction solution. On the other hand, intense signals at 8.07 ppm in the ¹H NMR and 168.9 ppm in the ¹³C NMR can be assigned to formic acid. Apart from the resonances due to FUR and formic acid, the spectra exhibit numerous weak to very weak signals in the ranges of 3.3–4.3 ppm ($\delta_{\rm H}$) and 65–85 ppm ($\delta_{\rm C}$), which are the typical regions for carbohydrate H–C–O or H₂C–O groups; weak peaks at $\delta_{\rm H}$ < 2 ppm may be assigned to methyl or methylene carbon atoms. These signals may be due to fragmentation products of xylose; however, product identification is complicated by the overlapping of individual signals, especially in the ¹H NMR spectrum.

The reaction mechanism of the acid-catalysed conversion of xylose into FUR involves a series of elementary steps with the formation of three molecules of water per molecule of FUR formed (Fig. 5; the cyclic form of xylose is presented based on the mechanistic assumptions made by Antal et al. [32]). In high temperature liquid water, organic acids may act as homogeneous catalysts in the reaction of xylose [10,32,33]. However, formic acid does not

seem to play an important role in the decomposition of FUR [10]. The reaction of FUR (instead of xylose) in the presence of catalyst gave 3% conversion at 6 h, suggesting that FUR is relatively stable under the reaction conditions used. It is possible that FUR reacts with intermediates to give heavier by-products [6,10].

When the reaction of xylose was carried out in the presence of BEATUD with only water as the solvent, a conversion of 81% was obtained at 6 h, but the FUR yield was poor (25%) in com-



Fig. 5. Schematic representation of the reaction of xylose into furfural under aqueous-organic biphasic conditions. The dots represent the powdered solid acid catalyst.



Fig. 6. Kinetic profiles of xylose conversion (A) and furfural (FUR) formation (B) at 170 °C using water (0.3 mL)-toluene (0.7 mL) solvents and BEA1.0 (\triangle), BEA0.4 (**a**), the physical mixture BEA0.4/TUD0.6 (×), or BEATUD (\bigcirc), or only water as the solvent and BEATUD (\bigcirc) or BEA (-). Reaction conditions: 30 mg D-xylose and 20 mg catalyst for BEA1.0 and BEATUD, 8 mg BEA for BEA0.4, 8 mg BEA + 12 mg TUD-1 for BEA0.4/TUD0.6.

parison to the W-T solvent system (Figs. 6 and 7). In the biphasic system, the reaction of xylose (insoluble in T) takes place in the aqueous phase, and the in situ extraction of FUR from the aqueous phase (containing xylose and polar intermediates) into the organic phase may enhance FUR yields by avoiding its decomposition through consecutive reactions with (non-polar) intermediates in the aqueous phase. The partition ratio of FUR, calculated as (moles of FUR in T)/(moles of FUR in W) varies in the range of 8-10 for different reaction times (measured at room temperature). Hence, changes in the product distribution with time do not significantly affect the partition ratio of FUR. Increasing the reaction temperature in the range of 160-180°C for the W-T system had a beneficial effect on initial conversions and FUR yields: initial reaction rate (mmol $g_{cat}^{-1} h^{-1}$) followed the order, 3.4 $(160 \,^{\circ}\text{C}) < 5.7 \,(170 \,^{\circ}\text{C}) < 8.2 \,(180 \,^{\circ}\text{C})$; FUR yield at 30 min followed the order, 4% (160 °C) < 14% (170 °C) < 27% (180 °C). Hence, increasing the reaction temperature may be advantageous for process intensification.



Fig. 7. Variation of FUR yield as a function of xylose conversion at 170 °C using water (0.3 mL)-toluene (0.7 mL) solvents and BEA1.0 (\triangle), BEA0.4 (\blacktriangle), the physical mixture BEA0.4/TUD0.6 (\times), or BEATUD (\bigcirc), or only water as the solvent and BEATUD (\bullet) or BEA (-). Reaction conditions are given in the caption to Fig. 6.

3.2.2. BEA versus BEATUD

The reaction of xylose in the presence of BEA, used in the same quantity (20 mg) as BEATUD, at 170 °C (experiment denoted BEA1.0) gave 42% FUR yield at 1 h (Fig. 6), which is comparable to that reported by Moreau et al. for dealuminated H-faujasite and H-mordenite zeolites possessing similar Si/Al ratio (10–15), used as catalysts in the same reaction under similar conditions (33–43% FUR yield at 50 min) [9]. The beneficial effects of using the W–T solvent system instead of just water as solvent mentioned above for BEATUD are also observed for BEA: FUR yield at 4 h is 17 and 54% for the W and W–T systems, respectively (Fig. 6).

The reaction of xylose using the W-T solvent system was faster for BEA1.0 than for BEATUD (Fig. 6). It is possible that the catalytic reaction takes place on the internal and external surface of the BEA nanocrystallites (micropore volume is much lower than the total pore volume, Table 2). The initial reaction rate calculated on the basis of the mass of catalyst correlates with the amount of acid sites in the catalysts, which is higher for BEA (Tables 1 and 3) [13,14]. On the other hand, the initial reaction rate calculated on the basis of the total amount of acid sites (L+B) is similar for BEA1.0 and BEATUD (26 and 27 mol $mol_{L+B}^{-1}h^{-1}$, respectively). A 2.5-fold decrease in the mass of BEA used (experiment BEA0.4) led to a slower reaction than that for BEA1.0 (Fig. 6), and initial reaction rate was similar (Table 3). In the studied range of catalyst bulk density $(8-20 g_{BEA} dm^{-3})$, the plots of FUR yield against conversion are roughly coincident (Fig. 7). The reaction in the presence of the physical mixture BEA0.4/TUD0.6 took place at a similar rate to that for BEA0.4, suggesting that the reaction rate is essentially governed by the acid properties of the zeolite fraction. Furthermore, considering the plots of FUR yield against conversion, BEA0.4/TUD0.6 and BEA0.4 give similar FUR yields for conversions up to ca. 80%, and for higher conversions slightly higher FUR yields are reached for the physical mixture: 60 and 56% yield at 97-98% conversion for BEA0.4/TUD0.6 and BEA0.4, respectively. A significant improvement in FUR yield at high conversion was observed for the composite BEATUD, which gave 74% FUR yield at 98% conversion. The silica surface in the surroundings of the zeolite nanocrystallites may account for favourable competitive adsorption effects.

The originally white BEATUD and BEA powders turned brown during the catalytic reaction, and remained so after washing with



Fig. 8. (a) ¹³C CP MAS NMR spectrum of BEA after catalysis (reaction of xylose using D₂O as solvent, under identical conditions to those described in the caption to Fig. 4). (b) ¹³C NMR spectrum of the solution obtained after washing used BEA with DMSO-d₆. (c) ¹³C NMR spectrum of FUR in DMSO-d₆.

toluene, methanol, ethanol and acetone, probably due to the presence of organic by-products. In a study of the reaction of xylose in the presence of H-ZSM-5, O'Neill et al. concluded that furfural loss reactions lead to the formation of bulky by-products, which become entrapped inside the micropores constituting coke deposits, which may cause pore blockage and passivation of the catalyst surface ('poisoning' acid sites) [10]. In the case of zeolite nanocrystallites it is possible that coke is formed on the internal (strongly adsorbed and/or entrapped) and external surface (strongly adsorbed). Thermal analyses (TGA, DSC) were performed under air for the solids recovered (washed and dried at 65 °C overnight) from the reaction in the presence of BEATUD, BEA1.0, BEA0.4 and BEA0.4/TUD0.6 after reaching 98% conversion of xylose. The presence of organic matter was confirmed by DSC, which showed exothermic features above 200 °C (not observed for the as-prepared samples). An endothermic peak was detected below 200°C, attributed to desorption of physisorbed water and volatiles. The amount of carbonaceous matter was estimated from the TGA curves in the temperature range of 200-600 °C (no significant variation in mass was observed for the as-prepared materials), which gave 24, 31 and 15 wt.% for BEA0.4, BEA1.0 and BEATUD solids, respectively. Hence, BEATUD possesses the lowest amount of carbonaceous matter and gives the highest FUR yields at high conversion.

In order to get more insight into the nature of the carbonaceous matter, used BEA catalyst was characterised by ¹³C CP MAS NMR spectroscopy (Fig. 8). The spectrum shows peaks characteristic of FUR (or related compounds) at 113, 117–137, 151 and 178 ppm, two very broad peaks centred at 33 and 208 ppm, and several relatively narrow and weak peaks in the region 60–80 ppm. The two broad peaks may correspond to saturated carbon–carbon bonds and aldehyde/ketone groups, respectively, while the narrow peaks

may be due to fragments related to xylose. The FTIR spectra of the as-prepared and used BEA are quite similar (Fig. S2 in the supporting information), with the main difference being the appearance of a new band centred at ca. 1700 cm⁻¹ which may be assigned to the aldehyde/ketone groups that give rise to the broad signal at ca. 208 ppm in the ¹³C CP MAS NMR spectrum; a very weak band at ca. 1470 cm⁻¹ is also observed which may be due to FUR or related by-products. The failure to observe additional IR bands from by-products may be due to overlap of these bands with the more intense bands of the aluminosilicate matrix, as well as to the low concentration and/or the amorphous "heterogeneous chemical nature" of the by-products. The comparison of the FTIR spectra of the as-prepared and used BEA suggests that the chemical nature of BEA is essentially preserved under the applied hydrothermal reaction conditions.

Attempts were made to remove organic compounds from the used BEA by further washing the catalyst with DMSO-d₆ (giving DMSO-d₆ catalyst wash), and obtaining the 13 C NMR spectrum of the resultant solution (Fig. 8). A comparison of the liquid and solid state ¹³C NMR spectra indicates that the compounds which gave rise to the peaks centred at 33, 60-80 and 208 ppm in the MAS NMR spectrum of used BEA were not removed by washing with DMSO-d₆, and are therefore essentially insoluble products. The liquid-state ¹³C NMR spectrum (DMSO-d₆ catalyst wash) exhibits the characteristic resonances of FUR and extra lines at 21.4, 125.7, 128.6, 129.3 and 163.4 ppm. The signals between 125 and 130 ppm can be assigned to alkenyl groups (RHC=CHR), while the single line at 21.4 ppm can be assigned to a methyl or methylene carbon atom. These results are congruent with the appearance of several overlapping signals or multiplets in the region 7.1–7.3 ppm and a singlet at 2.30 ppm in the ¹H NMR spectrum of DMSO-d₆ catalyst wash (not shown). More elaborate characterisation studies will be needed to identify the product(s) responsible for these signals. The weak line at 163.4 ppm in the ¹³C NMR spectrum and at 8.1 ppm in the ¹H NMR spectrum (not shown) is assigned to a residual amount of formic acid. It is noteworthy that the low field resonances between 125 and 130 ppm (¹³C NMR spectrum of DMSO-d₆ catalyst wash) match with the fairly narrow peak at 128.5 ppm and the shoulder at 125.7 ppm in the ¹³C CP MAS NMR spectrum of used BEA (prior to washing with $DMSO-d_6$). Overall, it seems that the carbonaceous matter contains aldehyde/ketone groups, fragments related to xylose and (un)saturated carbon-carbon bonds and it is possible to extract with DMSO compounds containing (un)saturated carbon-carbon bonds.

To examine the reusability of the BEA and BEATUD catalysts, a total of four consecutive 6 h batch runs were carried out (see Section 2.3 for details about the regeneration procedure applied after each run). As shown in Fig. 9, the xylose conversions and FUR yields at 6 h reaction remained fairly constant for the consecutive runs. The powder XRD patterns of the as-prepared and used catalysts were similar (Fig. 1), as were the Si/Al ratios determined by ICP-OES (33 and 13 for recovered BEATUD and BEA, respectively). These results suggest that BEA and BEATUD are quite stable under the applied reaction conditions. The total FUR productions for the four runs were 20 and 29 mmol_{FUR} g_{cat}⁻¹ for BEA and BEATUD, respectively (theoretical value = 40 mmol_{FUR} g_{cat}⁻¹). When BEATUD was recovered without applying the thermal treatment and reused in a second run, the FUR yield at 6 h decreased by a factor of ca. 1.8, revealing the negative effect of coke on FUR production.

Table 3 shows the catalytic results reported for other watertolerant inorganic solid acids (containing Al and Si) tested in the reaction of xylose using W–T solvent conditions at 170 °C, namely crystalline microporous silicoaluminophosphate SAPO-11, and a material obtained by swelling and ultrasonication of a layered precursor of Nu-6(2) (denoted del-Nu-6(1), Si/Al=29) [13,15]. In relation to these materials, the catalytic performance of BEATUD



Fig. 9. Catalytic performance of BEA and BEATUD in four consecutive 6 h batch runs, at 170 °C. Reaction conditions: 30 mg D-xylose, 20 mg BEA or BEATUD, using water (0.3 mL)-toluene (0.7 mL) solvents.

in terms of FUR yield at 6 h reaction compares quite favourably. Decreasing the catalyst bulk density from $20 g_{BEATUD} dm^{-3}$ to $5 g_{BEATUD} dm^{-3}$ leads to somewhat lower FUR yield at 6 h (69 and 59%, respectively), although this result still compares quite favourably with those reported for the previously investigated catalysts.

4. Conclusions

The composite consisting of commercial nanocrystalline zeolite Beta in the protonic form incorporated in a TUD-1 mesoporous matrix (denoted BEATUD) is an effective catalyst for the acidcatalysed conversion of xylose into furfural, without the need for catalyst replacement during at least four runs (similar FUR yields are reached). In comparison to the bulk nanocrystalline zeolite (BEA), BEATUD gives a lower reaction rate (on the same catalyst mass basis), which correlates with the lower total amount of acid sites (L+B) of BEATUD: initial reaction rate is about $27 \text{ mol mol}_{L+B}^{-1} \text{ h}^{-1}$ for both materials. The catalyst stability of BEA seems as good as that of BEATUD. However, the FUR yields at very high conversions of xylose (98%) are higher for BEATUD (74%) than for bulk BEA (54%) or the physical mixture consisting of BEA plus TUD-1 silica (60%). On the other hand, the amount of carbonaceous matter is lower for BEATUD than for BEA. Based on solid- and liquid-state NMR studies it seems that carbonaceous matter contains aldehyde/ketone groups, xylose-related fragments and (un)saturated carbon-carbon bonds.

The improved performance of the composite BEATUD may be due to favourable competitive adsorption effects caused by the surrounding silica matrix. Catalytic tests show that the strong adsorption/entrapment of organic matter in the catalyst has a major negative effect on the catalytic performance, although this drawback can be successfully overcome by, for example, thermally regenerating the catalyst.

Further improvements in catalytic performance for composites of the type BEATUD may be possible by fine tuning properties such as the Si/Al ratio, which will change the total amount of acid sites and catalyst surface polarity, and the zeolite loading, which may affect the dispersion and the number of accessible acid sites of the zeolite.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2010.08.040.

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