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Catalytic dehydration of D-xylose to 2-furfuraldehyde in the presence of Zr-(W,Al) mixed oxides. Tracing by-products using two-dimensional gas chromatography-time-of-flight mass spectrometry

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ABSTRACT

Zirconium-tungsten mixed oxides (ZrW) are effective catalysts in the aqueous-phase dehydration of D-xylose to 2-furfuraldehyde (Fur), at 170 °C. The texture and acid properties of ZrW materials were modified to enhance Fur yields. The catalysts prepared by co-condensation without a templating agent (ZrW(X), $X = NO_3$, Cl; X is related to the type of zirconium precursor) possess relatively low specific surface area and amounts of accessible acid sites, leading to a modest Fur yield of ca. 35% at 99% conversion. The use of a templating agent in the preparation of mesoporous ZrW (ZrW-MP) increased considerably the specific surface area and the amount of accessible acid sites, which resulted in enhanced Fur yields (42%) reached at comparable conversions. Further improvements in Fur yields at high conversions were accomplished by introducing aluminium in the catalyst preparation procedure to give ZrAlW-MP (51% yield at 98% conversion). Fairly good catalytic results were also obtained in the case of the ZrAlW-MP (atalyst, using solely water as solvent (46% yield at 93% conversion). A study of the identification of the reaction by-products by two-dimensional gas chromatography (GC × GC) combined with time-of-flight mass spectrometry (ToFMS) was carried out.

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1. Introduction

The production of non-petroleum derived energy, fuels and chemicals is nowadays a global concern, principally due to oil depletion. Plant biomass is a natural renewable resource that through chemical and/or biological transformations can give a plethora of bio-derived compounds which can become increasingly competitive alternatives to some petrochemicals [1–12]. Several low-cost kinds of plant biomass may be utilised, such as agricultural and forest waste and surpluses, plants grown on arid land, and aquatic plants. The major components of plant-derived biomass are carbohydrates which can be converted to furanic aldehyde compounds such as 2-furfuraldehyde (Fur) and 5-(hydroxymethyl)-2-furaldehyde (Hmf), with wide application profiles [13,14]. These reactions involve the hydrolysis of di/polysaccharides into hexoses (e.g. glucose, fructose) and pentoses (xylose is the most abundant), and the dehydration of these

0920-5861/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.cattod.2012.03.066 monosaccharides into Fur and Hmf, respectively: the two reaction systems are acid-catalysed.

Fur is produced worldwide on an industrial scale (e.g. China, South Africa, Dominican Republic), commonly using H_2SO_4 as the catalyst [15,16]. Liquid mineral acids pose risks to human health, the environment (due to the difficult catalyst recovery/recycling, formation of sulphur containing by-products, large amounts of neutralisation waste), and equipment (e.g. corrosion hazards). As an alternative to toxic liquid acids as catalysts for converting carbohydrates into furanic aldehydes, porous solid acids seem quite promising [17,18]; advantages may include the easier separation of the catalyst from the reaction products (separation processes typically constitute more than half of the total investment in equipment [13,19,20]), extended catalyst lifetimes and recycling, the avoidance of downstream neutralisation steps, and a plethora of families of porous solids with tunable texture/acid properties can be found.

The mechanism for the dehydration of xylose to Fur is complex, involving a series of elementary steps, and it may be accompanied by several types of undesirable side reactions such as fragmentation of xylose and reactions of Fur with other products (e.g. condensation) or with itself (so-called "resinification") [15,21–32]. The understanding of the influence of the acid/texture properties of



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porous solids on the catalytic reaction is not straightforward partly due to the complex reaction system (many types of side reactions may occur, leading to complex mixtures of by-products), and each step may depend differently on the catalytic properties. Recently, Weingarten et al., in a comparative study using different types of solid acids as catalysts in the aqueous-phase dehydration of xylose, reported that a commercial zirconium-tungsten mixed oxide catalyst (XZO 1251, MEL Chemicals, WO₃ content of 15 wt.%), with relatively high concentration of Lewis acid sites, was more active (and less selective to Fur) than an amorphous (mainly Brønsted type) zirconium phosphate catalyst, and less active than (Brönsted) microporous HY zeolite (Si/Al=30) in Fur loss reactions (strong adsorption and subsequent decomposition of Fur on the catalyst's microporous surface) [27]. In a different approach, one may focus on a specific family of catalysts to help establish structure-activity relationships by modifying the physicochemical properties.

Zirconium-tungsten mixed oxides (ZrW) are fairly stable, versatile solid acid catalysts (and commercially available) used in different types of catalytic reactions, including dehydrations such as those of 2-butanol [33-35], tert-butanol [36], methanol [34,37,38], 1-propanol and 2-propanol [36], 2-propenol [39], and of glycerol to acrolein [40-47]. The ZrW-type materials have also been used to study structure-activity relationships in different types of acid-catalysed reactions (the texture and acid properties of ZrW materials may be finely-tuned through different synthetic approaches/conditions). In the case of the dehydration of xylose into Fur, it may be advantageous to prepare mesoporous versions (denoted MP) of ZrW catalysts with enhanced amounts of effective acid sites. Catalyst preparation approaches in this direction can involve using a templating agent (for generating mesoporosity) and doping the catalyst with aluminium (attempting to enhance acidity) [48,49].

In the present work, mixed zirconium tungsten oxides prepared by co-condensation (ZrW(X), X = NO₃, Cl), or impregnation (with or without aluminium) on mesophases of zirconia (ZrW-MP, ZrAlW-MP), were investigated as solid acid catalysts in the aqueous phase dehydration of p-xylose into Fur, at 170 °C. A study of the identification of reaction by-products by two-dimensional gas chromatography (GC × GC) combined with time-of-flight mass spectrometry (ToFMS) was carried out.

2. Experimental

2.1. Preparation of the catalysts

Two samples of zirconium tungsten mixed oxide ZrW(X) (X=Cl, NO₃) with W/Zr atomic ratio of ca. 0.1 were prepared by the co-precipitation method, in a similar fashion to that reported in the literature [50]. Ammonium metatungstate hydrate ((NH₄)₆W₁₂O₄₀·13H₂O; Sigma-Aldrich, 99%) was used as the source of tungsten and ZrOCl₂·8H₂O (Sigma-Aldrich, 99%) or ZrO(NO₃)₂·6H₂O (Sigma–Aldrich, 99%) were used as the source of zirconium. For each ZrW(X) material, three solutions were prepared: 50 mL of 0.5 M ZrOCl₂·8H₂O or ZrO(NO₃)₂·6H₂O in deionised water (solution A); 1L of distilled water with pH adjusted to 10 using aqueous NH₄OH (solution B); 0.2 mmol ammonium metatungstate dissolved in 20 mL of solution B (solution C). Solution A was added drop-wise to solution C, and the pH was adjusted to ca. 10 using NH₄OH (Fluka, 25% NH₃, ca. 13.3 M). The resultant slurries were hydrothermally treated in teflon-lined stainless steel autoclaves heated at 195 °C for 24 h. Subsequently, the solids were filtered; in the case of ZrW(Cl) the solid was washed with deionised water and the AgNO₃ test was used to confirm the efficient removal of Cl⁻ ions. The prepared materials were dried overnight at 110 °C and then calcined under air at 800 °C for 3 h, and finally ground

using an agate pestle and mortar, and sieved to give particles of less than 150 μ m width. A zirconia material (denoted ZrO₂) was prepared in a similar fashion but without adding the tungsten precursor.

Two mesoporous ZrW-MP and ZrWAl-MP materials were prepared via the incipient wetness impregnation method for introducing tungsten (and aluminium) on a pre-prepared templated zirconium hydroxide support (denoted Zr(template)). The Zr(template) solid was prepared by following the procedure described by Ciesla et al. [51]. A solution of 70 wt.% Zr(O-nPr)₄ in 1propanol (11.34 mL, 25.64 mmol) was added slowly with stirring to a solution of hexadecyltrimethylammonium bromide (5.00 g, 13.72 mmol) in a mixture of water (230 g) and 37 wt.% HCl (37.6 ml, 457.9 mmol). After stirring for 30 min a solid was obtained, to which was added a solution of $(NH_4)_2SO_4$ (3.40 g, 25.73 mmol) in water (46g). The resultant mixture was stirred for 1h, and then transferred to a polypropylene bottle and heated at 100°C for 72 h. Finally, the suspension was filtered, and the solid washed consecutively with deionised water (200 mL), ethanol (200 mL), deionised water (200 mL), followed by drying at 100 °C overnight to give Zr(template).

The alumina-doped tungstated mesoporous zirconia (denoted ZrAlW-MP) was prepared as follows: a solution of ammonium metatungstate hydrate (0.213 g, 0.0668 mmol) and aluminium nitrate nonahydrate (0.210 g, 0.560 mmol) in a mixture of water and ethanol (10 mL, 1:1 v/v) was added drop-wise with stirring at 100 °C to Zr(template) (3.215 g) [49]. The drop-wise addition of small aliquots of the solution was alternated with partial drying of the solid at 120 °C for 1 h; after all the solution had been added, the mixture was dried in an oven at 100 °C for 24 h, and the solid was then calcined at 630 °C for 5 h. The tungstated mesoporous zirconia (denoted ZrW-MP) was prepared using the procedure described above for ZrAlW-MP: a solution of ammonium metatungstate hydrate (0.150 g, 0.047 mmol) in a mixture of water and ethanol (10 mL, 1:1 v/v) was added drop-wise with stirring at 100 °C to Zr(template) (1.332 g).

2.2. Catalyst characterisation

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 $_{\alpha}$ Xradiation, $\lambda = 1.54060$ Å) and a flat-plate sample holder, in a Bragg-Brentano para-focusing optics configuration (40 kV, 50 mA). Scanning electron microscopy (SEM), EDX analyses, and elemental mapping were performed using a HR-SEM-SE/EDS Hitachi SU-70 UHR Schottky instrument and Bruker Quantax 400. ICP-AES measurements for Zr, W and Al (error < 10%; detection limit, $20 \,\mu g \, L^{-1}$) were carried out using a Horiba Jobin Yvon Activa-M spectrometer. The BET specific surface areas (SBET, calculated for relative pressures in the range 0.01–0.10) were estimated from N₂ adsorption isotherms measured at -196 °C using a Micromeritics instrument Corp Germini model 2380 (sample pre-treatment: 250 °C, vacuum): the BJH pore size distribution curve was calculated from the adsorption branch of the isotherm. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out under air, with a heating rate of $10 \,^{\circ}$ C min⁻¹, using Shimadzu TGA-50 and DSC-50 systems, respectively. Raman spectra were recorded on a Bruker RFS FT-Raman spectrophotometer (100 s⁻¹, λ = 1064 nm, 200–5000 scans with a resolution of 4 cm^{-1}).

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 self-supported discs and pyridine as the basic probe. Gas-phase characterisation of acid sites has been quite useful for investigating the influence of the acid properties of solid acid catalysts in the aqueous phase reaction of xylose [16,25]. Pyridine was chosen since its critical dimension of ca. 6.5 Å [52] is comparable with the molecular diameters of xylose (6.8 Å along the longest axis, [53]). After in situ outgassing at 400 °C for 2 h (10^{-5} mbar), pyridine (99.99%) was contacted with the sample at 150 °C for 10 min and then evacuated at 150 °C and 350 °C (30 min) under vacuum (10^{-5} mbar). The IR bands at ca. 1540 and 1450 cm⁻¹ are related to pyridine adsorbed on Brønsted (B) and Lewis (L) acid sites, respectively, and were used for quantification [54].

2.3. Catalytic tests

Batch catalytic experiments were performed under nitrogen atmosphere 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, Dxylose (30 mg), powdered catalyst (20 mg) and either water (1 mL, denoted W) or a solvent mixture (denoted W-T) comprising H₂O (0.3 mL) and toluene (0.7 mL) were added to the reactor. 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; e.g. for ZrW(Cl), the initial reaction rates (based on conversion at 30 min reaction) were similar for stirring rates at or above 700 rpm (9.4, 12.4 and 12.1 mmol g_{cat}^{-1} h⁻¹ at 500, 700 and 900 rpm, respectively). Zero time (considered as the instant the reaction began) was taken to be the instant the micro-reactor was immersed in the oil bath. After a batch run, the catalyst was separated from the reaction mixture by centrifugation, thoroughly washed with deionised water and finally dried at 55 °C overnight (giving the washed/dried solid) and calcined at 450 °C (1 °C min⁻¹) for 5 h (giving the recovered solid).

The products present in the aqueous phase were analysed using a Knauer K-1001 HPLC pump and a PL Hi-Plex H 300 mm \times 7.7 mm (i.d.) 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 0.001 M H₂SO₄. The analytical conditions were the following: flow rate 0.6 mL min⁻¹, column temperature 65 °C. The Fur 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 37% v/v methanol and 63% v/v H₂O (flow rate of 0.5 mL min⁻¹). Authentic samples of D-xylose and Fur were used as standards and calibration curves were used for quantification. The Fur yield (%) was calculated using the formula: [(moles of Fur formed)/(initial moles of $xylose) \times 100$]. For each reaction time, at least two replicates of an individual experiment were made; the reported results are the average values.

2.4. Identification of the water-soluble reaction by-products by SPME/GC \times GC–ToFMS analyses

The liquid phase of the reaction mixture (after separating the solid phase by centrifugation) was analysed (qualitatively) on the same day that the respective catalytic test was performed. The vial containing the reaction solution was immersed in a thermostated bath adjusted to 40.0 ± 0.1 °C for 5 min. A solid-phase microextraction (SPME) device with a fused silica fibre coating (50/30 μ m divinylbenzene-carboxen-poly(dimethylsiloxane)) was immersed in the reaction solution for 20 min. After the extraction/concentration step, the SPME coating fibre was manually introduced into the GC × GC–ToFMS injection port at 250 °C and kept for 30 s for desorption. The injection port was lined with a 0.75 mm I.D. splitless glass liner; splitless injections were used (30 s). The LECO Pegasus 4D (LECO, St. Joseph, MI, USA) GC × GC–ToFMS system consisted of an Agilent GC 7890A gas

chromatograph, with a dual stage jet cryogenic modulator (licensed from Zoex) and a secondary oven. The detector was a high-speed ToF mass spectrometer. A non-polar/polar set of columns was used: a HP-5 column (30 m \times 0.32 mm I.D., 0.25 μ m film thickness, J&W Scientific Inc., Folsom, CA, USA) was used as first-dimension column and a DB-FFAP (0.79 m \times 0.25 mm I.D., 0.25 μ m film thickness, J&W Scientific Inc., Folsom, CA, USA) was used as a seconddimension column. The carrier gas was helium at a constant flow rate of 3.0 mLmin⁻¹. The primary oven temperature was programmed from 50°C (3 min) to 230°C (10 min) at a heating rate of 10 °C min⁻¹; the secondary oven temperature was programmed from 70 °C (3 min) to 250 °C (10 min) at 10 °C min⁻¹. The MS transfer line temperature and the MS source temperature was 250 °C. The modulation time was 5 s, and the modulator temperature was kept at 20 °C offset (above primary oven). The ToFMS was operated at a spectrum storage rate of 100 spectra s⁻¹. The mass spectrometer was operated in the EI mode at 70 eV using a range of m/z 33–500 and the voltage was -1626 V. Total ion chromatograms (TIC) were processed using the automated data processing software ChromaTOF (LECO) at signal-to-noise threshold of 100. Contour plots were used to evaluate the separation general quality and for manual peak identification; a signal-to-noise threshold of 50 was used. Two commercial databases (Wiley 275 and US National Institute of Science and Technology (NIST) V. 2.0 - Mainlib and Replib) were used. The majority (86%) of the identified compounds showed mass spectral similarity matches >850. Furthermore, a manual inspection of the mass spectra was done, combined with the use of additional data, such as the retention index (RI) value, which was determined according to the Van den Dool and Kratz RI equation [55]. For the determination of the RI, a C₈-C₂₀ n-alkanes series was used, and as some volatile compounds were eluted before C_8 , the solvent *n*hexane was used as C₆ standard. The experimentally calculated RI values were compared, when available, with values reported in the literature for similar chromatographic columns employed as the first dimension. The results were analysed qualitatively and thus the relative amounts of the products are not considered in this work.

3. Results and discussion

3.1. Characterisation of the catalysts

The physicochemical properties of the prepared catalysts are given in Table 1. The semi-quantitative analyses of the crystalline phases were performed using the Reference Intensity Ratio (RIR) method applied to the XRPD data (Fig. 1) of the prepared materials. The ZrW(X) materials are composed predominantly of tetragonal zirconia (t-ZrO₂) and contain ca. 20 wt% of (thermodynamically stable) monoclinic zirconia (m-ZrO₂); the ZrO₂ material prepared for comparison is predominantly monoclinic (contains 8 wt% t-ZrO₂). When tungsten is incorporated, the monoclinic phase tends to disappear due to stabilisation of the tetragonal phase [36,37,56–59]. Only t-ZrO₂ was detected for the ZrW-MP and ZrAlW-MP materials. For all prepared materials no crystalline phases of WO_x were detected [56].

The SEM images showed that the ZrW(X) materials are composed of particles (ca. 1–50 μ m size) with irregular morphologies; the mesoporous materials ZrW-MP and ZrAlW-MP consist of spherical particles with ca. 3 μ m diameter (Fig. 2). SEM-EDX and chemical mapping show fairly homogeneous dispersions of Zr, W and Al (in the case of ZrAlW-MP), and the atomic ratio W/Zr is ca. 0.1 for all the prepared materials (Fig. 2, Table 1); in the case of ZrAlW-MP the atomic ratio (W + Al)/Zr is 0.15 (Al/W = 0.07). The bulk atomic ratios measured by ICP-AES are comparable to those obtained by EDX (Table 1), further supporting fairly homogeneous dispersions

Physicochemical properties of the prepared materials.					
Sample	Crystalline phases (wt%) ^a	W/Zr ^b			

Sample	Crystalline phases (wt%) ^a		W/Zr ^b	$S_{\rm BET} (m^2g^{-1})$	$B+L(\mu mol g^{-1})$	L/B	L ₃₅₀ /L ₁₅₀	B ₃₅₀ /B ₁₅₀
	m-ZrO ₂	t-ZrO ₂						
ZrW(Cl)	19	81	0.11 (0.10)	48	38	1.4	0.2	<0.1
$ZrW(NO_3)$	23	77	0.09	51	39	1.2	0.2	<0.1
ZrW-MP	0	100	0.10 (0.13)	102	111	1.2	0.2	<0.1
ZrAlW-MP	0	100	0.09 (0.07) ^c	133	127	1.4	0.2	0.2
ZrO ₂	92	8	-	12	-	-	-	-

^a Semi-quantitative analyses of the constituent crystalline phases (monoclinic zirconia, m-ZrO₂; tetragonal zirconia, t-ZrO₂) determined by RIR method applied to the XRPD data.

^b Surface atomic ratio of W/Zr determined by EDX. Values in brackets are for the bulk elemental analyses using ICP-AES.

 c (W + Al)/Zr = 0.15 (EDX) or 0.14 (ICP-AES).



Fig. 1. XRPD patterns of the unused and recycled catalysts. For ZrW(Cl) and ZrW(NO₃) the main peaks of the ZrO₂ crystalline phases are marked as (\blacksquare) m-ZrO₂ and (\bullet) t-ZrO₂.

of the constituent elements (W, Zr, Al), and consistent with the absence of crystalline WOx phases in the XRPD patterns of all the prepared materials.

The N₂ sorption isotherms measured at $-196 \circ C$ for the ZrW(X) materials exhibit a hysteresis loop at high relative pressures (above 0.6) and very broad pore size distributions (exemplified in Fig. 3 for ZrW(Cl)); the values of S_{BET} for these materials are similar and in agreement with those reported in the literature for related materials [37,50,60–62]. The ZrW-MP and ZrAIW-MP materials exhibit type IV isotherms, and possess higher S_{BET} (Table 1) and narrower mesopore size distributions (between ca. 2 and 7 nm width, inset of Fig. 3) when compared against the ZrW(X) materials.

The Raman spectra of the prepared materials are shown in Fig. 4; that of (essentially monoclinic) ZrO_2 is given for comparison. The spectra of the tungsten-containing materials show similarities between each other and are very different from that of monoclinic ZrO_2 , partly due to the predominant t- ZrO_2 phase in the former materials [37]. Bands characteristic of crystalline WO₃ species (typically at ca. 800–810 cm⁻¹ and 710–720 cm⁻¹) are hardly detected (consistent with the XRPD data) [61]. Broad bands in the region 930–1020 cm⁻¹ may be assigned to the terminal W=O bonds which may be isolated or polymeric mono oxo tungsten species [37,63].

All the prepared materials possess both Brønsted (B) and Lewis (L) acid sites interacting with pyridine after outgassing at $150 \degree C$; the molar ratio L/B varies in the range 1.2-1.4 (Table 1). The acid properties of the ZrW(X) materials are similar in terms of the total

amount of acid sites (B+L) and acid strengths (based on the molar ratios of L and B acid sites measured at 350 °C and 150 °C, denoted L_{350}/L_{150} and B_{350}/B_{150} , respectively). The total amount of B + L acid sites is considerably greater for ZrW-MP than for the ZrW(X) materials which may be partly related to the higher S_{BET} in the former case, enhancing the accessibility of the acid sites to the base probe (the W/Zr molar ratios are similar for the three materials). The ZrW-MP possesses similar acid strengths to the ZrW(X) materials. In comparison to ZrW-MP, the ZrAIW-MP material possesses somewhat higher total amount of B + L acid sites (and S_{BET}), and slightly stronger B acidity.

3.2. Catalytic studies

3.2.1. Catalytic performances of the prepared catalysts

The mesoporous ZrW-MP and ZrAIW-MP catalysts lead to higher Fur yields at comparable reaction times, in comparison to the ZrW(X) catalysts (Fig. 5a), which correlates with the higher total amounts of acid sites of the former two catalysts (Table 1). In comparison to ZrW-MP, the ZrAIW-MP catalyst leads to higher Fur yields at high conversions (51% yield at 98% conversion, Fig. 5b), suggesting that the combined effects of enhanced S_{BET} and surface acidity favour the dehydration of xylose into Fur.

The thermally regenerated ZrW-MP and ZrAlW-MP catalyst (details given in Section 2.3) were re-used in three consecutive 4h-batch runs (similar conditions have been reported previously for efficiently regenerating a zirconia catalyst used in the conversion of cellulose at 180 °C [64]). The used catalysts were brownish in colour and the solvent washing procedures failed to restore the original white colour of the as-prepared catalysts (in contrast to that observed for the thermal treatment). For each catalyst, the Fur yields in recycling runs are comparable (Fig. 6). It is worth mentioning that for the washed/dried ZrW-MP catalyst which was not subject to the thermal treatment, the Fur yield dropped considerably from 41% for the first batch run to 13% for the second one, possibly due to catalyst surface passivation by adsorbed organic compounds. The XRPD patterns and Raman spectra for the used/recovered ZrW-MP and ZrAlW-MP catalysts are similar to those for the respective unused catalysts (Figs. 1 and 4; the Raman spectra for the used/recovered catalysts exhibit higher background noise). The stability of the mesoporous structure was confirmed by the similar texture properties (type IV isotherms, S_{BET} and pore size distribution) of the used/recovered ZrW-MP (109–133 m² g⁻¹; mesopore size distributions between ca. 2 and 7 nm width) and ZrAlW-MP (133–143 m² g⁻¹; mesopore size distributions between ca. 2.5 and 6 nm width) catalysts (exemplified in Fig. 3 for ZrW-MP). ICP-AES analyses of the aqueous phase of the reaction mixtures indicated no significant leaching of Zr, W or Al. Based on these results it seems that ZrW-MP and ZrAIW-MP are fairly stable catalysts.

The amount of water-insoluble organic matter (hereafter designated as InsolOrg) was determined by TGA of the washed/dried



Fig. 2. SEM image (top) and chemical mapping (Zr – red; W – dark blue; Al – light blue) for: (a) ZrW(Cl), (b) ZrW-MP and (c) ZrAlW-MP. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

solids (after reaching 98-100% xylose conversion), based on the mass loss in the temperature range 200-600 °C, and represented as [(mass of InsolOrg)/(initial mass of xylose)] (mg g_{xylose}⁻¹). DSC analyses (exemplified for ZrAlW-MP in Fig. 7) of the used catalysts exhibited two exothermic bands in the temperature range 200-550 °C which did not appear for the respective unused catalysts and are therefore attributed to the decomposition of InsolOrg. The amount of InsolOrg is similar for ZrAlW-MP ($154 \text{ mg g}_{xylose}^{-1}$) and ZrW-MP (133 mg g_{xylose}^{-1}). With respect to the water soluble by-products, only formic acid was detected by HPLC (using a UV diode array detector), although the yellow colour of the liquid phases of the reaction mixtures indicated the presence of different types of by-products. According to the literature, formic acid may be formed via fragmentation of sugars under acidic hydrothermal conditions [65,66], or hydrolytic fission of the aldehyde group of Fur [28-30,67]. A more detailed study on the water-soluble byproducts is discussed ahead (Section 3.2.2).

For comparison with the biphasic solvent system, the reaction of xylose in the presence of ZrAlW-MP was carried out using solely water as solvent, at $170 \degree C$ (the catalyst bulk density and

total volume of reaction mixture were the same for the two sets of reaction conditions). The Fur yields at similar conversions are lower for the water system than for the biphasic solvent system (Fig. 5a). The water and biphasic solvent systems lead to comparable Fur yields until ca. 90% conversion (46-48% Fur yield); afterwards the Fur yield drops to 36% as conversion reaches 100% in the case of the water system, whereas in the case of the biphasic solvent system the Fur yield increases to 51% at 98% conversion (Fig. 5b). A greater amount of InsolOrg is formed for the water system (197 mg g_{xylose}^{-1}) in comparison to the biphasic solvent system (154 mg g_{xylose}^{-1}), Fig. 7. The partition ratio of Fur, calculated as (moles of Fur in toluene)/(moles of Fur in the aqueous phase), measured at room temperature, varied in the range 7 ± 0.7 throughout the reaction. Hence, as Fur is formed it is dissolved favourably in the organic phase, which does not dissolve xylose (or polar intermediates). The higher Fur yields and lower amount of InsolOrg formed at high conversions in the case of the biphasic solvent system may be partly due to (i) reduction in the concentration of Fur in the aqueous phase and consequently the lower extension of Fur loss reactions involving xylose and/or polar intermediates [15,28-30,32] and (ii)



Fig. 3. Nitrogen adsorption–desorption isotherms at $-196 \degree C$ for ZrW(Cl) (\Box) , ZrW–MP (unused (\blacktriangle); recycled (\times)), and ZrAIW–MP (\blacklozenge); the inset shows the respective pore size distribution curves using the same symbols.

competitive adsorption effects minimising consecutive reactions of Fur (mainly toluene-solvated) on the catalyst surface (polar, hydrophilic). The reaction of Fur (as the substrate) in the absence or presence of ZrAlW-MP, at 170 °C (water system) gave 16% and 24% conversion at 4 h reaction, respectively; in the case of the biphasic solvent system no measurable conversion of Fur was observed, which is consistent with the favourable effects of the biphasic solvent system in avoiding Fur loss reactions.

3.2.2. Identification of by-products by SPME/GC \times GC–ToFMS analyses

The identification of the by-products may help to identify factors influencing the side reactions, important for tailoring the properties of solid acid catalysts for the target reaction. The identification of the InsolOrg compounds (also known as humins) is not trivial. Some of the authors have previously attempted the

Fig. 4. Raman spectra of the unused and recycled catalysts.

Fig. 5. Fur yields versus reaction time (a), and Fur yield versus conversion of xylose curves (b), for the catalysts $ZrW(Cl)(\Box)$, $ZrW(NO_3)(\Delta)$, $ZrW-MP(\bigcirc)$, and ZrAlW-MP((+) water-toluene solvent system; (\times) water system; the dashed lines are a visual guide). Reaction conditions: 30 mg xylose, 20 mg catalyst, 170 °C.

characterisation of the InsolOrg compounds formed in the reaction of xylose in the presence of micro/mesoporous aluminosilicate catalysts, under reaction conditions similar to those used in the present work, using FT-IR spectroscopy and ¹³C MAS NMR; the spectra were quite complex and it was only possible to identify clearly xylose, 2-furfuraldehyde and formic acid (the organic matter possessed aldehyde/ketone groups, fragments related to xylose and (un)saturated carbon–carbon bonds) [25,68].

Fig. 6. Fur yield in recycling runs of the reaction of xylose in the presence of ZrAlW–MP or ZrW–MP, using the biphasic water–toluene solvent system, at 170 °C. Reaction conditions: 10 wt% xylose, 20 mg catalyst, water–toluene (0.3:0.7 v/v), 170 °C, 4 h reaction.

Scheme 1. Products formed in the reaction of xylose in the presence of ZrAIW-MP, using solely water as solvent, at 170 °C, identified by GC × GC–ToFMS; TIC GC × GC–ToFMS representation (one- and three-dimensional) of the reaction mixture (on the right).

Fig. 7. TGA (represented as (mass of InsolOrg)/(initial mass of xylose)) and DSC curves for the ZrAIW–MP catalyst separated (washed/dried) from the reaction mixture after reaching at least 93% xylose conversion, using the biphasic water–toluene solvent system (black lines) or the water system (grey lines). Reaction conditions: 30 mg xylose, 20 mg catalyst, 170 °C.

In this work we set out to identify products of the reaction of xylose in the presence of ZrAlW-MP, using water as solvent, at 170 °C by GC × GC–ToFMS. This technique allows the separation and identification of water-soluble reaction products which are sufficiently volatile under the applied analytical conditions (details given in Section 2.4). For comparison, GC × GC–ToFMS was performed for the reaction of Fur in the presence of ZrAlW-MP, at 170 °C. A complex mixture of reaction products was obtained for the reaction of xylose (Scheme 1); the identified products are listed in Table S1 (many more products were detected, which were not clearly identified). For Fur as the substrate a much narrower spectrum of reaction products was detected (Fig. S1).

The products formed in the reaction of xylose may be grouped into aliphatic and aromatic compounds (Scheme 1). A major chromatographic peak was identified as Fur. The aliphatic byproducts consist of linear carbon chains of up to six carbon atoms, possessing hydroxyl, carbonyl and/or carboxylic acid functional groups. According to the literature monosaccharides may undergo fragmentations through complex reaction mechanisms involving retro-aldolisation, hydrolysis and/or oxidative fission pathways, which may be accompanied by enolisation and dehydration reactions leading to a variety of compounds [5,69,70–75]. The aliphatic by-products possessing less than five carbon atoms identified in the reaction of xylose include acetic acid, acetaldehyde, 1-hydroxy-2-propanone, 2,3-butanedione and 2-butanone (Table S1). The first four of these are possible sugar fragmentation products [65], and were not detected with Fur as the substrate. 2,3-Pentadione and hexadione products were formed in the reaction of xylose and not of Fur. According to the literature 2,3-pentadione may be formed through a series of reactions involving aldol reactions of butanedione (detected in this work) with formaldehyde, or of acetaldehyde (detected in this work) with 1-hvdroxy-2-propanone [76]. The mechanism of formation of the hexadiones is not clear: it has been reported that 2.5-hexadione is a possible product of the reaction of 2.5-dimethylfuran (not detected in this work) with water [77]. It is worth mentioning that the by-products may react with xylose (e.g. xylose bound to a non-carbohydrate moiety) and/or Fur, and fragmentation and recombination of carbohydrate fragments may take place, further enhancing the complexity of the overall reaction mechanism.

Furanone products were detected, namely 3-methyl-2(5H) furanone and 5-methyl-2(5H)-furanone, for xylose and not for Fur as substrate. A similar compound identified as 5-methyl-3(2H)furanone was previously reported as the product of the reaction of 2-deoxy-D-erythro-pentose in aqueous acidic medium [78].

Several compounds possessing one furan ring were detected and some (noted with the symbol * in Table S1, e.g. methyl furan-2-carboxylate) are common to the reactions of xylose and Fur. Furan derivatives possessing two furan rings were formed (e.g. di-2-furanyl-ethanedione); related by-products have been reported previously for the reactions of pentoses [17,79] and hexoses [5]. 2,5-Dimethyl-1,4-benzoquinone was detected for the reaction of xylose and not of Fur, as well as a variety of aromatic by-products possessing a benzene ring, suggesting that the formation of these by-products involves intermediates of the reaction of xylose; monocyclic compounds include hydroxyacetophenones. hydroxybenzaldehydes, and bicyclic compounds are benzopyrone and benzofuran derivatives. It is worth mentioning that phenolic compounds can be readily transformed into coloured products (as mentioned above the reaction solutions were yellow). Aromatic compounds of the type benzopyrone, toluene and acetophenone possessing hydroxyl functional groups have been identified as byproducts of the reaction of xylose under acidic conditions [80,81].

4. Conclusions

Zirconium-tungsten mixed oxides are relatively active catalysts in the aqueous phase reaction of p-xylose, at $170 \,^\circ$ C. The catalysts prepared by co-condensation led to more than 90% conversion within 2 h reaction, but 2-furfuraldehyde (Fur) yields were less than 35%. The Fur yields at similar xylose conversions could

be improved by using a templating agent to give ZrW-MP with enhanced specific surface area and amount of accessible acid sites (41% Fur yield at 100% conversion), and furthermore by doping the inorganic material with aluminium to give ZrAlW-MP (51% Fur yield at 98% conversion). Catalyst recycling tests and characterisation of the recovered solids revealed that ZrW-MP and ZrAlW-MP are fairly stable catalysts under the applied reaction conditions. For the ZrAlW-MP catalyst, the Fur yields were higher when using the biphasic water-toluene solvent system instead of solely water as the solvent (40% at 93% conversion). On the other hand, the Fur yields reached for ZrAIW-MP using solely water as the solvent (cheaper, cleaner), were higher than those for the ZrW(X) catalysts coupled with the biphasic solvent system. By fine-tuning the catalytic properties of these types of solid acid catalysts it may be possible to further improve their catalytic performances. Furthermore, tungsten/aluminium modified zirconias may be promising (versatile) catalysts for converting cellulose/glucose (most abundant terrestrial poly/monosaccharides) to added value products such as Hmf. The product distribution obtained in the aqueous reaction of glucose in the presence of aluminium-zirconium mixed oxides at 180 °C was found to be dependent on the acid-base properties of the catalysts [48]. ZrO₂ is effective in the isomerisation of glucose using water as solvent, at 200 °C [82]. McNeff et al. demonstrated the feasibility of using a continuous process coupled with a stable porous heterogeneous metal oxide catalyst (zirconia, titania) for the conversion of cellulose to Hmf in fairly good yields [64]. More recently, Essayem and co-workers reported that tungstated zirconia and tungstated alumina exhibited remarkable catalytic activity and stability in the depolymerisation of cellulose [42].

Finally, SPME/GC \times GC–ToFMS analyses were carried out for the reaction of xylose, showing that a complex mixture of watersoluble by-products was obtained. Detailed systematic studies using this technique may give valuable insights into the overall reaction mechanisms of the conversion of carbohydrate biomass, important for identifying factors (catalyst properties, reaction conditions) responsible for side reactions.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cattod.2012.03.066.

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