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Chemicals from biomass: Etherification of 5-hydroxymethyl-2-furfural (HMF) into 5,5′(oxy-bis(methylene))bis-2-furfural (OBMF) with solid catalysts

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Starting from 5-hydroxymethyl-2-furaldehyde (HMF), it has been possible to produce 5,5′-oxy(bismethylene)-2-furaldehyde (OBMF), which is an interesting prepolymer and antiviral precursor, using Lewis and Brönsted solid acid catalysts. Structured micro- and mesoporous aluminosilicates are active and selective, but Al-MCM-41 displays the best performance owing to smaller diffusion constraints. The yield obtained is higher than with homogeneous acid catalysts. Metal-substituted zeolites and mesoporous materials bearing Lewis acidity are also active and selective catalysts for the above reaction.

1. Introduction

The synthesis of fuels and chemicals from biomass makes an emphasis on the necessity to develop environmentally sustainable processes. Since sugars are abundant in nature, it is not surprising that one of the foremost target reactions has been the transformation of sugars into their immediate dehydrated derivative, i.e. 5-hydroxymethyl-2-furfural (HMF) and furfural from hexoses and pentoses, respectively [1,2].

The synthesis of an HMF derivative, such as 5,5′-oxy(bis-methylene)-2-furaldehyde (OBMF), is of much interest for the preparation of some imine-based polymers. For instance, the resulting polymer from the reaction between OBMF and 1,4-diaminobenzene exhibits a high glass transition temperature (300 °C) and high thermal and electrical conductivity [2]. A second important application of OBMF is for the preparation of hepatitis antiviral precursors. This is done by reacting OBMF with 4-amino-pyridine in presence of para-toluenesulphonic acid (pTSA) followed by its reduction with KBH_4 [3].

For the synthesis of OBMF, two different routes are found in the literature: (a) the etherification of two HMF molecules catalysed by homogeneous organic acids (e.g. pTSA) using organic solvents (e.g. toluene) to obtain 72 mol% yield [4–6]; (b) Williamson reaction between HMF and 5-chloro-methyl-2-furfural in presence of an excess of base [3]. These two routes are shown in Scheme 1.

When homogeneous acids and bases are used for the conventional synthesis of OBMF, large amounts of residues are generated. Moreover, in the preparation of OBMF with pTSA using toluene as a solvent, alkylation by-products between the reactant and the solvent are also formed. With the aim of improving the synthesis of OBMF, solid acids have been used. In this sense, it is worth noting the use of alumina [7], silico-aluminates [8], alumino-phosphates [9] and Nafion and Amberlist resins [10–14] to prepare symmetrical ethers. The latter ion-exchange resins are used industrially to synthesize ethers. However, the main disadvantage is their relatively low thermal stability, specially when the catalyst needs to be regenerated.

In order to overcome this limitation, we have thought on using zeolites and mesoporous aluminosilicates with Brönsted and Lewis acid sites. Indeed, the possibilities to modulate acidity and adsorption properties and pore dimensions and topology, together with their well-known thermal stability of the above materials, may offer further possibilities for designing a more efficient environmentally friendly process for the production of OBMF. This should be possible taking into account the work already done regarding the synthesis of ethers using beta and MCM-41 catalysts [15–20].

In this work, we will present a study on the synthesis of OBMF from HMF under mild reaction conditions, using zeolitic and mesoporous catalysts containing framework Brönsted and Lewis acid sites, with yields above 99%.

2. Experimental

2.1. Reactants

All the reactants used in this work were purchased from Aldrich unless indicated otherwise: 5-hydroxymethyl-2-furfural (99.8%),

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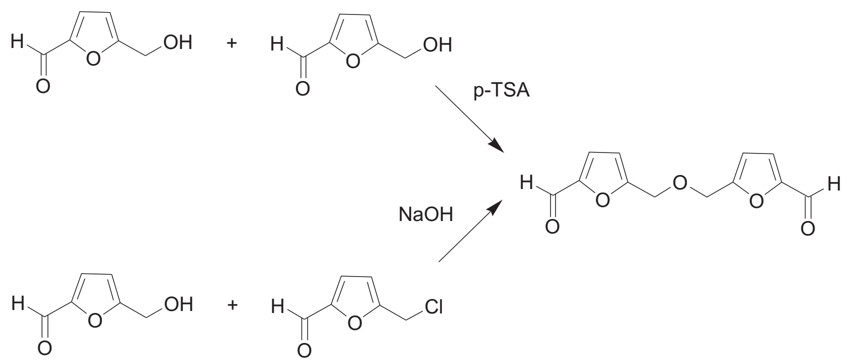

Scheme 1. Synthetic routes of OBMF.

furfural (99%), trifluorotoluene (TFT) (98%, ABCR), anhydrous toluene (99.9%), mesithylene (98%), durene (99%), 4-chlorotoluene (98%), nitrobenzene (99.9%) and para-toluenesulphonic acid (99.8%).

2.2. Catalysts preparation and characterization

H-Mordenite-12.5 (CBV-20A) and *H-Al-Beta 12.5* (CP 811) were purchased from PQ ZEOLITES B.V. and before use, they were calcined at 580 °C for 3 h. The following catalysts were prepared according to the literature: *H-Al-Beta-F 12.5-100* [21], *Nano-H-Al-Beta 19* [22], *Al-MCM-41 12.5* [23], *Sn-Beta* [24], *Zr-Beta* [25], *Nb-Beta, Ta-Beta* [26], *Sn-MCM-41* [27], *Zr-MCM-41, Si-Beta* [28,29] and *Si-MCM-41* [30].

Crystallinity and phase identification of the materials were determined by powder X-ray diffraction (XRD) in a Philips X'Pert MPD diffractometer equipped with a PW3050 goniometer (Cu Kα radiation, graphite monochromator) provided with a variable divergence slit. Infrared (IR) experiments with adsorption of pyridine were performed in a Nicolet 710 FTIR spectrometer using vacuum cells. Wafers of 10 mg cm^{-2} were degassed overnight under vacuum (10^{-4} to 10^{-5} Pa) at 400 °C. The spectra were recorded, then pyridine was admitted and, after equilibration, the samples were outgassed for 1 h at increasing temperatures (150/250/350 °C). After each desorption step, the spectrum was recorded at room temperature and the background subtracted. IR spectra were performed using a Nicolet 750 spectrophotometer. Hence, following the above procedure, the acidity of the catalysts was determined on the basis of a method already described in the literature [31]. The metal content of the calcined samples was determined by atomic absorption in a Varian SpectrAA-10 Plus, elemental analysis (C, H, N) in a Fisons EA1108CHN-S, and Si was calculated by difference. Specific surface area was measured by nitrogen and argon adsorption experiments at 77 and 85 K, respectively, using a Micromeritics ASAP 2000 apparatus. Thermogravimetric and differential thermal analyses (TGA-DTA) were performed in a Netzsch STA 409 EP thermal analyser with about 20 mg of sample and a heating rate of 10 °C/min in air flow (6 L/h). Gas chromatography (GC) analyses were performed with a Varian 3300 chromatograph equipped with a flame ionization detector, and the capillary column was TRB-5 (5% crosslinked phenyl-methyl silicone) (sizes 30–0.25–0.25) (Teknokroma). Mass spectra were performed by GC–MS (HP Agilent 5973 with a 6980 mass selective detector). Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a varian Gemini at a frequency of 300 MHz. The main characteristics of the catalysts are summarized in Tables 1 and 2.

2.3. Catalytic experiments

The catalytic reactions were carried out in a three-necked round bottom flask reactor equipped with a magnetic stirrer, immersed in a thermostatic oil bath, fitted with a reflux condenser. Prior to reaction, the catalyst was activated by in situ dehydration of the sample at 200 °C for 2 h under vacuum. As a general procedure, 1 mmol HMF was dissolved in 2.3 mL solvent and loaded into the reactor which contained the catalyst. The mixture was stirred at ca. 1000 rpm, and the progress of the reaction was followed by taking samples at regular periods of time and analysed by GC using nitrobenzene as internal standard. When the reaction was finished, the final product was filtered and the catalyst was washed several times with acetone. After evaporation of the solvent, OBMF was obtained as a solid whose structure was confirmed by ^{1}H NMR and MS spectrometry. The used solid catalyst was continuously washed

Table 1
Characterization of Brönsted acid catalysts.

Catalyst	Si/Al mol ratio	Crystal size (nm)	BET area (m^2/g)	Brönsted acidity[a,b] (μmol py/g)		
				150	250	350
H-Mord 12.5	12.5	50–300	550	67	54	29
H-Al-Beta 12.5	12.5	100–200	730	35	20	7
Nano-H-Al-Beta-F 19	19	20	580	62	52	21
Al-MCM-41 12.5	12.5	–	1100	20	5	4
H-Al-Beta-F 12.5	12.5	1000	470	80	57	18
H-Al-Beta-F 25	25	1220	460	55	44	13
H-Al-Beta-F 50	50	1400	475	33	30	12
H-Al-Beta-F 100	100	2000	470	28	20	9

[a] From extinction coefficients by Emeis [31].
[b] Pyridine (py) desorption at the temperatures indicated in °C.