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Liquid phase dehydration of D-xylose in the presence of Keggin-type heteropolyacids

Ana S. Dias, Martyn Pillinger, Anabela A. Valente *

Department of Chemistry, CICECO, University of Aveiro, Campus de Santiago,
3810-193 Aveiro, Portugal

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Abstract

The heteropolyacids (HPAs) $H_3PW_{12}O_{40}$ (PW), $H_4SiW_{12}O_{40}$ (SiW) and $H_3PMo_{12}O_{40}$ (PMo) were tested as catalysts for the homogeneous liquid phase dehydration of D-xylose to furfural. With dimethylsulfoxide (DMSO) as the solvent and a reaction temperature of 140 °C, the tungsten-based HPAs are comparable with H_2SO_4 and *p*-toluenesulfonic acid catalysts in terms of furfural yield achieved after 4 h (58–67%), whereas PMo yields less than half this amount of furfural. In the presence of PW, the temperature dependence of the initial reaction rate is approximated by the Arrhenius equation with the exponential term $\exp(-4767\ ^{\circ}\mathrm{K}/T)$. The initial rate of xylose conversion exhibits first-order dependence with respect to the initial xylose concentration and a non-linear dependence on initial HPA concentration. Catalytic results also vary according to the HPA composition and the nature of the solvent system (DMSO, water, water/toluene or water/isobutylmethylketone (IBMK)). Xylose conversions are higher in DMSO than in water-containing solvent systems. In DMSO, the turnover numbers (TON, mol/equiv. H^+ calculated at 4 h) follow the order PW > SiW > PMo, whereas in the water-containing systems the order changes to PMo > PW > SiW. In IBMK/water SiW is far more selective than PW (57 and 4% selectivity for SiW and PW, respectively, at 83–89% conversion) and yields more furfural (51% compared with <9% for PW and PMo, at 24 h). In DMSO selectivity to furfural is slightly higher with PW (64–69%) than with SiW (52–64%), but much lower with PMo (<27%), above 87% conversion. For PW and SiW selectivity towards furfural production is higher for toluene/water than for DMSO for conversions up to 80%.

Keywords: Xylose; Furfural; Dehydration; Acid catalysis; Heteropolyacid; Reaction kinetics; Solvent effects

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1. Introduction

Furfural is an important chemical produced on an industrial scale for the manufacture of furfuryl alcohol (for furan resin production), pesticides and tetrahydrofuran [1]. It is also used as a selective solvent for lube oil refining and for butadiene extraction. Furfural is prepared commercially by the acid-catalyzed degradation of pentosans obtained from agricultural raw (or waste) materials, e.g. corncobs, cottonseed hull bran, oat hulls, cottonseed hulls, bagasse and rice hulls. The reaction involves hydrolysis of the pentosan into pentoses and successive (much slower) dehydration of the latter to form furfural. Currently, there are furfural production plants experiencing technological and process maintenance problems which account for low operating rates. Batch processes, such as those used in China, the world's largest producer of furfural, involve the use of aqueous sulfuric acid as the catalyst, which is extremely corrosive, highly toxic and not easily handled. Improvement of the chemical technology for the production of furfural therefore remains of great interest for the growth of furan-based chemical industries [2–4]. Some of the alternative homogeneous catalysts that have been employed are hydrochloric, phosphoric and acetic acids, superphosphate, as well as chloride, phosphate and sulfate salts [5].

To the best of our knowledge, there are no reports in the literature concerning the use of heteropolyacids (HPAs) in the synthesis of furfural. HPAs and their salts are useful acid and oxidation catalysts for various reactions and they are

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* Corresponding author. Tel.: +351 234 378123; fax: +351 234 370084.
E-mail address: avalente@dq.ua.pt (A.A. Valente).

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found in several industrial applications [6–9]. The advantages of HPAs in homogeneous liquid phase catalysis are their low volatility, low corrosiveness, high flexibility, safety in handling and generally high activity and selectivity compared to conventional mineral acids. HPA catalysis lacks side reactions such as sulfonation, chlorination, nitration, etc., which occur with mineral acids [6]. Furthermore, due to the softness of HPAs they are quite soluble in organic solvents that are not usually suitable for dissolving inorganic salts. The Keggin-type HPAs typically represented by the formula $H_{8-x}[XM_{12}O_{40}]$, where X is the heteroatom, x is its oxidation state, and M is the addenda atom (usually Mo^{6+} or W^{6+}), are the most important for catalysis, with 12-tungstophosphoric acid ($H_3PW_{12}O_{40}$) being the strongest acid in the series [9–11]. Solutions of these materials exhibit acid strengths higher than that of typical mineral acids, including sulfuric acid. In the present work, the dehydration of D-xylose to furfural with different HPAs has been studied in liquid phase, and the effects of the reaction conditions (temperature, xylose and catalyst concentration) and of the solvent (aqueous and non-aqueous or biphasic) on the reaction is discussed.

2. Experimental

The HPAs 12-tungstophosphoric acid hydrate, 12-tungstosilicic acid hydrate and 12-molybdophosphoric acid hydrate were purchased from Fluka and used as received. Batch catalytic experiments were performed under nitrogen in a magnetically stirred micro-reactor (mixing speeds ≥500 rpm), heated with a thermostated oil bath, equipped with a valve for sampling the liquid phase. In a typical procedure, 30 mg D-xylose, 20 mg powdered catalyst and 1 ml solvent (in the case of solvent mixtures, 0.3 ml H_2O and 0.7 ml organic solvent) were poured into the reactor. Zero time was taken to be the instant the micro-reactor was immersed in the oil bath.

For the experiments carried out using dimethyl sulfoxide (DMSO) or water as solvent, D-xylose and furfural were quantitatively determined 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. Authentic samples of D-xylose and furfural were used as standards and calibration curves were used for quantification. When isobutylmethylketone (IBMK) or toluene were used as co-solvents, 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}).

3. Results and discussion

3.1. General considerations

The acid-catalyzed dehydration of pentose to furfural usually proceeds via consecutive protonation of the hydroxyl groups (forming H_2O^+ groups) and cleavage of the C–O bonds, leading to liberation of water molecules (three overall) and formation of trivalent carbocation intermediates which undergo deprotonation resulting in C=C bond formation [1]. The overall reaction is as follows:

$$C_5H_{10}O_5 \xrightarrow{H^+} C_5H_4O_2 + 3H_2O$$

Preliminary catalytic tests were performed in DMSO as the solvent since it dissolves both the organic (substrate) and inorganic (HPAs) substances used and, additionally, the HPAs tend to be more stable in organic solutions than in aqueous solutions [9]. Additionally, DMSO has a very low toxicity and is bio-degradable, leading to a low environmental impact. The reaction can therefore be assumed to be homogeneous, i.e. catalyzed by the heteropolyacids dissolved in the polar medium. A certain amount of water will always be present in the reaction media because it is formed as a by-product and is also present in the hydrated HPA. In a blank experiment carried out at 140 °C, xylose conversion takes place in the absence of a catalyst in DMSO (Table 1). However, the conversion after 4 h is only 34% compared with at least 94% in the presence of a HPA.

The turnover frequency (TOF) per unit weight of catalyst (calculated for a reaction time of 10 min) is the same for $H_3PW_{12}O_{40}$ (PW) and $H_4SiW_{12}O_{40}$ (SiW) (0.6 mmol $g_{cat}{}^{-1}$ min^{-1}), and higher for $H_3PMo_{12}O_{40}$ (PMo) (1.0 mmol $g_{cat}{}^{-1}$ min^{-1}). However, when TOF is expressed per proton [mmol (eq $H^+)^{-1}$ min^{-1}] a different trend is observed: SiW (439) < PW (595) ≈ PMo (608). The higher

Table 1
Catalytic performance of heteropoly acids in the dehydration of D-xylose[a]

Entry	Catalyst	Solvent	Conversion (%)[b]	Selectivity (%)[c]
1	None	DMSO	34	2
2	PTSA		100	67
3	H_2SO_4		100	58
4	PW		94 (100)	67 (59)
5	SiW		96 (100)	62 (52)
6	PMo		100 (100)	22 (27)
7	PW	Water	21 (44)	18 (68)
8	SiW		24 (47)	22 (63)
9	PMo		84 (97)	17 (39)
10	PW	IBMK/water	43 (83)	13 (4)
11	SiW		44 (89)	32 (57)
12	PMo		73 (98)	11 (9)
13	PW	Toluene/water	36 (77)	55 (68)
14	SiW		37 (80)	53 (67)
15	PMo		72 (98)	26 (35)

[a] Reaction conditions: 1 ml DMSO, 30 mg xylose, 20 mg HPA, 140 °C, 4 (24) h.
[b] Conversion of xylose.
[c] Selectivity to furfural.