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Microwave assisted efficient furfural production using nano-sized surface-sulfonated diamond powder

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ABSTRACT

Sulfonated nano-sized diamond powder (S-DP) was tested in a typical water-CPME (1:3, v/v) biphasic system and heated in a commercial monowave microwave oven to promote the dehydration of D-xylose into furfural as industrial platform molecule. This new heterogeneous catalyst with a propyl linker between the support and the sulfonyl group expressed remarkable sufficient hydrophilicity, affinity for D-xylose and catalytic activity in presence of NaCl. The solid can act as a strong acidic catalyst without detectable exchange between proton exclusively localized on the surface of the catalyst and sodium ion. It was also stable at 200 °C even after severe recycling treatment. The final optimized condition requires 10 wt% of the catalyst for a maximum furfural yield of 76% when the mixture is heated for 50 min in the current biphasicsystem.

Keywords: sulfonated diamond; furfural; microwave; biphasic system

1. Introduction

Furfural is a furanic compound obtained from dehydration of pentoses such as D-xylose and L-arabinose. Both pentoses are all monomers sub-units obtained from the hydrolysis of hemicellulose or xylan, or any biopolymers rich in xylose. Furfural is overall recognized as a top-value material source of fuel additives and usually it could become a key-compound for the production of furfuryl alcohol after reduction of its aldehyde function [1]. It is also known as the precursor of maleic acid through successive decarbonylation and ring opening oxidation [2]. Furfural is often employed as starting material for the catalytic transformation into organic solvents such as tetrahydromethylfuran (MeTHF) or tetrahydrofuran (THF) [3]. Under conventional heating, furfural is produced at temperature ranging from 170 to 180 °C, always in acidic conditions. Usually, strong mineral acids such as HCI [4, 5], H₂SO₄ [6] or H₃PO₄ [7] were put to good use to perform the dehydration of D-xylose in sole water.

However, industrially the distillation of this liquid product was necessary to isolate the material from the crude mixture with enough purity. In addition to the problems of corrosion, safety and handling, it seems difficult to avoid the associated large waste streams and the yield reduction caused by the formation of by-products derived from cross-polymerization between furfural and D-xylose, or from direct resinification of furfural itself, especially in a aqueous monophasic system. These reactions lead to the generation of insoluble carbonaceous black solid called humin. For preventing of all above reported concerns, conversion of D-xylose into furfural in a liquid biphasic system in a presence of NaCl or not with various acid catalysts has been reported [8,9]. Indeed, in a water-cyclopenthyl methyl ether (CPME) biphasic system with Nafion NR50 as commercial sulfonated perfluorinated resin [10], novel bio-based sulfonated sporopollenin [11] and a biobased sulfonated carbon-based material (ex Micanthus) [12] have successively demonstrated their potential for producing furfural under microwave heating at temperatures around 190 °C giving best furfural yields found between 60 and 70%. In order to have more economic variation in function of the price of the starting material, substitution of D-xylose to alginic acid extracted form a variety of microalgae has been described. In the presence of CuCl₂ as catalyst in a mixture of DMSO and γ -butyrolactone, furfural was obtained in competitive yield [13]. Whatever the starting material used, the presence of NaCl permitted to increase the productivity of furfural. NaCl induces a salt-out effect promoting the transfer of the furfural into the organic layer where the furanic compound was not subjected to degradation. When stored in a non water miscible organic layer, the furfural is not in contact with any acidic species, this kind of system is able to reduce the formation of all soluble and insoluble humin.

As a new catalyst, modified nanoscalled diamond powder by means of 1,3-propanesultone displays sulfonyl groups covalently bound on its surface (Fig. 1). This material was initially tested for production of ethylacetate from ethanol and acetic acid. It was also compared to Nafion NR50. Despite its lower surface acidity, it expressed good activity for esterification in atmospheric condition and conventional heating [14]. Besides in the literature, there are only a few examples of nanosized modified carbon based materials employed for the dehydration of D-xylose [15-17]. In this study,

sulfonated diamond powder (S-DP) with a propyl chain between the support and the sulfonic acid was tested for producing furfural starting from D-xylose in a typical water-CPME biphasic system under microwave heating by varying one by one the substrate to catalyst ratio, temperature, residence time, the salt-out effect and the xylose loading. Some attempts to regenerate the catalyst were also realized after one cycle.



Fig. 1. Schematic structure of the sulfonated diamond powder [14].

2. Experimental

2.1. Material and methods

Furfural (99% maximum) and D-xylose were purchased from Acros Organics. Cyclopentyl methyl ether was supplied by Sigma Aldrich. NaCl and other reagents were used without further purification. S-DP was synthesized by the procedure as reported in a previous paper [14]. A simple titration revealed that S-DP displayed 0.072 mmol g^{-1} of acid which is quite inferior to the value expressed by Nafion NR 50 which displays a capacity of 0.8 mmol of H⁺ g⁻¹. Besides, the Zeta-potential of a 0.0125 wt% S-DP aqueous dispersion was measured (result not shown here), and the value varied from - 35 to - 40 mV in a pH range from 3.5 to 11. This result confirmed the polarity of the S-DP surface. The water used in all experiments was a Millipore Milli-Q grade.

2.2. General procedure for the synthesis of furfural

In a typical experiment, 0.15 g (1.0 mmol) of D-xylose, 10 wt% of S-DP were introduced in a 10 mL vial closed with a septum, followed by addition of water or brine of different concentrations (1 mL) and CPME (3 mL). Biphasic batch reactions were carried out by way of microwave heating apparatus (Anton Paar Monowave 300) and stirred under magnetic stirring (600 rpm) for a desired period of time. The temperature in the reaction vessel was measured by means of an IR sensor and the vial was pressurized due to the normal vapor pressure of the solution at defined reaction temperature. At the end of the reaction, each sample was diluted with acetonitrile to obtain 100 mL of a diluted monophasic solution which was filtered prior HPLC analysis through a syringe filter (PTFE, 0.45 µm, VWR).

2.3. Product analysis

Each reaction sample was analyzed using a Shimadzu prominence HPLC. Unreacted D-xylose was detected with a low temperature evaporative light scattering detector (ELSD-LTII) and products were detected with a UV-vis detector (SPD-M20A) at a wavelength of 275 nm. The column used was a Grace C18 column (250 x 4.6 mm; 5 μ m). The mobile phase was MeOH-water (9:1, v/v) solution flowing at rate of 0.5 mL min⁻¹. The column oven was set at 40 °C. Regularly, the calibration curve was checked out in order to avoid eventual experimental errors associated with all measurements reported below.

D-Xylose conversion (X), furfural yield (Yi) and furfural selectivity (Yi) were calculated using the following equations :

 $X = \frac{(Initial xylose amount (mol) - Final xylose amount (mol))}{Initial xylose amount (mol)} x 100$ $Yi = \frac{Final \ furfural \ amount \ (mol)}{Initial \ xylose \ amount \ (mol)} x 100$ $Si = \frac{Furfural \ yield}{Conversion \ of xylose} x 100$

3. Results and discussion

3.1. Nature of the catalyst

Furfural has got a hydrophobic nature and could potentially expressed affinity to the surface of the catalyst when this one is hydrophobic such as Nafion NR50. This phenomenon could explain the degradation occurring during the process and the progressive deposit of humin on the surface reducing the accessibility of the sulfonyl groups for the D-xylose. S-DP has been chosen for this study for its hydrophilic nature compared with Nafion. S-DP displays carbonyl, hydroxyl and remaining epoxide groups proven by FT-IR spectra [14] which could prevent furfural adsorption.

3.2. Substrate to catalyst ratio for the production of furfural

The starting point of all experiments was taken from optimized conditions reported in our previous published papers [8-13]. In an aqueous biphasic system involving CPME as the extraction solvent, the best production of furfural was obtained in a H₂O-CPME (1:3, v/v) volume ratio, especially when the catalyst is a heterogeneous one [10,12]. By varying the catalyst loading from 10 to 40 wt% (Fig. 2) at 190 °C for 1 hour under microwave irradiation, the maximum of D-xylose conversion was observed in the presence of 30 wt% of catalyst. Interestingly, by using less amount of catalyst (20 wt%), a moderate furfural selectivity of 45% was obtained. However, if the catalyst content was multiplied by two, no real enhancement of the yield was observed and a decision was taken to save the catalyst (20 wt%) to produce furfural.



Fig. 2. Effect of catalyst loading on dehydration of D-xylose to furfural. Reaction conditions: D-xylose (150 mg), water (1 mL), CPME (3 mL), 190 °C, 60 min, MW.

3.3. Effect of reaction temperature and the amount of catalyst for the production of furfural

Impact of the temperature was measured in a range from 130 to 200 °C (Fig. 3). In our hands, higher temperature than 200 °C cannot be evaluated due to the detected overpressure generated in the microwave oven. For temperatures inferior to 170 °C, low conversion of D-xylose was observed. On the other hand, for all temperatures superior to 180 °C, the furfural yield started to increase until it reached a maximum value of 58% at 200 °C. The maximum of selectivity was observed at 180 °C but only half of xylose initial amount was consumed after one hour. At 200 °C, further reduction of the catalyst (10 wt% vs 20 wt%) gave surprisingly similar selectivity in furfural (58% vs 60%). In our conditions (200 °C, 60 min under microwave activation) dehydration of D-xylose did not require so much S-DP catalyst (10 wt%).



Fig. 3. Effect of reaction temperature on dehydration of D-xylose to furfural. Reaction conditions: D-xylose (150 mg), S-DP 20 wt%, water (1 mL), CPME (3 mL), 60 min, MW.

3.4. Effect of reaction time for the production of furfural

In the following step, it was important to determine the shorter residence time to get higher yield of furfural with the maximum of conversion. The previous conditions (D-xylose (150 mg), S-DP 10 wt%, water (1 mL), CPME (3 mL), 200 °C, MW) were applied with variation of the time of the reaction. Furfural yields increased with the reaction time till 50 min to obtain 54% yield and a selectivity of 60% (Fig. 4).





3.5. Salt-out effect of NaCl for the production of furfural

Early in the process, an excess of NaCl (1.5 mmol) was already added in an experiment involving 20 wt% of S-DP in presence of D-xylose (150 mg, 1 mmol). The resulted mixture was heated at 190 °C for 60 min and the furfural yield reached a value of 63% which is higher than that obtain without the presence of NaCl. In order to understand the mechanism of the reaction, a simple experience was carried out. After addition of the salt, the acid catalyst was filtered and pH of the recovered filtrate was unchanged. It was noteworthy that with Nafion NR50 in presence of an excess of NaCl, the resin pellets were able to release a great part of their protons in the reaction medium [10]. This result proved a clear difference between Nafion and sulfonated diamond powder.

Using the optimized conditions (D-xylose (150 mg), S-DP 10 wt%, water (1 mL), CPME (3 mL), 200 °C, 50 min, MW) with an added amount of NaCl (1.5 mmol), 85% conversion with 75% selectivity to furfural was observed. Then, the impact of NaCl concentration was also monitored (Fig. 5). Under 1.5 mM of NaCl, the furfural yield remained almost constant (60%). However, with higher NaCl concentration (2.0 mM), quantitative conversion and 76% yield were obtained with the current improved optimized conditions.



Fig. 5. Effect of salt-out study on dehydration of D-xylose to furfural. Reaction conditions: D-xylose (150 mg), S-DP 10 wt%, water (1 mL), CPME (3 mL), 200 °C, 50 min, MW.

3.6. Effect of xylose loading

Using the best furfural dehydration conditions without addition of NaCl, the catalytic activity of S-DP has been evaluated in samples of increasing concentration and viscosity (Table 1). In a viscous slurry (3 M), the furfural yields have fallen dramatically (40%) and a large amount of black insoluble humin was formed. This phenomenon could be connected to the growing difficulty for extracting the formed furfural by CPME when it was trapped in the sugar based slurry. Thus, furfural is obviously more easily subjected to the typical cross-polymerization with the neighbouring D-xylose molecules strongly adsorbed on the surface of S-DP. It should be interesting to notice that furfural yield was higher with diluted solution of D-xylose (66% vs 54%) even in absence of NaCl but the volumetric productivity was lower (0.037 mmol s⁻¹ L⁻¹ vs 0.045 mmol s⁻¹ L⁻¹). Even if the furfural yield decrease (from 54% to 34%) with the increase of the D-xylose concentration the volumetric productivity increase (from 0.045 mmol s⁻¹ L⁻¹ to 0.113 mmol s⁻¹ L⁻¹).

Entry	Xylose(M)	Yield (%)	Conversion (%)	Selectivity (%)	Productivity (mmol s ⁻¹ L ⁻¹)
1	0.7	66	100	66	0.037
2	1.0	54	86	63	0.045
3	2.0	50	80	62	0.083
4	3.0	40	72	56	0.100
5	4.0	34	56	60	0.113

 Table 1 Effect of D-xylose loading on dehydration of D-xylose to furfural.

^a Reaction conditions: D-xylose, S-DP 10 wt%, water (1 mL), CPME (3 mL), 200 °C, 50 min, MW.

3.7. Used catalyst treatment and recycling for reusability

After carried out the reaction, the sulfonated diamond powder as black insoluble material was recovered from the liquid by filtration. Then, the solid was immersed in aqueous hydrogen peroxide solution, recovered by filtration, washed with water and dried. The resulted brown powder was

washed further time with acetone to be finally exposed to a 10% HCl aqueous solution before being dried again. After this conventional treatment the resulted colored solid was re-injected in a fresh reaction medium and the reaction was performed in the optimized condition in presence of NaCl. Unfortunately after the first recycling a drop of the furfural yield (51%). Modification of both the sulfonated diamond powder or its treatment is in preparation.

3.8. Effect of the nature f the sulfonated catalysts for the furfural synthesis

Few sulfonated catalysts such as silica materials, carbonaceaous derivatives were reported in literature for the production of furfural. Unfortunately, in water silica materials as MCM-41-SO3H and SBA-15-SO3H lose their activity due to poisoning of acidic site during the process and their instability. In contrast, sulfonated carbonaceous materials have shown effective solid acid catalytic activities and stabilities for high temperature production of furfural in water. Most important, the sulfonated carbonaceous catalysts have the sulfonic acid function directly bonded onto the aromatic cores of the support. It is important to note that SDP is the first sulfonated carbonaceous catalyst having a propyl linker between the support and the SO₃H group used for the production of furfural. This linker with a propyl chain should added flexibility of the catalyst.

All things being equal, only reports concerning D-xylose as starting material and sulfonated graphene, graphene oxide, graphitic carbon nitride, biochar and biobased material as sulfonated carbonaceous materials have to be taken into account (Table 2). Except our excellent result obtained with sulfonated graphitic carbon nitride in term of yield, D-xylose loading and temperature, our new promising results clearly showed that SDP is a potent catalyst for the dehydration of biomass. Similar selectivities at same temperature (190-200°C) were obtained. Moreover, in our hands D-xylose loading was more than 3 times higher than this using graphene derivatives.

Entry	Xylose	Catalyst	Temperature	Time	Yield	Conversion	Selectivity	Ref
	(M)		(°C)	(min)	(%)	(%)	(%)	
1	0.20	Sulfonated	200	35	55	86	64	[17]
		graphene (2						
		wt%)						
2	0.20	Sulfonated	200	35	62	83	75	[17]
		graphene						
		oxide (2 wt%)						
3	1.00	Sulfonated	190	60	60	100	60	[12]
		biochar (10						
		wt%)						

Table	2	Recent	exemples	of	dehydration	of	D-xylose	to	furfural	in	water	using	sulfonated
carbon		00115 m2	torials		×								

4	3.0	Sulfonated	100	30	96	100	96	18
		graphitic						
		carbon						
		nitride (8						
		wt%)						
5	1.00	Sulfonated	190	40	69	100	69	[11]
		Sporopolenin						
		(10 wt%)						
6	0.70	Sulfonated	200	50	66	100	66	this
		Diamond						paper
		Powder (10						
		wt%)						

4. Conclusion

S-DP demonstrated strong acid capacity and stability to produce furanic dehydration products in good yields. The method used a mixture of S-DP and NaCl in a water-CPME biphasic system at 200 °C under microwave activation for 50 min. The association between S-DP and NaCl generated a synergetic effect in term of yield (76%). In relation to its hardness and its intrinsic hydrophilicity, it appeared us interesting to develop in the near future, a microwave or conventionally heated continuous flow system incorporating S-DP in a hard cartridge to produce rapidly solketal from glycerol or other furanic compounds of interest such as 5-hydroxymethyl furfural (HMF) or isosorbide.

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Highlights

- Microwave activation for the dehydration of xylose to furfural.
- Water-CPME as biphasic systems to limit the production of humin.
- Sulfonated Diamond Powder (S-DP) as efficient acid catalyst system for the synthesis of furfural.
- Use of waste from diamond industry
- The reusability of the catalyst was efficient.

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