



## Short communication

## Monolithic acidic catalysts for the dehydration of xylose into furfural



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## ABSTRACT

We report the application of hierarchically porous zirconium phosphate monoliths with high surface area as acidic heterogeneous catalysts for the dehydration of xylose into furfural. Analyses by  $\text{NH}_3$ -temperature programmed desorption and  $^{31}\text{P}$  solid state NMR reveal the presence of both Lewis and Brønsted acid sites in the as-synthesized zirconium phosphate monolith and that calcined at 600 °C. High accessibility and availability of the acidic sites and easy separation of the monolith from the liquid medium result in good catalytic activity (initial reaction rate for furfural production as  $8.7 \text{ mmol g}_{\text{cat}}^{-1} \text{ h}^{-1}$ ) with easy handling of the catalyst.

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## 1. Introduction

The reactivity and accessibility of active sites are two key factors for the efficiency of a reaction happening at a heterogeneous interface. The solution to the latter is to introduce a well-defined pore structure in heterogeneous catalysts, which not only ensures large interfacial area but also essentially minimizes the barrier from diffusion kinetics. Together with a satisfactory reactivity of the active sites, such materials with embedded optimized pore system commonly demonstrate catalytic behaviors as superior as those of homogeneous or enzymatic analogues. In this perspective, hierarchically porous monoliths may stand out from other material forms such as particles and thin films. The three-dimensionally interconnected macropores ( $d_{\text{pore}} > 50 \text{ nm}$  by IUPAC definition), typically in a few micrometer range, ensure efficient mass transfer over the whole substrate, especially when a pressure-driven flow is applied. Meanwhile, a network of mesopores ( $2 \text{ nm} < d_{\text{pore}} < 50 \text{ nm}$ ) and micropores ( $d_{\text{pore}} < 2 \text{ nm}$ ) veined in the continuous macropore skeletons provides high surface area as well as short diffusion paths to the catalytic sites [1–5]. Moreover, hierarchically porous monoliths can be easily applied to a continuous flow set-up, which has been proven as a good candidate to replace conventional fixed-bed reactors [6–8].

Zirconium phosphate (ZrP) as a well-known and studied acidic catalyst has been extensively applied for catalytic reactions, such as

dehydration [9–11], alkylation [12], acylation [13] and esterification [14] where acidic sites are required. The presence of both Lewis (exposed Zr sites) and Brønsted acidic sites ( $-\text{P}-\text{OH}$ ) in ZrP materials makes them highly adaptable to different reactions and reacting systems. However, the introduction of hierarchically porous structure into such ZrP materials is somehow difficult due to its low solubility in aqueous medium, which commonly leads to crystalline precipitates with low surface area. We have recently succeeded in the synthesis of hierarchically porous ZrP monolith via sol-gel process accompanied by phase separation starting from ionic precursors [15]. The micrometer-scale co-continuous macropores are formed as a result of phase separation (spinodal decomposition) during the sol-gel transition, while the nanometer-scale micro/mesopores derive from the interstitials between the constituent nanoparticles.

The catalytic properties of the obtained hierarchically porous ZrP monolith were studied adopting the dehydration of xylose into furfural as a model reaction. Furfural, its analogues (2-methyl furan, 2,5-dimethylfuran, 5-(ethoxymethyl)furfural, etc.) and derivatives (tetrahydrofuran, levulinic acid, 2,5-furandicarboxylic acid, maleic acid, etc.) have been envisaged as platform chemicals for biofuel, biochemical and biopolymer industries [16,17]. Due to the high activation barrier for the reaction to be catalyzed by the Brønsted acid, high operating temperature and long residence time are often required in order to obtain a high xylose conversion [18,19]. The combination of both Brønsted acid sites and Lewis acid sites in the ZrP monoliths successfully suppresses the energy barrier for the activation of the reaction, leading to higher furfural yield at relatively lower temperature [20,21].

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Furthermore the relatively slow kinetics allows the reaction to be conducted in a batch mode, making it easier to reveal more insights into the acidic nature of the obtained ZrP monolith.

## 2. Results and discussion

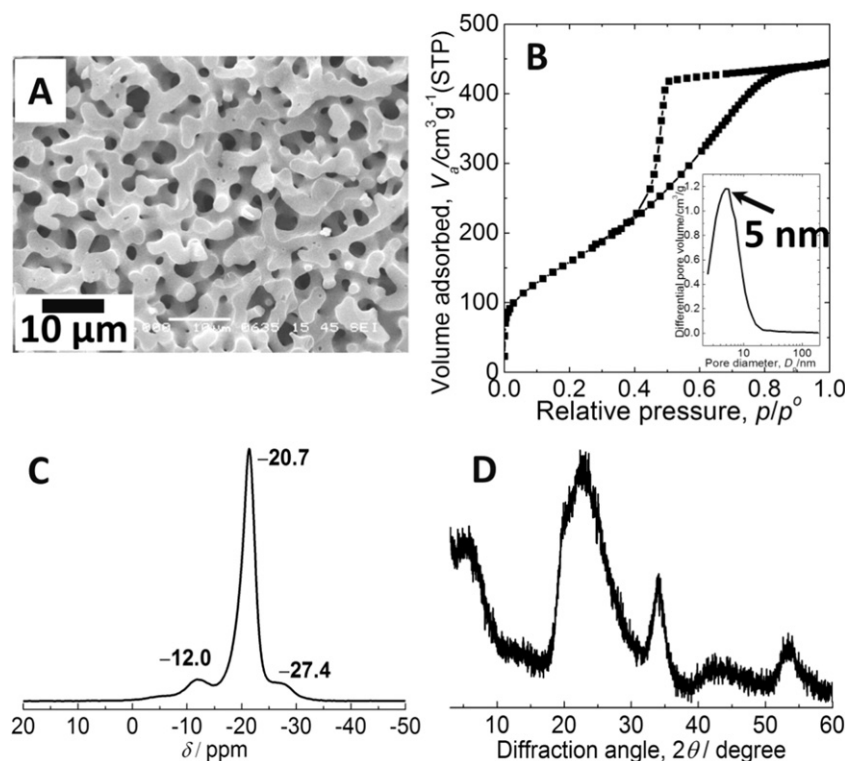
### 2.1. ZrP monolith synthesis

As reported previously [15], hierarchically porous ZrP monoliths can be obtained via sol-gel process accompanied by phase separation under the presence of polyethylene oxide (PEO) and polyacrylamide (PAAm) as the phase separation inducers. A preferential distribution of PAAm in the gel phase via strong coordination between amide groups and Zr stabilizes the as-formed nano colloids of ZrP from further growing into bulky entities. Meanwhile, a preferential distribution of PEO in the solvent phase increases the compatibility between the PAAm-containing gel phase and the PEO-containing solvent phase, leading to a controlled phase separation process. After removal of the solvent, a macroporous co-continuous structure, typical of the spinodal decomposition phase separation, is obtained (Fig. 1A). Beyond macropores, micro/mesopores, derived from the interstitials of the loosely packed ZrP nano colloids are also obtained, as shown by electron microscopies (Figs. S1 and S2). The presence of both micropores and mesopores is also supported by the  $N_2$  sorption isotherm shown in Fig. 1B. A BET surface area of  $600 \text{ m}^2 \text{ g}^{-1}$  can be determined together with a relatively sharp mesopore size distribution ranging from 2 nm to 7 nm with an average mesopore size of 5 nm and micro/mesopore volume as  $0.68 \text{ cm}^3 \text{ g}^{-1}$ .

Elemental analysis by EDS revealed a molar ratio between Zr and P of 1/2, in accordance with the molar ratio of both precursors added in the starting composition. Results of CHN elemental analyses confirm the presence of 7 wt% PAAm in the gel phase and ZrP is the dominant part of the gel. Results of  $^{31}\text{P}$  DDMA NMR show that phosphorous is mainly incorporated in the gel as  $\text{HPO}_4^{2-}$  ( $-20.7 \text{ ppm}$ ) with small amounts of  $\text{PO}_4^{3-}$  ( $-27.4 \text{ ppm}$ ) and  $\text{H}_2\text{PO}_4^-$  ( $-12.0 \text{ ppm}$ ) (Fig. 1C). The main composition of as-synthesized ZrP monolith is therefore  $\text{Zr}(\text{HPO}_4)_2$ , which is

compositionally in accordance with  $\alpha\text{-ZrP}$  ( $\text{Zr}(\text{HPO}_4)_2 \cdot \text{H}_2\text{O}$ ). XRD pattern further reveals the poorly crystalline nature of the monolith, which is commonly observed in ZrP materials synthesized at low temperature [22] (Fig. 1D). The broad diffraction peak indexed at around  $6^\circ$  indicates an expanded layered structure with the interlayer distance of 1.8 nm.

$\text{NH}_3$ -temperature programmed desorption (TPD) is commonly used for the determination of the surface acidity of heterogeneous acidic catalysts, due to the interaction between the acidic sites and ammonia molecules [23,24]. From the relationship between temperature and the desorption amount of adsorbed ammonia molecules, the relative amount of acidic sites can be detailed and their strength can be estimated. The constituent phase of the material should remain constant during the measurement at elevated temperatures in order to correctly measure the acidity of the material. Hence, due to the combustion of PAAm from the gel phase as well as the further dehydration of the ZrP network at elevated temperatures, the surface acidity of as-synthesized ZrP monolith cannot be measured with high enough accuracy. Instead, ZrP monolith calcined at  $600^\circ\text{C}$  was used for the  $\text{NH}_3$ -TPD measurement in order to obtain some information, though indirect, about the initial surface acidity of the as-synthesized ZrP monolith (Fig. 2). Significant desorption of ammonia starts from  $200^\circ\text{C}$  and completes at  $500^\circ\text{C}$ , during which a broad peak with a maximum rate of desorption at around  $300^\circ\text{C}$  together with a small shoulder at around  $400^\circ\text{C}$  is observed. The results indicate that the main acidic sites in the monolith are of medium strength ( $0.75 \text{ mmol g}^{-1}$ , desorbing ammonia from  $200^\circ\text{C}$  to  $400^\circ\text{C}$ ) together with the presence of a fraction of strong acidic sites ( $0.08 \text{ mmol g}^{-1}$ , desorbing ammonia from  $400^\circ\text{C}$  to  $500^\circ\text{C}$ ) [25]. The total amount of acidic sites ( $0.83 \text{ mmol g}^{-1}$ ) as well as the strength distribution is comparable with that of the well-known ZSM-5 zeolite ( $\text{Si/Al} = 15$ ,  $0.86 \text{ mmol g}^{-1}$  in total amount,  $0.09 \text{ mmol g}^{-1}$  as weak acidic sites ( $<200^\circ\text{C}$ ),  $0.68 \text{ mmol g}^{-1}$  as medium strong acidic sites ( $200\text{--}400^\circ\text{C}$ ) and  $0.09 \text{ mmol g}^{-1}$  as strong acidic sites ( $400\text{--}500^\circ\text{C}$ ), Fig. 2). According to the  $^{31}\text{P}$  DDMA NMR spectrum of ZrP monolith calcined at  $600^\circ\text{C}$  (Fig. S3), the main phosphorous species incorporated in



**Fig. 1.** (A) SEM image, (B)  $N_2$  adsorption-desorption isotherm (inset is the BJH pore size distribution obtained from the adsorption branch), (C)  $^{31}\text{P}$  DDMA NMR spectrum and (D) XRD pattern of the as-synthesized ZrP monolith.

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