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New zirconium hydrogen phosphate alkyl and/or aryl phosphonates with high surface area as heterogeneous Brønsted acid catalysts for aza-Diels–Alder reaction in aqueous medium

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A B S T R A C T

New zirconium hydrogen phosphate alkyl and/or aryl phosphonates of general formula $Zr(PO_3OH)_{2-(x+y)}(PO_3R)_x(PO_3R^1)_y$ have been prepared as amorphous solids. The presence of hydrophobic groups such as Me, Ph and Pr and their percentage have an important role in the definition of the corresponding solid structure. All the prepared solids are micro- and mesoporous and show an extraordinary surface area (200–380 m^2/g). The Brønsted acid catalytic activity of the solids was tested on the direct aza-Diels–Alder reaction of 2-cyclohexen-1-one with N-PMP-*p*Cl-benzaldimine in aqueous medium. The hydrophobic groups on the solid catalyst surface favor reagents' diffusion toward the acidic sites, aiding proton transfer to reagents, increasing the catalytic activity of the prepared solids compared with the layered α-zirconium hydrogen phosphate (α-ZrP).

1. Introduction

Heterogeneous catalysis on solid surfaces occurs at the active sites that promote a surface reaction by lowering the activation energy of a specific reaction pathway. Therefore, the surface structure (size, shape, composition and functionalities) exert a crucial influence on the activity and selectivity of heterogeneous catalyst [1].

Hydrophobic effects play a key role in several chemical phenomena in aqueous medium, while in heterogeneous catalysis, this parameter is not clearly defined [2]. It is well established that highly siliceous materials show a marked hydrophobicity on their surface and highly containing silica zeolites are expected to be very active as solid acid catalysts in aqueous solution [3]. The increase in Si/Al ratio in zeolite's framework leads not only to stronger hydrophobic interactions between organic substrates and zeolite's siliceous surface but also to a corresponding increase in the activity of the acidic sites [3b]. The more hydrophobic is the catalyst, the more active is the catalytic site and the stronger is the adsorption of the substrate.

In the last decade, solid acid catalysts such as zeolites, oxides, mixed oxides and heteropolyacids have received much attention for petroleum industry processes and for fine chemicals production since they are environmentally friendly with respect to corrosiveness, safety, waste minimization and ease of separation and recovery [4].

Development of processes in water is also desirable for environmental, economical and safety reasons. On the other hand, water may cause the severe poisoning of the acidic sites of solid catalysts that generally lose their catalytic activities in aqueous medium [4b]. The use of solid acid catalysts based on hydrophobic surfaces is preferable for conducting organic reaction in water.

In the last thirty years, an emerging class of inorganic–organic insoluble phosphates and phosphonates of tetravalent metals (mainly Zr^{IV}) with layered or pillared structure have attracted the attention of researchers because of their physical–chemical properties and high versatility [5]. The layered inorganic backbone may be considered as a hook onto which organic groups with different functionality (acidic, basic, polar, hydrophobic) may be attached, allowing for the control of both reactivity and selectivity of the organic process [5,6]. These materials can be easily prepared by a self-assembly approach, and since they are insoluble in water and organic solvents they are easy to be recovered and reused [5–7].

The layered α-zirconium hydrogen phosphate $\alpha\text{-}Zr(HPO_4)_2{\cdot}H_2O$, (α-ZrP), is a weak acid solid compound (p*K*a 2.0–3.0) with regularly spaced P–OH groups; it has a relatively small surface area of 2–10 m^2/g, is not considered to be porous and it does not possess a hydrophobic surface [4b,5a,5d].

Recently, we have been involved in the development of novel solid catalysts to be used in benign reaction media for the

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definition of environmentally efficient organic processes [6b,6c,8]. We have shown that at room temperature α-ZrP effectively catalyzes (yields 70–84%) the direct aza-Diels–Alder reaction between 2-cyclohexen-1-one and benzaldimines in water only in the presence of 0.4 equiv. of sodium dodecyl sulfate (SDS) [6b]. The role of SDS has not been proven, but we hypothesized that in aqueous medium SDS favors, most likely through Na^+/H^+ surface exchange [9], the proton transfer from the P–OH groups of the heterogeneous α-ZrP to the reagents. Both the solid catalyst (α-ZrP) and the aqueous mother liquor in toto (water, α-ZrP and SDS) were recovered and reused for several cycles without loss of activity [6b]. Also, a porous zirconium hydrogen phosphate (p-ZrP) with a larger surface area (83 m^2/g) and a mesoporosity (mesopore volume 0.17 cm^3/g) was prepared by template method [10] in order to compare its catalytic effectiveness to that of α-ZrP in the aza-Diels–Alder reaction of Danishefsky's Diene with benzaldimines [6c]. It has been proven that p-ZrP was more effective than the crystalline analogous α-ZrP both in water and under solvent-free condition, but also in this case the presence of SDS is essential for increasing the reactivity and the selectivity of the process. The recycling of p-ZrP and of the entire p-ZrP/SDS catalytic system gave very satisfactory results [6c].

The aza-Diels–Alder reaction is one of the most powerful synthetic methods in organic chemistry for the synthesis of nitrogen-containing heterocyclic compounds, including pyridines, quinolines, isoquinolines and azabicycloalkane, which are precursors of important biologic compounds such as alkaloids, peptides and aza-sugars [11]. On the other hand, it is known that water as reaction medium plays an important role in the development of new synthetic processes both by improving the chemical efficiency and by reducing the environmental impact [12].

In this paper, we have planned to develop new zirconium hydrogen phosphates with hydrophobic surface, in order to steer the reagents to the catalytic sites of catalyst's surface and avoid the use of SDS. We have therefore decided to prepare several zirconium hydrogen phosphates by inserting different hydrophobic R groups (R = methyl, propyl, phenyl) to modulate the hydrophobicity of the corresponding catalyst's surface. In this paper, we report the preparation of these novel catalysts and the results obtained by testing their catalytic activity in the direct aza-Diels–Alder reaction in water of 2-cyclohexen-1-one **1** with N-PMP-*p*-chloro-benzaldimine **2**, an effective route to isoquinuclidines **3** and **4** (azabicyclo[2.2.2]octanes) [13] that are the structural elements of numerous naturally occurring alkaloids with interesting biologic properties [14].

2. Experimental section

2.1. General remarks

All chemicals were purchased and used without any further purification. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded at 400 MHz, 100.6 and 161.9 MHz, respectively. IR spectra were recorded with a FT-IR instrument. TG and DTA analysis were performed by STA 449 C Jupiter (thermal analyzer). Molar ratio P/Zr^{IV} by elementary analysis by Inductively Coupled Plasma-Optical Emission Spectrometers (ICP-OES). Nitrogen adsorption–desorption isotherms [15] were determined with a Micromeritics ASAP 2010 instrument at 77 K on samples outgassed overnight at 373 K. The specific surface area was calculated by B.E.T. method [16]. Micropore volume and external surface area were evaluated by *t*-plot [17] method using non-porous α-ZrP as reference material [18]. Mesopore characterization has been performed by Barrett et al.'s method [19]. The evaluation of surface acid strength (H_0) has been obtained according to the Benesi methods [20]. The color test was made by adding a few drops of benzene solution of chosen indicator (Methyl Yellow, p*K*a = 3.3; Thymol Blue, p*K*a = 1.7; Crystal violet, p*K*a = 0.8) to a dispersion of about 50 mg of dried (150 °C for 24 h) powdered solid acid catalyst in 3 ml of dry benzene and observing the color of adsorbed indicator [20]. Centrifugation was performed at 12,000 rpm for 15 min. Thin-Layered Chromatography analysis was performed on silica gel on aluminum plates (Silica gel 60 F_{254}, Fluka). Column chromatographies to purify the aza-Diels–Alder adducts **3** and **4** were performed by using silica gel 230–400 mesh (Silica gel 60, Merk) eluting with petroleum ether/ethyl acetate 80:20; we isolated the Mannich adducts as mixture (**5**:**6** = 46:54) proceeding with two chromatographic separations eluting with petroleum ether/ethyl acetate 70:30 in the first and with dichloromethane/ethyl acetate 95/5 in the second. The Mannich adducts *syn* **5** and *anti* **6** are thermal instable, and warming at $T > 70$ °C, they were converted to the aza-Diels–Alder adducts *endo* **3** and *exo* **4**.

2.2. General procedure for preparation of zirconium phosphates

2.2.1. Amorphous solid (***a***,***c***,***d***,***f***-***j*** and a-ZrP)

A $ZrOCl_2$ aqueous solution (2 mmol in 4 mL of water) was slowly added, under stirring, at r.t. to an aqueous solution of phosphoric acid and alkyl and/or aryl phosphonic acids (6 mmol in 18 mL of water). The molar ratio between phosphoric acid and phosphonic acid used during the preparation is reported in Table 2. The preparation conditions were as follows: molar ratio $P/Zr^{IV} = 3$, precipitation temperature 25 °C, precipitation time 3 h. The obtained solid was separated from aqueous medium by centrifugation, washed with water (4 × 100 mL) and finally dried at 80 °C for 24 h.

2.2.2. Crystalline solid α-$Zr(PO_3OH)_{0.88}(PO_3Me)_{1.12}\cdot H_2O$ (***b***)

A $ZrOCl_2$ (2 mmol in 0.5 mL of water) and HF aqueous solution (4.15 mL, 2.89 M) was added, under stirring, to a 1:1 aqueous solution of phosphoric acid and methanphosphonic acid (6 mmol in 18 mL of water). The preparation conditions were as follows: molar ratio $HF/Zr^{IV} = 6$, molar ratio $P/Zr^{IV} = 3$, precipitation temperature 60 °C, precipitation time 24 h, in a closed vessel. The obtained crystalline solid was separated from aqueous medium by centrifugation, washed with water (4 × 100 mL) and finally dried at 80 °C for 24 h.

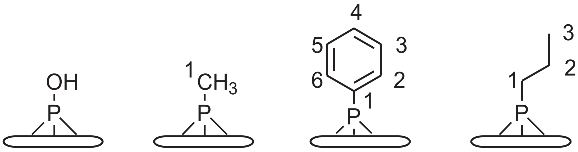
2.2.3. Crystalline solid α-$Zr(PO_3OH)_{0.96}(PO_3Ph)_{1.04}\cdot 0.8H_2O$ (***e***)

An aqueous solution of $ZrOCl_2$ (10 mmol in 23.08 mL of water) and conc. HF (6.92 mL, 28.9 M) was added, under stirring, to an aqueous solution of phosphoric acid (0.5928 mol) and phenylphosphonic acid (0.0072 mol) in 70 mL of water ($PhPO_3H_2$ molar fraction = 0.012). The preparation conditions were as follows: total phosphorus in solution = 6 M, molar ratio $HF/Zr^{IV} = 20$, molar ratio $P/Zr^{IV} = 60$, precipitation temperature 80 °C, precipitation time 40 h, in a open vessel maintaining the volume constant. The obtained crystalline solid was separated from aqueous medium by centrifugation, washed with water (4 × 100 mL) and finally dried at 80 °C for 24 h.

2.2.4. Porous Zirconium Hydrogen Phosphate (p-ZrP)

p-ZrP was prepared by the template method as described in Ref [10]. Briefly, sodium bis(2-ethylhexyl)sulfosuccinate (AOT) (0.2 g, 0.45 mmol) was mixed with 100 mL of deionized water and stirred until all the surfactant was dissolved. Zirconyl chloride octahydrate (1.28 mmol) and phosphoric acid (5.12 mmol) were added to the solution and stirred for 16 h ([P] = 0.05 M, [Zr] = 0.0125 M, P/Zr = 4). The white gel product was separated from aqueous medium by centrifugation, washed with water (3 × 100 mL) and

Table 1
^1H NMR, ^{13}C NMR and ^{31}P NMR spectral data of solids **a**–**j**.[a]



	^1H NMR				^{13}C NMR				^{31}P NMR
	H	Molt.	δ (ppm)	J (Hz)	C	Molt.	δ (ppm)	J (Hz)	δ (ppm)
P–OH	–	–	–	–	–	–	–	–	0.0
P–Me	H_1	d	1.15	17.4	C_1	d	11.2	134.4	30.8
P–Ph	H_3, H_5	m	7.19	–	C_3, C_5	d	128.3	15.0	17.4
	H_4	t	7.27	7.4	C_2, C_6	d	130.1	10.6	
	H_2, H_6	dd	7.43	13.6, 8.0	C_4	d	132.1	2.9	
					C_1	d	129.8	183.8	
P–Pr	H_1	m	1.32	–	C_1	d	27.8	133.5	32.8
	H_2	m	1.13	–	C_2	d	15.5	5.0	
	H_3	m	0.54	–	C_3	d	14.2	17.1	

[a] Recorded in D_2O/HF solution.

ethanol (3 × 100 mL) to remove the surfactant and finally dried under vacuum at 60 °C for 24 h.

Table 1 shows the ^1H NMR, ^{13}C NMR and ^{31}P NMR spectral data of solids.

2.3. General procedure for aza-Diels–Alder reaction

N-PMP-*p*Cl-benzaldimine **2** (0.125 mmol), catalyst (0.0375 mmol of P–OH groups, 30 mol%) and H_2O (0.150 mL) were put in a 2-mL vial. After stirring for 10 min at r.t., cyclohexenone (**1**) (0.625 mmol, 5 equiv.) was added and the mixture stirred at 50 °C for 24 h. The reaction mixture was extracted with ethyl acetate (3 × 2 mL). The organic phase was separated from the aqueous medium by centrifugation, and the combined organic layers were dried (Na_2SO_4) and evaporated under reduced pressure. The crude products were purified by column chromatographies (see Section 2.1).

2.3.1. Rel (1S,3R,4S)-3-(4′-Chlorophenyl)-2-(4″-methoxyphenyl)-2-azabicyclo[2.2.2]octan-5-one (endo **3**)[6b]

White crystals; m.p. 170–172 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.75 (m, 1 H), 2.0 (m, 1 H), 2.14 (m, 1 H), 2.26 (m, 1 H), 2.48 (dd, *J* = 18.8, 2.4 Hz, 1 H), 2.71 (dd, *J* = 5.6, 2.7 Hz, 1 H), 2.75 (dt, *J* = 18.8, 3.1 Hz, 1 H), 3.73 (s, 3 H), 4.43 (m, 1 H), 4.56 (d, *J* = 2.3 Hz, 1 H), 6.61 (m, 2 H), 6.78 (m, 2 H), 7.27 (m, 4 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 22.25, 22.46, 46.06, 49.51, 52.09, 55.59, 65.51, 114.71 (2C), 114.73 (2C), 127.12 (2 C), 129.07 (2C), 133.12, 140.74, 142.08, 152.27, 211.50 ppm. IR ($CHCl_3$): ν = 1731.3, 1510.6, 1252.6, 1040.1, 817.1 cm^{-1}. MS *m/e* (rel.int.): 77 (9), 115 (13), 117 (4), 134 (22), 149 (36), 165 (23), 188 (31), 202 (9), 230 (29), 245 (14), 247 (5), 298 (17), 300 (8), 341 (M, 100), 343 (M + 2, 35).

2.3.2. Rel (1S,3S,4S)-3-(4′-Chlorophenyl)-2-(4″-methoxyphenyl)-2-azabicyclo[2.2.2]octan-5-one (exo **4**)[6b]

Pale yellow crystals; m.p. 60–62 °C (*n*-hexane/ethyl acetate). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.63–1.76 (m, 2 H), 1.90 (m, 1 H), 2.24 (m, 1 H), 2.39 (dd, *J* = 18.8, 1.8 Hz, 1 H), 2.63 (dd, *J* = 5.8, 2.8 Hz, 1 H), 2.76 (dt, *J* = 18.8, 3.0 Hz, 1 H), 3.72 (s, 3 H), 4.43 (m, 1 H), 4.68 (d, *J* = 2.4 Hz, 1 H), 6.54 (m, 2 H), 6.76 (m, 2 H), 7.37 (m, 4 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 16.23, 26.29, 41.88, 48.95, 50.84, 55.63, 62.08, 114.35 (2C), 114.87 (2C), 127.66 (2C), 128.98 (2C), 133.07, 139.02, 142.32, 152.21, 213.40 ppm. IR ($CHCl_3$): ν = 1725.7, 1511.0, 1246.6, 1040.1, 817.4 cm^{-1}. MS *m/e* (rel.int.): 77 (11), 115 (15), 117 (5), 134 (28), 149 (22), 165 (7), 188 (29), 202 (6), 230 (25), 245 (13), 247 (6), 298 (64), 300 (26), 341 (M, 100), 343 (M + 2, 35).

2.3.3. Syn and anti 6-{(4′-chlorophenyl)[(4”-methoxyphenyl)amino]methyl}cyclohex-2-en-1-one (mix. **5**:**6** = 46:54)

^1H NMR (400 MHz, $CDCl_3$): δ = 1.82–2.00 (m, 4 H), 2.24–2.40 (m, 2 H), 2.50 (db, *J* = 16.7, 2 H), 2.83 (m, 1 H), 2.93 (m, 1 H), 3.69 (s, 6 H), 4.30 (d, *J* = 6.4 Hz, 1 H, CHNH *anti*), 4.44 (d, *J* = 5.8 Hz, 1 H, CHNH *syn*), 6.08 (td, *J* = 10.4, 2.6 Hz, 2 H), 6.47 (m, 4 H), 6.69 (m, 4 H), 6.86 (d broad, *J* = 10.8 Hz, 1 H); 7.03 (d broad, *J* = 10.2 Hz, 1 H); 7.29 (m, 8 H) ppm. ^{13}C NMR (100.6 MHz, $CDCl_3$): δ = 24.2, 26.89 (C5); 36.9, 37.0 (C4); 42.9, 43.3 (C6); 55.6 (OMe); 61.6 (CH–NH); 114.7, 114.8 (C3″, C5″); 115.0, 115.4 (C2″, C6″); 128.1, 128.3 (C3′, C5′); 128.89, 128.94 (C2′, C6′); 131.0, 131.2 (C2); 133.2, 139.5, 140.2 (C1′, C4′, C1″); 149.70, 151.0 (C3); 152.6 (C4″); 198.9, 199.0 (C=O) ppm. IR ($CHCl_3$): ν = 1677.3, 1512.8, 1244.9, 1037.7, 821.8 cm^{-1}. MS *m/e* (rel.int.): 77 (5), 107 (3), 122 (3), 134 (7), 167 (6), 202 (7), 230 (15), 232 (6), 246 (100), 248 (54), 341 (M, 3), 343 (M + 2, 1).

3. Results and discussion

3.1. Catalysts preparation and characterization

The first examples of Zr(IV) organophosphonates and Zr(IV) organophosphates with general formula $Zr(RPO_3)_2$ or $Zr(ROPO_3)_2$, respectively, were prepared (R being an organic group) in 1978 [21]. Nowadays, a large number of metal(IV) phosphonates are known and many other can be prepared for special purposes as they constitute a very large and versatile class of layered materials [22].

The preparation of zirconium phosphate and phosphonates is closely related to the methods employed for the preparation of α-$Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP), i.e. refluxing the amorphous precipitates in phosphoric or phosphonic acid solutions, or by precipitation of an aqueous solution containing the suitable phosphoric or phosphonic acids with $ZrOCl_2$ in the presence of hydrofluoridric acid. These organic–inorganic materials have a layered structure similar to that of α-ZrP. Amorphous materials can be obtained by direct precipitation in the absence of hydrofluoridric acid. It is possible to vary the acid properties of the phosphates from neutral (e.g. P–CH_3) or weak acid (e.g. P–CH_2COOH) to strong acid (e.g. P–$C_6H_4SO_3H$) or even to basic (e.g. P–$C_2H_4NH_2$), or to anchor an optically active amino acid [6a,23]. The only limitation to the synthesis is the use of organic groups with a cross-section equal or less than 24 $Å^2$. This is the free area around each phosphorous atom on the surface of the layers. However, more voluminous groups may be attached to the α-layers if their dimensions are compensated by introducing a small group R^1 (R^1 being H, OH, CH_3) to obtain bifunctional compounds of formula $Zr(PO_3R)_{2-x}(PO_3R^1)_x$ [5b,24].

In this paper, several zirconium hydrogen phosphates alkyl and/or aryl phosphonates of general formula $Zr(PO_3OH)_{2-(x+y)}(PO_3R)_x(PO_3R^1)_y$ have been prepared as amorphous and crystalline solids. Fig. 1 shows the general structure of a layer of functionalized zirconium hydrogen phosphates. We prepared the amorphous zirconium phosphates/phosphonates by direct precipitation adding $ZrOCl_2$ to the aqueous solutions of phosphonic and phosphoric acids ($P/Zr^{IV} = 3$). The crystalline zirconium phosphates/phosphonates have been prepared through the slow decomposition of the zirconium fluorocomplexes by slow evaporation of the HF at 80 °C in open vessel or at 60 °C in closed vessel [5,24]. The solids obtained were washed with water and dried at 80 °C for 24 h. They were characterized by ^1H NMR, ^{13}C NMR and ^{31}P NMR, TG, DTA, X-rays, by nitrogen adsorption–desorption isotherms at 77 K and by surface acid strength measurement (H_0).

The X-ray of the solids **a**, **c**, **d**, **f**–**j**, prepared by direct precipitation, showed the amorphous nature of the materials (data not shown). The X-ray of the solids **b** and **e**, prepared by HF methods, showed a layered crystalline structure with an interlayer distance of 8.56 Å, typical of a $Zr(PO_3OH)_{2-x}(PO_3Me)_x$ phase, and 24.2 Å typical of a crystal arise from the packing of alternate layer with different interlayer distance, one richer in phosphate (PO_3OH) the other in phosfonate (PO_3Ph), respectively [24]. The P/Zr and P–OH/P–R molar ratios were obtained by P, Zr elemental analysis, performed by ICP, and by ^{31}P NMR, respectively. These data allow to discuss the thermogravimetric (TG) and differential thermal analysis (DTA) curves. As a representative example, the TG-DTA curves of catalyst **j** is reported in Fig. 2. Thermal decomposition occurs in two steps: the first, between 50 and 200 °C, corresponds to the loss of 3.5% of the initial weight and is due to the water of crystallization, the second, between 200 and 900 °C, corresponds to the loss of 22.4% of the initial weight and is due to the oxidation of the organic groups. At 900 °C, the formation of cubic ZrP_2O_7 is considered, as shown by the XRPD spectrum of a sample heated at 900 °C (data not shown). The total weight loss amounts to 26%, which is in good agreement with those calculated (25%).

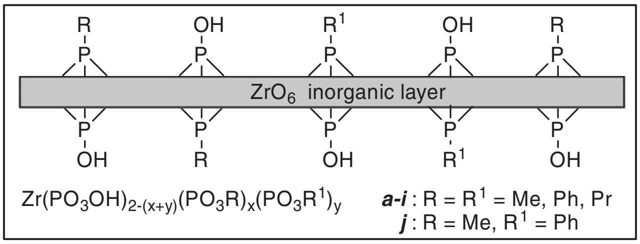


Fig. 1. Schematic arrangement of phosphate and phosphonate groups on a layer of functionalized zirconium hydrogen phosphates.

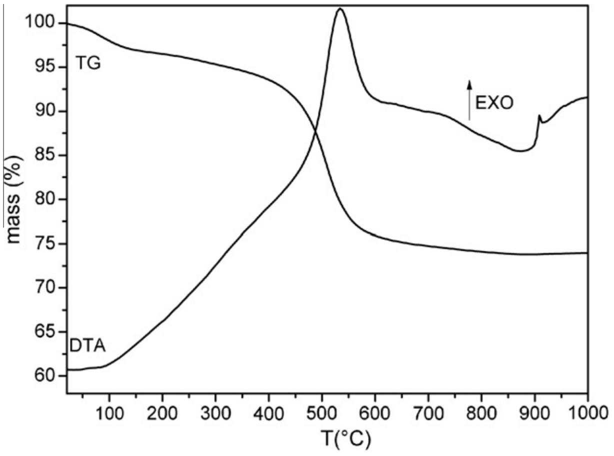


Fig. 2. Thermogravimetric (TG) and differential thermal analysis (DTA) curves of catalyst **j** obtained at a heating rate of 10 °C/min under air atmosphere.

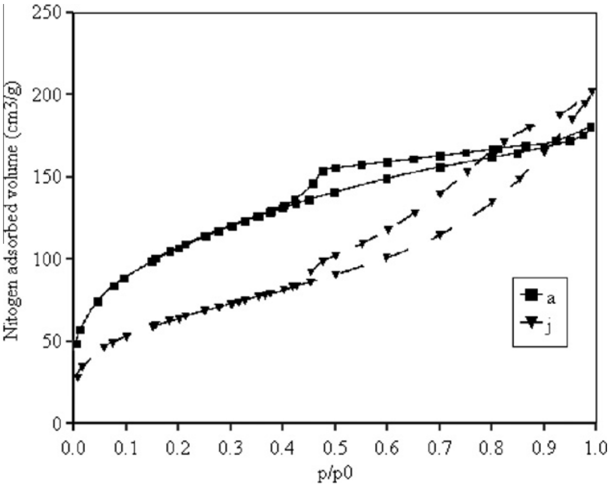


Fig. 3. Nitrogen adsorption–desorption isotherm plots obtained with catalysts **a** and **j**.

Fig. 3 reports, as representative examples, two nitrogen adsorption–desorption isotherm plots [15], performed at 77 K, obtained with catalysts **a** and **j**. Type IV nitrogen adsorption–desorption isotherms [25] were obtained. The hysteresis loops between desorption and adsorption curve indicate that capillary condensation occurs and, thus, mesopores are present in the catalysts. The shapes of hysteresis loops can be classified as intermediate between H_2 and H_4 type [25], which often associated with 'ink bottle' pores or with slit-shaped pores, respectively.

Attempts have been made to estimate the surface acid strength of the solids **a**, **d**, **i**, **j**, a-ZrP and α-ZrP as comparison, quantitatively expressed by H_0 function, by the indicator methods [20] as described in Section 2.1. It has been found that methyl yellow ($pKa = 3.3$) and thymol blue ($pKa = 1.7$), adsorbed on the surface of the solids, assume the color of the acid form, while crystal violet ($pKa = 0.8$) assumes the color of basic form. These observations led to conclude that all the prepared solids possess an acid strength comparable with that of α-ZrP and with H_0 values in the 0.8–1.7 range. The sole difference observed is the rate of absorption of the indicators on the surface of solids: much faster for the newly prepared solids **a**, **d**, **i**, **j**, than the solids a-ZrP and α-ZrP, due to the increased hydrophobicity of the solids surface.

In Table 2 are listed, for all the catalysts, the molar ratio between phosphoric acid and phosphonic acid used during the preparation, the P–OH/P–R molar ratio in the solid with the molecular formula and molecular weight, the calculated B.E.T.-specific surface area [16], the micropore volume calculated by *t*-plot [17] analysis using non-porous α-ZrP as reference material [18], and mesopore volume calculated by B.J.H. analysis [19].

Table 2 reports also the data about amorphous and porous zirconium hydrogen phosphates (a-ZrP and p-ZrP) in comparison with the newly prepared functionalized phosphates (solids **a**–**j**).

Table 2
Chemical and surface properties of prepared solids **a**–**j** and of porous (p-ZrP) and amorphous (a-ZrP) for comparison.

Solid[a]	R	P–OH/P–R solution molar ratio	P–OH/P–R solid molar ratio	Molecular formula	MW uma	B.E.T. surface area (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
a	Me	1/1	1/1.4	$Zr(PO_3OH)_{0.82}(PO_3Me)_{1.18}\cdot 0.7H_2O$	293.4	382	0.20	0.17
b[b]	Me	1/1	1/1.3	$Zr(PO_3OH)_{0.88}(PO_3Me)_{1.12}\cdot H_2O$	299.0	15	<0.01	0.01
c	Ph	1/0.5	1/0.8	$Zr(PO_3OH)_{1.10}(PO_3Ph)_{0.90}\cdot 1.3H_2O$	360.6	100	0.05	0.03
d	Ph	1/1	1/1.8	$Zr(PO_3OH)_{0.72}(PO_3Ph)_{1.28}\cdot H_2O$	378.0	205	0.06	0.15
e[b]	Ph	1/0.01	1/1.1	$Zr(PO_3OH)_{0.96}(PO_3Ph)_{1.04}\cdot 0.8H_2O$	360.0	9	<0.01	0.02
f	Pr	1/0.3	1/0.4	$Zr(PO_3OH)_{1.39}(PO_3nPr)_{0.61}\cdot 1.4H_2O$	324.3	23	0.01	<0.01
g	Pr	1/0.7	1/0.9	$Zr(PO_3OH)_{1.04}(PO_3nPr)_{0.96}\cdot H_2O$	326.2	210	0.11	0.06
h	Pr	1/1	1/1.6	$Zr(PO_3OH)_{0.77}(PO_3nPr)_{1.23}\cdot H_2O$	333.2	236	0.14	0.13
i	Pr	1/1.7	1/2	$Zr(PO_3OH)_{0.66}(PO_3nPr)_{1.34}\cdot 0.6H_2O$	328.8	216	0.12	0.13
j	Me, Ph	1/1/1	1/1.7/2.6	$Zr(PO_3OH)_{0.37}(PO_3Me)_{0.65}(PO_3Ph)_{0.98}\cdot 0.7H_2O$	353.3	238	0.05	0.30
a-ZrP	–	–	–	$Zr(PO_3OH)_2\cdot H_2O$	301.2	6	<0.01	<0.01
p-ZrP[c]	–	–	–	$Zr(PO_3OH)_2\cdot H_2O$	301.2	83	–	0.17

[a] Amorphous solid prepared by direct precipitation from an aqueous mixture of phosphoric acid and alkyl and/or aryl phosphonic acid with $ZrOCl_2$ under magnetic stirring at r.t.

[b] Crystalline solid prepared by HF method.

[c] Prepared by template method [10].

From the data in Table 2, it can be observed that the texture properties of the solids prepared are related both to the method of preparation (amorphous precipitation or HF methods) and to the replacement of a certain amount of hydrophilic phosphate groups with hydrophobic phosphonate groups. In any case, the presence of hydrophobic groups and their percentage have a very important role on solid surface texture.

As expected, the crystalline solids **b** and **e** present a relatively low B.E.T surface area (15 and 9 m^2/g, respectively) and low or negligible micro- and mesopore volume. Taking into account the amorphous samples listed in Table 2, it can be observed that by replacing the phosphate groups with hydrophobic phosphonate groups to reach a phosphate/phosphonate molar ratio equal or smaller than 1/1, the measured B.E.T. surface area is higher than 200 m^2/g, the micropore volume is higher than 0.05 cm^3/g and the mesopore volume is higher than 0.06 cm^3/g.

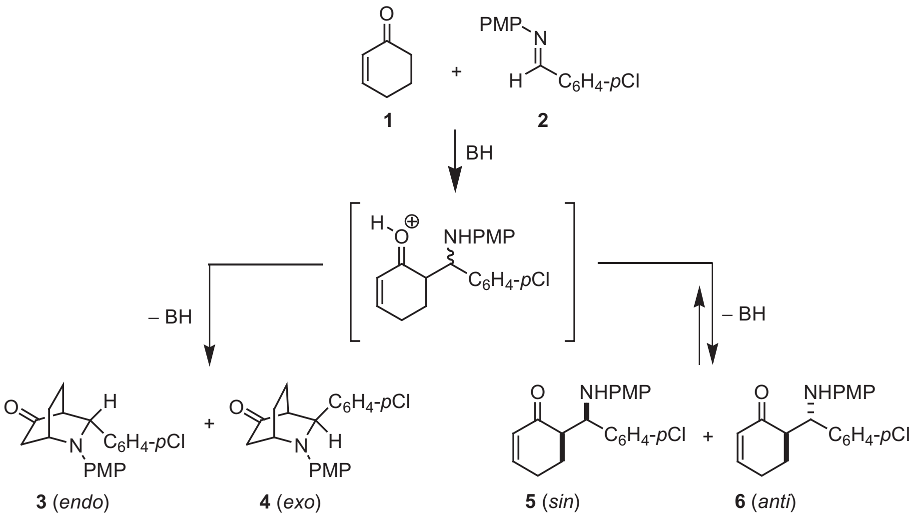
When R is a phenyl group, the B.E.T.-specific surface area increases with the percentage of phenyl groups (solid **c** P–OH/P–Ph = 1/0.8, solid **d** P–OH/P–Ph = 1/1.8) from 100 m^2/g to 205 m^2/g. The same trend is more evident when R is a propyl group (solids **f**–**i**): the B.E.T.-specific surface area, which is low when the percentage of P–Pr is small (solid **f**, P–OH/P–Pr = 1/0.4, 23 m^2/g), greatly increases to 210–236 m^2/g in the solids **g**–**i** where the amount of P–Pr is larger (P–OH/P–Pr = 1/0.9, 1/1.6, 1/2). A similar trend is observed for the mesoporous volume that increases with the percentage of propyl group from <0.01 cm^3/g for solid **f** to 0.13 cm^3/g for solids **h** and **i**.

A mixed acidic solid **j**, which contains phosphate, phenylphosphonate and methylphosphonate groups, has been prepared as amorphous. It has been characterized and showed a high B.E.T. surface area (238 m^2/g) and also a high external surface area (144 m^2/g) together with high micro- and mesopore volume.

These observations about the effect of hydrophobic groups are confirmed by surface properties of amorphous zirconium hydrogen phosphate (a-ZrP) that contains only P–OH groups: its B.E.T.-specific surface area is low (6 m^2/g) and similar to that reported in literature for layered α-zirconium hydrogen phosphate (<5 m^2/g) [5a], and it is characterized by negligible micro- and mesopore volume. The surface areas of the new prepared amorphous solids are very high (100–382 m^2/g), and this interesting result opens important ways for their future applications.

3.2. Catalytic activity

With the aim of understanding the hydrophobicity surface effect on catalytic activity of solids Brønsted acids catalysts **a**–**j**, we studied the direct aza-Diels–Alder reaction of 2-cyclohexen-1-one (**1**) with N-PMP-*p*-chloro-benzaldimine (**2**) in water and in absence



Scheme 1. Direct Brønsted acid catalyzed aza-Diels–Alder reaction of cyclohexenone **1** with N-PMP-*p*-chloro-benzaldimines **2**.

of any additive (Scheme 1). As reported in our previous work [6b], in acidic conditions cyclohexenone (**1**) is enolized and undergoes a Mannich reaction with the protonated aldimine, followed by an intramolecular aza-Michael reaction to give the *endo* and *exo* isoquinuclidines **3** and **4**, regenerating the acid catalyst. With this work we demonstrated this mechanism, since we isolated the Mannich's products, *syn* **5** and *anti* **6**, never detected previously (Scheme 1).

We started with the optimization of the process in water using as catalyst the first prepared solid **a** (R=Me) compared with layered (α-ZrP), amorphous (a-ZrP) and porous (p-ZrP) zirconium hydrogen phosphate. The results are reported in Table 3.

In water, at 30 °C for 24 h in the presence of solid acid catalyst **a** or α-ZrP (30 mol%, determined on the bases of mol/equiv. of P–OH group in the solid) the adducts were not detected (Table 3, Entries 1 and 2). At 50 °C, only the catalyst **a** gave traces of products (Table 3, Entries 3 and 4). Decreasing the volume of water, we observed an increase in conversion and the best result was obtained with 0.150 mL of water (Table 3, Entry 6) that represents the minimum volume that allows a good homogenization of the heterogeneous system by magnetic stirring.

Decreasing the amount of cyclohexenone (**1**) from 10 to 5 equiv. (Table 3, Entry 7), the reactivity did not change. These optimized conditions (cyclohexenone (**1**) 5 equiv., water 0.150 mL, catalyst 30 mol% in P–OH groups, 50 °C, 24 h) were used to compare the activity of the other phosphates.

In the absence of catalyst or in the presence of layered α-ZrP the products were not detected (Table 3, Entries 8 and 9), while in the presence of porous p-ZrP or amorphous a-ZrP low conversions were observed (Table 3, Entries 10 and 11); the crystalline catalyst **b** with R=Me, analog of amorphous **a**, gave a comparable conversion (Table 3, Entry 12 vs Entry 7), but the ratio between Diels–Alder and Mannich products ((**3** + **4**)/(**5** + **6**)) was smaller (60/40 vs 71/29).

The results obtained with non-functionalized zirconium phosphates (Table 3, Entries 9–11) showed that the catalytic activity increases with the surface area, but the comparable conversions obtained by using solid catalyst **a** (B.E.T. surface area 382 m^2/g) and **b** (B.E.T. surface area 15 m^2/g) demonstrated the important effect of the surface hydrophobicity on the reactivity. Thus, to reach a good catalytic activity, both the area and the hydrophobicity of the catalyst surface should be increased.

Table 3
Optimization of direct aza-Diels–Alder reaction of 2-cyclohexen-1-one (**1**) and N-PMP-*p*-chlorobenzaldimine (**2**) catalyzed by the solid Brønsted acid **a** compared with layered (α-ZrP), amorphous (a-ZrP) and porous (p-ZrP) zirconium hydrogen phosphate.

Entry[a]	Catalyst	*T* (°C)	V_{H2O} (mL)	Conv. (%)[c,d]	(**3** + **4**)/(**5** + **6**)[c]	**3**/**4**[c]
1	α-ZrP	30	1	0	–	–
2	**a**	30	1	0	–	–
3	α-ZrP	50	1	0	–	–
4	**a**	50	1	5	71/29	63/37
5	**a**	50	0.50	12	70/30	62/38
6	**a**	50	0.15	48	71/29	65/35
7[b]	**a**	50	0.15	50	71/29	64/36
8[b]	–	50	0.15	0	–	–
9[b]	αZrP	50	0.15	0	–	–
10[b]	a-ZrP	50	0.15	23	71/29	67/33
11[b]	p-ZrP	50	0.15	30	72/28	65/35
12[b]	**b**	50	0.15	52	60/40	65/35

[a] Reaction conditions: N-PMP-*p*-chlorobenzaldimine (**2**) (0.125 mmol), 2-cyclohexen-1-one (**1**) (1.25 mmol, 10 equiv.), catalyst (30 mol% in P–OH groups), 24 h.
[b] 2-Cyclohexen-1-one (**1**) (0.625 mmol, 5 equiv.).
[c] Determined by ^{1}H NMR analysis.
[d] The complement to 100% is unreacted benzaldimine **2**.

To evaluate the importance of the nature of organic group on the surface of the solid, we studied the reaction with the Brønsted acid catalysts **c**–**j** (R=Ph, Pr). The results are illustrated in Table 4 together with those obtained with solids **a** and **b** (R=Me) for comparison.

When R is a phenyl group (solids **c** and **d**), more hydrophobic than methyl (Table 4, Entries 3 and 4), the reactivity increases considerably (conversion 78–95%) and it increases with the percentage of Ph groups on the surface of the solid acid catalyst. The crystalline catalyst **e**, analog in chemical composition of amorphous **c**, that presents non-symmetrical layers (one rich of PO$_3$OH and one rich of PO$_3$Ph) gave, as expected, a low conversion (Table 4, Entry 5). The same trend of reactivity was observed when R is a propyl group (Table 4, Entry 6–9): the reactivity increases with hydrophobic group percentage and we observed not only a higher conversion, but a higher chemoselectivity, too (Table 4, Entry 9 vs Entries 6–8). The best result is obtained with catalyst **i** (P–OH/P–Pr = 1/1.7) with 99% conversion and a 70:30 Diels–Alder/Mannich adducts ratio (Table 4, Entry 9). We obtained a similar result with the mixed catalyst **j** (P–OH/P–Me/P–Ph = 1/1.7/2.6), (Table 4, Entry 10) that has a high surface area but also a high external surface (144 m^2/g), a high micro- and mesoporosity and high hydrophobicity.

In all cases (Table 4, Entries 1–10), we observed the formation of Mannich products *syn* (**5**) and *anti* (**6**) (30–44%), and the *endo*/*exo* ratio is unchanged (about 65/35).

Table 4
Direct aza-Diels–Alder reaction of 2-cyclohexen-1-one (**1**) and N-PMP-*p*-chlorobenzaldimine (**2**) catalyzed by the solid Brønsted acid **a**–**j**.

Entry[a]	Catalyst	Conv. (%)[b,c]	(**3** + **4**)/(**5** + **6**)[b]	**3**/**4**[b]
1	**a**	50	71/29	64/36
2	**b**	62	60/40	65/35
3	**c**	78	58/42	64/36
4	**d**	95	56/44	66/34
5	**e**	55	57/43	63/37
6	**f**	46	65/35	67/33
7	**g**	82	61/39	65/35
8	**h**	98	64/36	63/37
9	**i**	99	70/30	65/35
10	**j**	99	70/30	64/36

[a] Reaction conditions: N-PMP-*p*-chlorobenzaldimine (**2**) (0.125 mmol), 2-cyclohexen-1-one (**1**) (0.625 mmol, 5 equiv.), catalyst (30 mol% in P–OH groups), 24 h, 50 °C.
[b] Determined by ^{1}H NMR analysis.
[c] The complement to 100% is unreacted benzaldimine **2**.

Table 5
Optimization of aza-Diels–Alder reaction of 2-cyclohexen-1-one (**1**) with N-PMP-*p*-chloro benzaldimine (**2**) catalyzed by solid **j**.

Entry[a]	Catalyst (mol%)[b]	Conv. (%)[c,d]	(**3** + **4**)/(**5** + **6**)[c]	**3**/**4**[c]
1	30	99	70/30	64/36
2	20	98	69/31	64/36
3	15	99 (90)[e]	71/29	65/35
4	10	92	69/31	64/36
5	5	88	68/32	64/36
6[f]	5	99 (53)[e]	89/11	64/36
7[f]	–	99 (47)[e]	93/7	65/35

[a] Reaction conditions: N-PMP-*p*-chlorobenzaldimine (**2**) (0.125 mmol), 2-cyclohexen-1-one (**1**) (0.625 mmol, 5 equiv.), catalyst **j**, H$_2$O 0.150 mL, 24 h, 50 °C.
[b] mol% of P–OH groups.
[c] Determined by ^{1}H NMR analysis.
[d] The complement to 100% is unreacted benzaldimine **2**.
[e] Yield of isolated products.
[f] Reaction temperature 70 °C.

We continued our study using catalyst **j**, cheaper and with more interesting surface properties than catalyst **i**, to determine the best reaction conditions (Table 5).

Decreasing the amount of catalyst from 30 mol% in P–OH groups to 5 mol%, the catalytic activity did not change drastically. The best result was obtained with 15 mol% in P–OH groups of catalyst **j** (Table 5, Entry 3, conv. 99%) with a total yield of isolated products of 90%. The Mannich adducts **5** and **6** are not stable and in thermal conditions undergoes to aza-Michael to give the *endo* and *exo* isoquinuclidines **3** and **4**. To favor the aza-Diels–Alder reaction, we increased the temperature from 50 to 70 °C, the (**3** + **4**)/(**5** + **6**) ratio was higher (89/11 vs 70/30), but the yield of isolated products was lower (47%) (Table 5, Entry 6). While at 50 °C, in absence of any catalyst, the reaction did not proceed (Table 3, entry 8); running the reaction at 70 °C, we observe a similar result to that obtained in presence of catalyst **j** (Table 5, Entry 7 vs 6) demonstrating that the reaction proceeds via thermal conditions and not through a Brønsted acid catalysis.

4. Conclusion

In this work, we report the preparation and characterization of new amorphous zirconium hydrogen phosphates alkyl and/or aryl phosphonates, which can be used as solid Brønsted acid catalysts. The solid acids have been tested in the aza-Diels–Alder reaction of cyclohexenone (**1**) with benzaldimine **2** in water without any additive. In fact, the hydrophobic groups as Me, Ph and Pr on solid catalyst surface favor reagents' diffusion toward acidic sites, aiding proton transfer to reagents. The best results were obtained with the solid **j**, which has a high surface area and also a high external surface (144 m^2/g). The presence of a high content of alkylphosphonic groups, like methyl-, phenyl- and propyl-phosphonic, in the catalysts is associated with the presence of a high micro- and mesopore volume together to a high hydrophobicity of their surface. We also isolated, for the first time, the Mannich products, confirming the hypothesized mechanism for the direct aza-Diels–Alder reaction.

The newly prepared amorphous solids are micro- and mesoporous, and they have surprising high specific surface area and this is interesting for a large number of applications.

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