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- Titel: Phosphonate-modified UiO-66 Brønsted acid catalyst and its use in dehydra-decyclization of 2-methyltetrahydrofuran to pentadienes
- Autoren: Matheus Dorneles de Mello, Gaurav Kumar, Tarnuma Tabassum, Sheetal K Jain, Tso-Hsuan Chen, Stavros Caratzoulas, Xinyu Li, Dionisios G. Vlachos, Songi-i Han, Susannah Scott, Paul J. Dauenhauer, and Michael Tsapatsis

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# **RESEARCH ARTICLE**

# Phosphonate-modified UiO-66 Brønsted acid catalyst and its use in dehydra-decyclization of 2-methyltetrahydrofuran to pentadienes

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Abstract: Phosphorus-modified all-silica zeolites exhibit activity and selectivity in certain Brønsted acid catalyzed reactions for biomass conversion. In an effort to achieve similar performance with catalysts having well-defined sites, we report the incorporation of Brønsted acidity to metal-organic frameworks with the UiO-66 topology, achieved by attaching phosphonic acid to the 1,4benzenedicarboxylate ligand and using it to form UiO-66-PO<sub>3</sub>H<sub>2</sub> by post-synthesis modification. Characterization reveals that UiO-66-PO<sub>3</sub>H<sub>2</sub> retains stability similar to UiO-66, and exhibits weak Brønsted acidity, as demonstrated by titrations, alcohol dehydration, and dehydra-decyclization of 2-methyl-tetrahydrofuran (2-MTHF). For the later reaction, the reported catalyst exhibits site-time yields and selectivity approaching that of phosphoric acid on all-silica zeolites. Using solid-state NMR and deprotonation energy calculations, the chemical environments of P and the corresponding acidities are determined.

#### Introduction

Phosphorus-based materials<sup>[1–12]</sup> are reported to have Brønsted acidity and have been extensively studied as catalysts, including for the catalytic upgrading of lignocellulosic biomass. For example, niobium phosphate is a selective catalyst for fructose dehydration to 5-hydroxymethylfurfural (HMF), exhibiting 78.2% HMF selectivity at 58% fructose conversion.<sup>[13]</sup> Similarly, phosphoric acid supported on all-silica zeolites (zeosils) are highly selective catalysts in the production of p-xylene from 2,5dimethyl furan (2,5-DMF) and ethylene.<sup>[14]</sup> Furthermore, we have recently reported their utility for the tandem ring-opening and dehydration (dehydra-decyclization) of tetrahydrofuran (THF) to produce butadiene selectively.<sup>[15]</sup> However, the heterogeneous

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and dynamic nature of phosphoric acid species on these zeosils under reaction conditions makes the identification and tuning of the active sites challenging.<sup>[14]</sup>

Functionalized MOF-derived solid acids have found numerous applications in catalysis and separations.<sup>[16]</sup> For example, MIL-101 (Cr) and UiO-66 (Zr) were functionalized with sulfonic acid, introducing Brønsted acidity and making these materials active for fructose dehydration.<sup>[17]</sup> Functionalized UiO-66-CO<sub>2</sub>H and UiO-66-SO<sub>3</sub>H also showed enhanced selectivity towards  $CO_2/CH_4$  separation.<sup>[18]</sup> The COOH moiety was introduced into the framework of UiO-67 by C-H activation using a rhodium catalyst. The resulting Brønsted acidity from the free acid was active for an epoxide ring-opening reaction with high selectivity.<sup>[19]</sup> Also, Farha and coworkers succeeded in impregnating the Zr clusters of the MOF NU-1000 with H<sub>3</sub>PO<sub>4</sub> for applications in glucose dehydration.<sup>[20]</sup>

Inspired by the existing MOF-derived solid acids and with our goal to prepare tunable materials with well-defined catalytic sites that show high selectivity for acid-catalyzed reactions, we investigated the synthesis of phosphonate-modified MOFs by ligand functionalization and their activity for Brønsted acidcatalyzed reactions. We report the installation of phosphonate and phosphonic acid functionalities into benzene-1,4-dicarboxylic acid (BDC) ligands and their use to form UiO-66-PO<sub>3</sub>H<sub>2</sub> by a postsynthesis modification (PSM) method while maintaining the stability, crystallinity, and topology of the parent material. The resulting P-sites were characterized by a combination of solidstate NMR and deprotonation energy DFT calculations. Brønsted acidity in the synthesized materials was probed using four acidcatalyzed chemistries (dehydration of ethanol and isopropyl alcohol (IPA), Hoffman elimination of tert-butylamine, and dehydra-decyclization of 2-methyl-tetrahydrofuran (2-MTHF)). The performance of P-modified MOFs for dehydra-decyclization of 2-methyl-tetrahydrofuran was found to be comparable with phosphoric acid supported on zeosils. To our knowledge, this is the first demonstration of pendant phosphonic-acid in MOFs functioning as a selective Brønsted-acid catalyst.

#### **Results and Discussion**

2-(Diisopropylphosphonate)terephthalic acid (PO(OPr)<sub>2</sub>-TPA) was synthesized and used in the PSM of UiO-66 to incorporate P-O groups into the framework (P-UiO66-PSM). The synthesis details of P-UiO66-PSM are described in the Supporting Information (Section S1). The introduction of different functional groups into MOFs can be challenging because, in many cases, the use of thermally labile ligands can be limited by solubility and coordination issues.<sup>[21]</sup> In the case of phosphonic acid modified MOFs, the direct synthesis approach leads to densely packed or even amorphous materials.<sup>[22]</sup> Here, the PSM method was used to overcome such issues. Briefly, parent UiO-

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66 was submitted to solvent-assisted ligand exchange for five days (Scheme 1) in a KOH/THF solution in the presence of the phosphorus ligand. The exchanged materials were washed with water and methanol and then heated (180 °C for 20 h under vacuum) for solvent removal. Finally, P-UiO66-PSM was further treated with acidified water (AW: 1M HCI) to install POH moieties in the ligands by removing protecting isopropyl groups and potassium; the obtained material is called P-UiO66-PSM-AW.



 $\label{eq:scheme 1. Post-synthesis modification (PSM) of UiO-66 using 2-diisopropyl phosphonate-terephthalic acid.$ 

The PXRD patterns in Figure 1A show no changes for Pexchanged UiO-66 relative to the parent material; relative peak intensities remain the same after PSM. Figure 1B shows the Arsorption isotherms of these materials. The pristine, defect-free UiO-66, shows inflection points in Ar uptake at P/P<sub>0</sub> values of 10<sup>-4</sup> and 10<sup>-2</sup>. They are attributed to the filling of 4 and 6 Å micropores, respectively.<sup>[23]</sup> In general, P-exchanged UiO-66 exhibits lower Ar uptake in the low P/P<sub>0</sub> (10<sup>-4</sup>, microporous) range and higher Ar uptake in the high P/P<sub>0</sub> (>10<sup>-2</sup>) range. The latter indicates the presence of larger pores, most likely created by the introduction of defects during the ligand exchange process.<sup>[24]</sup>

TGA profiles of the materials are presented in Figure 1C. P-UiO66-PSM and P-UiO66-PSM-AW exhibit the onset of decomposition at 510 °C compared to 540 °C for UiO-66. The treatment with acidified water does not affect the MOF decomposition temperature, which can be attributed to the high stability of UiO-66 under acidic conditions.<sup>[25]</sup> Finally, Figures 1D-1F show SEM images of the parent and modified MOFs, where no apparent changes in morphology are visible. The particles retain their size of about 260 nm after PSM and acid water treatment. Particle size distributions can be found in Figure S2.

Having established that the P-exchanged materials retain the topology of the parent UiO-66, their chemical composition was investigated. Ligand exchange was confirmed by digesting the materials and analyzing the liquid solution by <sup>1</sup>H NMR (Section S6.1). The <sup>1</sup>H NMR spectrum shows a singlet at 7.8 ppm attributed to the magnetically equivalent protons in unmodified BDC<sup>2-,[26]</sup> The aromatic region also includes three multiplets at 8.1, 7.7, and 7.2 ppm, that match the chemical shifts of H<sub>2</sub>PO<sub>3</sub>-BDC<sup>2-</sup> in solution (see ligand characterization in the SI, section S5).<sup>[27]</sup> The <sup>1</sup>H NMR spectra of digested MOFs reveal that about 23 % of the original BDC ligands in UiO-66 were exchanged with phosphonate-TPA (Table 1).



Figure 1. Structural characterization of PSM UiO66 materials: (A) PXRD patterns, (B) Ar sorption isotherms (closed symbols refer to adsorption and open symbols to desorption), (C)TGA profiles, and SEM images of (D) UiO66, (E) P-UiO66-PSM, and (F) P-UiO66-PSM-AW.

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We also analyzed the materials by XPS (Table 1). The nearsurface P/Zr atomic is 0.22 for both P-UiO66-PSM and P-UiO66-PSM-AW, which agrees with the values observed by solutionstate <sup>1</sup>H NMR after digestion. More details on XPS analysis can be found in Figure S3. Furthermore, ICP analysis shows a P/Zr atomic ratio between 0.17 - 0.19. In three independently performed syntheses using identical procedures, the P/Zr determined by XPS is 0.22 ± 0.03, while the ligand exchange by digestion NMR is 21 ± 4 %, indicating good reproducibility and agreement between these characterization methods (Table S2). ATR-IR of the exchanged MOFs (Figure S4) shows a band at 1100 cm<sup>-1</sup>, attributed to the presence of P=O stretching,<sup>[28]</sup> further supporting the presence of the phosphonate ligand.

 Table 1. Near-surface (from XPS) and bulk (ICP) composition of P-UiO66 materials.

Material	Ligand exchange (%) <sup>a</sup>	P/Zr <sup>b</sup> (at/at)	P/Zr <sup>c</sup> (at/at)	K/P <sup>c</sup> (at/at)		
P-UiO66-PSM	20 ± 4	$0.22 \pm 0.03$	0.17	0.44		
P-UiO66-PSM-AW	21 ± 4	$0.22 \pm 0.03$	0.19	0.04		
a From NMR: h From XPS: c From ICP						

a From NMR; b From XPS; c From ICP.

To further probe the chemical environment of phosphorus, we acquired solid-state <sup>31</sup>P NMR spectra (Figure 2). There are four distinct signals. Three are present in the <sup>31</sup>P MAS-NMR spectrum of heated P-UiO66-PSM, which shows a main peak at 6 ppm representing 60 % of the total intensity, with a shoulder at 11 ppm (25 %), and a tail at -2 ppm (15 %). The other signal appears in the spectra of P-UiO66-PSM-AW, which shows a main peak at 9 ppm representing 49 % of the total intensity, with a shoulder at 6 ppm (31 %) and a tail at -2 ppm (20%). Spectral deconvolution is also shown in Figure 2, and a summary of the chemical shifts from it can be found in Table S3. The peaks are assigned as follows: according to solution <sup>31</sup>P NMR (see Section S5.1), the fully protected PO(OPr)<sub>2</sub>-TPA ligand appears at 12 ppm, and the fully deprotected H<sub>2</sub>PO<sub>3</sub>-TPA ligand at 9 ppm. The peak at 11 ppm in the P-UiO66-PSM is then assigned to PO(OPr)2-TPA but slightly shifted because of its interaction with the MOF framework or from partially protected sites like P(O)(OR)(OH)-TPA. The peak at 9 ppm in the P-UiO66-PSM-AW is assigned to deprotected H<sub>2</sub>PO<sub>3</sub>-TPA. The peak at 6 ppm is assigned to different structures for the two materials. In the case of P-UiO66-PSM, it is assigned to PO<sup>-</sup>K<sup>+</sup> groups, as suggested by Harris et al. for several pairs of phosphonic acid/salt derivatives<sup>[29]</sup> and supported by ICP results, which show a K/P atomic ratio of 0.44. The lower experimental K/P value compared to 0.6 obtained by spectral deconvolution suggests the presence of some hydrogenbonded phosphonic acid sites whose chemical shift overlap with

that of the PO<sup>-</sup>K<sup>+</sup> sites. In the case of P-UiO-66-PSM-AW, ICP indicates that acid washing removes a significant amount of potassium (K/P of 0.04, Table 1). Therefore the shoulder at 6 ppm in this material is likely from hydrogen-bonded POH groups, as suggested by Davidowski et al. [30] and Bibent et al. [31]. Finally, the peak at -2 ppm is assigned to phosphonates that are bonded to zirconium. The resulting POZr bonds with the cluster can account for the more significant decrease in chemical shifts due to the low electronegativity of Zr.<sup>[30]</sup> The assignments invoke the expected decrease in the chemical shift of the "free" phosphonic acid signal at 9 ppm upon the interaction between the phosphonic acid and the Zr cluster. The magnitude of the decrease depends on the strength of this interaction, ranging from hydrogen bonding to bonding directly with the cluster by a POZr bond.<sup>[30]</sup> In the case of the 6 ppm peak, this shift decrease is relatively small ( $\Delta\delta$ =-3 ppm), in accordance with hydrogen bonding involving either a P=O...HOZr, or a POH...POH interaction between nearby phosphonates.<sup>[31]</sup> Solid-state NMR data suggests that P-UiO66-PSM-AW has the majority of P-sites (~about 80 %) as deprotected P-OH, with small or no interactions with the cluster. However, a small portion of the ligands binds strongly to Zr during the PSM process.



Figure 2. Solid-state <sup>31</sup>P NMR spectra of P-UiO66 in (A) P-UiO66-PSM and (B) P-UiO66-PSM-AW, all recorded at 18.8 T with 20 kHz MAS frequency.

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Figure 3. Optimized clusters modeling Brønsted sites in phosphonate-modified UiO-66: (A) structure 1: free -PO(OH)<sub>2</sub>; (B) structure 2: -P=O hydrogen-bonded with -ZrOH; (C) structure 3: phosphonate group acts as a bidentate ligand to  $Zr_6O_4(OH)_4$ ; (D) structure 4: -PO(OH)<sub>2</sub> on one terephthalate ligand hydrogen-bonded to a second -PO(OH)<sub>2</sub> located on an adjacent ligand. Acidic protons are indicated by green circles. Note that, for structure 4, a circle also indicates the proton in -COOH, which could be acidic (DPE values in Table S3). Blue dashed lines indicate hydrogen bonds. Atoms shown: H (white), O (red), C (gray), P (orange), Zr (blue).

To identify the sites most likely to participate in acid catalysis, we estimated deprotonation energy (DPE) using quantum chemical calculations. Four sites were modeled according to the major possibilities from solid-state NMR. The detailed structures can be found in Figure 3, and the results are presented in Table S4. Across all the P-structures probed, the DPE values varied by up to 80 kJ mol<sup>-1</sup>. Phosphonate without interactions with the cluster ('free' P-O(OH)<sub>2</sub>) (Figure 3A) exhibits the lowest DPE (1306 kJ mol<sup>-1</sup>). Phosphonates in which the P=O sites engage in a hydrogen-bond with a ZrOH (Figure 3B) have a slightly higher DPE (1315 kJ mol-1) followed by mutually Hbonded neighboring phosphonates (1341 kJ mol<sup>-1</sup>, Figure 3D), and phosphonates bonded to Zr cluster (1386 kJ mol<sup>-1</sup>, Figure 3C). These results suggest that the 'free' P-OH sites and sites in which the P=O engages in hydrogen-bonding with ZrOH sites are expected to be the most active in Brønsted acid catalysis. Most notably, the DPE values obtained in all cases are >100 kJ mol<sup>-1</sup> higher than those previously calculated for aluminosilicate zeolites (1200  $\pm$  11 kJ mol<sup>-1</sup>),<sup>[32]</sup> consistent with a much weaker acidity in P-UiO66-PSM-AW relative to bridging hydroxyls in aluminosilicates.

Combining the solid-state <sup>31</sup>P NMR signals and the DFT calculations, we conservatively assume that 80 % of the P-sites are active sites in P-UiO66-PSM-AW, including both 'free' P-OH and H-bonded P-OH to Zr-OH. The remaining 20 % of P-sites are bonded to the Zr-cluster, and the associated protons are probably

not acidic enough for catalysis given their high DPEs, even when compared to the bridging OH in the Zr-cluster of UiO-66 (Table S4), which does not show any catalytic activity for the reactions tested (see below).

We studied the catalytic performance of the P-modified material in several Brønsted acid-catalyzed reactions (Scheme 2). First, the number of Brønsted acid sites (BAS) was determined by the Hoffman elimination of two different alkylamines using the Reactive Gas Chromatography (RGC) technique details of which are reported elsewhere.<sup>[33]</sup> Dehydration of two alcohols (ethanol and isopropyl alcohol) and the dehydra-decyclization of 2-methyltetrahydrofuran (2-MTHF) were performed to benchmark the catalytic performance of the material against those of a traditional, strong solid acid (the aluminosilicate H-ZSM-5) and a structurally analogous weak acid (the P-containing all-silica zeosil P-SPP).<sup>[14,15]</sup>

BAS densities measured by the Hoffman elimination of both *tert*-butylamine and *tert*-amylamine are listed in Table 2. The corresponding values for P-SPP (Si/P=27, 136 µmol g<sup>-1</sup>) and ZSM-5 (Si/Al=140, 94 µmol g<sup>-1</sup>) are included for reference. The BAS counts for both UiO66 and P-UiO66-PSM are low but non-zero. There are likely  $\mu_3$ -bridging OH sites on the clusters or defect sites (i.e., terminal OH groups from missing ligand-defects) present in the materials that are capable of protonating these investigated amines. In contrast, the production of isobutene from the Hoffman elimination of *tert*-butylamine is significantly higher

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for P-UiO66-PSM-AW, giving a BAS count of 66 µmol g<sup>-1</sup>. Nevertheless, its BAS counts are only ~10-14% of the theoretical value assuming one BAS per P-site, indicating that the alkylamines either are not protonated at most P sites, or they could desorb without undergoing Hoffman elimination. Unlike in aluminosilicates, the BAS count was found to be dependent on the identity of probe alkylamine.[33] Thus, the BAS count is ~ 1.5x higher using tert-amylamine (proton affinity 938 kJ mol<sup>-1</sup>) (Table 2) than using tert-butylamine (proton affinity 934 kJ mol<sup>-1</sup>). Both observations are consistent with results obtained in P-SPP, and confirm the weakly acidic nature of POH sites in such materials, as previously noted.<sup>[14,34]</sup> The BAS counts obtained from Hoffman elimination of amines reflect the probe-dependent nature of the active sites in these materials. However, using these counts to normalize rates would overestimate them. Instead, the site-time yields (STYs) reported in the probe reactions below were normalized by the active phosphorus content (assuming 80% of total phosphorus, see Figure 2B). We further compared the acidity of these materials by ammonia TPD (Figure S5 and Table S5). The data agree well with the expectation of weak acidity observed by titration with the alkylamines.



**Scheme 2.** Brønsted-acid reactions catalyzed by P-UiO66-PSM-AW: (1) Hoffman elimination of *tert*-butylamine (analogous for *tert*-amylamine); (2) ethanol dehydration; (3) isopropyl alcohol dehydration; (4) 2methyltetrahydrofuran dehydra-decyclization.

Next, the catalytic performance of P-UiO66-PSM-AW was probed in the acid-catalyzed dehydration of two alcohols (namely, ethanol, and isopropyl alcohol). Alcohols can undergo unimolecular dehydration to the corresponding olefin, or bimolecular dehydration to the di-alkyl ether.<sup>[35,36]</sup> P-UiO66-PSM-AW gives unimolecular dehydration products, namely, ethylene and propylene, at reaction temperatures of 130-150 °C. STYs for ethylene and propylene production can be found in Figure S6, and are analyzed in more detail in the SI.

We compared the activity and selectivity for propylene formation from IPA by P-UiO66-PSM-AW with the parent UiO66, as well as P-UiO66-PSM, and P-SPP. The results are shown in Figure 4A. UiO-66 is inactive for IPA dehydration. P-UiO66-PSM shows weak activity (STY 0.03 h<sup>-1</sup>) with high selectivity to propylene (98%). As suggested by solid-state NMR and ICP data, most of the sites in P-UiO66-PSM are either protected by

isopropyl groups or occupied by potassium sites. The observed low activity probably comes from a small number of POH sites available. P-UiO66-PSM-AW, on the other hand, shows considerably higher activity compared to UiO66 and P-UiO66-PSM (i.e., before hydrolysis). Relative to P-SPP, the propylene formation rate of P-UiO66-PSM-AW is similar (STYs within a factor of ~2, Figure 4A), although the latter shows higher propylene selectivity (~98% per C basis) than P-SPP (~80%) under identical reaction conditions at strictly differential conversions (<1%). Both P-materials exhibit lower activity compared to aluminosilicates.<sup>[33]</sup>

 Table 2. Brønsted-acid site (BAS) densities of P-UiO-66 and other materials.

Material	BAS (TBA) (μmol g⁻¹)	BAS (TAA) (μmol g <sup>-1</sup> )	BAS theor. (μmol g <sup>-1</sup> )
UiO66	20	-	-
P-UiO66-PSM	32	-	-
P-UiO66-PSM-AW	66	92	673
P-SPP	136	169	680
ZSM-5 <sup>[33]</sup>	100	95	119

We then probed the activity of P-UiO66-PSM-AW for dehydra-decyclization of 2-MTHF (Figure 4B). This reaction is studied for the production of bio-renewable linear pentadienes. [37] As in the case of IPA dehydration, UiO66 showed nearly no dehydra-decyclization reactivity, while P-UiO66-PSM exhibited a low but non-zero activity for pentadiene production. The dehydradecyclization activity and selectivity to linear pentadienes for P-UiO66-PSM-AW are similar to the corresponding values reported for P-SPP.<sup>[15]</sup> The performance of P-UiO66 and its weak Brønsted acidity shows very high selectivity at the expense of activity of one order-of-magnitude lower than other aluminosilicate zeolites.[37] Kumbhalkar et al. tested zeolites of different pore sizes, as the 10 MR ZSM-5 and the 12 MR BEA. They did not observe a significant change in the activity or selectivity (about 65 % at 35 % 2-MTHF conversion), providing no direct evidence for confinement effects. Other catalysts, such as the Lewis acid Al<sub>2</sub>O<sub>3</sub> or Al-Sn-BEA, also performed poorly.<sup>[38]</sup> On a recent report, Kumar et al. reported activity data on MCM-22 and its pillared derivative MCM-36. It was observed that mesopores were detrimental to dienes production. In the same paper, the authors show that introducing boron into the framework of the all-silica zeolites MWW, BEA and MFI yield selective materials for 2-MTHF dehydra-decyclization as a consequence of the weak acidity of the boron sites.[39] The phosphoric acid impregnated zeosils were not extensively investigated for dehydra-decyclization of 2-MTHF, but the related reaction of 3-MTHF to pentadienes and isoprene. The Al-free phosphorus-containing zeolites were all active and relatively selective to isoprene (30 % < S< 70 %), especially compared with regular aluminosilicates like ZSM-5 and FAU (5 - 40 % selective).[40]

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Figure 4. STYs (green bars) and selectivities (blue bars), for two reactions catalysed by various P-containing materials: (A) Isopropyl alcohol dehydration to propylene (0.050 g cat. 30 Torr IPA, 130 °C, WHSV 3.8 h<sup>-1</sup>, conversions maintained below 1 %); and (B) dehydra-decyclization of 2-MTHF (0.050 g cat, 4.9 Torr 2-MTHF, 280 °C, WHSV 0.31 h<sup>-1</sup>, determined at 25 % conversion). STYs were calculated for P-UiO-66-PSM-AW using the estimated of accessible P sites (80% of total P determined by <sup>31</sup>P solid-state NMR, see Figure 2B) and for P-UiO66-PSM and P-SPP based on total P content. UiO66 did not show any activity (STYs are shown as zero just for comparison purposes). All carbon balances close to ±10 %.

The catalytic activities and selectivities to products for different P-UiO-66 materials and different reaction conditions are summarized in Table S6. Notably, P-UiO66-PSM-AW retains high selectivity to pentadienes (~90% on a per C basis) at low (<2%) and moderate (~23%) 2-MTHF conversion. Some catalyst deactivation was observed, but it is less severe for P-UiO66-PSM-AW than for P-SPP (Figure S7). Furthermore, regeneration performed by heating the catalyst in air at 320 °C for 10h, restored 90 % of its activity (Figure S8). We also performed three consecutive reaction-regeneration cycles and did not observe any changes in selectivity. Moreover, the material retained its crystallinity (Figure S9), confirming the stability of the framework.

Overall, the weak acidity in the pendant P-OH sites of P-UiO-66-PSM-AW, as evidenced by <sup>31</sup>P solid-state NMR, DPE calculations, and probe reactions, provides an appropriate chemical environment for its high selectivity towards pentadienes in the dehydra-decyclization of 2-MTHF.

#### Conclusion

A combination of ligand synthesis and a post-synthesis modification method led to the successful incorporation of P-OH Brønsted acid sites into the Zr-UiO-66 framework. According to <sup>31</sup>P MAS-NMR, the material after hydrolysis contains three different types of P sites, with ~ 80% of them expected to be active for Brønsted acid catalysis based on DFT calculations. P-UiO66-PSM-AW catalyzes the Hoffman elimination of alkylamines.

Consistent with its weak acidity, it is moderately active for the dehydration of both ethanol and isopropyl alcohol. For the dehydra-decyclization of 2-methyl-tetrahydrofuran, P-UiO-66-PSM-Hy exhibits site-time yields and selectivity similar to that of highly selective phosphoric acid supported on zeolites (P-SPP), holding promise for this and other reactions for the biomass conversion to chemicals. The tunability of MOFs combined with the PSM method and synthesis of phosphonic acids can provide a more uniform distribution of acid sites throughout the framework compared to the wide distribution observed in supported phosphoric acid catalysts.

### **Experimental Section**

Experimental procedures, other characterization, and reaction data are given in Supporting Information.

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Matheus Dorneles de Mello, Gaurav Kumar, Tarnuma Tabassum, Sheetal K. Jain, Tso-Hsuan Chen, Stavros Caratzoulas, Dionisios G. Vlachos, Songi-I Han, Susannah L. Scott, Paul Dauenhauer, and Michael Tsapatsis\*

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Phosphonate-modified zirconium metal-organic frameworks with intrinsic Brønsted acidity and its use in dehydra-decyclization of 2methyltetrahydrofuran to pentadienes