Improving the selectivity to 4-tert-butylresorcinol by adjusting the surface chemistry of heteropolyacid-based alkylation catalysts

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Article info
Article history:
Received 12 September 2017
Revised 5 January 2018
Accepted 10 January 2018
Available online 3 February 2018

Keywords:
Keggin
Heteropolyacids
Alkylation
Methyl-tert-butyl ether
4-tert-Butyl resorcinol
SBA-15

Abstract
Keggin tungstophosphoric acid (H₃PW₁₂O₄₀, HPW) was immobilized onto Santa Barbara Amorphous (SBA-15) type silica to obtain selective catalysts for the resorcinol tert-butylation with methyl-tert-butyl ether. The challenge was to enhance the reaction selectivity to the mono-alkylated product i.e. 4-tert-butylresorcinol at the expenses of other more thermodynamically favored products as the 4,6-di-tert-butylresorcinol. Using HPW@SBA15 catalysts, remarkable selectivity to 4-tert-butylresorcinol was obtained, up to 42% (at 20% of resorcinol conversion). Our finding is that the change in the product distribution was dependent on the catalyst surface chemistry: 4TBR selectivity can be increased adjusting the fraction of Brønsted acid sites versus Lewis ones at the catalyst surface.

1. Introduction
Resorcinol tert-butylation is an electrophilic aromatic substitution giving a mixture of alkylated benzenediols and ethers [1]. Being thermodynamically favored, the di-alkylated 4,6-di-tert-butylresorcinol (46DTBR) is the major product. However, the mono-alkylated 4-tert-butylresorcinol (4TBR) is of particular interest as antioxidant in food conservation [2] and in skin diseases treatment [3]. Thus, it is important to enhance 4TBR production and increase the selectivity of the resorcinol alkylation to it. Typically, soluble Brønsted acids like sulfuric acid have been used to catalyze the resorcinol tert-butylation but several adversities are linked to its usage. For example, they are difficult to handle and cause equipment corrosion. Moreover, the product separation is complicated, requiring solvent extraction and a long procedure. Furthermore, distillation and purification are required for catalyst recovery and it is more feasible to dispose it than regenerate and ultimately reuse it.

Heterogeneous catalysts would represent a valid solution since they are easy to separate from the reaction mixture by filtration and therefore can be handily reused. However, they should offer competitive performances with respect to traditional homoge-
1. The active phase is dissolved in a solution of the support precursors, which are first hydrolysed and then condensed to form a solid network in which the active phase molecules are immobilized. This inhibits their mobility and prevents the formation of big active phase aggregates.

2. The synthesis parameters can be adjusted to force the active phase to be embedded in the support pore walls, which allows the immobilization of considerable amount of active phase and helps to prevent HPW leaching.

3. During the synthesis, the active phase establishes strong interactions with the support, which stabilizes the active phase. Formation of H-bond or even covalent bond are reported [12]. These interactions protect the active phase from thermal decomposition and leaching.

In this context, SBA-15 textural properties make it particularly suitable to be used as framework for HPW immobilization. Its homogeneous mesoporous texture consists of long parallel hexagonal channels which allow to prevent diffusional limitations, and walls with a thickness of 3–4 nm which are adequate to host the 1 nm HPW, while their stability allows to hypothesize they will maintain their integrity during the catalytic reaction, so avoiding leaching of HPW through liquid phase [14]. Furthermore, the weakly acidic character of SBA-15 allows the HPW immobilization without deforming its structure as reported by Thorat et al. [15] and neutralizing its acidity, thus not inhibiting the catalytic activity of the active phase.

Unlike the case of homogeneous catalysis, resorcinol tert-butylolation catalyzed by solids is regulated by reagents adsorption and products desorption mechanisms. The catalyst surface chemistry appears then to be crucial, since its ability to adsorb the reactants depends on its characteristics. The amount of adsorbed resorcinol molecules with respect to the number of tert-butyl cations formed affects the overall reaction selectivity. Besides this, the surface acidity was already reported to influence the catalytic activity: the Lewis to Brønsted acid sites ratio was found to have an impact on resorcinol conversion [16,17].

Therefore, in this study, three HPW/SBA-15 catalysts featuring a mesoporous homogeneous texture with well dispersed, intact and immobilized HPW were synthesized. Even though sol-gel technique is not new in the literature, the simultaneous heteropolyacid incorporation in the SBA-15 walls and the pore size tuning of SBA-15 was never reported before, to our knowledge. This introduces a first element of novelty of this work. The second element of novelty consists in using heteropolyacid-based catalyst to catalyse the resorcinol alkylation with methyl-tert-butylether. At the best of our knowledge, the use of HPWSBA-15 for this reaction was not reported before. Several synthesis parameters were varied to reach different Brønsted/Lewis sites ratios at the catalysts surface: the addition order of HPW with respect to TEOS during the synthesis, the active phase establishes strong interactions with the support, which stabilizes the active phase.

**2. Materials and methods**

**2.1. Chemicals**

Ethanol (Normapur, absolute), hydrochloric acid (hereafter noted HCl, Sigma Aldrich, 37 wt.%), tetra ethyl orthosilicate (hereafter noted TEOS, Janssen Chimica, 98%), resorcinol (hereafter noted RES, Sigma Aldrich, ReagentPlus®, 99%), methyl-tert-butyl ether (hereafter noted MTBE, Sigma Aldrich, ≥99%), 1,3-di-nitrobenzene (Sigma Aldrich, 97%), phosphotungstic acid hexahydrate H₃PW₁₂O₄₀·H₂O (hereafter noted HPW, Sigma Aldrich, reagent grade), 4 tert-butyl hydroquinone (Sigma Aldrich, HPLC grade), 4,6-di-tert-butylresorcinol (hereafter noted 46DTBR, Sigma Aldrich, HPLC grade), Tungsten anhydride (hereafter noted WO₃, UCB, reagent grade), Cetyltrimethylammoniumbromide (hereafter noted CTAB, Sigma-Aldrich), Pluronic P-123 (hereafter noted P-123, Sigma-Aldrich), 4-tert-butoxyphenol (hereafter noted 4TPPh TCI chemicals), hydroquinone (hereafter noted HQ, Sigma Aldrich ≥99%), catechol (hereafter noted CAT, Sigma-Aldrich, ReagentPlus®, ≥99%), phenol (Sigma-Aldrich, ACS reagent, ≥99%), benzene (Merck, pure), o-xylene (ACROS Organics, 99%, pure), m-xylene (ACROS Organics, 99%, extra pure), p-xylene (ACROS Organics, 99%, pure), were purchased and used as received. Being 4-tert-butylresorcinol (hereafter noted 4TBR) not commercially available, in the first instance its isomer 4-tert-butylhydroquinone was used as analytical standard. 4TBR was then isolated from the reaction products, characterized and used as standard.

**2.2. Catalysts synthesis**

HPW containing mesoporous silicas were synthesized adapting two different protocols reported by Dufaud at al. [18] and Gagea et al. [19]. These parameters were explored as summarized in **Table 1**: addition order of HPW with respect to TEOS during the catalysts synthesis, temperature during the hydrothermal treatment and presence of CTAB as co-surfactant. The general protocol consisted of four main steps: co-condensation of silica precursors in presence of HPW to obtain a powder which was first dried, then calcined, washed and finally dried again under vacuum.

The surfactants weight percentages in the initial HCl/H₂O solution were kept at P-123 = 2.64 w/w% and CTAB = 0.27 w/w%. The molar ration CTAB/Si was equal to 0.028. Those are typical conditions, as already reported by Boissière et al. [20] and from Zhao et al. [21]. In the general synthesis protocol, 3 g of P-123 (and the appropriate amount of CTAB, when required) was poured in a two neck round bottom flask of 500 mL together with 125 g of a solution HCl 1.9 M. The mixture was put under magnetic stirring until complete P-123 dissolution. The flask was then placed in an oil bath at 40 °C and one of the necks was connected to a refrigerator. 8.16 g of TEOS (or 2.3 g of HPW) was then added dropwise to the flask and kept under agitation at 40 °C for 30 min (or 24 h) then the appropriate amount of HPW (or 8.16 g of TEOS) were dissolved in 5 mL of distilled water and added dropwise to the solution in the flask. The flask was kept 20 h (or 30 min) under magnetic stirring at 40 °C before being transferred in a Teflon lined autoclave equipped with a stainless-steel jacket. The autoclave was closed and placed in an oven at 80 °C for the decided duration without stirring. After that, the precipitated catalyst was filtered and dried under vacuum (20 kPa) at 70 °C prior to calcination at 500 °C during 6 h. The temperature was increased from room temperature to 500 °C at a rate of 2 °C/min. The solid was then placed in a Soxhlet extractor and washed with methanol overnight before being dried again at 20 kPa for 3 h and then grinded in an agate mortar and sieved to obtain particles below 100 μm in size.
The washing step was important to remove the HPW units which were not immobilized onto the support during the synthesis. The removal of those Keggin units was necessary to avoid their leaching in the liquid medium during the reaction. In this manner, the measurement of the HPW in the Soxhlet washing solvent made it also possible to indirectly estimate the amount of HPW efficiently immobilized.

2.3. Estimation of HPW immobilization efficiency

During the hydrothermal treatment in autoclave, the solid phase (gel) precipitated at the bottom and was separated from the residual supernatant liquid which contained traces of surfactant, hydrochloric acid and HPW not incorporated in the solid. After the hydrothermal treatment, this liquid was recovered and analysed by UV–vis spectroscopy to estimate the amount of HPW which was not incorporated in the silica matrix. Such measurement was also done on the methanol recovered after the catalyst washing by Soxhlet extraction. Knowing the amount of HPW which was not incorporated during the hydrothermal treatment and the HPW amount lost during the Soxhlet extraction, it was possible to assess the amount of HPW incorporated in the silica matrix at the end of the synthetic process by subtracting the losses from the initial quantity engaged in the synthesis.

UV–vis spectra were collected on a Beckman Coulter DU800 spectrometer in absorption mode between 200 nm and 800 nm at a speed of 1200 nm/min. The liquid was placed in a quartz cuvette. The blanks were collected placing distilled water or methanol, correspondingly, in the quartz cuvette. Calibration was done by analyzing solution of HPW in methanol and HPW in water at known concentrations.

2.4. Characterization of the solids

Raman spectra were collected using a RAMAN Microscope DRX, Thermo-scientific, equipped with a 780 nm laser focused on the samples via an optical microscope (10× magnification lens). The analysis parameters were set as follows: exposure time 30 s, laser power 10 mW, aperture 50 μm in pinhole mode. The wavenumber scanned was in the range 400–1800 cm⁻¹ with a resolution range of 3.0–4.1 cm⁻¹.

X-ray diffractograms were collected using a Siemens D5000 diffractometer equipped with a Cu Kα source working at 40 kV–40 mA and a scintillation detector. The 2theta range scanned was between 5 and 80° at a rate of 0.01°/s. Peaks identification and data treatment have been performed using the software QualX matching the experimental data with the PDF-2 database.

Specific surface area, pore volume and pore size distributions were obtained through nitrogen adsorption-desorption experiments performed using a Micromeritics Tristar 3000. Before the analysis, samples were degassed overnight under vacuum (6 Pa) at 150 °C. The measurements were performed at −196 °C and with relative pressures in the range of 0.01–1.00 (p/p0). The specific surface area was calculated from the adsorption isotherm in the p/p0 relative pressure range of 0.05–0.30 using the Brunauer–Emmett–Teller method (BET) and denoted afterwards S BET. The pore size distribution, mean pore diameter and pore volume were calculated by the Barrett–Joyner–Halenda method (BJH) using the data from the isotherm desorption branch.

For Transmission electron microscopy, the samples were grinded and suspended in ethanol, then sonicated for 30 min. A drop (7 μl) of the slurry obtained was deposited onto carbon film copper grids (Electron microscopy science CF200-CU, 200mesh) and placed under vacuum (20 kPa) for 4 h to remove the solvent. The electron microscope was a LE0922 Zeiss equipped with an EDX detector. The analysis was performed at 120 kV. The images were obtained in the bright field. The catalyst pore diameter was estimated using the software i-Tem. The pore size distribution was calculated using not less than 100 measured diameters.

Acidity measurements of the catalyst surface were done by Pyridine adsorption and temperature programmed desorption as follows. The catalysts were pressed to obtain a wafer. The wafer was weighted and then placed in a sample holder inside a Pyrex cell especially designed for the controlled heating of the sample under vacuum and equipped with an optical NaCl window. The sample holder was movable and it allowed the sample placement in the infrared beam for the recording of IR spectra or in the furnace for the thermal treatments. In a typical measurement, the sample was heated at 300 °C under vacuum (between 10⁻⁴ and 10⁻³ Pa) for 3 h in order to desorb physisorbed molecules from the surface. After cooling under vacuum, 1000 Pa of pyridine was sent at room temperature in the cell and adsorption was allowed for 30 min. The sample was then outgassed at 10⁻³ Pa in five steps: at room temperature and at 100 °C, 150 °C, 200 °C, 250 °C. For each desorption step, once the value of 10⁻³ Pa was reached, the sample was kept under vacuum for 1 h. FT-IR spectra were taken in transmission mode before and after pyridine adsorption and after each desorption step using a spectrometer IFS55 Equinox (Bruker) equipped with a DTGS detector. The spectra were recorded with 100 scans between 400 and 4000 cm⁻¹ with a resolution of 4 cm⁻¹.

Affinity of the reaction reagents and products for the catalyst surface was estimated through their retention times measured by HPLC with a method used by Van der Perre et al. [22]. A slurry of the catalyst as the stationary phase in toluene was prepared in an ultrasonically agitated reservoir. Using a slurry packer, a stainless-steel column (usually 50 mm in length and 2.1 mm in inner diameter, except the one used for the sample SBA-15 which inner diameter was 4 mm) was packed and allowed to settle at 35 °C for 1 h. MTBE was used as eluent. The retention factors were calculated using m-xylene as an unretained compound, because its retention time corresponds very well with the zero-void volume. The retention factor, k, was calculated using the formula

\[ k = \frac{t_{R} - t_{m-xylene}}{t_{m-xylene}} \]
where $t_i$ is the retention time of the compound $i$ (in minutes) and $t_m$ is the retention time of $m$-xylene (in minutes) which acts as a $t_0$ marker.

2.5. Catalytic activity and products identification

7 g of resorcinol was dissolved in 45 mL of methyl-tert-butyl ether in a 100 mL three necks round bottom flask surmounted by a refrigerator. The reactor was placed in an oil bath under magnetic stirring (1500 rpm) and heated at 60 °C under atmospheric pressure. Then, 0.7 g of catalyst was added. The reaction was monitored by GC–FID analysis. A solution of 1,3-dinitrobenzene in MTBE was used as internal standard (1:109 molar ratio of 1,3-dinitrobenzene: MTBE). For the sampling, 7 µL of reaction mixture was mixed with 0.2 mL of standard solution and diluted in 1.2 mL of MTBE.

The separation was performed by Gas Chromatography using a VARIAN 3800 equipped with a capillary column SGE HT5 12 m × 0.53 mm with an internal diameter of 0.15 µm. The temperature program was composed of three steps: a first segment at 55 °C hold for 1 min, then a ramp from 70 °C to 85 °C at a rate of 2 °C/min and a third ramp from 85 °C to 180 °C at a rate of 2 °C/min. The injector and detector temperatures were 320 °C and 360 °C, respectively. Helium was used as carrier gas at a flow rate of 20 mL/min. 1 µL of sample was injected in split mode 50.

After catalytic test, the catalyst was removed by filtration and the filtrate was evaporated to remove the solvent and deposited onto Celite® 545 (VWR) and placed at the top of a column of preparative flash chromatography. Flash chromatography was performed using petroleum ether/ethyl acetate solvent system and on normal phase silica gel (ROCC 60, 40 63 Dm). The eluent was analysed by thin Layer Chromatography (TLC) analyses performed on commercial aluminium plates bearing a 0.25 mm layer of Merck Silica gel 60® 254. The eluent was then eliminated by evaporation in rotary evaporator and the compounds in the solid state were recovered to be further analysed by NMR and HR-MS.

The alkylated products recovered by flash chromatography in the solid state were diluted in deuterated chloroform (CDCl₃) and then identified and characterized by $^1$H and $^{13}$C NMR. Spectra were recorded on Bruker 300 spectrometer at 300 MHz. $^1$H NMR and $^{13}$C NMR chemical shifts are reported relative to Tetramethylsilane (TMS), (0 ppm) or CDCl₃ (7.26 ppm for $^1$H, 77.0 ppm for $^{13}$C).

For further confirmation of the structure of the alkylated products, high resolution mass spectra were obtained using a Thermo scientific QExactive Reactive Electron spray. The analysis was run in negative polarity. The components identification was done using the Xcalibur software, with accurate mass reported for the molecular ion or suitable fragment ions.

3. Results

3.1. Heteropolyacids immobilization inside the SBA-15 matrix

After the hydrothermal treatment, the solid catalyst was filtered from the remaining liquid, which was recovered and analysed by UV–vis spectroscopy to estimate the amount of HPW which was not incorporated in the silica matrix. Such measurement was also done on the methanol recovered after the catalyst washing by Soxhlet extraction. Knowing the amount of HPW which was not incorporated during the hydrothermal treatment and the HPW amount lost during the Soxhlet extraction, it was possible to assess the amount of HPW incorporated in the silica matrix at the end of the synthetic process by subtracting the losses from the initial quantity engaged in the synthesis.

While catalysts HPW@SBA15-1 and HPW@SBA15-3 presented similar overall HPW losses of 16% and 22% respectively if compared with the initial HPW mass engaged, the catalyst HPW@SBA15-2

![Fig. 1. Quantification of HPW losses by UV–vis spectroscopy and calculation of immobilized HPW.](image-url)
presented the highest HPW losses of 47% (Fig. 1). HPW losses were distributed between the hydrothermal treatment and the washing step in the Soxhlet extractor. The HPW losses were the most significant during the hydrothermal treatment, with 16%, 33% and 15% of lost HPW for the catalysts HPW@SBA15-1, 2 and 3 respectively. HPW losses during Soxhlet extraction with methanol were lower: 14% for HPW@SBA15-2 and 7% for HPW@SBA15-3. For the catalyst HPW@SBA15-1, no losses of HPW during Soxhlet extraction were detected, indicating that for this sample the HPW immobilized during the hydrothermal treatment was highly resistant to leaching.

The mass fraction of HPW immobilized in the final solid catalysts was recalculated and falls in the range 30.2–41.9 wt% (Table 2).

3.2. Characterization of the solids

Raman spectra collected on the catalysts HPW@SBA15-1 and HPW@SBA15-3 showed presence of peaks assignable to the symmetric and antisymmetric stretching of W-Od in HPW at 1010 and 995 cm\(^{-1}\) respectively [23]. No peaks were detected when the catalyst HPW@SBA15-2 was analysed, which is probably due to high HPW dispersion on the catalyst surface. No peaks assignable to WO\(_3\) (essentially antisymmetric O\(\overline{A}\)W\(\overline{A}\)O stretching at 717 cm\(^{-1}\), symmetric O\(\overline{A}\)W\(\overline{A}\)O stretching at 808 cm\(^{-1}\)) or P\(_2\)O\(_5\) (at 258, 420, 555 and 723 cm\(^{-1}\) assigned to P=O wagging, P–O–P bending, P–O stretching and P–O–P bending respectively) were detected for any of the samples [24–26] (Fig. 2).

The diffractograms of the HPW@SBA15 catalysts are compared with the ones of HPW and WO\(_3\) in Fig. 3. No peaks were found in the diffractograms of any of the HPW@SBA15 samples even though HPW at the solid state is a highly crystalline material of which most intense peak is visible at 2theta = 25.44\(^\circ\). No WO\(_3\) peaks were detected as well, which is readily distinguishable by a series of peaks in the 2theta range between 20\(^\circ\) and 40\(^\circ\), at 23.62, 24.4, 26.9, 29.08 and 34.16\(^\circ\). Finally, no peaks were detected in the SBA-15 diffractogram, which is in this case expected for an amorphous material (see Table 3).

For all samples, nitrogen adsorption-desorption isotherms were of type IV, having a hysteresis loop indicating presence of mesopores open at both ends (Fig. 4). The specific surface area decreased when HPW was present in the samples. The pore volume showed the same decrease and varied between 0.21 and 0.98 cm\(^3\)/g.

The correct estimation of the pore size was affected by the nitrogen instability during desorption. At the instant nitrogen reaches a value called tensile strength while pressure is decreasing, sudden desorption takes place. This well-known phenomenon, called tensile strength effect, provokes an underestimation of the pore size, as an artificial peak appears on the pore size distribution, calculated using the BJH desorption model, below 4 nm [27]. The BJH approach cannot thus be used here to precisely measure the pore size. To avoid this problem, the pore diameter was then directly determined using Transmission Electron Microscopy.

All the catalysts showed an ordered mesoporous structure typical of SBA-15 (Fig. 5). The mesostructure presented hexagonal arrangement as expected from the use of P-123 as surfactant [28].

The pore size distribution (PSD) could be recalculated for each catalyst (Fig. 6). The average pore size for the catalysts varied from 3 to 7 nm (Table 4).

Infrared analysis of adsorbed pyridine allowed the identification of Brønsted (B) and Lewis (L) sites at the catalysts surface. Pyridine adsorbed onto SBA-15 showed very intense bands of the C\(\overline{A}\)C\(\overline{A}\)N stretching, assignable to pyridine coordinatively bonded onto strong L sites at 1450 cm\(^{-1}\) and weak L sites 1600 cm\(^{-1}\) (Fig. 7) [17]. An additional very weak band at 1490 cm\(^{-1}\) was detected and assigned to pyridine bonded to weak B sites. The Lewis acid sites onto SBA-15 are assumed to be formed by silicon unsaturated atoms present at the SBA-15 surface and/or by silica

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Estimated HPW content in the solid catalysts.</th>
</tr>
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<tbody>
<tr>
<td>Catalyst</td>
<td>HPW@SBA15-1</td>
</tr>
<tr>
<td>Estimated HPW content (wt.%)</td>
<td>41.9</td>
</tr>
</tbody>
</table>

![Fig. 2](image) Raman spectra of the HPW@SBA15 catalysts.

![Fig. 3](image) XRD patterns of the HPW@SBA15 catalysts. Patterns of tungsten trioxide (WO\(_3\)), phosphotungstic acid hydrate (HPW), and mesoporous silica (SBA-15) are also given for reference.

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Specific surface area and pore volume of HPW@SBA15 and SBA-15 obtained by nitrogen physisorption.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalyst</td>
<td>Specific surface area S(_{BET}) (m(^2)/g)</td>
</tr>
<tr>
<td>SBA-15</td>
<td>862</td>
</tr>
<tr>
<td>HPW@SBA15-1</td>
<td>330</td>
</tr>
<tr>
<td>HPW@SBA15-2</td>
<td>479</td>
</tr>
<tr>
<td>HPW@SBA15-3</td>
<td>306</td>
</tr>
</tbody>
</table>
dehydroxylation [29]. Condensation reactions involving isolated vicinal Si-OH groups causes the formation of rings containing 3 or 4 Silicon members: the change in the tetrahedral geometry around Silicon activates the d-acceptor orbitals allowing Silicon to act as a Lewis acid site. The weak B sites are probably formed by silanol groups.

The HPW@SBA15 catalysts showed the same bands (shoulder at 1600 cm\(^{-1}\) and peak at 1450 cm\(^{-1}\)) plus bands corresponding to pyridine bonded to strong L sites at 1613 cm\(^{-1}\). The presence of B sites was also revealed via peaks at 1540 and 1637 cm\(^{-1}\). These ones were not observed on SBA-15. The insertion of HPW inside the silica matrix introduced strong Brønsted acid sites at the catalyst surface. As a further consequence of HPW insertion the presence of stronger Lewis sites arose from the interaction between HPW and the silica network [30].

Several interpretations are reported in the literature for the pyridine band at 1490 cm\(^{-1}\). This band is very often assigned to the simultaneous presence of B and L sites at the catalysts surface [31], which was reported by several authors to rise from the contribution of both sites to pyridine adsorption [17]. Ward et al. [32] reported the band at 1490 cm\(^{-1}\) to be simultaneously characteristic of pyridinium ion and thus attributable to B acidity and characteristic of coordinatively bonded pyridine, thus attributable to L acidity. This combination band of pyridine on Lewis and Brønsted sites rises from simultaneous excitation of the two pyridine fundamental frequencies \(8a\) and \(19b\) [33]. More precisely, Kumar et al. [34] also reported this band to rise from the presence of sites of the kind M-OH-M in which the pyridine could bond simultaneously to the H atom (B site) and the metal atoms M (L sites).

![Fig. 4. Nitrogen adsorption-desorption isotherms (77 K) of the catalysts HPW@SBA15 and of SBA-15.](image)

![Fig. 5. TEM micrographs of HPW@SBA15 and SBA-15.](image)
Nevertheless, this band was already present, even though very weakly, in our SBA-15 without any trace of other bands assignable to pyridine bonded to strong B sites. Concerning this, Swoboda et al. [35], assigned the band at 1490 cm$^{-1}$ to pyridine bonded to weak Brønsted sites present at the surface. In our case, these weak sites could be represented by silanol groups.

The relative percentage of L and B sites out of total acidity was calculated using the intensity of the bands at 1450 cm$^{-1}$ and 1540 cm$^{-1}$ respectively, which are well resolved in the spectrum (Table 5).

### Table 4
Average pore diameter calculated from TEM micrographs.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Average pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>3.7</td>
</tr>
<tr>
<td>HPW@SBA15-1</td>
<td>5.7</td>
</tr>
<tr>
<td>HPW@SBA15-2</td>
<td>6.2</td>
</tr>
<tr>
<td>HPW@SBA15-3</td>
<td>7.0</td>
</tr>
</tbody>
</table>

3.3. Catalytic activity and products identification

The catalysts were tested in the resorcinol alkylation with methyl-tert-butyl ether. NMR and HRMS revealed that the reaction products consisted of a mixture of mono and poly-alkylated molecules. Alkylation occurred both on the aromatic ring (C-alkylation) and on the oxygen (O-alkylation) forming: resorcinol-mono-tert-butyl ether (RmTBE); 2-tert-butylresorcinol (2TBR); 4-tert-butylresorcinol (4TBR); 4,6-di-tert-butylresorcinol (46DTBR) (see NMR and HRMS data in the additional information, Table 1S. The NMR spectra are reported as well in Fig. 1N–4N in the additional information). Two additional products (named hereafter “other products”) were also detected but could not be identified. A hypothesis could be that the structure of this compounds are of C- and O-alkylated mixed type. Devassy et al. [1] also reported the same. However, during our work those products could not be isolated and characterized, hence their selectivity was calculated from the chromatographs assuming a response factor equal to one.

The resorcinol alkylation with MTBE was carried out in the temperature range from 60°C to 80°C. This was to limit the energy expenses and make the process greener. In addition, the catalyst was inactive below 60°C and the solution of resorcinol in methyl-tert-butylether was boiling above 80°C. Here, only the results obtained performing the reaction at 60°C were reported for comparison.

Resorcinol conversion was monitored during about 24 h (Fig. 8). After 1400 min of reaction, resorcinol conversion had reached 24% for the catalyst HPW@SBA15-2, 29% for the catalyst HPW@SBA15-1 and 35% for the catalyst HPW@SBA15-3. SBA-15 was tested as well and showed no activity.

Reaction selectivity was reported with respect to the resorcinol conversion for the HPW@SBA15-3 catalyst (Fig. 9). RmTBE was the first product to appear, followed by 2TBR, 46DTBR and finally 4TBR. While RmTBE, 2TBR and the other products are produced and then consumed during the reaction, 4TBR and 46DTBR accumulate with time. After 1400 min of reaction, 4TBR was the major product. When the other catalysts were tested, the reaction selectivity showed a similar trend (Fig. 2S and 3S in the additional information).

For the sake of comparison, the reaction selectivity for the three catalysts was reported at 20% iso-conversion (Table 6).

The selectivity for 4TBR decreased in the order HPW@SBA15-3 > HPW@SBA15-2 > HPW@SBA15-1. Simultaneously, the selectivity
to all the other products (identified and not identified) generally increased.

### 3.4. Affinity of the reaction reagents and products for the catalysts

The affinity of resorcinol and of the alkylated products for the catalyst surface was investigated via HPLC adsorption experiments. The retention time of the alkylated compounds was compared with the retention time of the reagent resorcinol and decreased in the order 4TBR > (or \( > \)) resorcinol > 4TBPh > 46DTBR (Fig. 10). Since only few milligrams of RmTBE could be isolated after reaction, its isomer 4TBPh was used as replacement during the HPLC experiments. The higher 4TBR retention time with respect to the other compounds suggested a slightly higher affinity for the catalyst surface.

### 4. Discussion

#### 4.1. Efficiency of HPW immobilization

The efficiency of HPW immobilization during the synthesis was investigated by UV–vis spectroscopy. The HPW losses during the hydrothermal treatment depended on the interaction between the Keggin anion and the forming silica network. The catalysts HPW@SBA15-1 and 3 showed good encapsulation yields and the losses were limited to 16% and 22% of the initial HPW mass introduced in the synthesis medium. As a counterpart, despite the higher initial HPW mass used, the catalyst HPW@SBA15-2 had almost 50% of HPW quantity left in the filtrate.

One hypothesis to explain this phenomenon is that, HPW being a super-acid in water, the higher amount added in the medium decreased the pH too much during the synthesis. Even though a pH lower than 2 is required to keep the silica positively charged during the synthesis, a too low pH can dissolve the already formed silica particles and disperse the Keggin anions in solution.

CTAB addition was supposed to increase the amount of immobilized HPW. As already reported in the literature by Boissière et al. [20], the assembly mechanism of the H₃PW₁₂O₄₀/SBA15 catalysts depends on the addition order of HPW with respect to TEOS and can be described as follows. First, P-123 was dissolved in an acidic solution of HCl. The dissociated protons from HCl protonated the micellar corona (schematized as I+) and the Cl⁻ anions arranged around the micelles forming a negative charged layer. When HPW was added to the aqueous environment, it was completely dissociated into 3H⁺ and PW₁₂O₄₀⁻. The PW₁₂O₄₀⁻ anion exchanged with the Cl⁻ ions at the micelles periphery (Fig. 11a). The following TEOS addition made the system evolve toward the configuration S⁺-PW₁₂O₄₀⁻I⁺, where S⁺ represents the silicic acid H₅SiO₄⁺, which simultaneously polymerizes in the acidic environment to form the silica network.

During the synthesis of HPW@SBA15-2 catalyst, TEOS was added before HPW. The interaction can be written as PW₁₂O₄₀⁻S⁻-
Cl⁻ with the HPW in contact with the poly-condensing silica [18] (Fig. 11b). The addition of CTAB does not disturb the self-assembly mechanism described above. Once dissolved in the aqueous medium it dissociates in CTA⁺ and Br⁻. The hydrophobic long chains of the CTA⁺ cation enter in the P-123 micelles close to the hydrophobic core while the charged head groups form an addi-

Fig. 11. Self-assembly mechanism during the synthesis of HPW@SBA15 catalysts.
tional positive charge distribution deep in the PEO chains layer. In this way CTA⁺ was supposed to interact with some of the PW₁₂O₄₀⁻⁻ to form the corresponding ammonium salt, hence forcing the HPW to remain between the forming silica network and the surfactant micelles and consequently favoring HPW immobilization [18] (Fig. 11c).

In our case, the addition of CTAB did not increase the amount of immobilized HPW, probably because it was added after TEOS during the synthesis. In this manner, the HPW had no chance to directly interact with CTAB during the self-assembly mechanism (Fig. 11d).

HPW losses during the Soxhlet extraction were limited to the Keggin units which could not establish a strong interaction with the support during the synthesis and the following drying and calcination steps. This was the case for catalysts HPW@SBA15-2 and 3, which released residual weakly bonded HPW during the extraction. The catalyst HPW@SBA15-1 did not show HPW loss and this can be due to the synthesis conditions: in this case TEOS was added first and left for hydrolysis for 30 min prior to HPW addition. In this way, HPW was put in contact with at least partially hydrolyzed TEOS in the form R₃Si-OH (R = OCH₂CH₃), favoring the establishment of interaction of the kind (≡Si-OH)⁺(H₂PW₁₂O₄₀⁻⁻). Furthermore, the HPW quantity added was not too much as in the case of HPW@SBA15-2, preventing the pH to be lower than 2 which would dissolve the silica particles. Finally, for HPW@SBA15-1, the hydrothermal treatment lasted only 24 h, thus probably preventing the weak immobilization of excess HPW units. Longer hydrothermal treatment duration (72 h in the case of HPW@SBA15-3) did not improve the HPW amount, which was lost during the Soxhlet extraction. This suggests that after a certain time, further HPW units do not longer interact strongly with the silica matrix and are leached during the washing. This could also be due to saturation of the silica network charge.

In all the three syntheses, although the HPW losses were not negligible, still a good quantity of HPW could be immobilized in the silica matrix, leading to the synthesis of catalysts containing HPW in an appreciable quantity (30.2–41.9 wt%).

4.2. State of incorporated HPW

Raman spectroscopy has been widely used in the literature to assess the stability of HPW when exposed to high temperature [36]. This is because the HPW spectrum shows completely different features with respect to the spectrum of WO₃, which is a product of HPW decomposition (Fig. 15 in the additional information). Raman spectra taken on our catalysts HPW@SBA15-1 and 3 confirmed the presence of intact HPW and absence of WO₃ (of which the presence would reflect a partial decomposition). P₂O₅ also presents peaks in Raman but was never observable on any of our HPW@SBA15 catalysts. Even in the case of HPW decomposition, P₂O₅ would be unlikely to detect due to its high volatility when exposed to high temperature as during the calcination step. On the contrary, WO₃ is stable at high temperature and could have grown on the surface sample upon HPW decomposition [24].

The calcination temperature of 500 °C was chosen to allow the complete surfactant removal and free the catalysts surfac from organic residuals. Although it was higher than the decomposition temperature of HPW, the intimate contact between the HPW and the support obviously prevented the decomposition.

The high HPW dispersion inside the silica matrix was confirmed by X-ray diffraction. X-ray diffractograms did not show the presence of any peak assignable to HPW, thus suggesting the absence of large crystalline HPW aggregates. Simultaneously, as just mentioned above, the presence of HPW was proved by Raman spectra. Thus, the combination of Raman and XRD allows claiming that HPW aggregates are not larger than 3–4 nm.

In Raman, the HPW signal strongly depends on the degree of crystallinity and on the environment. The more isolated the HPW in the sample, the lower the signal intensity. The absence of signal of HPW in the Raman spectra of HPW@SBA15-2 can be considered as a sign of high HPW dispersion in the corresponding silica matrix, indicating that HPW units may be individually dispersed.

TEM micrographs confirmed that the catalysts possessed mesoporous and homogeneous SBA-15-like texture. This means that the long range textural order was kept despite the HPW incorporation. EDX analysis showed the presence of tungsten in the mesostructured particles, indicating that the HPW did not form a separate phase aside (Figs. 4S, 5S and 6S in the additional information).

To summarize, the three samples HPW@SBA15-1, HPW@SBA15-2 and HPW@SBA15-3 featured mesoporous homogeneous texture with well dispersed, intact and immobilized HPW and therefore possessed the suitable characteristics for drawing a link between surface chemistry and reaction selectivity.

4.3. Link between HPW location, surface acidity, retention factors and selectivity

Infrared analysis of adsorbed pyridine showed that the three catalysts have different proportions of Brønsted and Lewis acid sites at their surface. HPW@SBA15-1 showed the highest amount of accessible Brønsted sites, representing 64% out of its total acidity. The percentage of B sites out of total acidity decreased in the order HPW@SBA15-1 > HPW@SBA15-2 > HPW@SBA15-3. Infrared analysis of adsorbed pyridine revealed the presence of Lewis sites at the SBA-15 surface. Those sites are generated by silicon unsaturated atoms present at the SBA-15 surface and/or by silica dehydroxylation. The insertion of HPW, which are strong Brønsted acids, inside the silica matrix introduced strong Brønsted acid sites at the catalyst surface. As a further consequence of HPW insertion, stronger Lewis sites arose from the interaction between HPW and the silica network.

The difference in the Brønsted to Lewis acid sites ratio can be linked to the variation of the synthesis parameters. Brønsted to Lewis sites proportion could be first linked to the heteropolyacids loading. The catalyst HPW@SBA15-1, having the highest HPW loading, showed the highest fraction of Brønsted sites (Table 5). Concerning the other two samples, an alternative explanation was reported by Dufaud and others [12], who linked the HPW location inside the silica matrix to the synthesis conditions, explaining that pre-hydrolysis of TEOS in the presence of P-123 followed by HPW introduction (as in the case of HPW@SBA15-2) resulted in the HPW tendency to be embedded in the support walls [18,37,38]. On the other hand, the dissolution of HPW in the aqueous surfactant suspension followed by TEOS addition (as in the case of HPW@SBA15-3) was reported to push the HPW to the pore walls surface [19]. These hypotheses are contradictory with our findings since HPW@SBA15-2 was found to be more Brønsted acidic than HPW@SBA15-3. In our case, a combination of both, HPW loading and synthesis conditions, are considered affecting the B/L ratio and it is difficult to disentangle the effect of one from the other.

Concerning the hydrothermal treatment duration, it was already found to have poor effect when not being detrimental for the HPW immobilization. It was also found to give no improvement on the surface acidity: for the catalysts HPW@SBA15-1 and 2, for which the B sites % of sites was higher (64% and 58%, respectively), the hydrothermal treatment lasted only for 24 h, while for the catalyst HPW@SBA15-3 (42% of B sites) it was 72 h. Additional time did not increase the density of B sites at the surface as the eventual additional HPW units were only weakly adsorbed and removed upon Soxhlet extraction.
The catalysts were active in the resorcinol alkylation with MTBE. Resorcinol conversion decreased in the order HPW@SBA15-3 > HPW@SBA15-1 > HPW@SBA15-2 from 35% to 24% of resorcinol converted after 24 h of reaction. Regarding this, Nur et al. already reported that B/L ratio affected the resorcinol conversion, which was found to reach a maximum when the B % approached 50%[39]. This is well in agreement with our findings, since HPW@SBA15-3 possess B% equal to 42% (the closest to 50%) thus confirming the importance of tailoring the catalyst surface chemistry to improve not only the catalyst selectivity but also the conversion.

Other authors have already reported about resorcinol tert-butylolation conversion over different catalysts. As an example, Nur et al. already reported that B/L ratio affected the resorcinol conversion, which was found to reach a maximum when the B % approached 50%[39]. This is well in agreement with our findings, since HPW@SBA15-3 possess B% equal to 42% (the closest to 50%) thus confirming the importance of tailoring the catalyst surface chemistry to improve not only the catalyst selectivity but also the conversion.

Retention times were measured in HPLC columns packed with the catalysts to evaluate the affinity between the reaction reagents and products for the various catalysts. As a general trend, the compounds show only a weak affinity for the catalysts surface, as is visible from the very low retention factor values (Fig. 10). The retention factors of resorcinol and 4TBR were higher than those of 46DTBR and 4TBPh, due to the availability of both the hydroxyls group present on the resorcinol and 4TBR rings for surface adsorption. Dihydroxybenzenes are indeed reported to adsorb onto oxide surfaces through their phenolic oxygens[40]. 4TBPh possesses only one —OH group available for adsorption, since the second —OH group is hindered by the presence of one tert-buty1 group. 46DTBR hydroxyls are hindered by the presence of two tert-buty1 groups on the adjacent carbon positions, which inhibits the adsorption.

4TBR retention time decreased in the order HPW@SBA15-3 > HPW@SBA15-2 > HPW@SBA15-1, indicating higher affinity of this compound for the surface of HPW@SBA15-3. The latter was also the catalyst most selective for 4TBR.

The reaction selectivity at 20% of conversion was correlated with the surface acidity for the three catalysts. The selectivity for 4TBR increased from 24% for the catalyst HPW@SBA15-1 to 33% for the catalyst HPW@SBA15-2, to 41% when HPW@SBA15-3 was used (Fig. 13).

The comparison between surface chemistry and catalytic activity suggests the following reaction mechanism: in the first step of the reaction, MTBE is converted to methanol and tert-buty1 cation onto B sites. Then, resorcinol, which was adsorbed onto Lewis sites, is converted to RmTBE (Fig. 14a and b) which is quickly desorbed.
from the Lewis site, because of its low affinity with the catalyst surface (Fig. 14c). As the resorcinol conversion to RmTBE increases, RmTBE concentration in the catalyst pores increases. If RmTBE enters into the pore system of the catalyst and comes in contact with, in this case, a Brønsted site, it can be isomerized to 4TBR which is released in the reaction medium (Fig. 14d and e). However, the isomerization is slow because of the competitive adsorption of RmTBE and MTBE onto B sites. The adsorption of MTBE is preferred, because of its high concentration in the reaction medium (MTBE is used in excess as solvent). That is why 4TBR appears later than RmTBE. Due to its affinity for the catalyst surface, part of 4TBR can be re-adsorbed onto Lewis sites to be converted to 46DTBR (Fig. 14f and g). 46DTBR is finally desorbed and accumulates in the reaction medium because its adsorption (either on Brønsted or Lewis sites) is hindered by the two tert-butyl groups (Fig. 14h).

The 4TBR conversion to 46DTBR was expected to be fast and was supposed to go to completion because 4TBR adsorption is preferred onto HPW@SBA15-3 L sites as shown by its higher retention factor. Despite this, we observed slow 4TBR conversion to 46DTBR. In addition, a plateau in the resorcinol conversion was found to appear after 5 h of reaction. We hypothesize that this phenomenon is due to presence of methanol in the reaction medium, which is obtained as by-product of the MTBE conversion during the first step. Methanol was found to be prone to interact strongly with Keggin heteropolyacids [41] and in particular to be a Brønsted site.
blocking molecule which acts as a poison for the catalyst [42]. To confirm this, catalytic tests were carried out using methanol as solvent and the catalysts were found to be inactive in such conditions. So, as the reaction proceeds methanol molecules bond to HPW protons inhibiting the catalytic activity. As the MTBE conversion increases, the B sites are gradually poisoned and, consequently, there is no more tert-butyl cation available to alkylate 4TBR to 46DTBR. The reaction followed the same mechanism for all the HPW@SBA15 catalysts. SBA-15 was tested as well in the resorcinol tert-butylation and showed no activity. This underlines the importance of having strong B sites available at the catalyst surface.

The difference in 4TBR selectivity can be explained considering the difference in B/L ratio at the catalysts surface. Among them, HPW@SBA15-3 possesses the right B percentage with respect to HPW@SBA15-1 and 2, for the 4TBR selectivity improvement. At the beginning of the reaction the catalysts B sites are free and active to convert MTBE and RmTBE. As the reaction proceeds, the B sites are gradually deactivated by the adsorbed methanol. The number of B sites onto HPW@SBA15-3 allows the poisoning to occur at the right reaction coordinate to avoid the 4TBR conversion to 46DTBR. Even though 4TBR presents high affinity for the HPW@SBA15-3 catalyst surface, once it is adsorbed onto Lewis sites it finds less and less active B sites in proximity to be alkylated. HPW@SBA15-1 and 2 possess a higher number of B sites, so that upon 4TBR adsorption, still a relevant number of active B sites is available to convert it into 46DTBR. Therefore, onto HPW@SBA15-3, the 4TBR production is higher despite the fact of higher thermodynamic stability of 46DTBR.

5. Conclusion

Immobilization of HPW in the SBA-15 silica framework resulted in the synthesis of active catalysts for the resorcinol tert-butylation. The three catalysts synthesized in this work, HPW@SBA15-1, HPW@SBA15-2 and HPW@SBA15-3, featured a mesoporous homogeneous texture with well dispersed, intact and immobilized HPW, suitable for assessing the impact of the catalyst surface chemistry onto the reaction selectivity. The alkylation product distribution of resorcinol with methyl–butyl ether (MTBE) over solid acid catalysts, Green Chem. 3 (2010) 682–703.


D. Zhao, J. Sun, Q. Li, G.D. Stucky, Masonry transport and with the project PDR-T.0064.16. François Devred is thanked for the technical support.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.01.010.


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