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

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ABSTRACT

Keggin tungstophosphoric acid ($H_3PW_{12}O_{40}$, 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 homogeneous catalysts in terms of reactant conversion and product selectivity.

Different classes of materials have been studied and utilized as heterogeneous catalysts for the alkylation reaction, including zeolites [4], metal oxides [5], sulphated zirconia [6], clays [7], supported triflates [8]. Alternatively, heteropolyacids can be used as catalysts as they are strong and thermally stable Brønsted acids [9]. In spite of their solubility in polar reaction media, heteropolyacids have been widely used in the development of insoluble solid acid catalysts for liquid-phase reactions [10]. Among the heteropolyacids, the Keggin-type phosphotungstic acid ($H_3PW_{12}O_{40}$, hereafter noted HPW) is known to be an effective catalyst when supported on different silica supports, for the Friedel-Crafts type alkylation and acylation [11].

In literature, the HPW incorporation in silica has been the object of many studies and several encapsulation techniques in a silica matrix are available [12]. One very effective method, which has been selected in this study as the most suitable synthetic route, is the direct synthesis of HPW immobilized on Santa Barbara Amorphous (SBA) silica, specifically SBA-15, via hydrolytic sol-gel encapsulation [13].

The synthesis of HPW@SBA15 catalysts via the sol-gel method presents indeed several advantages for the achievement of well dispersed and strongly immobilized active phases in the support matrix:

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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*-butylation 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@SBA15 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 HPW@SBA-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 tetra ethyl orthosilicate (TEOS) with respect to HPW during the synthesis, the mass of HPW engaged, presence/absence of cetyltrimethylammoniumbromide (CTAB) as co-surfactant and the hydrothermal treatment duration. To fully characterize the catalysts, UV–Vis spectroscopy, Raman spectroscopy, nitrogen physisorption, X-ray powder diffraction, Transmission Electron Microscopy, Energy Dispersive X-ray analysis were used. Special attention was given to the characterization of the catalysts surface chemistry, namely the catalyst surface acidity and its impact on catalytic selectivity. Therefore, High Performance Liquid Chromatography (HPLC) was used to determine the affinity of the reagents and products for the catalysts surface in liquid phase, which regulates the adsorption-desorption phenomena during the reaction. Infrared analysis of adsorbed pyridine was used to characterize the catalysts surface acidity and calculate the relative amount of Brønsted and Lewis acid sites.

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-dinitrobenzene (Sigma Aldrich, 97%), phosphotungstic acid hexahydrate $H_3PW_{12}O_{40}*6H_2O$ (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 WO_3, UCB, reagent grade), Cetyltrimethylammoniumbromide (hereafter noted CTAB, Sigma-Aldrich), Pluronic® P-123 (hereafter noted P-123, Sigma-Aldrich), 4-*tert*-butoxyphenol (hereafter noted 4TBPh 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/H_2O 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.