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Supplementary information

"Fishing" of heteropolyacids into carbonaceous seine via coking

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Preparation of catalysts

The silica supported HPW/SiO_2 sample was prepared by incipient wetness impregnation of amorphous silica (Q-40c, Fuji Silica) with aqueous solution of $H_3PW_{12}O_{40}$ acid followed by drying at 383K in air and calcination at 773K in air flow for 3 hours.

Controlled coking for the synthesis of HPW/SiO_2@C was carried out in a fixed bed flow reactor under atmospheric pressure at 573K. Formaldehyde and isobutene mixture with C_4H_8/CH_2O molar ratio of 5 were fed for 5 hours with the weight hourly space velocity of formaldehyde of 0.3 g/g·h. After coking the sample was purged with flow of helium at 623 K for 1 hour to remove physically adsorbed species. For silica matrix leaching 40 wt% HF water solution was used. 10g of HPW/SiO_2@C was stirred in 100 ml of HF at 353K for 3 hours, than the mixture was filtered, washed with distilled water to remove traces of HF and dried at 393K overnight. The prepared material was denoted as HPW@C.

Characterization

The elemental analysis was performed using energy dispersive X-ray fluorescence spectroscopy (EDXRF). Prior to the analysis the samples were mixed with $B(OH)_3$ and pressed in self-supporting wafers. The wafers were analyzed using a Thermo Scientific ARL Perform'x WDXRF.

N_2 sorption-desorption isotherms were measured at 77K using a Micromeritics ASAP-2000 automatic surface area and pore size analyzer.

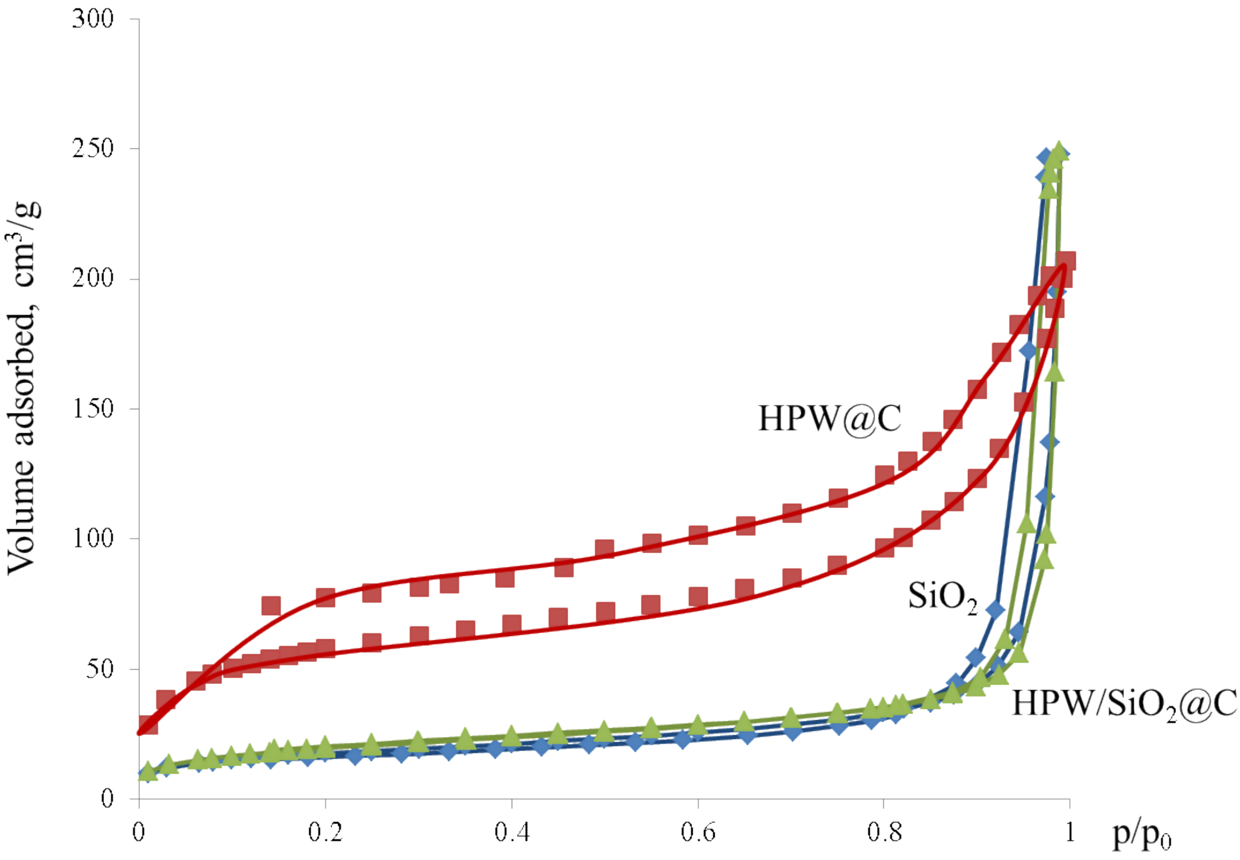

Figure S1. Nitrogen adsorption/desorption isotherms obtained at 77K over catalysts.

The ^{13}C and ^{31}P MAS NMR measurements were carried out on AVANCE-400 Bruker spectrometer.

Used catalysts were characterized by TG analysis on “TA SDT Q600” instrument in a flow of dry air in the temperature range of 300 to 1073K with the rate of heating of 10K/min.

The TEM analyses were carried out on a Jeol 2100F (field emission gun) microscope operating at 200 kV and equipped with the Tridiem GIF filter with an energy resolution of 0.7 eV. The zero loss TEM imaging procedure consists in imaging only the electrons elastically scattered by applying an energy “filter” on the zero loss peak within the EELS spectra. As consequence, the image contrast is considerably improved when compared to the conventional TEM imaging.

The EFTEM imaging is based on the Electron Energy Loss spectroscopy (EELs) and therefore the choice of the filtering windows is crucial. It is performed on the associated EEL spectra. In practice, the windows widths are chosen as function of the element and its intensity. In this case, the energy windows W1 and W2 marked in Figure S2 (a) were chosen for the background extraction whereas Figure S2 (b) displays from left to right: the W2 micrograph, the

W3 post-edge image acquired using on the carbon edge and the carbon map after images extraction, respectively.

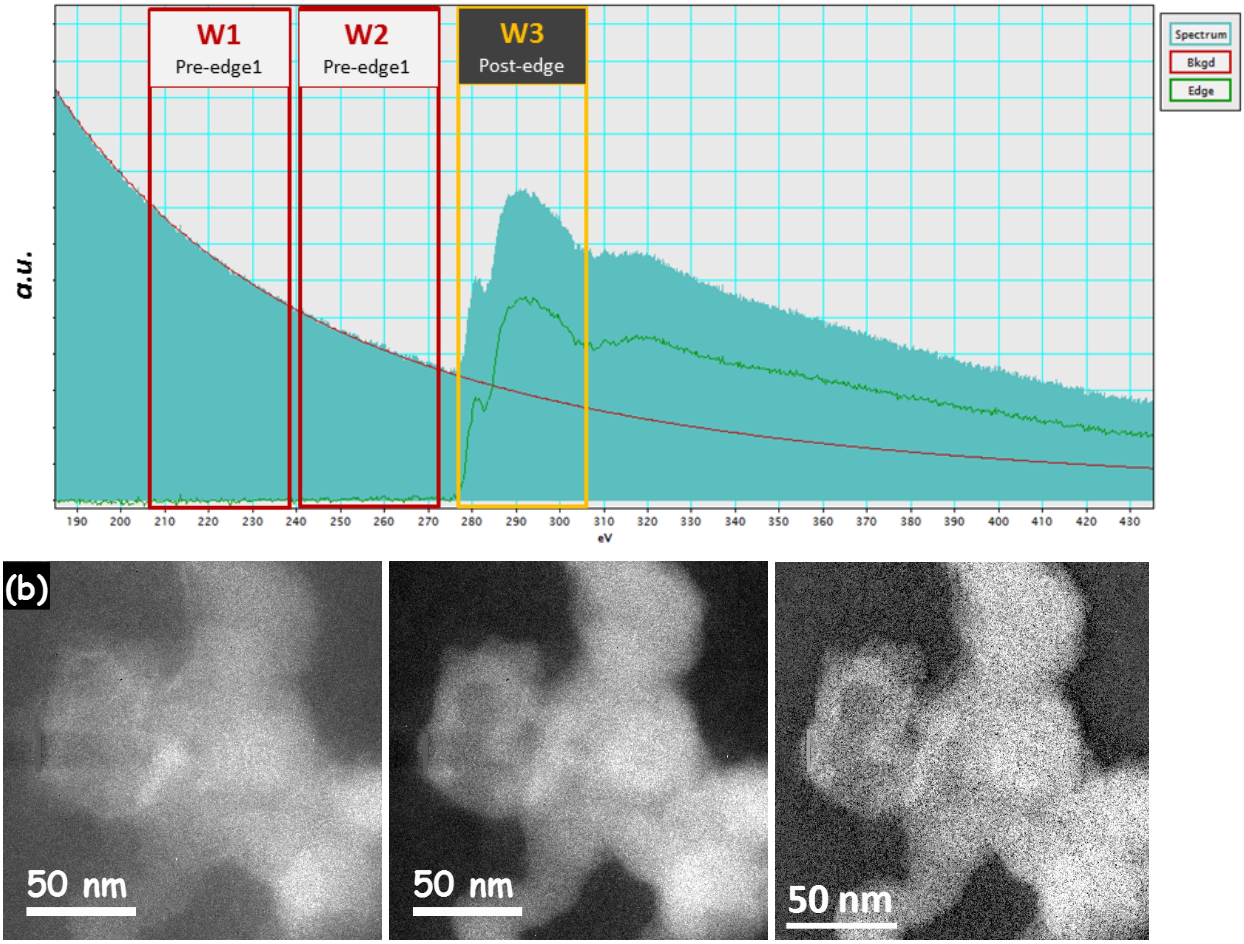

Figure S2. EFTEM imaging procedure. (a) the EEL spectra with the two pre-edge and one post-edge windows; (b) EFTEM micrographs acquired using the W2 and W3 windows and the carbon map ahieved by the “three-windows” method of signal extraction.

Catalytic tests

Catalytic tests of acetic acid esterification with ethanol were performed in batch type reactor at 333K. A reaction mixture of 10 g of ethanol with 10 g of acetic acid was used. The products were analysed by GC. Amount of the catalyst used for each test was normalized to 0.1 g of pure $H_3PW_{12}O_{40}$.