Supporting information for

HKUST-1 silica aerogel composites: the novel materials for separation of saturated and unsaturated hydrocarbons by conventional liquid chromatography

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1. FT-IR spectroscopy

The FT-IR spectroscopic analysis was performed using Bruker Vertex 70v spectrometer equipped with a diamond ATR accessory (Specac, Ltd., UK) and DLaTGS detector. The spectrum of sample was recorded from 5000 cm^{-1} to 370 cm^{-1} using 128 scans at a resolution of 2 cm^{-1}. These spectra were transformed with ATR correction function with refractive indices (n = 1.5) on Opus software.

Figure S1 are shown FTIR-ATR spectra of pure silica aerogels, HKUST-1 and HKUST-1@SiO_2 aerogel composite in region 370–1800 cm^{-1}. Silica aerogels is characterized absorption bands 1072, 810 и 450 cm^{-1}, that can be assigned to the stretching vibration of Si–O–Si and Si–O groups, it is described in detail in Ref. [1]. Absorption bands at 1627 cm^{-1} are assigned to O–H bending vibrations of adsorbed water. Spectra of HKUST-1 have absorption bands around 1700–1500 и 1500–1300 $см^{-1}$ which are attributed to $\upsilon_{asym}(COO^-)$ and $\upsilon_{sym}(COO^-)$ stretching modes, bands 710–758 cm^{-1} characterize the out-of-plane vibrations of C–H of the benzene ring. Absorption band at 510 cm^{-1} is due to a vibrational mode directly involving the Cu center [2].

HKUST-1@SiO_2 aerogel composite is characterized by the same set of absorption bands that have both spectra SiO_2 aerogel and HKUST-1. At HKUST-1@SiO_2 aerogel composite spectrum there is no appearance of new absorption bands, disappearances and the displacement of the absorption bands observed earlier for SiO_2 aerogel and HKUST-1, there is only a strong decline in the intensity of bands HKUST-1 in aerogels. This is due to the different density of HKUST-1 and HKUST-1@SiO_2 aerogel composite and, correspondingly, different volumetric concentration of HKUST-1. IR-spectroscopy data show no noticeable interactions between HKUST-1 and SiO_2.

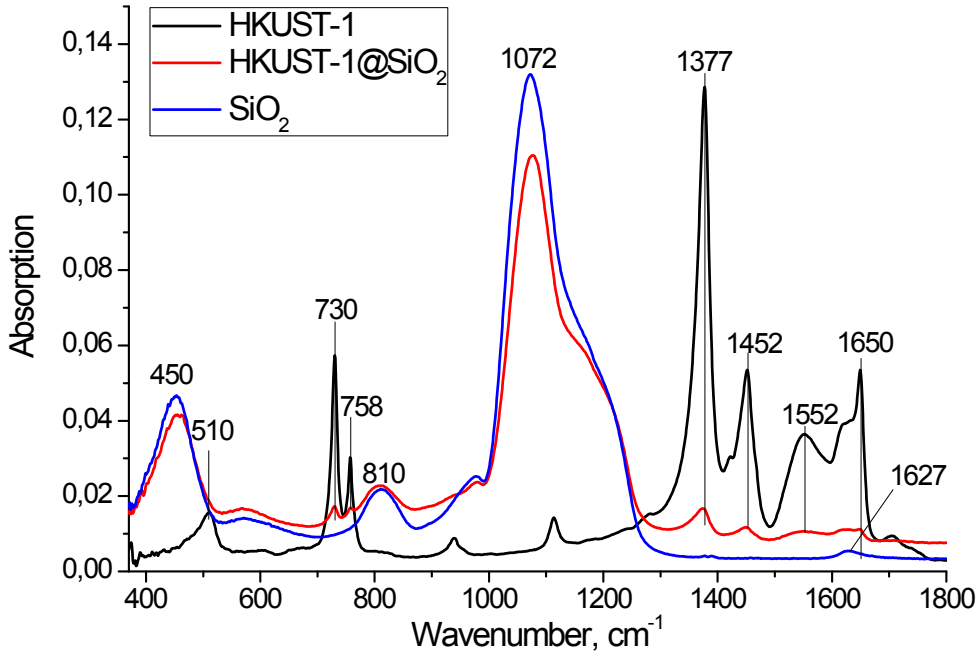

Figure S1. FT-IR spectra of HKUST-1, SiO_2 aerogel and HKUST-1(30%)@SiO_2 aerogel composite. All samples were activated at 200°C *in vacuo* for 3 h.

2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectra were recorded on a SPECS (Germany) photoelectron spectrometer using a hemispherical PHOIBOS-150-MCD-9 analyzer (Mg Kaα radiation, hnν = 1253.6 eV, 100 W). The binding energy (BE) scale was pre-calibrated using the positions of the peaks of $Au4f_{7/2}$ (BE = 84.0 eV) and $Cu2p_{3/2}$ (BE = 932.67 eV) core levels. The samples in the form of powder were loaded onto a conducting double-sided copper scotch. For the survey were recorded at pass energy of the analyzer of 50 eV; that for the narrow spectral regions was 20 eV. The concentration ratios of elements on the sample surface were calculated from the integral photoelectron peak intensities which were corrected with theoretical sensitivity factors based on Scofield's photoionization cross sections [3].

The X-ray photoelectron spectra of HKUST-1 and HKUST-1@SiO_2 aerogel composite are shown in Figure S2. Two characteristic peaks of divalent Cu^{2+} were observed at 934.9 and 954.8 eV corresponding to $Cu2p_{3/2}$ and $Cu2p_{1/2}$, respectively [2, 4]. The $Cu2p_{3/2}$ and $Cu2p_{1/2}$ binding energies of HKUST-1 and HKUST-1@SiO_2 aerogel composite are equal. XPS data show no noticeable destruction of HKUST-1 and interactions between HKUST-1 and SiO_2 matrix.

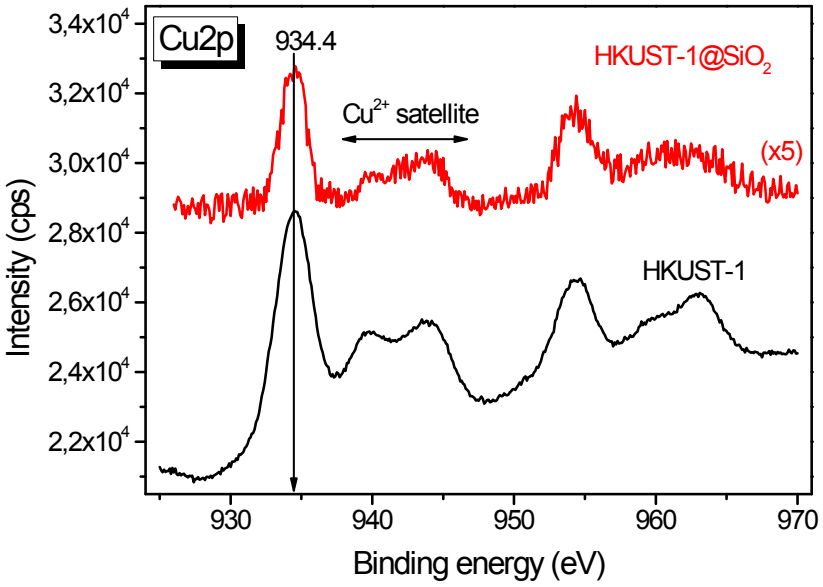

Figure S2. Cu2p XPS spectra of HKUST-1 and HKUST-1@SiO_2 aerogel composite

3. Scanning Electron Microscopy

The microstructure and element mapping was checked by SEM (JEOL, model JSM 6460-LV) with energy-dispersive spectrometer INCA Energy350 (Oxford Instruments). Test samples were previously coated with carbon film of 30–50 nm thick to reduce noise in the micrographs caused by the effects of charging samples. Micrographs were obtained with the electron energy of 20 keV. To analyze the morphology of the surface the images were obtained in the detection mode of secondary electrons.

SEM image and Cu, Si element maps of HKUST-1@SiO_2 aerogel composite are shown on Figure S3. It is seen that the HKUST-1 domains embedded in the surface of silica aerogels. Element maps are shown the absence of silicon, the presence of copper in HKUST-1 domains embedding locations. Consequently, the HKUST-1 domains uniformly are distributed in the bulk silica aerogel.

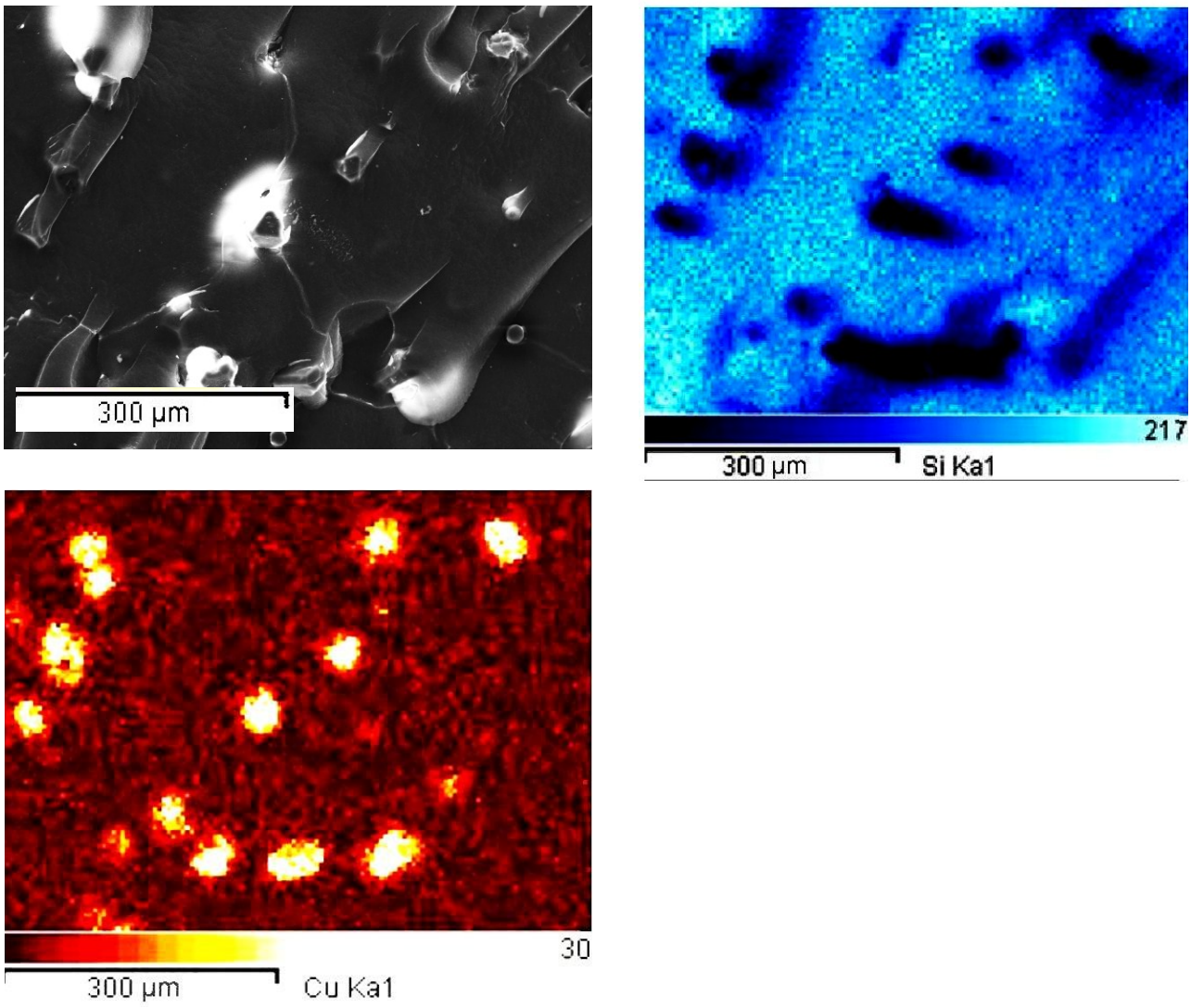

Figure S3. SEM images of HKUST-1(30%)@SiO_2 aerogel composite with Si, Cu element maps.

References

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