

SUPPLEMENTARY MATERIAL

Enhancing Catalytic Properties of Silicalite-1 through Ammonium Fluoride Modification for Waste Glycerol Acetalization

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Table S1. Mass loss of the modified Silicalite-1 due to NH₄F treatment.

Sample	Concentration of NH ₄ F [mol/dm ³]	Mass loss [%]
Sil-1(0.5F)	0.5	15
Sil-1(1F)	1	23
Sil-1(2F)	2	39
Sil-1(3F)	3	48

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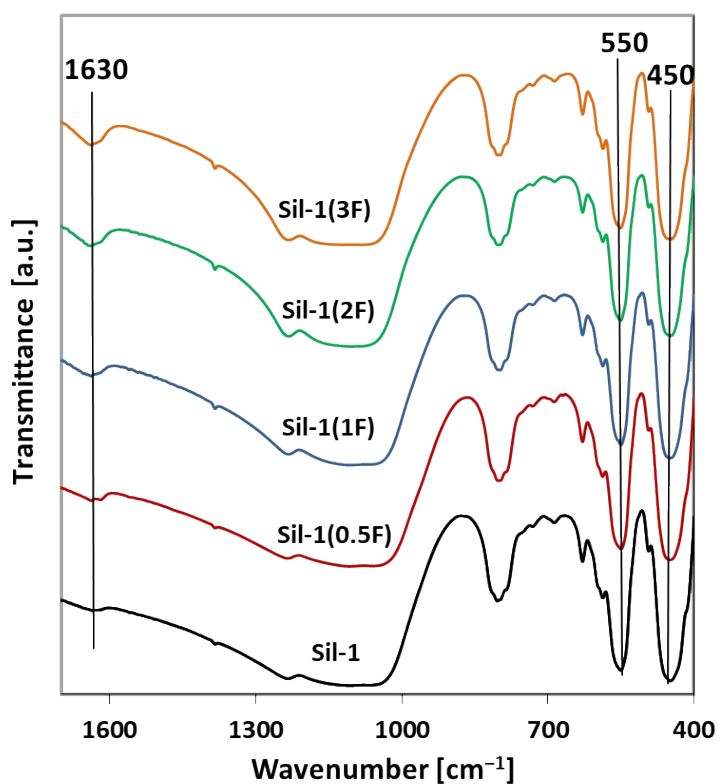


Figure S1. FTIR spectra (KBr) of pristine and modified Silicalite-1 samples in the region of skeletal vibrations.

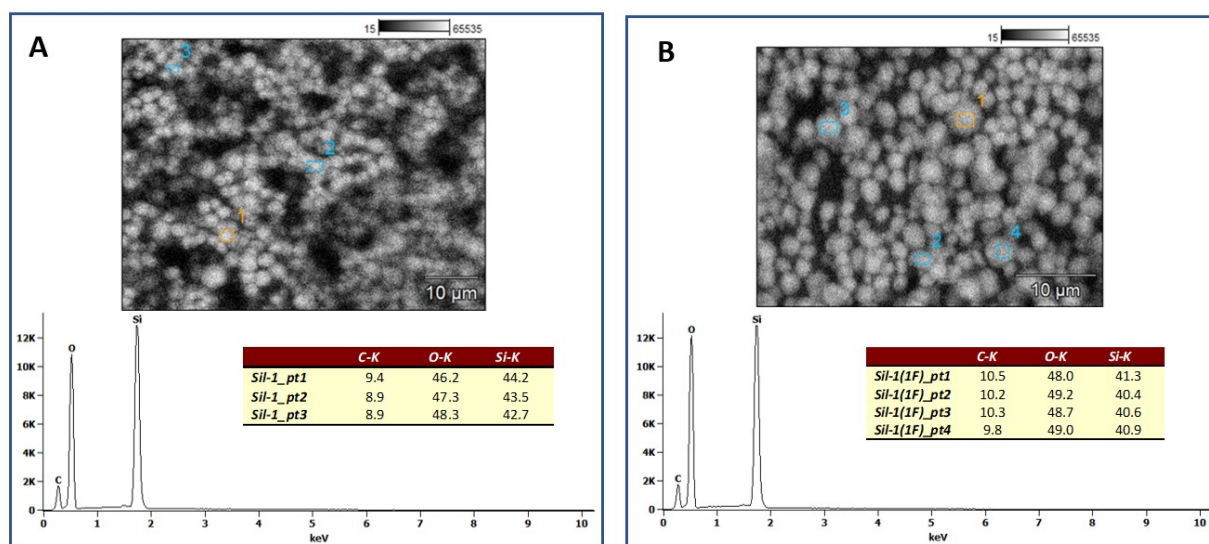


Figure S2. SEM micrograph and EDS spectra of Sil-1 (A) and Sil-1(1F) (B).

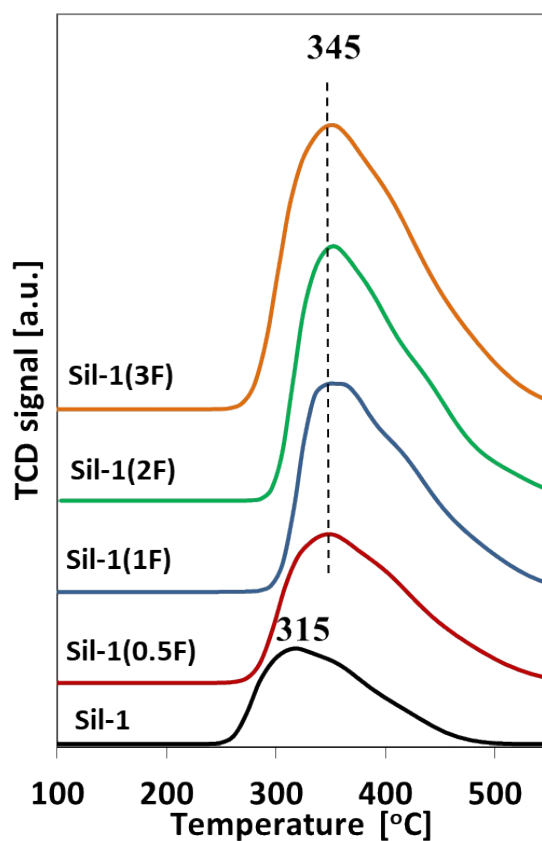


Figure S3. TPD-NH₃ profiles of pristine and modified Silicalite-1 samples.

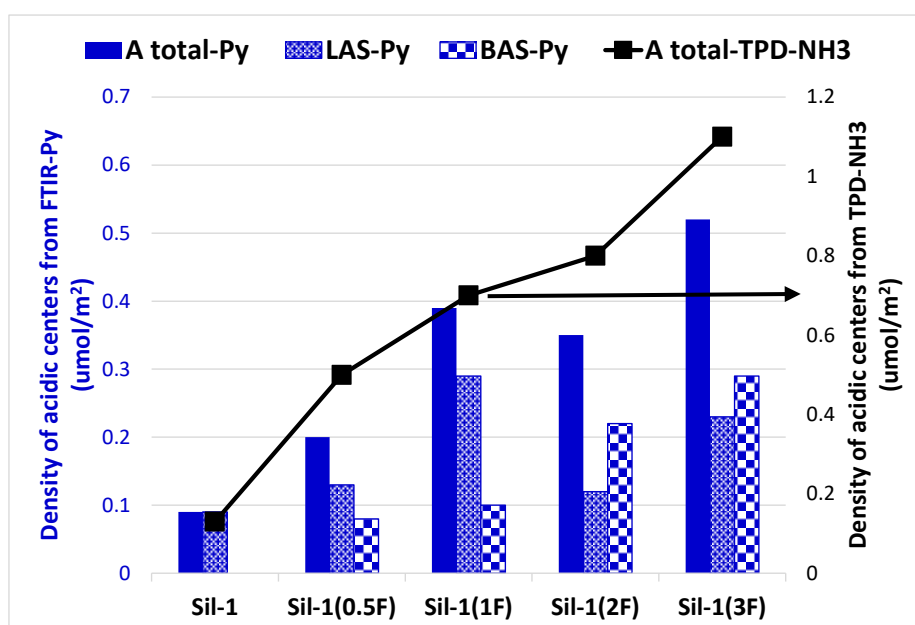


Figure S4. The density of total Lewis and Brønsted acid centres estimated from the FTIR of adsorbed pyridine and TPD-NH₃ measurement.

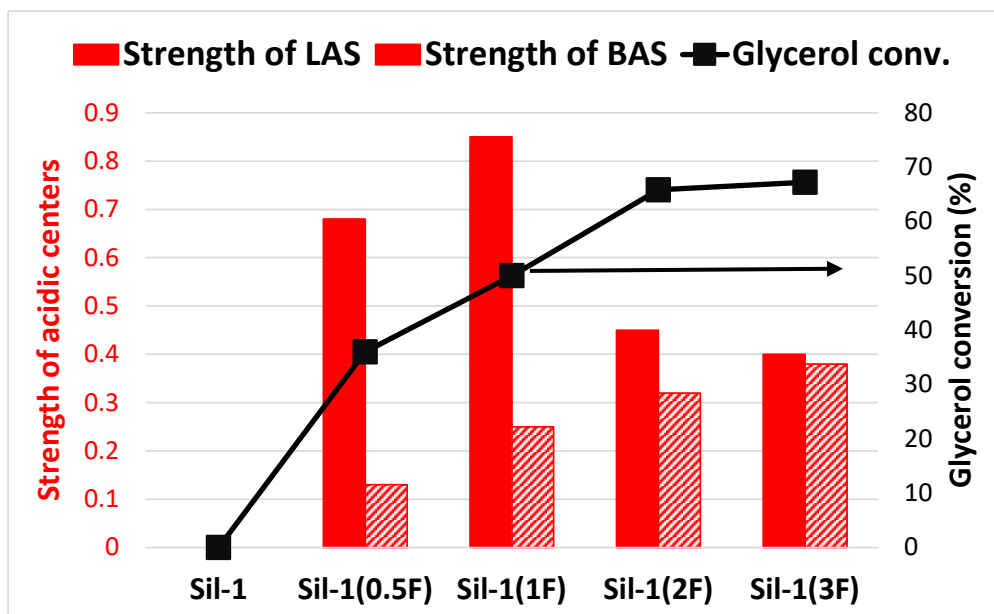


Figure S5. The dependence of the strength of Lewis and Brønsted acid sites on glycerol conversion in the acetalization reaction. The strength of acidic centres was obtained from FTIR studies of pyridine thermodesorption expressed as A_{300}/A_{150} .

Extended experimental section:

Procedure of synthesis

Silicalite-1 was synthesized in a non-stirred autoclave by hydrothermal procedure using water glass as a source of silicon, tetrapropylammonium bromide as a template, and phosphoric acid to adjust the pH of the initial gel. The molar composition of the synthesis gel was $0.08\text{TPABr}/1\text{SiO}_2/20\text{H}_2\text{O}$. At first, the template was dissolved in distilled water, then the water glass was added while stirring. In next step, the pH of the initial mixture was adjusted to 11 using concentrated H_3PO_4 . The obtained gel was stirred for 0.5 hours, then transferred into a Teflon-lined stainless steel autoclave and crystallized at $170\text{ }^\circ\text{C}$ under autogenous pressure for 22 hours. The resulting product was filtered, washed with distilled water, dried, and calcined in air at $550\text{ }^\circ\text{C}$ for 5 hours to remove the template.

The FTIR studies

The FTIR spectra of adsorbed pyridine (Py) and pivalonitrile (Pn), recorded on an Invenio Bruker spectrometer with an MCT detector, were used to estimate the number and strength of acid sites. Due to different kinetic diameters of the applied probe molecules [1, 2] (pyridine – 0.57 nm and pivalonitrile – 0.65 nm), the acidity resulted from pyridine adsorption was treated

as total acidity, while the acidity related to Pn adsorption was attributed to external acid sites. On the base of measurements of Py and Pn adsorption the accessibility of acid sites has also been estimated. Hydroxyl groups in silicalite-1 were detected in the range of 3200-3800 cm^{-1} . All spectra have been normalized to equal weight. Samples, prepared as self-supporting wafers, were weighed, placed inside a bespoke quartz IR cell, and outgassed at 400 °C for 1 h under high vacuum prior to the measurements. Quantitative in-situ IR studies determined acid sites concentrations. Excess of pyridine vapors ($\geq 99.8\%$, Sigma-Aldrich) was adsorbed at 110 °C under static conditions and evacuated at 150 °C to remove the gaseous and physisorbed pyridine molecules, tracked by evaluating spectra over time (until the disappearance of the bands attributed to physisorbed Py). Subsequently, the FTIR spectrum at 150 °C was recorded. The band intensities in those spectra were used to calculate the total concentration of Brønsted and Lewis sites. The total concentration of Lewis sites was estimated using the intensities of the 1445-1450 cm^{-1} band of pyridine coordinatively bonded to Lewis sites (PyL) assuming the extinction coefficients of 0.11 cm^2/mol [1]. The 1545 cm^{-1} band was used to estimate the total number of Brønsted acid sites using the extinction coefficient of 0.07 $\text{cm}^2/\mu\text{mol}$. The Lewis and Brønsted acid sites strength were determined by the amount of pyridine desorbed under vacuum at given elevated temperature. The bands at 1445-1450 cm^{-1} (Lewis sites) and 1545 cm^{-1} (Brønsted sites) maintained upon evacuation at elevated temperature (300 °C) were assumed as measures of acid site strength. Weak acid sites release adsorbed Py during desorption treatment at 300 °C for 10 minutes, whereas strong sites retain Py after this evacuation. The ratio A_{300}/A_{150} , where A_{150} and A_{300} correspond to the intensities of IR bands of Py coordinatively bonded to Lewis sites or of pyridinium ion (PyH^+) upon evacuation at 150 °C and 300 °C, respectively, was taken as the measure of the acid strength of the Lewis and Brønsted acid sites. In order to estimate the concentration of the acid sites on the external crystal surface, pivalonitrile (98%, Sigma Aldrich) was adsorbed on the samples at room temperature evacuated for 20 minutes at the same temperature to remove the excess of physisorbed molecules. The concentrations of the Brønsted and Lewis acid sites detected by the Pn were calculated from the maximum intensities (band height) of the respective bands at 2277 cm^{-1} and 2305 cm^{-1} and their extinction coefficients (0.11 and 0.15 $\text{cm}^2/\mu\text{mol}$, resp.). The accessibility factor (AF) for the pivalonitrile probe molecule was defined as the number of sites detected by adsorption of the Pn (external sites) divided by the total amount of acid sites in the studied materials quantified by pyridine sorption (external and internal sites).

[1] K.A. Tarach, K. Góra-Marek, J. Martinez-Triguero, I. Melián-Cabrera, *Catal. Sci. Technol.* 7 (2017) 858-873. <https://doi.org/10.1039/c6cy02609e>

[2] K. Sadowska, K. Góra-Marek, J. Datka, *J. Phys. Chem. C*, 117 (18) (2013) 9237-9244. <https://doi.org/10.1021/jp400400t>