Supplementary Material

Combination of Chemo- and Biocatalysis: Conversion of Biomethane to Methanol and Formic Acid

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Characterization of the Chemocatalyst

1.Methods

Powder X-ray diffraction (XRD) patterns of SBA-15 and V/SBA-15 were measured in a small angle range from 0.5-10° 2theta-scale and a wide angle range from 5-80° 2-theta-scale on a Theta/Theta diffractometer X'Pert Pro from Panalytical, Almelo, Netherlands using Ni-filtered Cu-K_α radiation (λ = 1.5418 Å, 40 kV, 40 mA). The data were recorded with the X'Celerator (RTMS) detector.

Specific surface area (after BET-Method) and pore size distribution (after BJH Method) were determined by N_2 sorption at -196 °C applying the NOVA 4200e characterization unit (Quantachrome, Boynton Beach, FL, US). Before measurement, the calcined samples were evacuated (0.13 Pa) *in situ* at 200 °C for 2 h for the removal of physisorbed water.

The vanadium contents were determined using a Varian 715-OES-ICP emission spectrometer. Before the measurement, the samples were digested with a mixture of hydrofluoric acid and aqua regia and then treated in a microwave at 200 °C and 80 bar. The residue was used to determine the Si content by means Atom Absorption Spectroscopy (Analyst 300 Perkin Elmer).

The IR-Spectra were recorded with Diffuse Reflection Infrared Fourier Transform Spectroscopy measurements on a Nicolet 6700 spectrometer (Thermo Scientific) equipped with a commercial reaction cell (Harrick) using CaF_2 windows with connection to a gas-dosing system. The reaction cell was modified as described by Bellmann *et al.* (Appl. Catal. B: Enviromental 230 (2018) 184-193.) using a quartz window in the dome to implement a high-temperature reflection probe (Avantes) of a Ava Spec-2048 spectrometer (Avantes). The reflection probe is in contact with the sample without disturbing the optical path of the infrared beam. SBA-15 and V/SBA-15 were heated in a flow of dry synthetic air (32 mL·min^{-1}) to 600 °C and treated at this temperature for 2 h. Afterwards the sample was cooled to 25 °C in dry synthetic air flow (32 mL·min^{-1}). At the latter conditions IR and UV-Vis spectra were recorded.

Raman spectra were measured on a Lab RAM HR (Horiba Jobin Yvon) Raman microscope using a laser excitation wavelength of 532 nm (objective 50x).

1.1. X-ray Diffraction

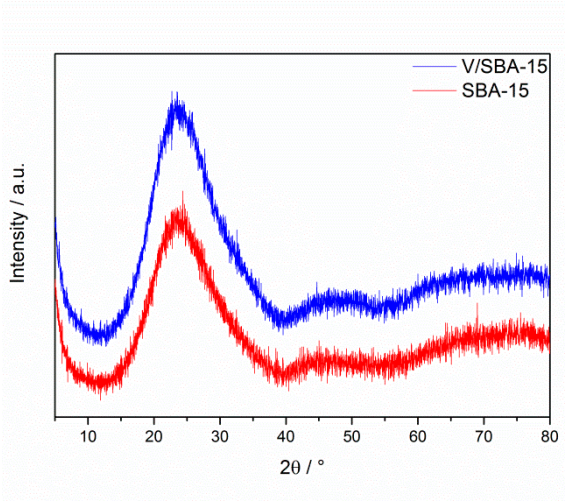

Figure S1 X-ray diffraction patterns of V/SBA-15 and SBA-15.

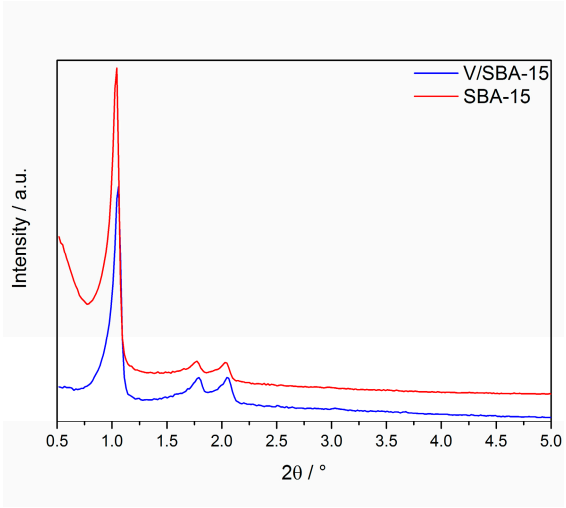

Figure S2 Small angle X-ray diffraction patterns of V/SBA-15 and SBA-15

1.2. Nitrogen Adsorption

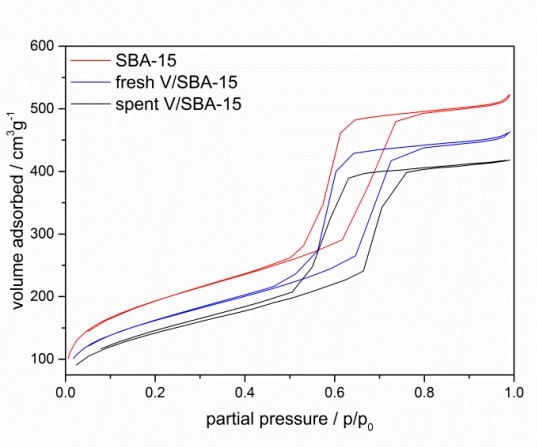

Figure S3 BET isotherms of SBA-15,V/SBA-15 and spent V/SBA-15.

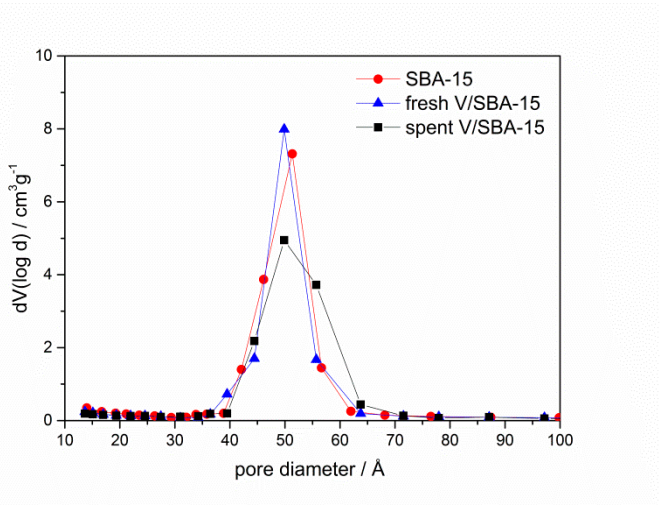

Figure S4 Pore size distributions of SBA-15,V/SBA-15 and spent V/SBA-15

1.3. Spectroscopic Methods

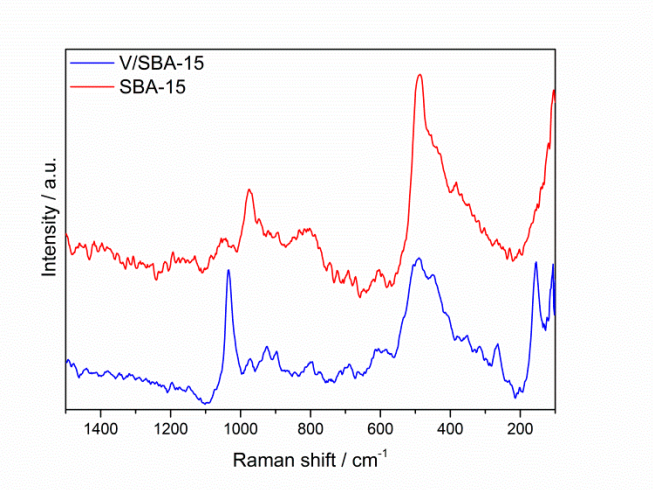

Figure S5 Raman spectra of of V/SBA-15 and SBA-15 under ambient conditions. Excitation at 532 nm.

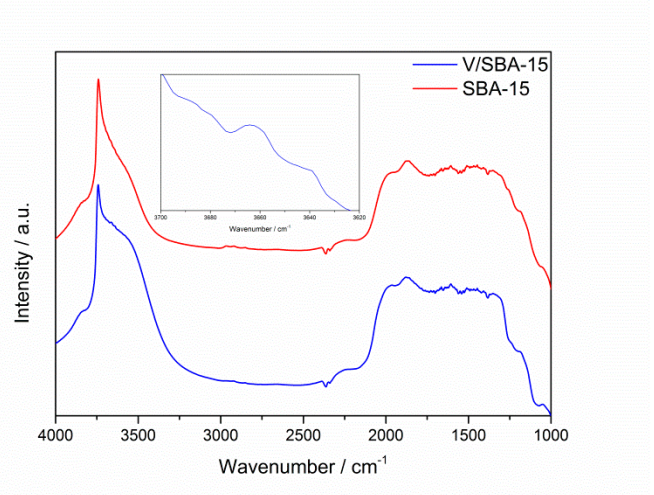

Figure S6 DRIFTS spectra of V/SBA-15 and SBA-15 at room temperature after drying at 600 °C for 2 h.

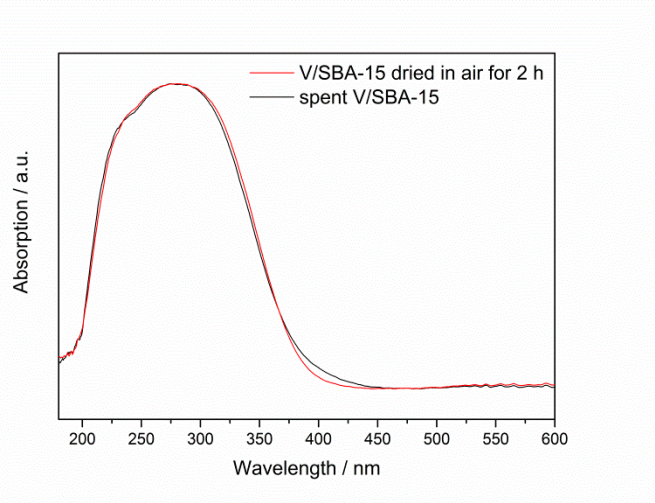

Figure S7 UV-vis DRS spectra of V/SBA-15 after 2 h at 600 °C in air (V/SBA-15) and spent after application in the chemocatalytic part of the cascade process.

Biocatalysis

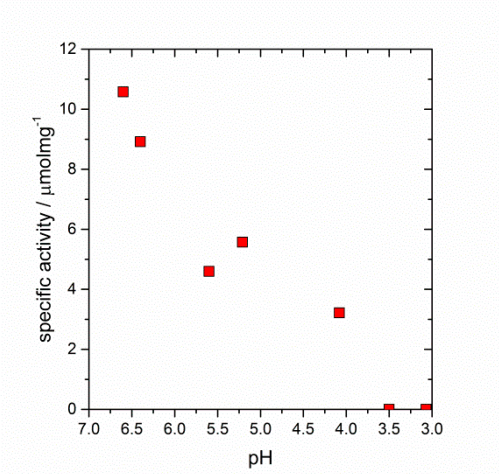

Figure S8 Specific FDM acitivity at different pH values.

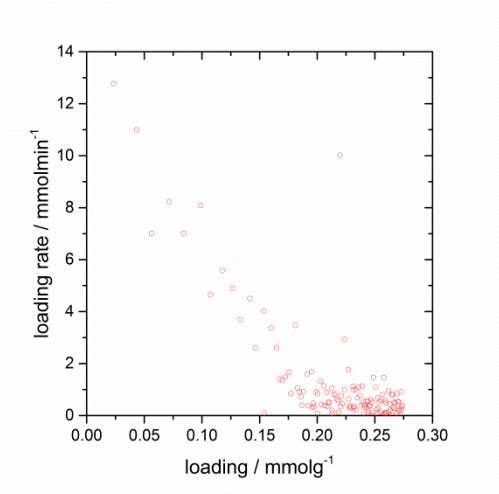

Figure S9 Loading rate at different loadings of ion exchanger Purolite A111.