Electronic supplementary materials *Mendeleev Commun.*, 2023, **33**, 832–835

HMFI/SiC – a novel efficient catalyst for green hydrocarbon production *via* bioisobutanol conversion

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Catalyst characterization. Powder X-ray diffraction (XRD) data were collected at a scanning speed of 1.4 °/min on a Rigaku MiniFlex 600 (Cu – K_α radiation, λ = 1,54187 Å) diffractometer operated at 40kV and 20mA. The morphology of the catalysts was analysed by scanning electron microscopy (SEM) on a JEOL JIB 4501 Multibeam SEM-FIB system. The textural properties were examined by low temperature nitrogen physisorption on an Autosorb–1 analyzer. The specific surface area was calculated by the BET method. The total pore volume was calculated at p/p_0 = 0.945 from the adsorbtion branch of the isotherm. Micropore volume was calculated by the t-plot method. The acidic properties of the catalysts were evaluated by temperature programmed desorption of ammonia (NH_3-TPD) on a USGA-101M chemisorption analyzer. Each sample was pretreated at 550°C at 30 min in a He flow of 30 ml min^{-1}. After that the sample was cooled to 60°C and was saturated with 10 vol.% He-NH_3/He for 30 min. Subsequently, the physically adsorbed NH_3 on the sample was purged by He at 100 °C. The signal of NH_3 desorption was recorded in the temperature range up to 650 °C with a heating rate of 8 °C/min.

Al and Si content was determined by the ICP-OES method. An aliquot of 0.05 g of sample was taken and transferred to microwave digestion vessel (Multiwave GO Plus, Anton Paar), into which a mixture of 4 ml HF, 1 ml H_2SO_4, and 6 ml HNO_3 was added. After dissolving the sample, the resulting solution was stabilized with a saturated solution of boric acid to bind free hydrofluoric acid, and diluted with de-ionized water 18.2 MΩ·cm (Arium Comfort II, Sartorius) to a volume of 50 ml with further dilution with 2 % solution of nitric acid. A blank sample was prepared in the same way. The samples were analyzed by the ICP-OES method on Agilent 5800 spectrometer.

The zeolite content in the composite, determined by the presence and intensity in the IR spectra of characteristic bands related to zeolite, and the acidic properties of the surface of the samples, determined by infrared spectroscopy of adsorbed pyridine with Fourier transform (FT-IR), were studied using a Nicolet Protégé 460 spectrometer. The samples were activated at 400°C for 1 hour at a pressure of 10^{-5} Torr. Pyridine adsorption was carried out at 150°C at a pressure of 2 Torr of pyridine for 30 minutes. At the end of the adsorption cycle, a stepwise desorption of pyridine was carried out at 150, 200, 250, 300, 350 and 400°C for 15 minutes at each temperature. The concentration of Brønsted and Lewis acidic centers was determined by the intensity of the bands of adsorbed pyridine (1547 and 1455 cm^{-1}, respectively), the extinction coefficients from [1] were used in the calculations.

Catalyst test. The catalysts were tested in isobutanol conversion in a heated quartz flow-type fixed-bed reactor (300 mm in length, inner and outer diameters of 30 and 32 mm, respectively) with an axial thermocouple pocket with the outer diameter of 8 mm. The catalyst (2.49 g, particle size 0.5–2 mm) was loaded in the isothermal zone of the reactor. The free volume of the reactor upstream and downstream of the catalyst was filled with quartz chips. The catalyst was heated to the test temperature in a nitrogen flow, after that, isobutanol was fed by a micropump either simultaneously with the nitrogen flow or without one. The gas products were analyzed chromatographically. The carrier gas was helium. Steel packed columns (2 m ×5 mm) were used. A Porapak Q column was used to separate CH_4, CO_2, C_2H_4 and C_2H_6 at 70 °C. H_2, O_2, N_2, CO and CH_4 were separated at 30 °C by a column with the NaX zeolite. The C_{3+} hydrocarbons were determined at 70 °C using a column with 5%Na_2CO_3/Al_2O_3. The liquid products were collected for 2 h in a cooled receiver at −80 °C and analyzed using a Crystallyx-4000 gas chromatograph and a 100 m×0.25 mm×0.5 µm DB-PETRO column according to ASTM D5134.

The isobutanol conversion ($X_{isobutanol}$) and products yields (Y_i) were calculated using equations S1 and S2, respectively.

$$X_{isobutanol} = \frac{m_{inj.\ isobutanol} - m_{det.\ isobutanol}}{m_{inj.\ isobutanol}} \times 100\% \qquad \textbf{(S1)}$$

$$Y_i(wt) = X_{isobutanol} \times Sel_i \qquad \textbf{(S2)}$$

The products yields and hydrocarbon composition over the HMFI/SiC catalyst at 600 °C; WHSV = 2.2 h^{-1}; time on stream of 2 h; 1.8 l/h flow of N_2 are presented in Table S1. Isobutanol conversion was 100%.

Table S1 Products yields and hydrocarbon composition in catalytic conversion of isobutanol under the above-described conditions.

Product	**Yield, wt.%**
$CO+CO_2$	Traces
H_2O	20
Oxygenates	Traces
Heavy ends	5
Hydrocarbons	75
Total:	100
Hydrocarbon composition, wt.%	
Alkanes C_1–C_4	11
Ethylene	20
Propylene	31
Isobutene	6
Other butenes	9
Benzene	3
Toluene	9
Ethylbenzene	0.4
p-Xylene	2
m- and o-Xylenes	3
Aromatic hydrocarbons C_{9+}	0.6
Other nonaromatic hydrocarbons C_5–C_{12}	5
Total:	100

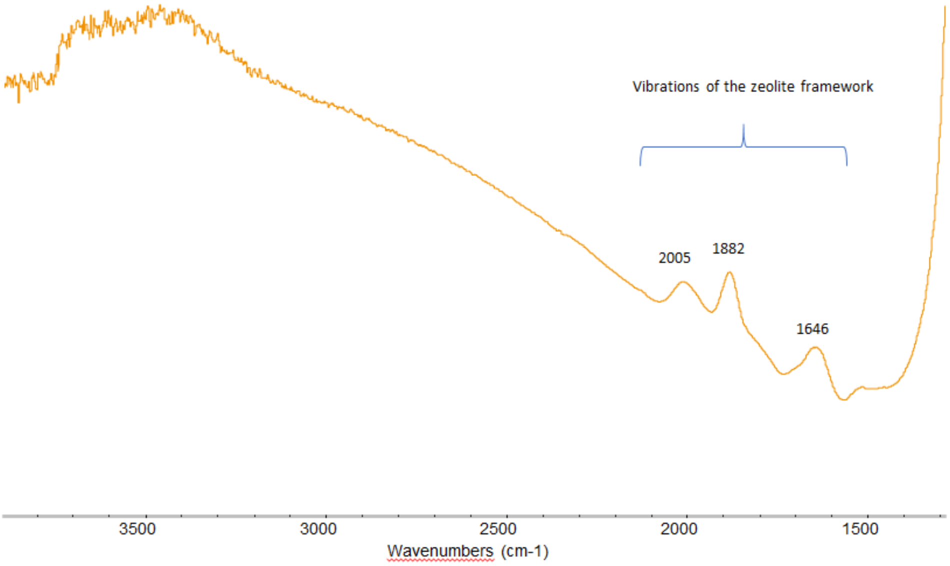

Figure S1. IR spectrum of fresh HMFI/SiC.

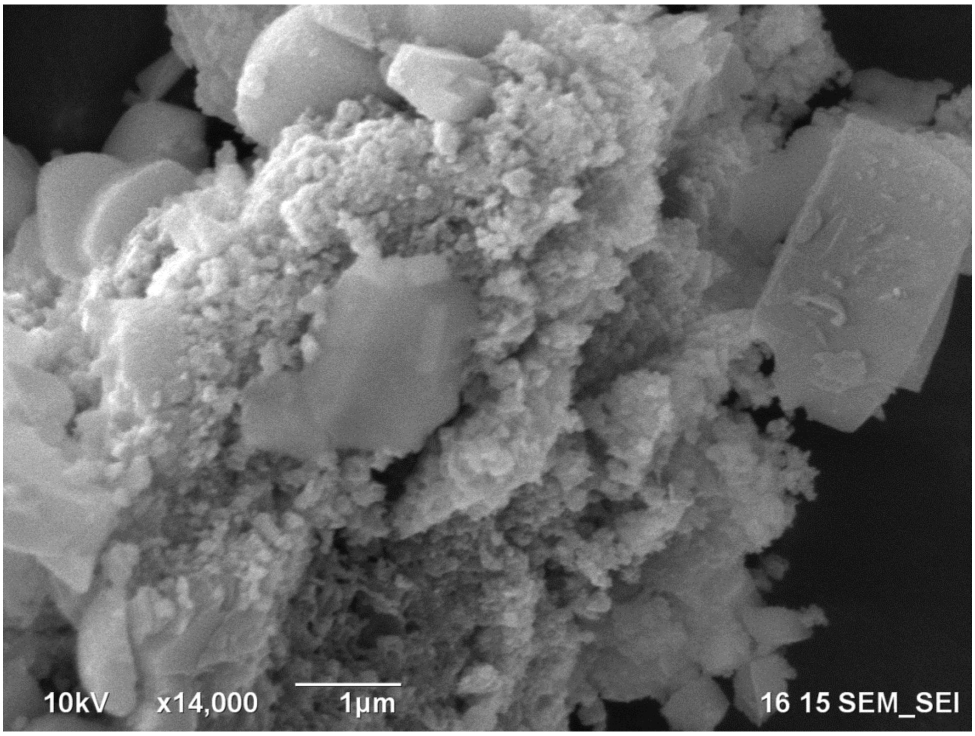

Figure S2 SEM image of fresh HMFI/SiC.

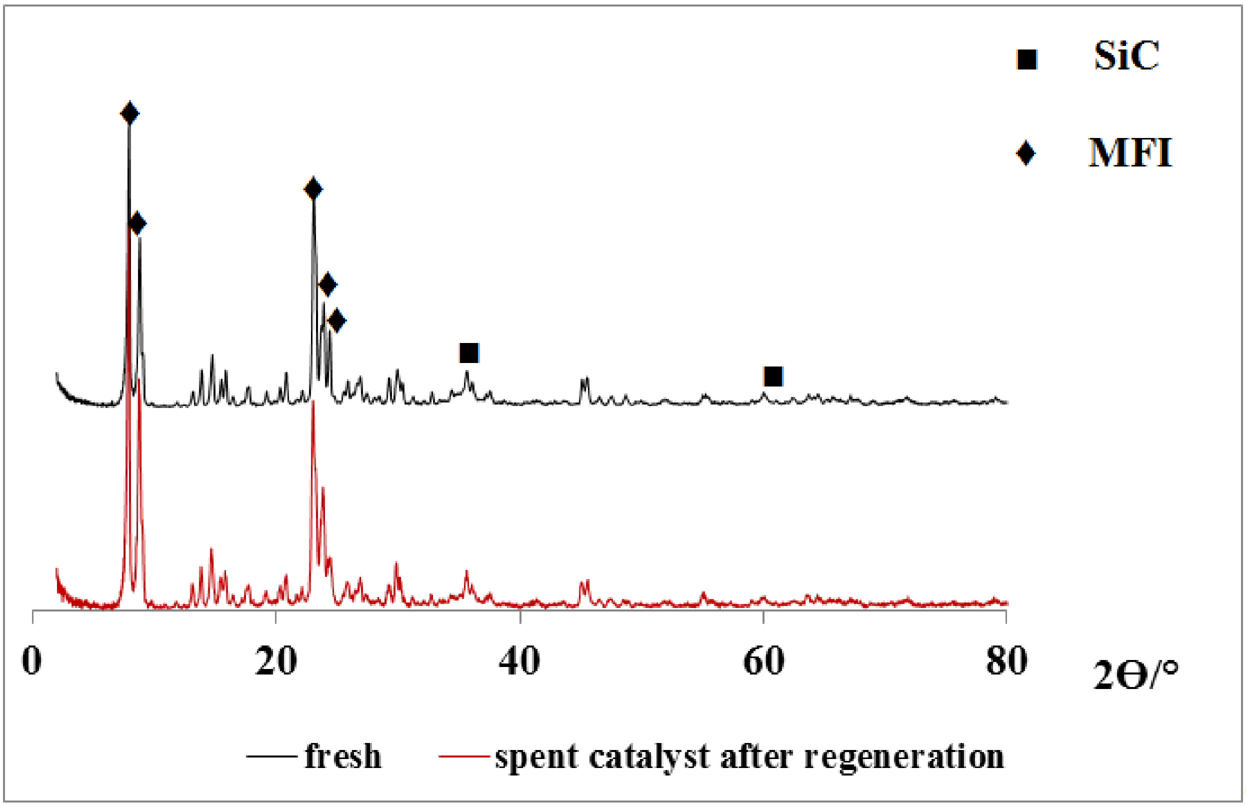

Figure S3 XRD pattern of fresh HMFI/SiC and spent HMFI/SiC after regeneration.

Table S2 Textural properties of fresh HMFI/SiC and spent HMFI/SiC after regeneration.

	S_{BET} (m^2/g)	S_{micro} (m^2/g)$^{a)}$	V_{micro} (cm^3/g) $^{b)}$	V_{meso} (cm^3/g) $^{c)}$	V_{total} (cm^3/g)
Fresh HMFI/SiC [2]	393	371	0.16	0.06	0.22
Spent HMFI/SiC after regeneration	361	351	0.16	0.04	0.20
Fresh HMFI	432	431	0.18	0.01	0.19
Spent HMFI after regeneration	398	383	0.17	0.03	0.2

a) Calculated by the t-plot method.
b) Determined from the BJH pore size distribution calculated from the adsorption branch of the isotherm.
c) Calculated as: Vmeso=Vtotal-Vmicro.

Table S3 Number of acidic centers (µmol/g) in catalysts measured by NH_3-TPD.

Catalyst	**Medium strength** [a]	**Strong** [b]	**Total**
Fresh HMFI_136	113	107	220
Fresh HMFI/SiC	133	69	202
Fresh SiC	14	2	16
Spent HMFI/SiC after regeneration	**56**	**17**	**73**

[a] Calculates as amount of NH_3 (µmol/g) desorbed below 300°C.
[b] Calculates as amount of NH_3 (µmol/g) desorbed above 300°C.

Table S4 Products yields and hydrocarbon composition over SiC at 550 °C; WHSV = 2.6 h^{-1}; time on stream of 2 h; 2.2 l/h flow of N_2.

Isobutanol conversion	**65%**
Products	**Yield, wt.%**
$CO+CO_2$	Traces
H_2O	21
Oxygenates	2
Heavy ends	9
Hydrocarbons	33
Total yield:	65
Hydrocarbon, wt.%	
Isobutene	28
Other butenes	4
Other nonaromatic hydrocarbons C_5–C_{12}	1
Total amount:	33

1 M. Tamura, K.-I. Shimizu and A. Satsuma, *Appl. Catal., A,* 2012, **433-434**, 135.

2 A. G. Dedov, A. A. Karavaev, A. S. Loktev, A. S. Mitinenko, K. A. Cherednichenko and I. I. Moiseev, *Mater. Lett.*, 2021, **290**, 129497.