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A new way to produce green *p*-xylene: rapeseed oil conversion over HMFI/SiC catalytic material

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Catalyst synthesis method

The chemicals for MFI/SiC synthesis directly in proton form were tetraethyl orthosilicate $Si(O\text{-}Et)_4$ (99%, Sigma ALDRICH), aluminum isopropoxide $Al(O\text{-}i\text{-}Pr)_3$ (>98%, Sigma-Aldrich), tetra-n-propylammonium hydroxide TPA-OH (1 M, Alfa Aesar), and silicon carbide (β-SiC, metallurgical grade, SICAT). The molar ratio of reagents was as follows: $Si(O\text{-}Et)_4$: H_2O: TPA-OH: $Al(O\text{-}i\text{-}Pr)_3$: SiC = 1: 37,1: 0,127: 0,014: 0,562. Aluminum isoproxide and tetra-n-propylammonium hydroxide were added to distilled water under vigorous stirring. After that, tetraethyl orthosilicate was added dropwise. The obtained gel was mixed for 2 h. Then, SiC powder was added to the gel. The final suspension was placed in Teflon autoclaves and subjected to the Berghof SpeedWave 4 microwave system (maximum power of 1500 W, 2.45 GGz). Zeolite crystallization was performed for 180 min at 190–200 °C. The MFI/SiC obtained in proton form was filtered, washed with distilled water and dried at 190 °C for 2 h. Finally, the MFI/SiC composite was calcined at 550 °C for 7 h to remove the organic template, resulting in HMFI/SiC.

Catalyst characterization.

Powder X-ray diffraction (XRD) data were collected at a scanning speed of 1.4 °/min on a Rigaku MiniFlex 600 (Cu – Kα radiation, λ = 1,54187 Å) diffractometer operated at 40 kV and 20 mA. The low temperature nitrogen physisorption were examined 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 adsorption branch of the isotherm. Micropore volume was calculated by the t-Plot method.

Temperature programmed desorption of ammonia (NH_3-TPD) was studied 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.

A JEOL JEM-2100 (UHR) microscope operated at 200 kV (the lattice resolution of 0.19 nm) and equipped with an Olympus Quemesa 11-megapixel CCD camera and an EX-24065JGT energy dispersive X-ray (EDX) analyzer was employed to investigate the structure, morphology and chemical composition of the samples. The fine powders were dispersed in ethanol and dropped onto a carbon coated formvar TEM Cu grid (300 mesh, Ted Pella, Inc.). The images were acquired in the TEM and STEM modes. The EDX elemental mappings was recorded in the STEM mode.

Thermogravimetric analysis was carried out on a Mettler Toledo TGA/DSC 3+ analyzer in the temperature range of 25-1000 ºC, in an air flow with a heating rate 10 ºC/min. TGA data processing was performed using the NETZSCH Proteus Thermal Analysis package.

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 were used in the calculations.[S1]

Catalyst test. The catalysts were tested in rapeseed oil 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 (2.5 g, particle size 0.5–2 mm) was loaded in the isothermal zone of the reactor. The particle size of the catalyst is selected empirically in order to avoid a noticeable pressure drop on the catalyst layer in the reactor used. The free volume of the reactor upstream and downstream of the catalyst was filled with quartz chips. The catalyst was heated to the experimental temperature in a hydrogen flow, after that, rapeseed oil was fed by a micropump either simultaneously with the hydrogen flow. The liquid products were collected for 2 h in a cooled receiver at −80 °C. After a two-hour experiment,

nitrogen was supplied to the reactor for 1 hour at an increase in temperature to 800 ° C. Next, the catalyst was annealed at 800 °C in an air stream, cooled to room temperature and reused.

Liquid products were analyzed using a Crystallyx-4000 gas chromatograph and a 100 m×0.25 mm×0.5 μm DB-PETRO column according to ASTM D5134. Additionally, the liquid phase products were analyzed by Fourier transform infrared spectroscopy (FTIR). Fourier transform IR spectra were recorded at room temperature in the wavenumber range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} on a Nicolet 6700 instrument with an ATR attachment. The OMNIC Spectra Material Characterization software package was used to process the data.

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 yield of products (wt. %) was calculated using the formula:

$$Y_i = \frac{m_i}{m_{oil}} * 100\%$$

m_i – weight of the i-th product, g;

m_{oil} – the weight of the feeded rapeseed oil, g.

Figure S1 XRD data of HMFI/SiC

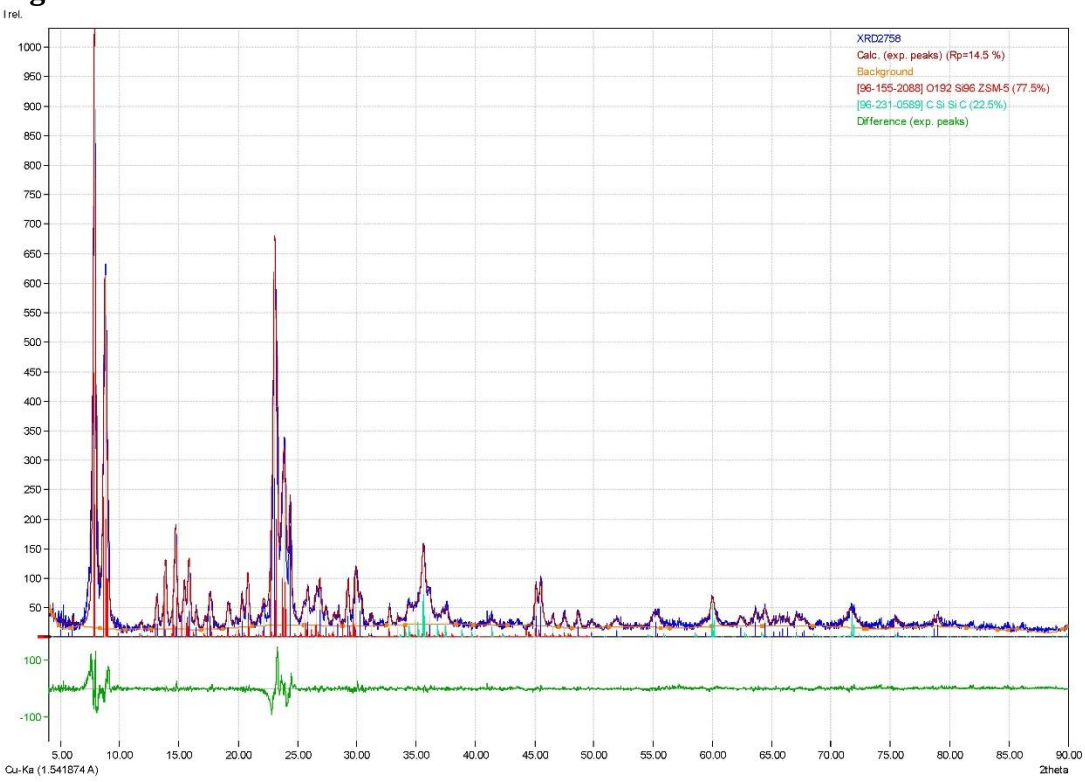


Table S1. Brønsted and Lewis acidity of HMFI/SiC and HMFI, synthesized by similar method without SiC (for comparison)

Sample	Brönsted acidity, μmol/g	Lewis acidity, μmol/g
HMFI	74	13
HMFI/SiC	82	22
Recalculated to HMFI mass in HMFI/SiC	106	29

Table S2. Contents of Al and Si in HMFI/SiC and HMFI synthesized by similar method without SiC (for comparison)

Sample	Al, wt.%	Si, wt.%	Si/Al, molar	SiO_2/Al_2O_3 in zeolite phase, molar
HMFI	0.36 ± 0.04	50.9 ± 0.4	137	274
HMFI/SiC	0.58 ± 0.05	47.7 ± 0.2	79	122

Table S3. Fatty acid composition of rapeseed oil used

Fatty acids	**Content, wt. %**
Myristic	0.03
Palmitic	3.71
Palmitoleic	0.16
Stearic	1.46
Oleic	61.22
Linoleic	19.96
Linolenic	11.45
Arachidic	0.4
Gondoic	1.06
Behenic	0.25
Lignoceric	0.09
Erucic	0.03
Selacholic	0.12

Table S4 Products yields (the mass balance closure) in experiments on catalytic conversion of rapeseed oil at 450 °C; WHSV = 3.1 h^{-1}; time on stream of 2 h; 2 l/h flow of H_2.

Product	Yield, wt.%		
	Fresh catalyst	No regeneration	Calcination in air
H_2	1	1	traces
$CO+CO_2$	1	2	1
H_2O	4	2	6
Oxygenates	1	6	traces
Heavy ends	26	8	24
Sum of Hydrocarbons	67	81	69
Total:	100	100	100
Hydrocarbon's yield, wt.%			
Alkanes C_1–C_4	1	2	3
Ethylene	1	1	2
Propylene	3	1	5
Isobutene	2	1	2
Other butenes	3	traces	4
Benzene	3	1	3
Toluene	7	2	8

Ethylbenzene	3	1	3
p-Xylene	6	1	6
m- and o-Xylenes	2	1	2
Aromatic C_{9+}	10	17	11
Nonaromatic C_5–C_{15}	26	53	23
Total:	67	81	69

Table S5. Comparison of the literature data on the production of *p*-xylene from biogenic feedstocks and toluene over catalysts containing non-promoted zeolite ZSM-5 with the results of this work

Catalyst, experimental conditions, feedstocks	**Yield of p-xylene, wt. %**	**Content of p-xylene in the mixture of isomeric xylenes, wt. %**	**References**
ZSM-5 (450°C, 1 atm, jatropha oil)	4	50	[S2]
ZSM-5 (450°C, 1 atm, fatty acids)	4	57	[S3]
ZSM-5 (430°C, 1 atm, toluene disproportionation)	1	23	[S4]
HMFI/SiC (450°C, 1 atm, rapeseed oil, hydrogen supply)	**6**	**75**	**This work**

Figure S2 IR spectrum of the liquid product obtained in H_2 flow at 600 ºC catalyzed by HMFI/SiC

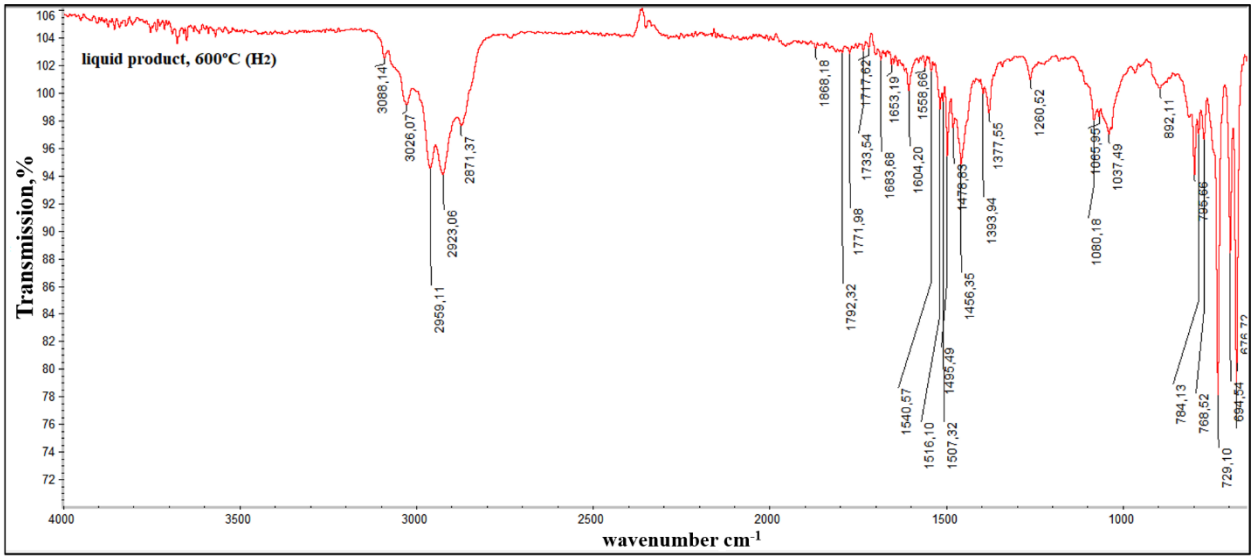


Figure S3 IR spectrum of the liquid product obtained at 500 ºC catalyzed by HMFI/SiC

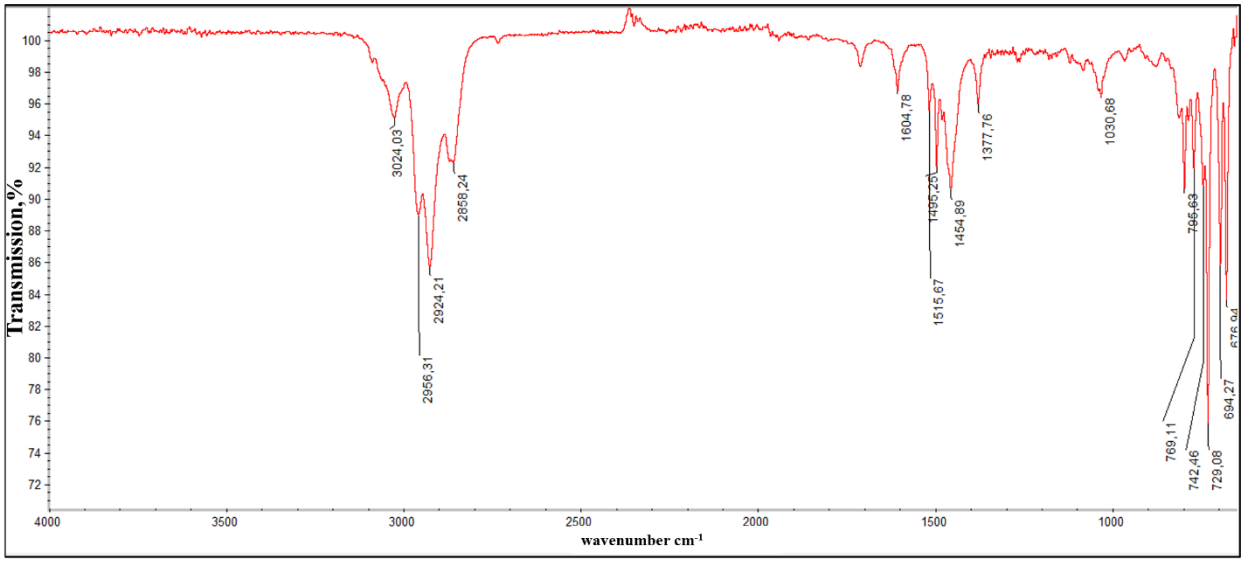
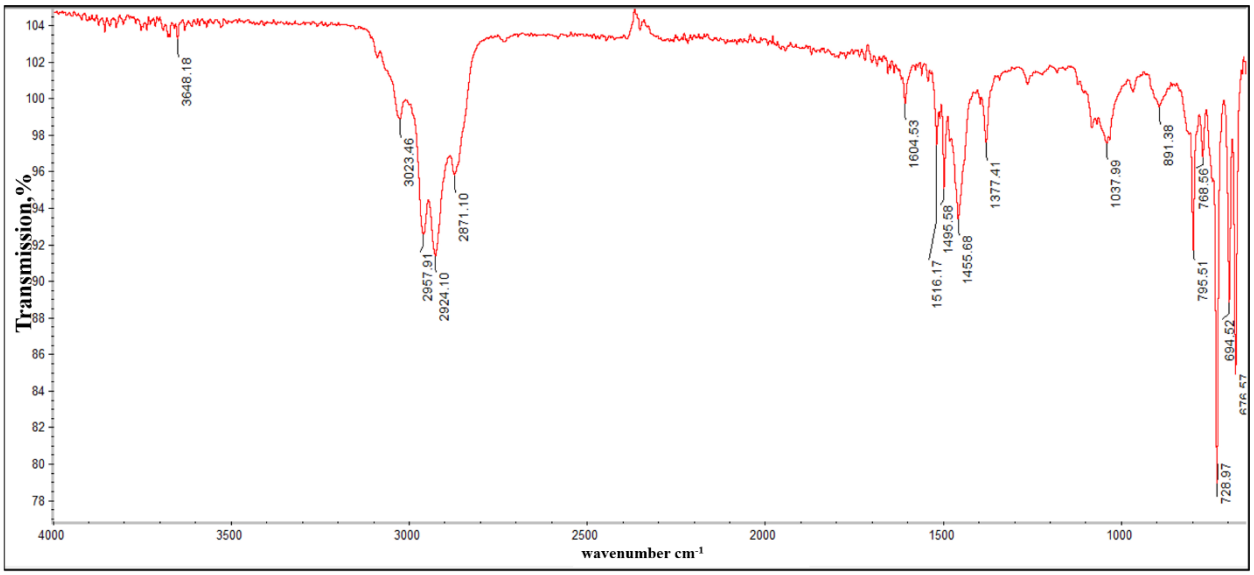


Figure S4 IR spectrum of the liquid product obtained at 550 ºC catalyzed by HMFI/SiC



References

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