Experimental part

Catalyst

Before every test, catalyst samples were heat treated in a muffle oven in air atmosphere to eliminate impurities and adsorbed water. For comparison two procedures were used: calcination at 300°C to eliminate adsorbed water, and calcination at 600°C to convert Brønsted into Lewis acid sites and generate new types of active centers.[1-4] For the lower temperature, the catalyst sample was heated at 100°C, after 1h temperature was raised to 200°C and remained constant for 0.5h, raised to 300°C and remained constant for 5h. For the higher temperature, the catalyst sample was heated at 100°C, after 1h temperature was raised to 200°C and remained constant for 0.5h, raised to 300°C and remained constant for 0.5 h, and finally, raised to 600°C and remained constant for 5h. To dehydrate its surface and generate strong Lewis acid sites, γAl_2O_3 calcination was conducted at 500°C in air atmosphere.[5] Applied heating rate was in all cases 5 °C/min.

Catalyst characterization

The N_2 adsorption isotherms were collected on a Micromeritics ASAP 2020 insturment at 77 K. Prior each measurement the catalyst sample was outgassed (6 h at 463 K) under vacuum. The BET method was used to determine the surface area and mean pore diameter.

The zeolite acidity was determined by ammonia temperature programed desorption (POROTEC). An exact amount of catalyst (about 200mg) was firstly kept under N_2 flow (20 mL/min) at 350°C for 1 h and exposed to ammonia (3% of NH_3 in N_2, 30 mL/min) at 80°C for 2 h. Afterwards, the sample was flushed with N_2 (20 mL/min) at 80°C K for 1 h. The ammonia desorption up to 1100°C (20 °C/min) was performed under He flow (20 mL/min) using a TCD detector.

Thermogravimetric analysis, coupled with a mass spectrometer (TGA-MS), was performed on a METTLER TOLEDO TGA/DSC 1 STAR system and a THERMOStar mass spectrometer. The sample was prepared by incipient wetness impregnation. 12.1 μL of reacting solution (formic acid in water or DMF / DEF) was added to 50 mg of the calcined catalyst (300°C). ~10mg of such prepared sample was placed in a 70 μL aluminum oxide crucible. Before the measurement, the TGA furnace was purged with Ar (20 mL/min) for one hour at 50°C. During the measurement the sample was heated up to 900°C (5 °C/min) under constant Ar flow (20 mL/min).

For molecular simulations, the geometries were optimized with the STATPT module of Turbomole, until the Cartesian gradients were smaller than 10^{-4} Hartrees/Bohr and the energy change was smaller than 10^{-6} Hartrees. No symmetry constraints were applied. The optimized minimum-energy structures were verified as stationary points on the potential energy surface by performing analytical harmonic vibrational frequency calculations, using the AOFORCE module of Turbomole.

Catalytic tests and product analytics

All experiments with formic acid and its derivatives were carried out in a plug-flow fixed bed reactor of 8mm in diameter. The reaction set-up consisted of a syringe pump connected to an evaporator. The vapors were directly fed through the catalyst bed (64-125 µm sieve fraction) without the use of any carrier gas. The reaction temperature was controlled by a thermocouple placed in the catalyst bed. All experiments were carried out under atmospheric pressure.

Formic acid (98% or 88% content in water; Sigma Aldritch), dimethylformamide (99%; Sigma Aldritch), and diethylformamide (99%; Sigma Aldritch) were used as a feedstock. FA acidic nature and decomposition thermodynamic result in lower decomposition temperature compared to its derivatives. Therefore, experimental procedures and analytic techniques, applied in FA decomposition tests, differ in some points from those applied in the FAD decomposition experiments (see below).

Unreacted substrate and liquid reaction products were collected in a cold trap placed directly behind the reactor. Collected gaseous products were injected into a GC (Shincarbon ST 100/200) equipped with 2m, 1mm ID column and coated TCD.

In an improved setup, an online GC (Thermo Scientific Focus GC with a Porapak Q and a molecular sieve 5A column, equipped with a TCD) was used. In this case, to allow an efficient transport of the products to the analytics, a minimal amount of Ar as carrier gas was employed (Ar flow = 275 ml/h). This flow was kept as low as possible to avoid dilution of the stream and keep vapor pressure to the reacting gas as constant as possible. In industrial conditions the use of any carrier gas should be avoided.

The collected liquid products were also analyzed. Different analysis methods were used in formic acid and formamides decomposition experiments. The analysis of collected liquid products from FA decomposition tests was carried out by HPLC (Agilent Technologies 1200 Series) equipped with RID and INERSIL ODS-3 column. Water was used as a mobile phase. Analysis of liquid products coming from formamide decomposition was carried out by a GC (Hewlett Packard HP6890). Unreacted substrate and corresponding amine were separated in a CP-Sil-PONA-CB column and detected by a FID. Additionally, H-MAS-NMR technique (Bruker 400 MHz) was used for analysis of liquid products coming from a formamide decomposition. 0.2 ml of the liquid sample was placed in an NMR tube and mixed with 0.2ml D_2O.

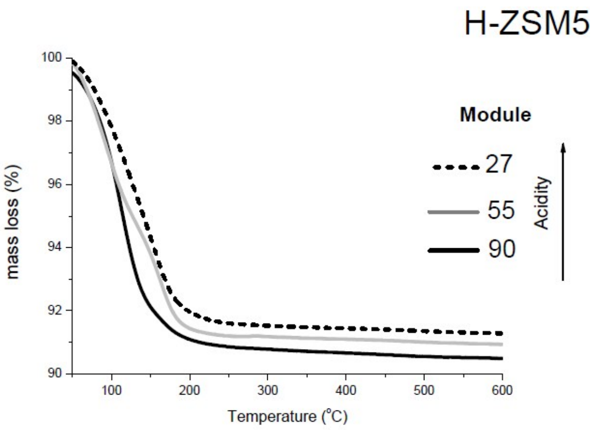

Fig. S1 *TGA measurement of H-ZSM5 catalyst with different module values, impregnated with 88% FA in water.*

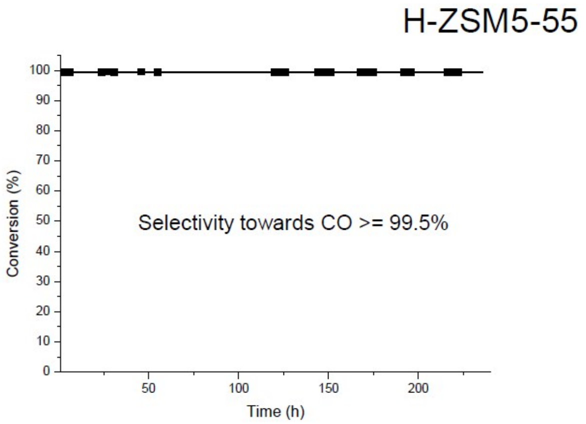

Fig. S2 *Long term stability test* - Formic acid conversion over time on stream over *H-ZSM5-55. Test temperature 190 °C, 1.2 g of catalyst, HCOOH (88% in water) flow 1 mL/h.*

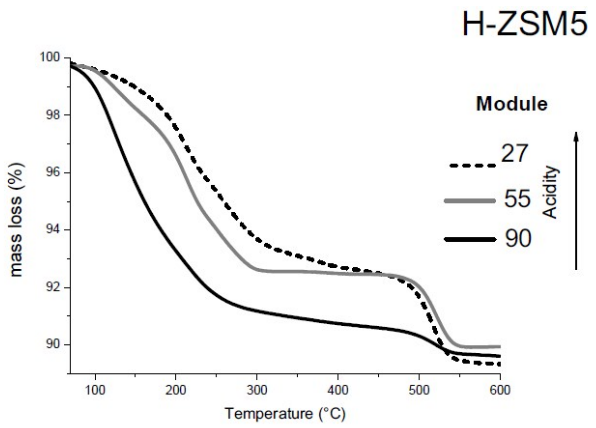

Fig. S3 *TGA measurement of H-ZSM5 catalyst with different module values, impregnated with dimethylformamide - DMF.*

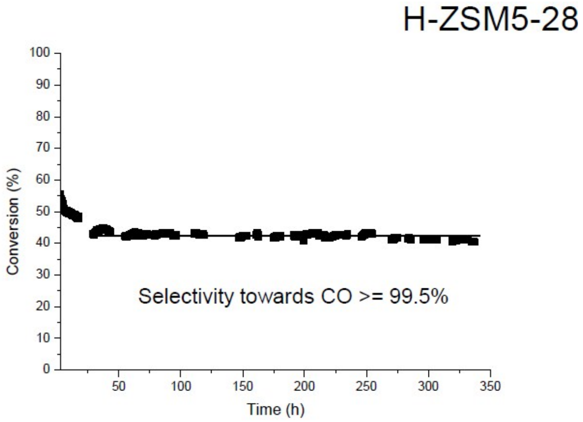

Fig.S4 *Long term stability test - d*iethylformamide conversion over time on stream over *H-ZSM5-28 catalyst with different crystallite sizes. Test temperature 280 ^{o}C, 0.6 g catalyst, DEF flow 0.5 mL/h.*

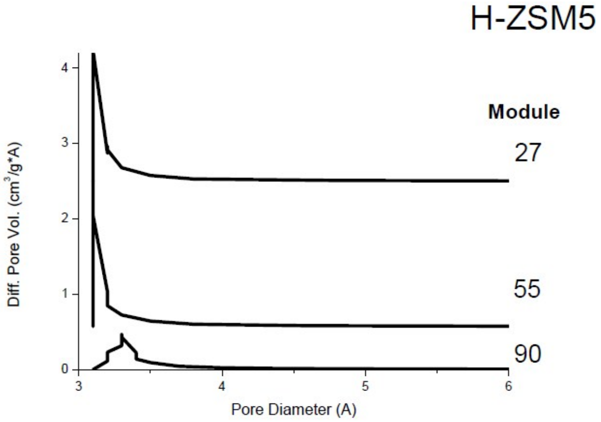

Fig. S5 *Pore size distribution of H-ZSM5 catalyst with different module values.*

Notes and references

1 J. Weitkamp, *Solid State Ionics*, 2000, **131**, 175-188.

2 V.B. Kazansky, *J. Catal.*, 2003, **216**, 192-202.

3 L. Kiwi-Minsker, D. A. Bulushev and A. Renken, *J. Catal.*, 2003, **219**, 273-285.

4 S.M.T. Almutairi, B. Mezari, G.A. Filonenko, P.C.M.M. Magusin, M.S. Rigutto, E.A. Pidko and E.J.M. Hensen, *ChemCatChem*, 2013, **5**, 452-466.

5 X. Liu, *J. Phys. Chem. C*, 2008, **112**, 5066-5073.