Electronic Supplementary Material (ESI) for Catalysis Science & Technology.


# SUPPORTING INFORMATION

## Hydrodeoxygenation of fatty acid esters catalyzed by Ni on nano-sized MFI type zeolites

Moritz W. Schreiber, Daniella Rodriguez-Niño, Oliver Y. Gutiérrez*, and Johannes A. Lercher*

*TU München, Department of Chemistry and Catalysis Research Center, Lichtenbergstrasse 4, D-84747 Garching, Germany*

*Corresponding authors:

Oliver.Gutierrez@mytum.de

Tel. 0049 89 28912827, Fax 0049 89 28913544

Johannes.Lercher@ch.tum.de

Tel. 0049 89 28913540, Fax 0049 89 28913544

**Table S1:** Fatty acid composition in triglyceride mixture of microalgae oil

| Fatty acid composition [wt%] | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $C_{14:0}$ | $C_{16:0}$ | $C_{18:2}$ | $C_{18:1}$ | $C_{18:0}$ | $C_{20:4}$ | $C_{20:0}$ | $C_{22:6}$ | $C_{22:4}$ | $C_{22:1}$ | $C_{22:0}$ | $C_{24:0}$ | Sterol |
| 0.04 | 4.41 | 56.2 | 32.2 | 4.41 | 0.07 | 0.43 | 0.13 | 0.19 | 0.97 | 0.44 | 0.36 | 0.12 |

Nomenclature in lipid numbers: $C_{X:Y}$:x number of carbon atoms in fatty acid chain; y number of double bonds in fatty acid chain

Crude microalgae oil was obtained from Verfahrenstechnik Schwedt GmbH.

**Table S2.** Diameter, dispersion, and concentration of accessible Ni atoms on different materials as determined from XRD, TEM, and hydrogen chemisorption.

| | XRD | | |
|---|---|---|---|
| Catalyst | Diameter [nm] | Dispersion [%] | Accessible Nickel atoms [µmol/g] |
| Ni/H-ZSM-5 | 10.5 | 9.6 | 157 |
| Ni/Silicalite 1 | 10.0 | 10.1 | 174 |
| Ni/n-H-ZSM-5 | 3.6 | 28.0 | 445 |
| Ni/n-Silicalite 1 | 2.6 | 38.8 | 668 |
| | TEM | | |
| Catalyst | Diameter [nm] | Dispersion [%] | Accessible Nickel atoms [µmol/g] |
| Ni/H-ZSM-5 | 8.8 | 11.5 | 187 |
| Ni/Silicalite 1 | 8.0 | 12.6 | 218 |
| Ni/n-H-ZSM-5 | 2.3 | 43.7 | 693 |
| Ni/n-Silicalite 1 | 2.4 | 41.9 | 721 |
| | Hydrogen chemisorption | | |
| Catalyst | Diameter [nm] | Dispersion [%] | Accessible Nickel atoms [µmol/g] |
| Ni/H-ZSM-5 | 12.9 | 7.9 | 128 |
| Ni/Silicalite 1 | 8.4 | 12.0 | 207 |
| Ni/n-H-ZSM-5 | 4.5 | 22.0 | 349 |
| Ni/n-Silicalite 1 | 4.7 | 21.5 | 370 |

XRD: particle diameters were calculated based on deconvoluted XRD signals for the (111) plane reflection of Ni *via* the Scherrer equation (1), where τ is the particle size in Å, K is the shape factor (0.9 for spherical particles used), β is the line broadening at half the maximum intensity of the reflection [2θ] after subtraction of the instrumental line broadening (0.1 for used instrument), Λ is the X-Ray wavelength of the used cathode and θ is the Bragg angle of the signal.

$$\tau = \frac{K\,\lambda}{\beta\,cos\theta} \qquad (1)$$

TEM: Particle diameters were calculated based on at least 300 particles obtained from at least 5 different areas of the catalyst on the carbon grid. The dispersion D based on the mean particle size was calculated following formula (2), with $v_{Ni}$ being the volume occupied by a Ni atom (10.95 Å³) and $a_{Ni}$ is the surface area of Nickel atom (6.51 Å²) and $d_{VA}$ is the mean particle size. The concentration of accessible Ni atoms was calculated based on the amount of Ni on the catalyst per gram and the dispersion based on formula (3).

$$D = 6\,\frac{(v_{Ni}/a_{Ni})}{d_{VA}} \qquad (2)$$

$$c_{accessible\ Ni\ atoms} = D\,\frac{(m_{Ni}/M_{Ni})}{m_{catalyst}} \qquad (3)$$

References


1 P.Scherrer, *Nachr. Ges. Wiss., 1918*, **2**, 96.

2 G. Ertl, H. Knözinger, J. Weitkamp, *Handbook of Heterogeneous Catalysis*, 2008, **3**, Weinheim, Wiley VCH.

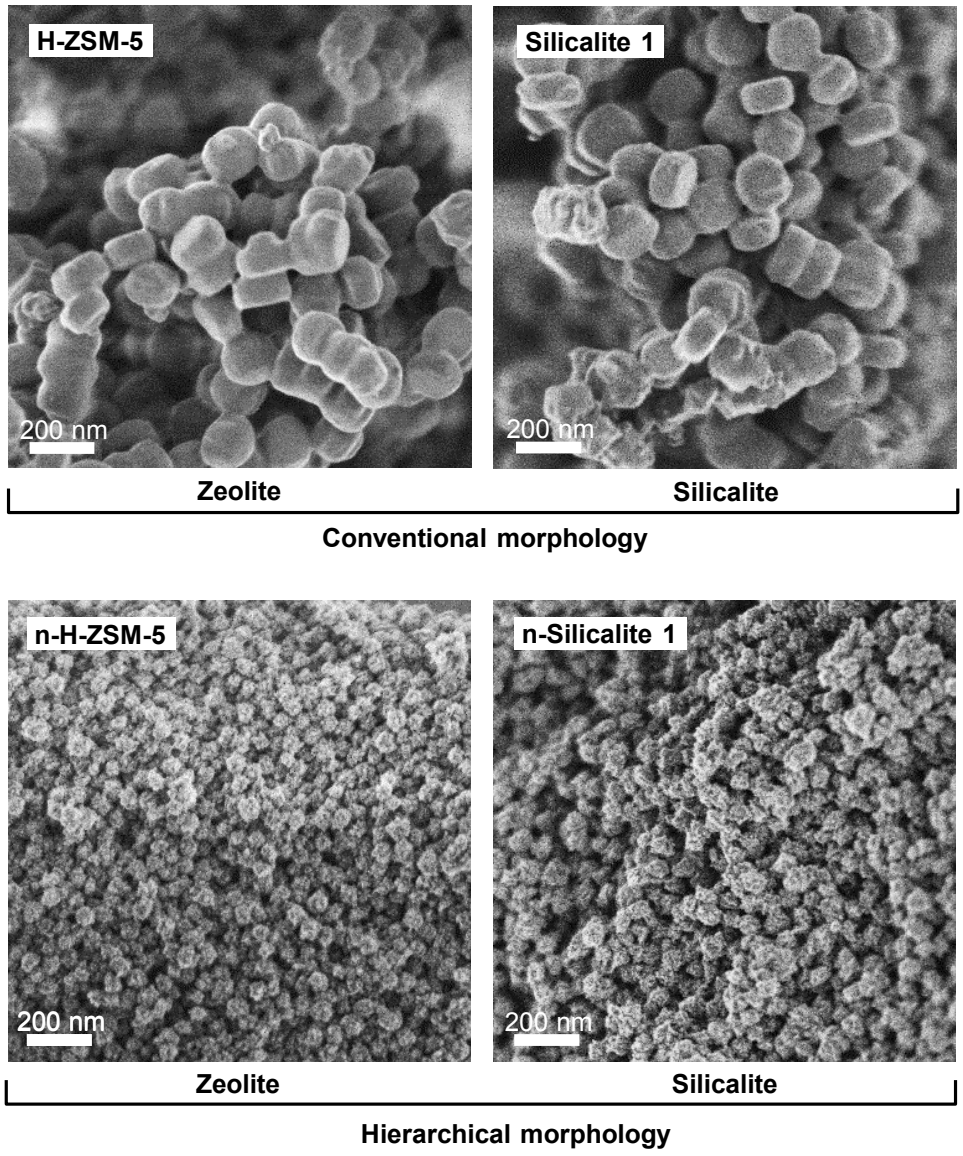


**Figure S1.** Representative micrographs of (n)-H-ZSM-5 and (n)-Silicalite 1 materials.

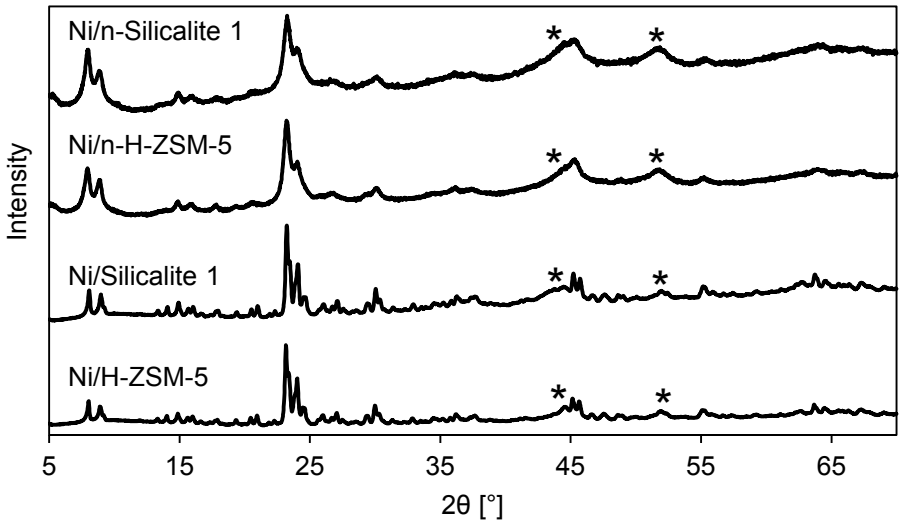


**Figure S2.** X-ray diffractograms of the catalysts based on (n)-H-ZSM-5 and (n)-Silicalite 1 materials. Nickel reflections are highlighted with a star (*).

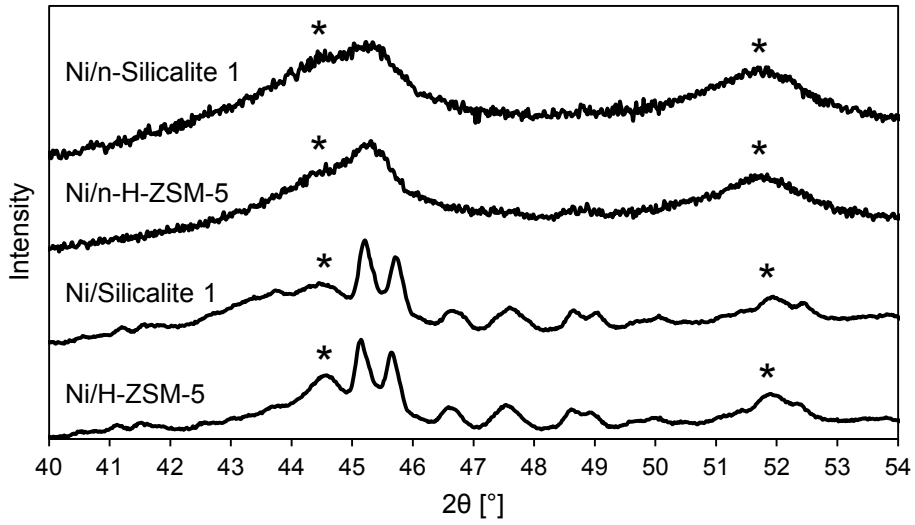


**Figure S3.** Detail of X-ray diffractograms in the region of Ni reflections of the catalysts based on (n)-H-ZSM-5 and (n)-Silicalite 1 materials). Nickel reflections are highlighted with a star (*).

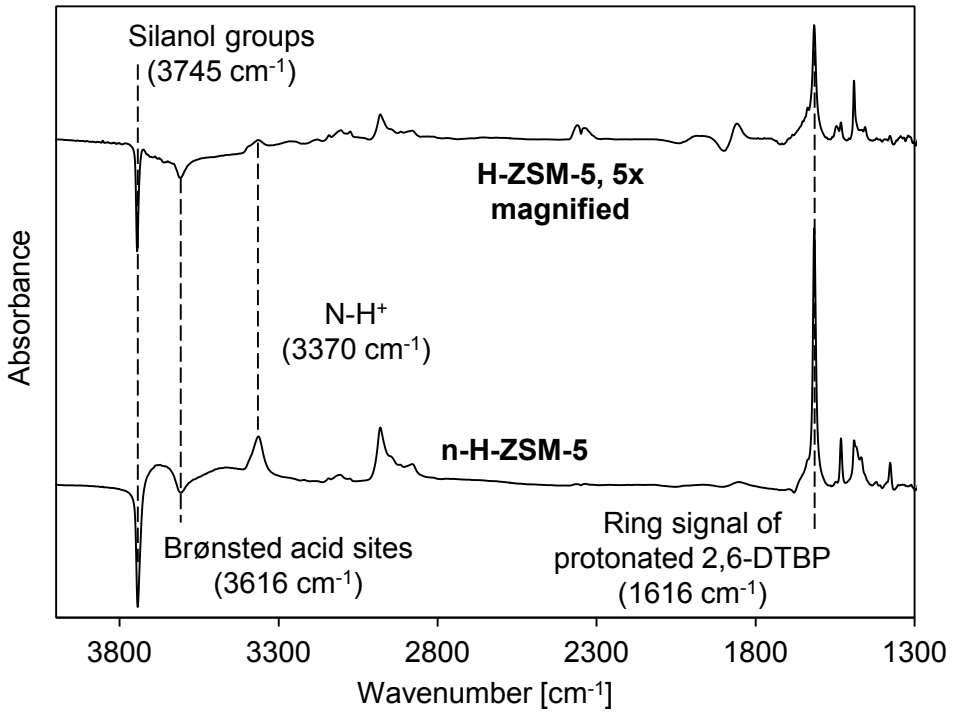


**Figure S4.** Changes in IR spectra after adsorption of 2,6-di-tert-butyl-pyridine (2,6-DTBPy) at 423 K, 0.01 kPa and outgassing for 1 h in vacuum. The characteristic bands at 3370 $cm^{-1}$ ($N\text{-}H^{+}$ vibration) and 1616 $cm^{-1}$ (C=C vibration) appear from 2,6-DTBPy interaction with the zeolite.

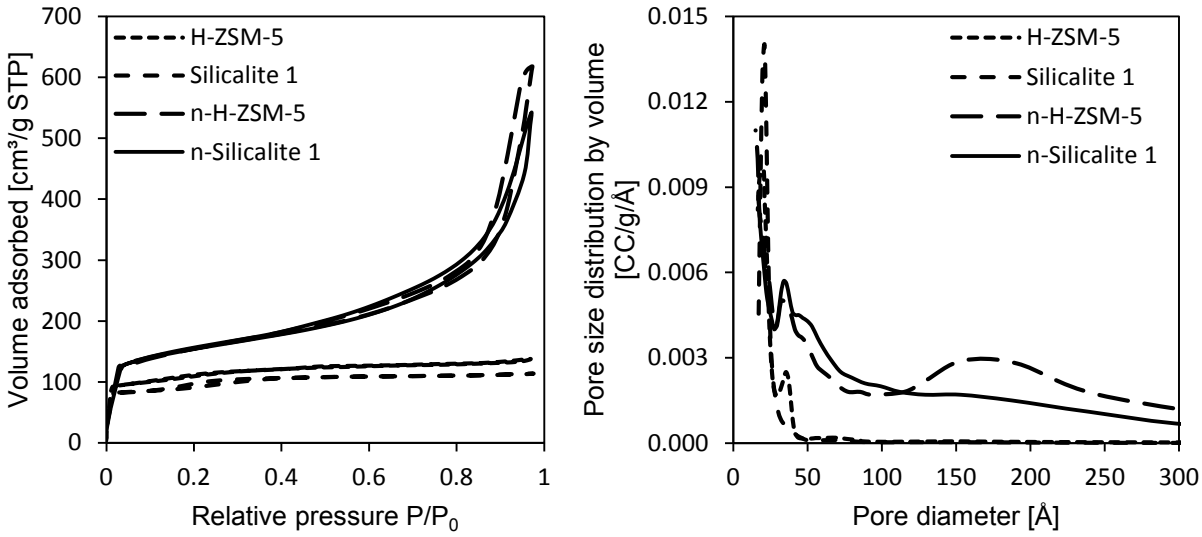


**Figure S5.** $N_2$-physisorption isotherms and pore size distributions of unloaded parent materials.

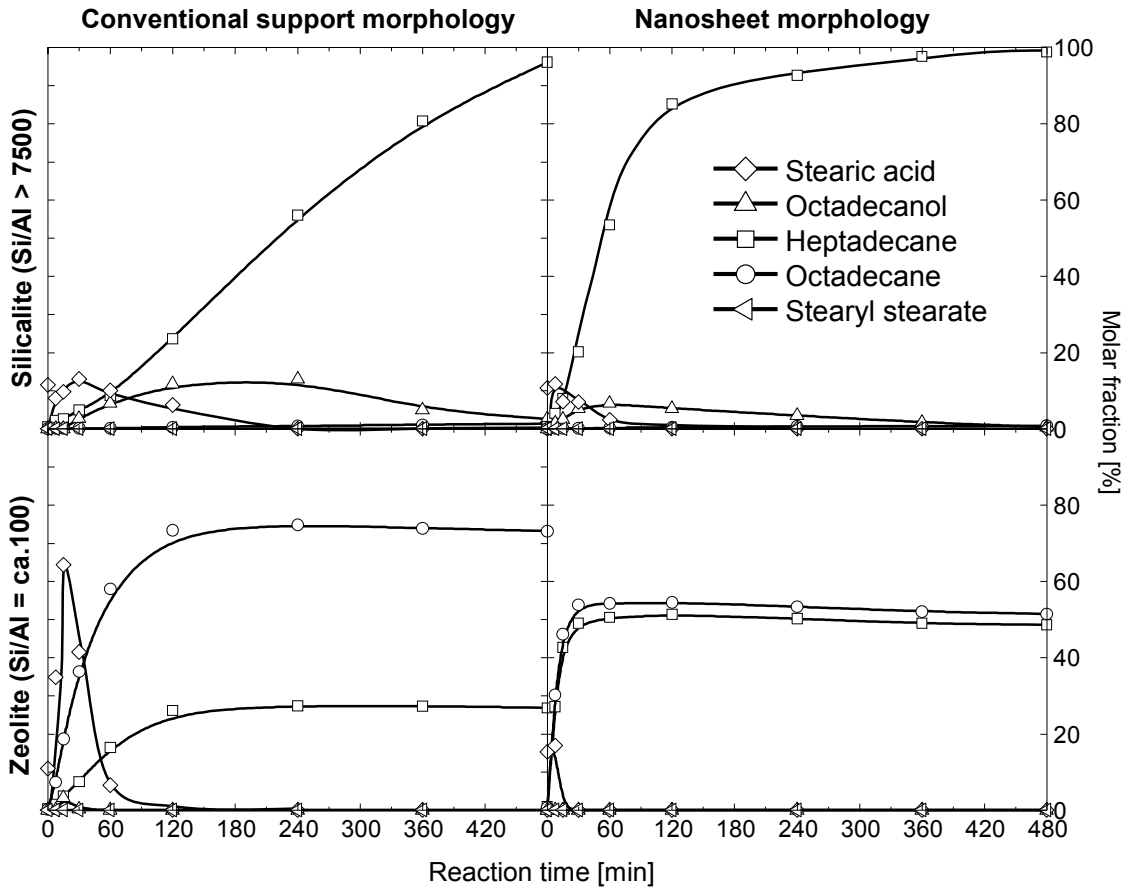


**Figure S6.** Evolution of the concentrations of reaction products of algae oil conversion over time.

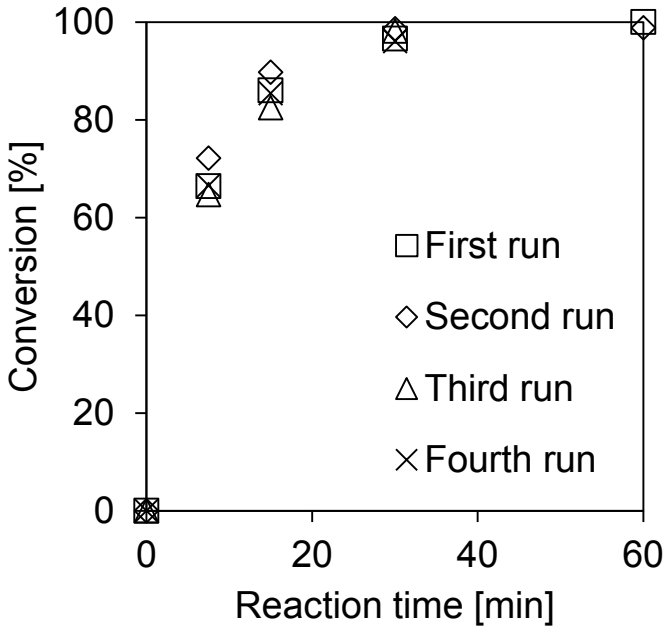


**Figure S7.** Evolution of algae oil conversion over time for four consecutive recycling experiments of Ni/n-H-ZSM-5.

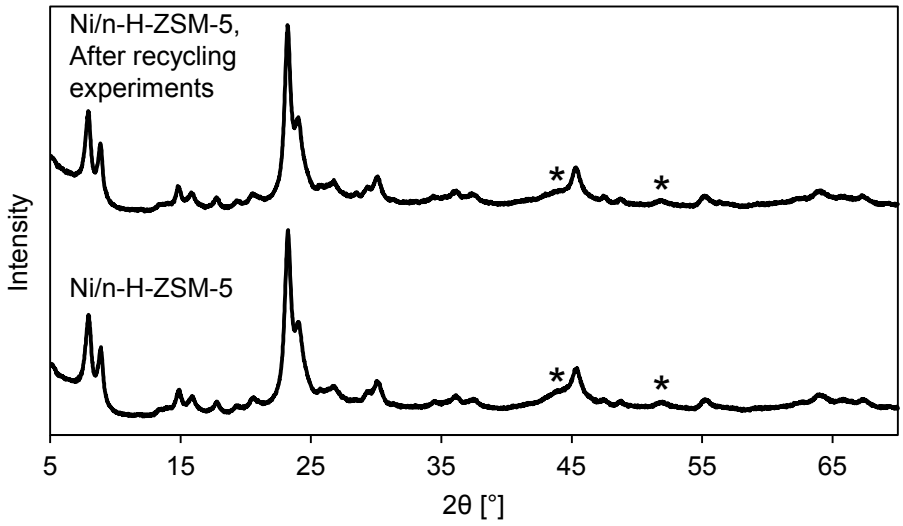


**Figure S8.** X-Ray diffractograms of Ni/n-H-ZSM-5 before and after four consecutive recycling experiments. Nickel reflections are labeled with "*".

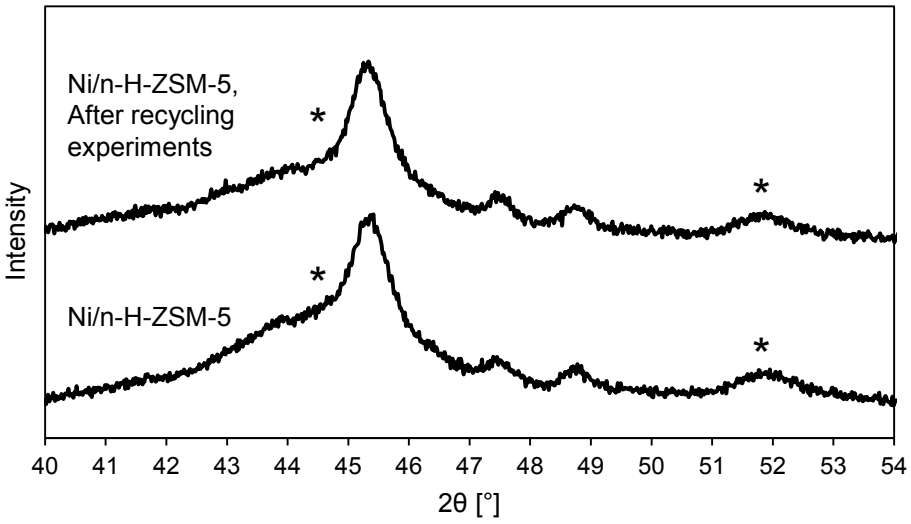


**Figure S9.** X-ray diffractograms of Ni/n-H-ZSM-5 before and after four consecutive recycling experiments. Nickel reflections are labeled with "*".