

Supporting Information

Influence of the Synthesis Protocol on the Catalytic Performance of PHI-Type Zeolites for the Dehydration of Lactic Acid

Dorothea Häussermann, Richard Schömig, Barbara Gehring and Yvonne Traa*

Institute of Technical Chemistry, University of Stuttgart, 70550 Stuttgart, Germany.
* Correspondence: yvonne.traa@itc.uni-stuttgart.de.

1. Catalytic Performance of the Catalysts over TOS

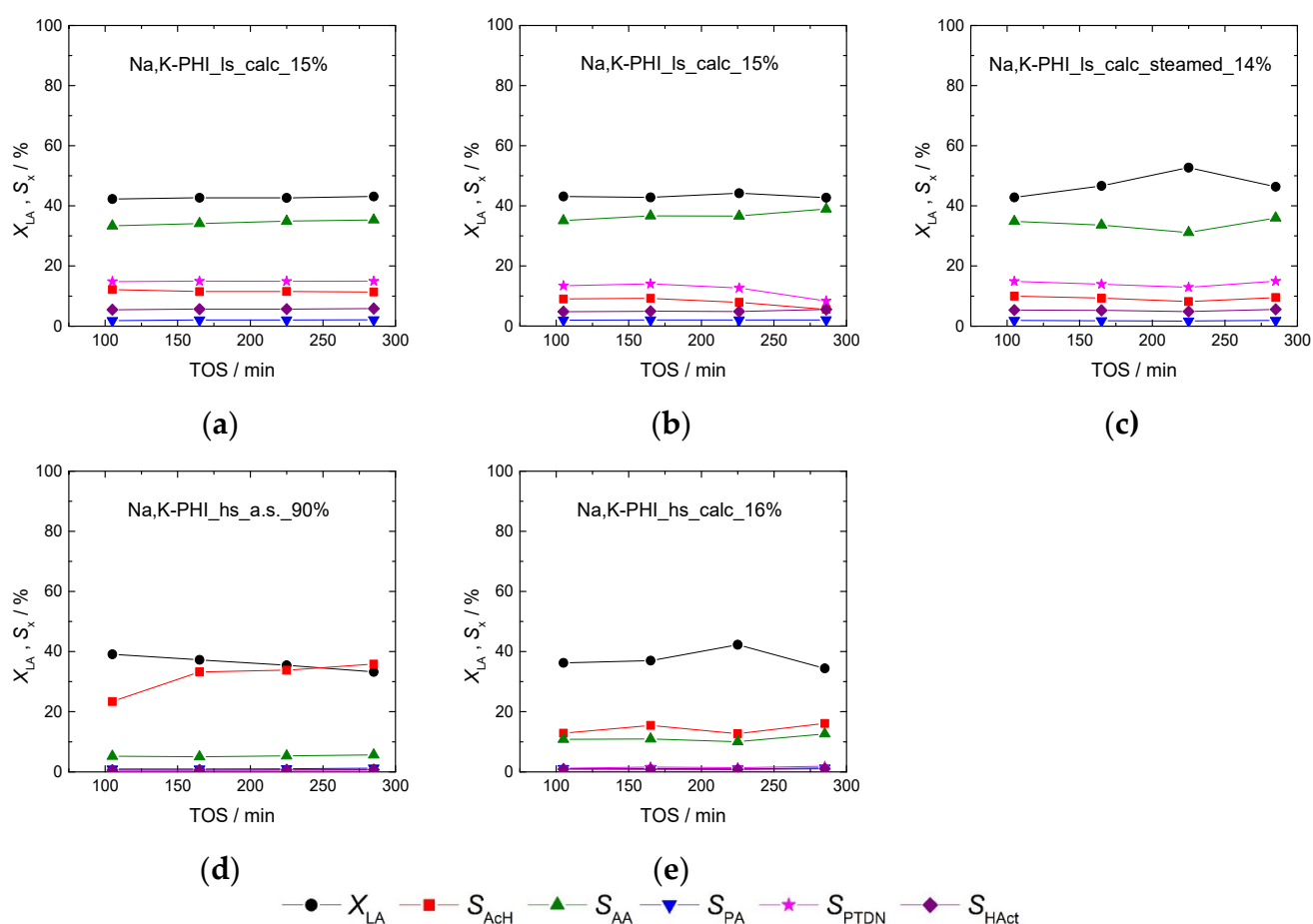


Figure S1. Catalytic performance of the catalysts. Conversion of lactic acid X_{LA} and selectivities to acrylic acid S_{AA} , acetaldehyde S_{AcH} , propionic acid S_{PA} , 2,3-pentanedione S_{PTDN} and hydroxyacetone S_{HAct} as a function of time-on-stream TOS. Na,K-PHI_ls_calc_15% was measured twice freshly (a+b). Thus the reproducibility of the measurements is demonstrated. Na,K-PHI_ls_calc_steamed_14% (c), Na,K-PHI_hs_a.s._90% (d) and Na,K-PHI_hs_calc_16% (e) were measured once. The lines are interpolations to guide the eye. Reaction conditions: 0.5 g catalyst, LHSV = 3 h⁻¹, 598 K.

2. CO₂ Physisorption Isotherms

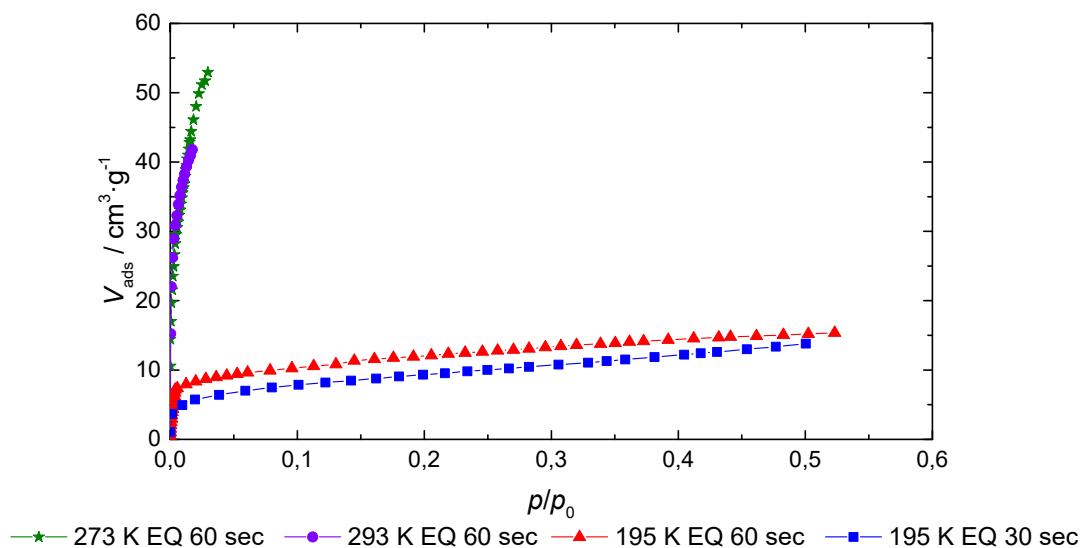


Figure S2. CO₂ physisorption isotherms for Na,K-PHI_hs_a.s._90% at 273 K and 195 K and different equilibration times (EQ). At 195K, the kinetic inhibition is clearly visible.

3. Pore Size Distributions

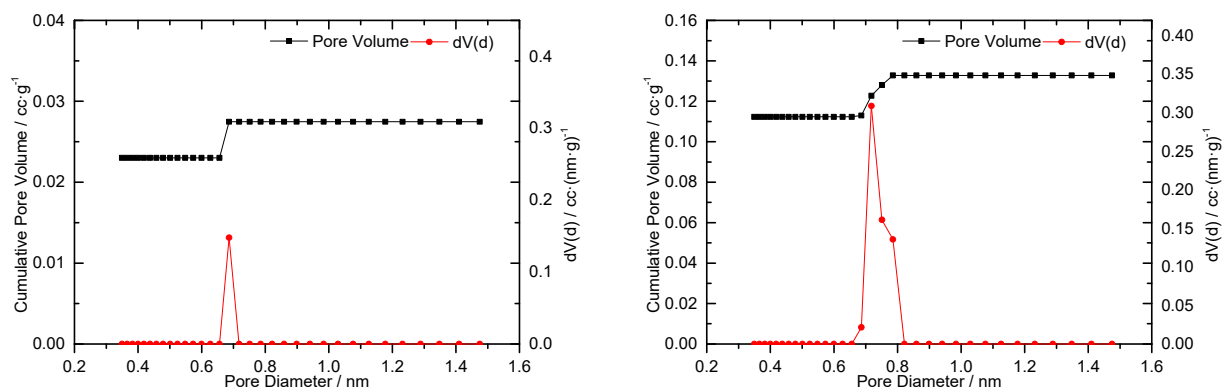


Figure S3. Pore size distributions calculated with Grand Canonical Monte Carlo Simulation (CO₂ at 273 K on carbon (GCMC model)) for the CO₂ physisorption measurements at 273 K for Na,K-PHI_hs_a.s._90% (left) and Na,K-PHI_hs_calc_16% (right). The fitting error for Na,K-PHI_hs_a.s._90% was 18.359 % and for Na,K-PHI_hs_calc_16% was 3.832 %.

4. ^{27}Al MAS NMR Spectra of the Hydrated Zeolites

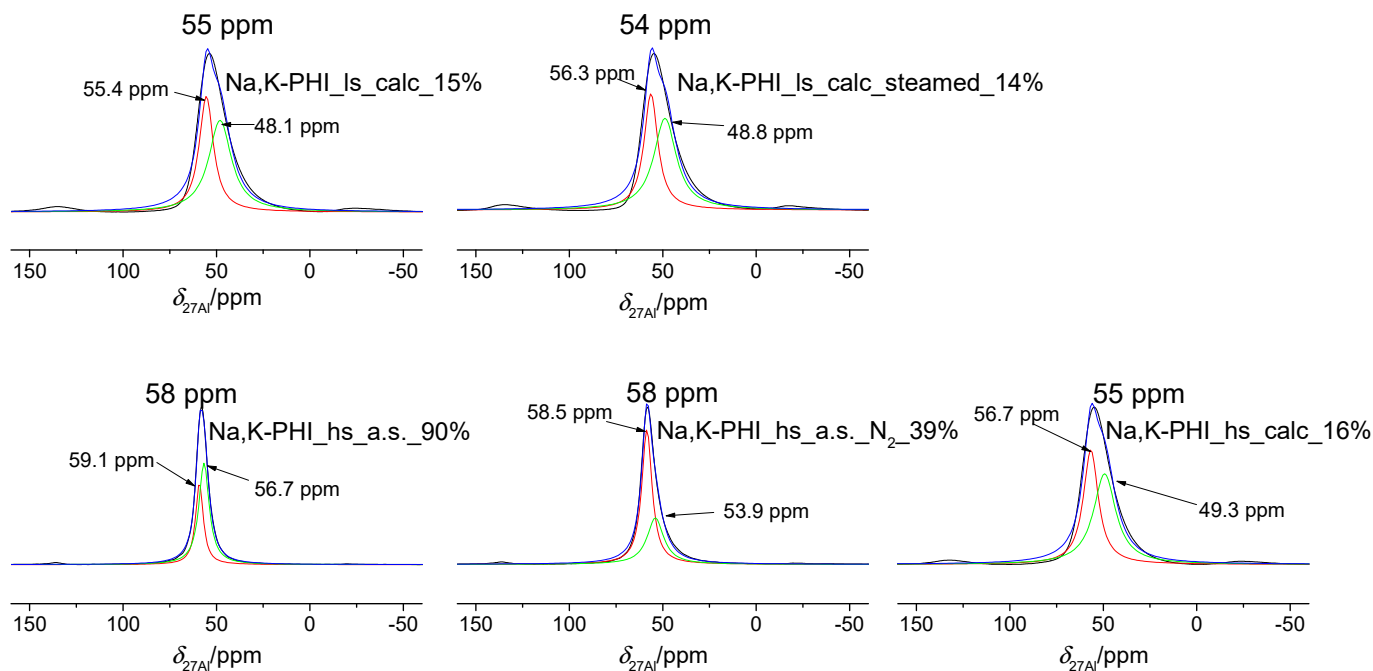


Figure S4. ^{27}Al MAS NMR spectra of the hydrated zeolites. Experimental spectra (black) and mathematically deconvoluted spectra using Lorentzian lines (red and green) and overall mathematical fit (blue).

5. Carbon Contents of the Catalysts after the Reaction

Table S1. Carbon content w_c of the catalysts after the reaction.

	Na,K-PHI_ ls_calc_15%	Na,K-PHI_ ls_calc_steamed_14%	Na,K-PHI_ hs_a.s._90%	Na,K-PHI_ hs_calc_16%
w_c / wt.-%	1.2	1.3	0.5	0.4

6. Calculation of the Size of the Lactic Acid Molecule

The molecule size was investigated by density functional theory (DFT) and the semi-empirical GFN2-xTB [42] method. All DFT calculations were performed in Turbomole V7.4.1 [43] in ChemShell [44,45] via DL-FIND [46]. After initial optimization at the GFN2-xTB level, subsequent use of the Conformer Rotamer Ensemble Sampling Tool (CREST) [47] resulted in various conformers at the GFN2-xTB level. For these conformers, geometry optimizations were performed at the B3LYP-D3(BJ)/def2-SVP level followed by a single-point energy calculation of the optimized geometry at M06/def2-TZVP level. For all DFT-optimized structures, the molecule sizes were determined as the smallest diameter of a cylinder through which the rigid ligand would fit. Each atom is delimited by its van-der-Waals radius. The analysis was performed visually in VMD [48]. This procedure is analogous to the one described in Rieg et al. [49][50].

References

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