



Supporting Information

© Wiley-VCH 2008

69451 Weinheim, Germany

Supplementary information for

In situ Synchrotron-based IR Microspectroscopy to study Catalytic Reactions in Zeolite Crystals

Eli Stavitski, Marianne H.F. Kox, Ingmar Swart, Frank M.F. de Groot and Bert M. Weckhuysen

1. IR spectra for ZSM-5/styrene and ZSM-5/4-chlorostyrene

To verify that the experimental observation outlined in the main text are general for different styrene derivatives, H-ZSM-5 crystals were contacted with styrene and 4-chlorostyrene, and thermally treated in the spectroscopic cell following the same experimental procedure. IR spectra (aromatic region) obtained from the $5\ \mu\text{m} \times 5\ \mu\text{m}$ area in the centre of the crystal are shown in Figure S1. In both cases, two sharp features, are detectable in the spectrum (1491 and $1539\ \text{cm}^{-1}$ in for styrene and 1493 and $1532\ \text{cm}^{-1}$ for 4-chlorostyrene). By comparing the spectra with those of starting compounds, lower wavenumber bands can be attributed to the styrene and 4-chlorostyrene. Following the reasoning for the case of the 4-fluorostyrene, outlined in the main text, absorption at higher wavenumbers can be assigned to the 1,3-bisphenyl-2-buten-1-ylum cation and 1,3-bis(4-chlorophenyl)-2-buten-1-ylum cation, respectively. Intensities of the the latter bands are strongly dependent on the incident IR light polarization suggesting they are due to long molecules aligned in the zeolite pores. This observation confirms the assignment to the styrene dimeric species.

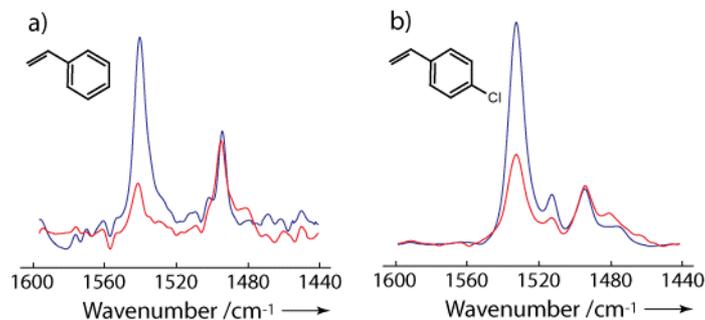


Figure S1. a) IR spectrum of an individual H-ZSM-5 crystal contacted with styrene. $5\ \mu\text{m} \times 5\ \mu\text{m}$ area in the center of the crystal was probed. Spectra were taken with two different polarization of the incident light: parallel (blue) and perpendicular (red) to the main axis of the crystal; b) same as a) but for 4-chlorostyrene.

2. Details of the theoretical calculations

For self consistent field calculations, the energy convergence criterion was set to 10^{-7} H. Geometries were considered to be converged when the gradient dropped below 10^{-3} H bohr $^{-1}$ and the energy change below 10^{-6} H.

The effect of basis set size on the calculated vibrational spectrum was tested for the 4-fluoro styrene monomer (figure 3C, i). The molecular geometry was optimized and the vibrational spectrum was calculated using the B3LYP parameterization of the exchange-correlation functional in combination with the SVP, TZVP and QZVP basis sets as implemented in the TURBOMOLE package. The IR spectra are convoluted with a Gaussian of $2\ \text{cm}^{-1}$ width. The results are shown in figure S2.

Note that no frequency scaling factor was applied. Increasing the basis set size beyond TZVP does not lead to significant changes in the calculated IR spectra and hence this basis set was used for all other calculations.

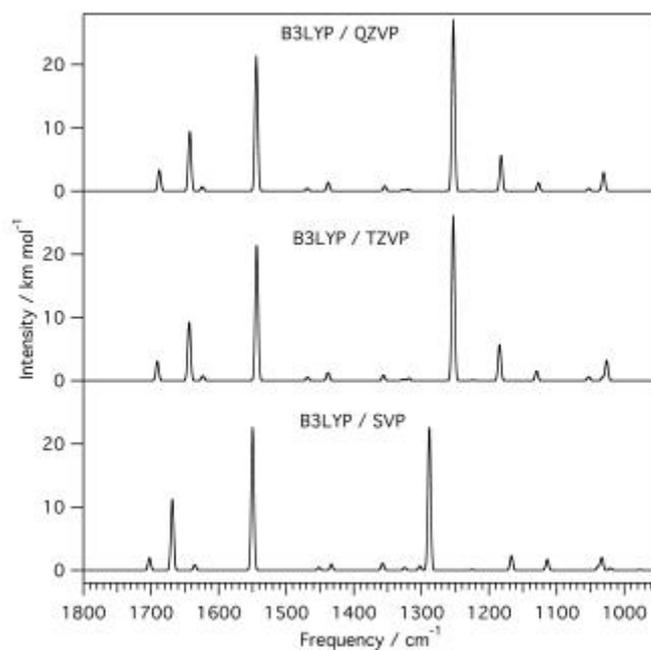


Figure S2. Calculated vibrational spectrum of the fluorinated styrene monomer using the B3LYP functional and the SVP, TZVP and QZVP basis sets (bottom to top) respectively. No frequency scaling factor was applied.

Also the effect of exchange-correlation functional on the calculated spectrum was tested. The vibrational spectrum of the fluorinated styrene monomer was calculated using a hybrid functional (B3LYP) and two generalized gradient approximation (GGA) functionals (BP86 and PBE) in combination with a TZVP basis set. The IR spectra are convoluted with a Gaussian of 2 cm^{-1} width. The results are shown in figure S3. The peak positions calculated with the B3LYP functional are shifted to higher frequency compared to the peak positions calculated using the BP86 and PBE functionals. However, the overall shape of the vibrational spectrum does not depend on the exchange-correlation functional. Also note that different functionals in general give rise to different scaling factors. The agreement of the overall spectrum is a good indication of the reliability of the theoretical results.

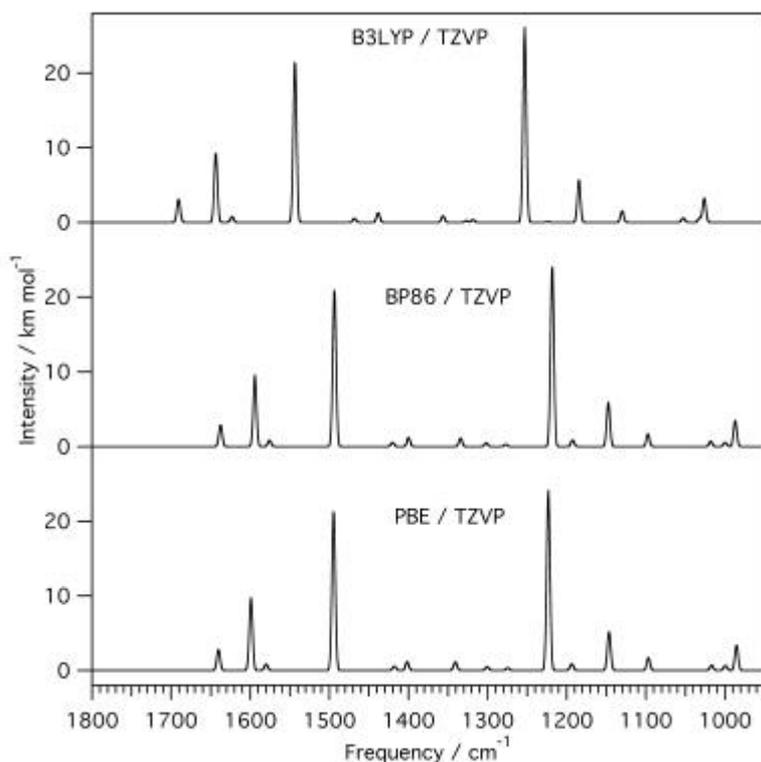


Figure S3. Calculated vibrational spectrum of the fluorinated styrene monomer using the PBE, BP86 and B3LYP functionals (bottom to top) in combination with a TZVP basis set. Note that no frequency scaling factor was applied.

3. Other carbocationic intermediates

Besides the 1,3-bisphenyl-2-buten-1-ylum cation, considered as the most probable reaction product in the styrene oligomerization reaction, other carbocationic species can be formed. In more detail, the reaction scheme, given in Figure S4 suggests that the reaction starts with the protonation of styrene on a Brønsted acid site of H-ZSM-5 (A). The carbocation reacts with a neutral styrene molecule, forming a secondary 1,3-bis(phenyl)-1-butylium cation (B), which further reacts via transfer and hydride shift to form the stable allylic 1,3-bis(phenyl)buten-1-ylum cation (C).

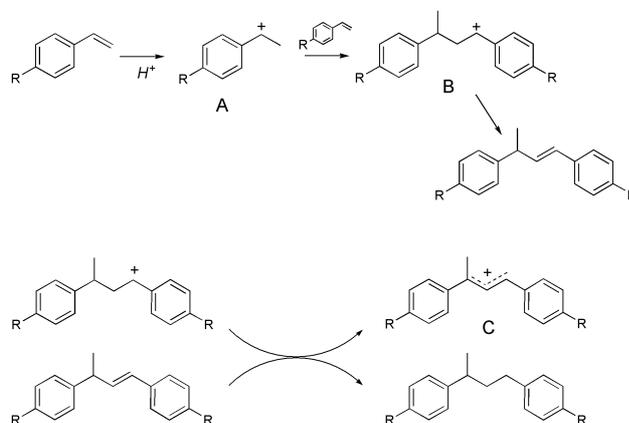


Figure S4. Oligomerization reaction pathways of styrene derivatives on acidic zeolites.

We have calculated the IR absorption spectrum of several intermediate products, based on the reaction scheme shown in Figure S4. More specifically, the absorption spectrum of protonated styrene (struc A), the secondary 1,3-bis(phenyl)-1-butylium cation (struc B) and the 1,3-bisphenyl-2-buten-1-ylium cation (struc C) were calculated. The vibrational spectra of these species are shown in figure S5. Note that the frequencies were scaled by a factor of 0.97.

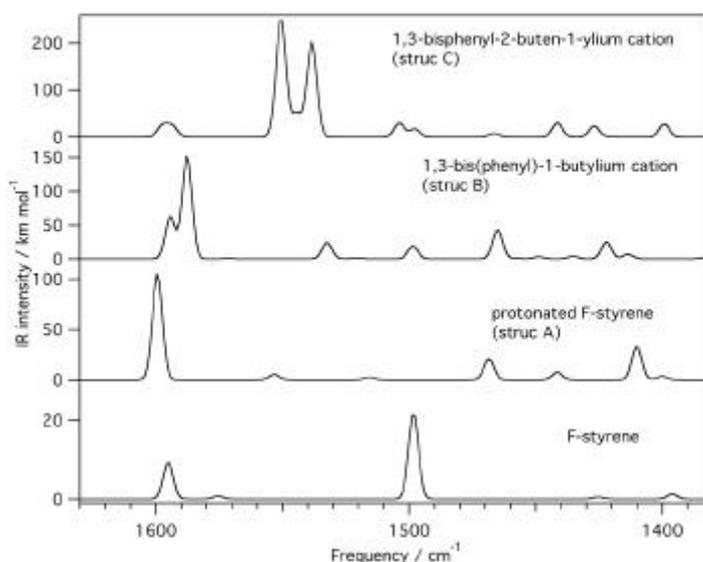


Figure S5. Calculated vibrational spectra (frequency scaling factor: 0.97) of possible intermediate reaction products of the styrene oligomerization reaction and the spectrum of the reactant.

The spectra of all intermediate species exhibit at least one strong absorption band in the 1610 – 1530 cm^{-1} range. The bands for the protonated F-styrene monomer and the secondary 1,3-bis(phenyl)-1-butylium cation are located at significantly higher frequencies. Based on this, it is most likely that the band observed experimentally at 1534 cm^{-1} is due to the 1,3-bisphenyl-2-buten-1-ylium cation. However, a definitive assignment cannot be made as other, species specific, absorption bands are masked by broad absorption bands of the zeolite matrix.