Nanoscale infrared imaging of zeolites using photoinduced force microscopy
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Donglong Fu, a Katie Park, b Guusje Delen, a Özgün Attila, a Florian Meirer, a Derek Nowak, b Sung Park, b Joel E. Schmidt b and Bert M. Weckhuysen a,b,*

Characterizing the structures of zeolites and their catalytic performance with high-spatial-resolution is vital to developing new solid catalysts. We demonstrate the application of photoinduced force microscopy (PiFM), with nanometer scale resolution across the infrared spectral range, for the study of zeolite ZSM-5 thin-films with various Si/Al ratios after the methanol-to-hydrocarbons reaction. This first-of-its kind nanometer scale infrared imaging of zeolite materials demonstrates the possibility of PiFM for the study of functional porous materials.

Zeolite ZSM-5, with the MFI framework topology, plays a pivotal role in petroleum refining and industrial chemical manufacturing, but acquiring nanometer scale insights into its structure-performance relationships in order to engineer superior materials is still a challenge. Recent advances in micro-spectroscopic approaches, such as synchrotron-based infrared (IR) spectroscopy, synchrotron-based X-ray diffraction (XRD), atom probe tomography (APT), stimulated Raman scattering (SRS) and single molecule fluorescence (SMF) have allowed researchers to obtain a more complete picture of the structural and catalytic properties of zeolite catalysts. However, these methods suffer from limitations including the use of probe molecules, being diffraction limited or being inherently destructive techniques. The recently developed, probe molecule-free photoinduced force microscopy (PiFM) can offer a lateral spatial resolution of ~10 nm and probing depth of ~30 nm by probing the mid-IR dipole–dipole moment interaction between the atomic force microscopy (AFM) tip and the catalyst (Fig. 1). Herein, the incorporation and spatial distribution of framework Al into zeolite ZSM-5 thin-films have been studied using PiFM, and nanometer scale structure-performance relationships have been established by mapping the surface of the zeolite thin-film (Si/Al = 45) after the methanol-to-hydrocarbons (MTH) reaction.

Zeolite ZSM-5 thin-films, prepared using the secondary growth method by immersing an as-prepared pure-Si mono-layer into the secondary growth media (SGM) solutions with various Si/Al ratios (i.e., 45, 125, 250 and 450) as we reported recently (see Fig. S1, ESI†), were studied using PiFM after the MTH reaction at 623 K for 4 h. Large zeolite ZSM-5 crystals were also studied after a 1.5 h MTH reaction (623 K) to confirm the
Fig. 2  (a and b) Atomic force microscopy (AFM) topography (top) and photoinduced force microscopy (PiFM, bottom) image at 1100 cm$^{-1}$ of zeolite ZSM-5 thin-films grown in a secondary growth media with ethanol as the structure directing agent and Si/Al = (a) 0.5 and (b) 45. (c and d) PiFM point spectra show (c) zeolite framework vibration and (d) hydrocarbon vibration distributions at different locations indicated by the stars with corresponding colors in (a and b) in the zeolite ZSM-5 thin-films after a 4 h methanol-to-hydrocarbons (MTH) reaction at 623 K. (e) High resolution PiFM image of the framework vibration at 1100 cm$^{-1}$ of the zeolite thin-films from the region highlighted in (b). (f) Product/coke distribution in the same area measured with PiFM at 1480 cm$^{-1}$ representing the C=C stretch of hydrocarbons. The black and red scale bars represent 1 μm and 55 nm, respectively. Images (e) and (f) are shifted with respect to each other due to thermal drift between the tip and the sample.

As shown in Fig. 2a and b, the ethanol-directed pure-Si zeolite thin-films were measured using the AFM mode and PiFM mapping mode, with the zeolite asymmetric framework vibration (T–O–T, 1100 cm$^{-1}$) serving as a marker for the formation of zeolite framework (discussed further in the ESI†). As shown in Fig. 2, the surface topography and crystallinity of zeolite thin-films were measured using the AFM mode and PiFM mapping mode, with the zeolite asymmetric framework vibration (T–O–T, 1100 cm$^{-1}$) serving as a marker for the formation of zeolite framework (discussed further in the ESI†). As shown in Fig. 2a and b, the ethanol-directed pure-Si zeolite thin-film and aluminosilicate zeolite ZSM-5 thin-film with Si/Al = 45 have smooth, well-crystallized surfaces. However, the tetrapropylammonium (TPA$^+$) directed zeolite ZSM-5 thin-film with Si/Al = 45 has a very rough surface that consists of well-crystallized needle-like zeolite features (Fig. S2, ESI†), as well as isolated amorphous structures. These observations provide nanometer scale confirmation of the conclusions of our recent work, that ethanol can serve as an overgrowth suppressing structure-directing agent for aluminosilicate ZSM-5 thin-films.†

Different locations across the aluminosilicate thin-films were also measured with PiFM to examine its sensitivity to framework Al$^{3+}$ incorporation and its potential for probing nanometer scale Brønsted acidity variations (based on Si/Al ratio) across zeolite thin-films/crystals. In Fig. S3 (ESI†) we show the gradual red shift from 1107 cm$^{-1}$ to 1100 cm$^{-1}$ and finally a split to ~1109 and ~1082 cm$^{-1}$ in the asymmetric vibration band in four different thin-films with increasing Al content. This can be attributed to the longer Al–O bond (1.75 Å) than Si–O bond (1.61 Å), as well as the lower mass of Al compared to Si. Moreover, the results (Fig. S3, ESI†) demonstrate the high sensitivity of PiFM for the examination of heteroatom incorporation and zeolite framework defects.

The product/coke formation from the MTH reaction was studied in the same locations with PiFM, as shown in Fig. 2d, using the C=C stretch at ~1480 cm$^{-1}$ as the fingerprint band of hydrocarbon species.† The zeolite thin-film with Si/Al = 45 shows similar peak location and intensity in both locations, while the aluminosilicate thin-film has a different peak intensity ratio of 1082/1109 cm$^{-1}$ bands in different locations, which is attributed to potential differences in the Al content in the center and at the edge of the aluminosilicate thin-film. These results demonstrate the high sensitivity of PiFM for the examination of heteroatom incorporation and zeolite framework defects.

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Transmission Electron Microscopy (TEM) and attributed to the assembly by rubbing.\textsuperscript{29} As shown in Fig. 2f, the PiFM image of the same area at 1480 cm\textsuperscript{-1}, the characteristic C=C aromatic stretch, shows that the amorphous region is free of product/coke. Similar results are observed by scanning in the reverse direction, ruling out the possibility that the observation is from the height difference. The results highlight the potential of PiFM for building surface structure-performance relationships with nanometer scale resolution.

This study has explored the nanometer scale framework structure and product/coke distribution in zeolite thin-films using the recently developed PiFM technique. The results suggest that PiFM is highly sensitive to the surface chemical structure and product/coke distribution in zeolite thin-films with nanometer scale resolution. The height difference. The results highlight the potential of PiFM for building surface structure-performance relationships with nanometer scale resolution.

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Conflicts of interest

There are no conflicts to declare.

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