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ARTICLE TYPE

## Electronic Supplementary Materials

### Probing the surface of nanosheet H-ZSM-5 with FTIR spectroscopy

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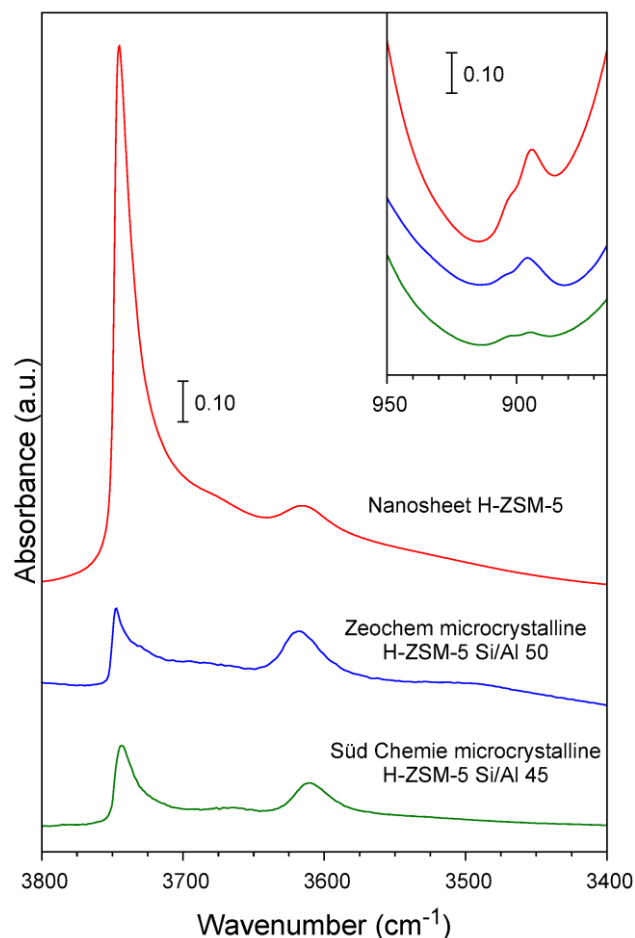
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Fig. S1 compares H-ZSM-5 nanosheet (Si/Al=50 from MP-AES) with two commercial microcrystalline materials with similar Si/Al ratios (50 and 45). Microcrystalline H-ZSM-5 shows distinct signals for the SiOH and Si(OH)Al in the  $\nu(\text{OH})$  region.

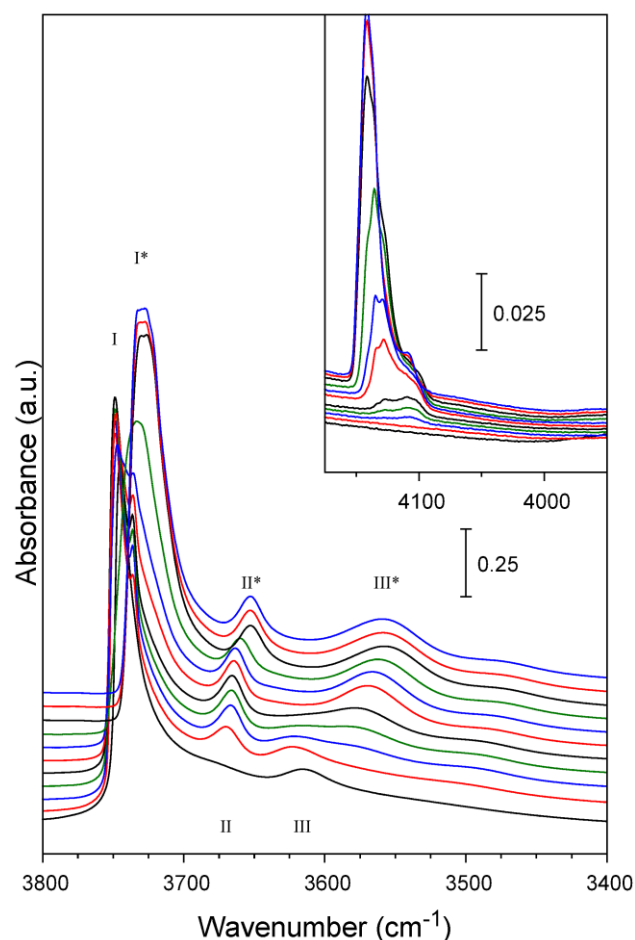
10 As these microcrystalline samples have more classical dimensions, several hundred nanometres along each crystal edge,

normalised by the framework overtone. Data from Saepurahman *et al.*<sup>1</sup> and Svelle *et al.*<sup>2</sup>

the SiOH signal is of the same magnitude in intensity as the  
20 Si(OH)Al signal.



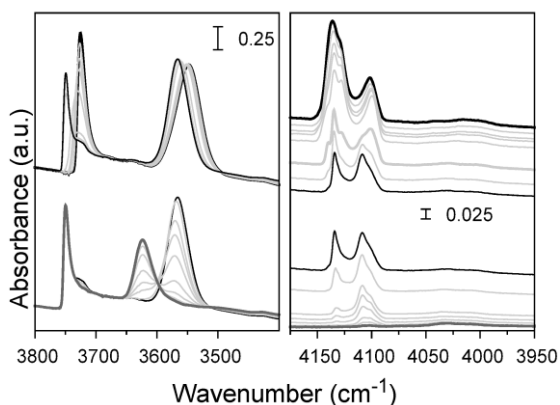
15 **Fig. S1** FTIR spectra of dehydrated H-ZSM-5 samples in the  $\nu(\text{OH})$  region and the  $950\text{-}875\text{ cm}^{-1}$  region with signals related to strained Si-O-Si bridges. Nanosheet H-ZSM-5 in comparison with two commercial microcrystalline H-ZSM-5 samples with similar Si/Al. All spectra were



25 **Fig. S2** FTIR spectra of H<sub>2</sub> adsorption on nanosheet H-ZSM-5 with emphasis on the  $\nu(\text{OH})$  region and the  $\nu(\text{HH})$  region (inset). Line I is the sample after activation at 250 K with H<sub>2</sub> present in the cell. The consecutive spectra 2-X reports the effect of progressive cooling to reach 15 K (line X).

Fig. S2 shows the effect of progressive cooling from 250 K till 15 K on an activated nanosheet H-ZSM-5 with H<sub>2</sub> present in the cell.

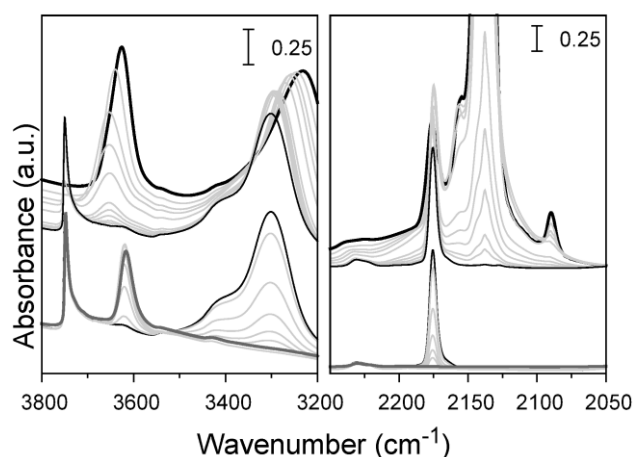
Fig. S3 displays FTIR spectra of H<sub>2</sub> desorption from a microcrystalline H-ZSM-5 sample with few defects (Si/Al=40). In the ν(OH) region the spectrum of the activated sample is characterised by two main components at 3750 and 3623 cm<sup>-1</sup> associated to SiOH and Si(OH)Al respectively. Upon interaction with H<sub>2</sub>, both components are progressively eroded: bottom spectra report data associated to low H<sub>2</sub> coverage; top spectra refer to high H<sub>2</sub> coverage. The formation of H<sub>2</sub> adducts with strong Brønsted sites causes erosion of the band at 3623 cm<sup>-1</sup> and the growth of a new band at 3570 cm<sup>-1</sup> (isosbestic point at 3595-3600 cm<sup>-1</sup>). At high H<sub>2</sub> coverage also silanols are engaged in the interaction, as testified by the total disappearance of the band at 3750 cm<sup>-1</sup> and the appearance of a new absorption at 3725 cm<sup>-1</sup> (isosbestic point around 3732 cm<sup>-1</sup>). In the ν(HH) region more fine resolved signals are observed than for the nanosheet H-ZSM-5. At low loading of H<sub>2</sub> two signals and a shoulder are clearly seen. At higher loading of H<sub>2</sub> at least five components can be identified (bold light grey curve in Fig. S3) due to H<sub>2</sub> molecules being entrapped in small cavities.



**Fig. S3** H<sub>2</sub> desorption with emphasis on the ν(OH) region (left panel) and the ν(HH) region (right panel). Upper set of curves relate to high coverage of H<sub>2</sub> and the bottom set is related to lower coverage of H<sub>2</sub>. This H-ZSM-5 sample (Si/Al=40) has very few defects. Note the fine resolved bands in the ν(HH) region in the upper set of curves.

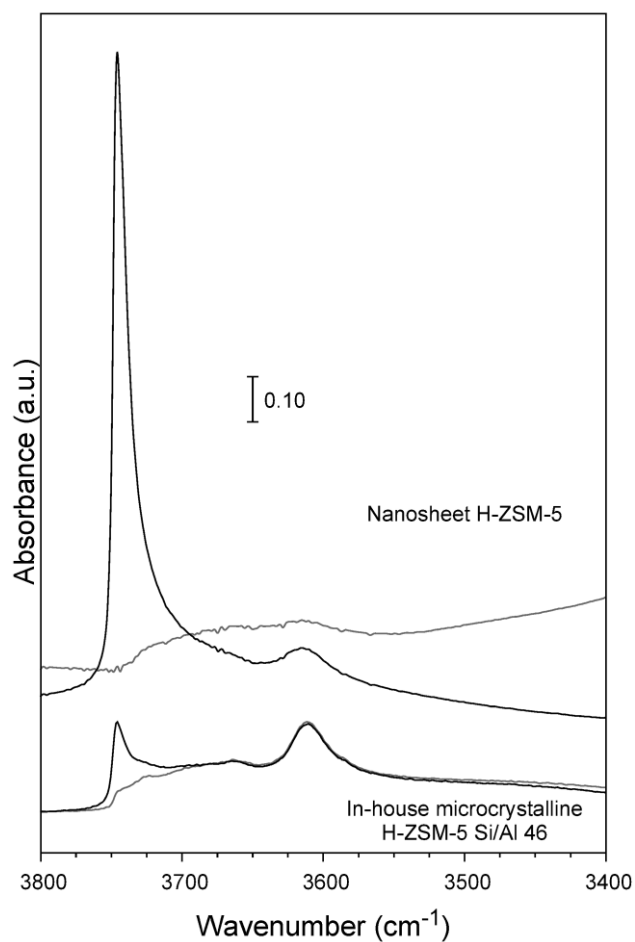
Fig. S4 displays FTIR spectra of a parallel experiment performed on the same zeolite, using CO as probe. Bottom spectra report data where CO is interacting with strong acidic sites, while top spectra show the effect of CO interaction with silanols and filling of the pores. At low CO coverage the band due to strong Brønsted sites is eroded and a corresponding band is growing at 3300 cm<sup>-1</sup> (isosbestic point at 3534 cm<sup>-1</sup>). Note the complex nature of the absorption observed after CO interaction (at least 2 maxima at 3413 and 3300 cm<sup>-1</sup>) even if the original Si(OH)Al group is characterised by a single component. This has been

recently explained not in term of heterogeneity of sites but to the presence of Fermi resonance of the O-H stretching with the 3δ(OH) modes of the bridged hydroxyls<sup>3</sup>. At high CO converges silanols are eroded and new band grows at 3654 cm<sup>-1</sup>. The right panel of the figure reports the CO stretching counterpart. At low CO coverage, a sharp band at 2174 cm<sup>-1</sup> testifies the formation of the adducts with strong Brønsted sites; a weak complex absorption at 2230 cm<sup>-1</sup> reveals a small amount of extraframework Al<sup>3+</sup>. At high CO coverage Si-OH...CO adducts are confirmed by the appearance of a component at 2157 cm<sup>-1</sup>, on the left side of the main absorption centered at 2138 cm<sup>-1</sup> associated to liquefied CO inside the pores.



**Fig. S4** CO desorption with emphasis on the ν(OH) region (left panel) and the ν(CO) region (right panel). Upper set of curves relate to high coverage of H<sub>2</sub> and the bottom set is related to lower coverage of CO. This H-ZSM-5 sample (Si/Al=40) has very few defects.

Fig. S5 compares the IR spectra of the ν(OH) region of 2 dehydrated H-ZSM-5 (black curves) with collidine adsorbed (grey curves). All spectra were normalised by the framework overtone. The in-house made microcrystalline H-ZSM-5 (top spectra) shows literary no change in the Si(OH)Al band intensity when collidine is adsorbed. This proves that relatively few Brønsted acid sites are close to the external surface. In the nanosheet H-ZSM-5 sample (bottom spectra) the FTIR spectrum shows that most Brønsted acid sites are in vicinity of the external surface. Data from Holm *et al.*<sup>4</sup>



**Fig. S5** FTIR spectra of the  $\nu(\text{OH})$  region of dehydrated H-ZSM-5 (black curves) with collidine adsorbed (grey curves). All spectra were normalised by the framework overtone.

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## References

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