Supplementary Material (ESI) for Chemical Communications

Problems in the IR measuring the acidity of zeolite bridging hydroxyls by low-temperature CO adsorption

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Supporting information

1. Background IR spectra.

The background FTIR spectra of the activated H–ZSM-5 and H–D–ZSM-5 samples are presented in Fig. S1.

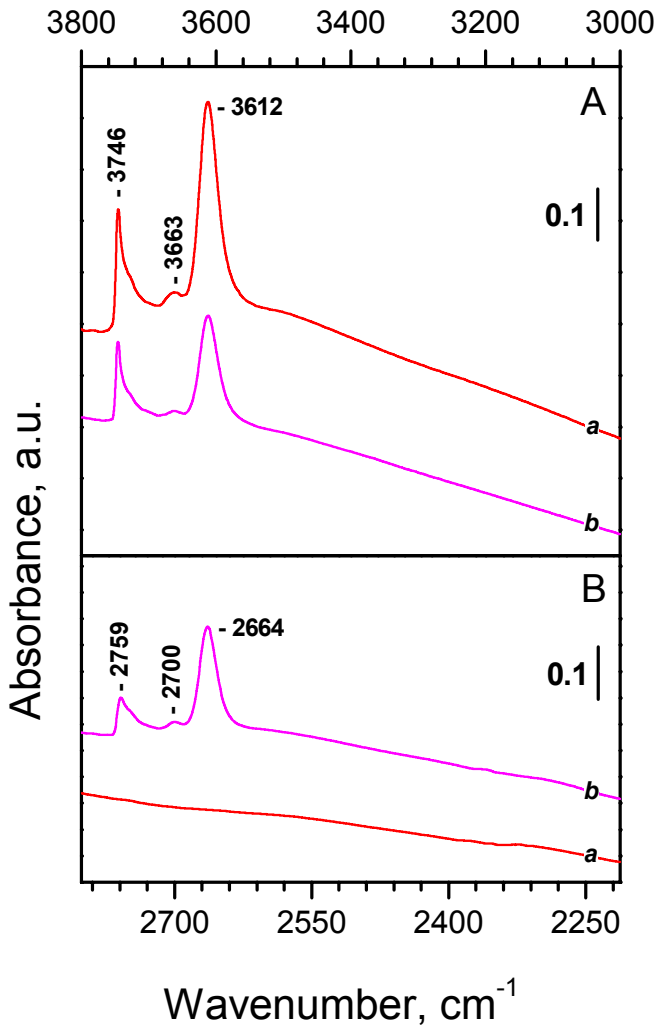

Fig. S1. FTIR spectra of activated H–ZSM-5 sample (a) and partly deuteroxylated H–D–ZSM-5 sample (b) registered at room temperature.

2. Changes in the OH and OD regions induced by low-temperature CO adsorption of H–D–ZSM-5.

The changes in the OH and OD regions induced by low-temperature CO adsorption are presented in Fig. S2.

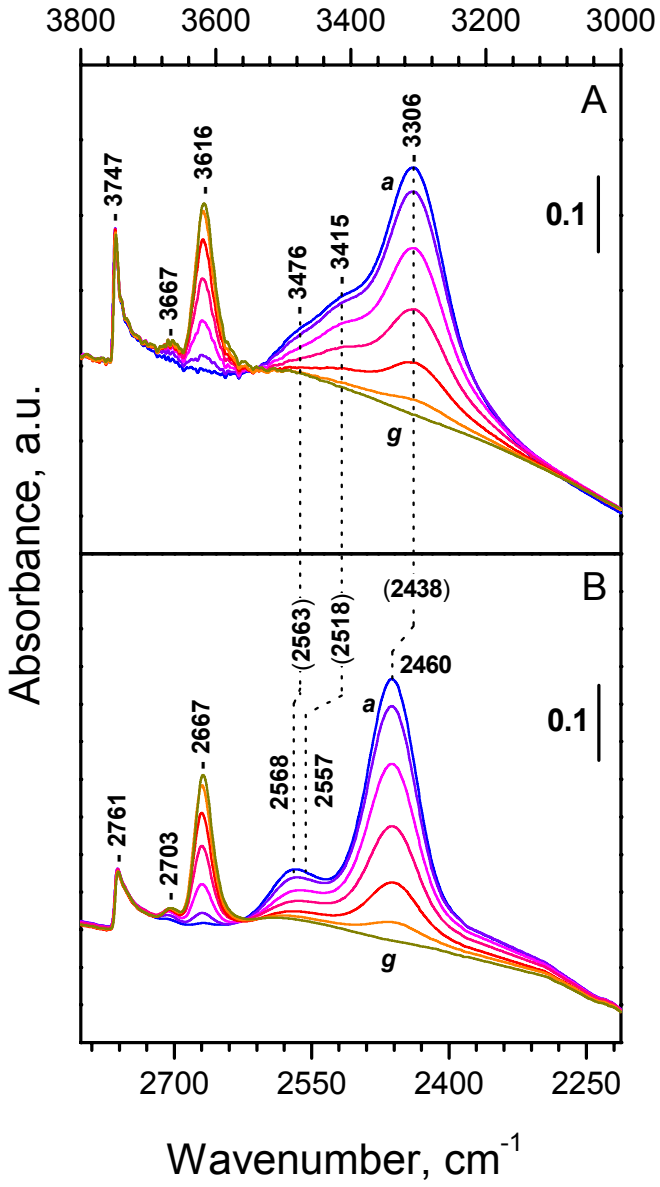

Fig. S2. FTIR spectra of CO (500 Pa initial equilibrium pressure) adsorbed at 100 K on H-D-ZSM-5: evolution of the spectra under dynamic vacuum at 100 K (a-g).

3. Changes in the carbonyl region induced by low-temperature CO adsorption of H–D–ZSM-5.

The carbonyl spectra, corresponding to the spectra presented in Fig. 1 are shown in Fig. S3. A single band at 2174 cm^{-1} is detected at low coverages (CO interacting with zeolite acidic hydroxyls). With coverage increase a shoulder at 2167 cm^{-1} (CO interacting with Al–OH groups) develops.

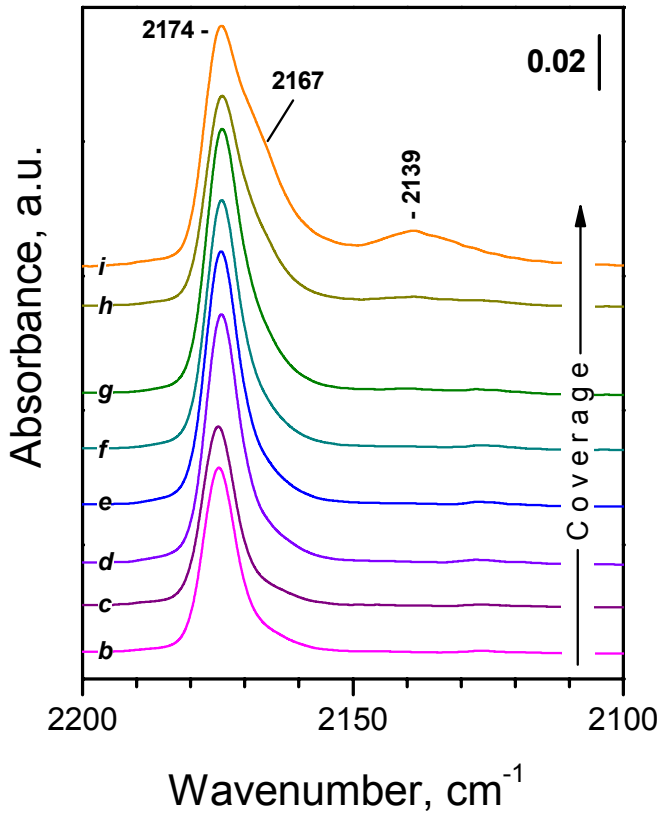

Fig. S3. Changes in the FTIR spectra of H–D–ZSM-5 induced by small changes in the CO coverage (b-i). The spectra are the same with those presented in Fig. 1 but show the carbonyl region.

4. Low-temperature adsorption of $^{15}N_2$ on H–D–ZSM-5.

The changes in the OH and OD regions induced by low-temperature $^{15}N_2$ adsorption are presented in Fig. S4. The bands of the bridging OH (3616 cm^{-1}) and OD groups (2667 cm^{-1}) are shifted to single bands at 3496 and 2585 cm^{-1}, respectively. On the basis of the H-D isotopic shift factor the shifted OD band is expected at 2578 cm^{-1}, i.e. at wavenumber lower by 7 cm^{-1}. These results evidence: (i) lower acidity of the OD groups, as compared to OH, and (ii) homogeneity of the bridging acidic OH and OD groups.

At higher coverages the Al-OH (3667 cm^{-1}) and Al-OD (2703 cm^{-1}) band are shifted to ca. 3600 and 2660 cm^{-1}, respectively.

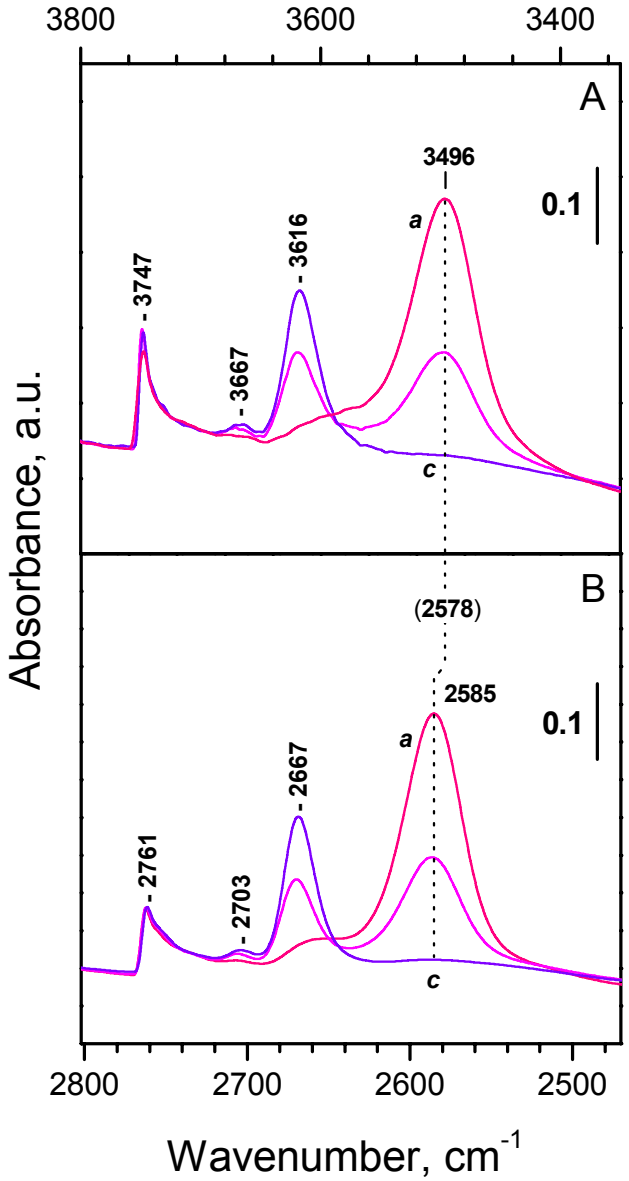

Fig. S4. FTIR spectra of $^{15}N_2$ (1 kPa equilibrium pressure) adsorbed at 100 K on H–D–ZSM-5: evolution of the spectra under dynamic vacuum at 100 K (a-c).

5. Low-temperature CO adsorption on H–ZSM-5 and D–ZSM-5.

The changes in the OH (sample H–ZSM-5) and OD regions (sample H–ZSM-5) induced by low-temperature CO adsorption are presented in Figs. S5 and S6, respectively. Comparison with Fig. 1 clearly shows that analogous changes are observed with the H–D–ZSM-5 sample.

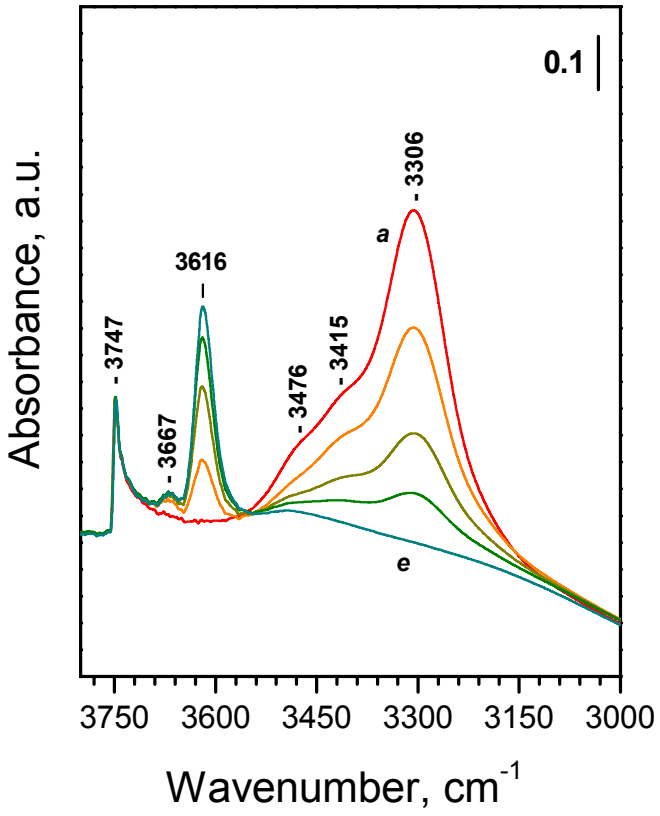

Fig. S5. FTIR spectra of CO (500 Pa initial equilibrium pressure) adsorbed at 100 K on H–ZSM-5: evolution of the spectra under dynamic vacuum at 100 K (a-e).

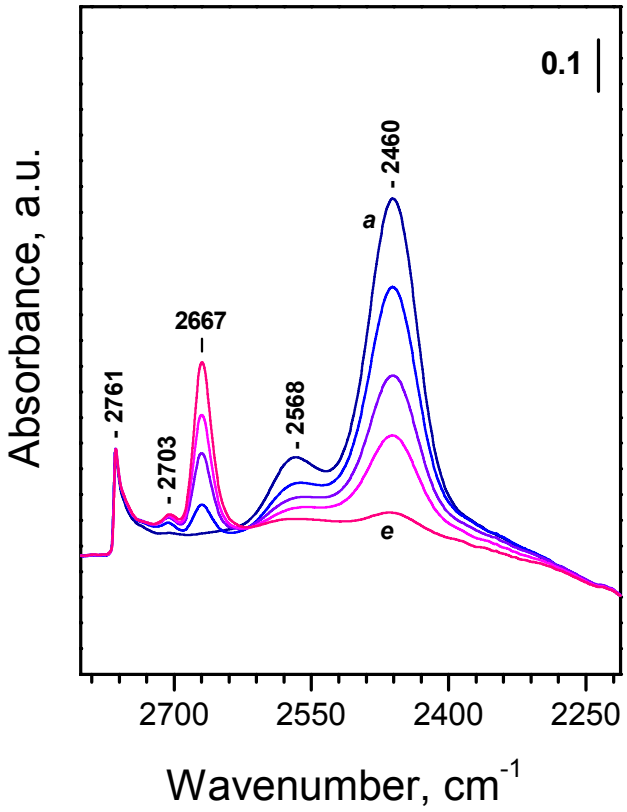

Fig. S6. FTIR spectra of CO (500 Pa initial equilibrium pressure) adsorbed at 100 K on D–ZSM-5: evolution of the spectra under dynamic vacuum at 100 K (a-e).