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Defect-engineered zeolite porosity and accessibility

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Figure S1 Magnified N_2 adsorption-desorption isotherms highlighting the isotherms shape in the 0 - 0.1 relative pressure range.



Figure S2 TEM images of MOR-AF (A) and MOR-A-AF (B) showing obvious difference in mesopore density between these two samples.



Figure S3 TEM images of the MOR-OA-AF revealing aligned rectangle pores (A) and pores with an ill-defined shape (B).



Figure S4 The IR spectra of MOR (A), MOR-A (B), MOR-AF (C) and MOR-A-AF (D) after activation at 450 °C and under 1×10^{-6} torr vacuum (lines "OH-IR" in A-D), and after the adsorption of 1 torr collidine at room temperature (lines "RT" in A-D), as well as the subsequent heating of the sample at 200 °C in 1 torr collidine atmosphere for up to 210 min (lines "15", "30", "45"... mean that IR spectra were collected after each 15 min of heating.).

As can be seen from the dotted lines "RT" in Figure S4A-D, the collidine adsorbed at room temperature mainly interact with the silanol groups (see the peak at ca. 1617 cm⁻¹), although there are also some adsorption of collidine on zeolite Brønsted acid sites (see the peak at ca. 1643 and 1637 cm⁻¹ in Figure S4C, for example). The heating of the sample at 200 °C accelerates the diffusion of collidine and an increasing amount of Brønsted acid sites are accessible to collidine.



Figure S5

(A) The subtraction result of the IR spectra of MOR after 15 (line 1) and 30 min (line 2) of collidine adsorption at 200 °C in 1 torr collidine atmosphere. Line 3 is the difference spectra between line 1 and 2.

(B) The subtraction result of the IR spectra of MOR-A after 15 (line 1), 30 min (line 2) and 120 min (line 3) of collidine adsorption at 200 °C in 1 torr collidine atmosphere. Line 4 is the difference spectra between line 1 and 2. Line 5 is the difference spectra between line 1 and 3.

(C) The subtraction result of the IR spectra of MOR-AF after 15 (line 1), 30 min (line 2) and 105 min (line 3) of collidine adsorption at 200 °C in 1 torr collidine atmosphere. Line 4 is the difference spectra between line 1 and 2. Line 5 is the difference spectra between line 1 and 3.

(D) The subtraction result of the IR spectra of MOR-A-AF after 15 (line 1), 30 min (line 2) and 210 min (line 3) of collidine adsorption at 200 °C in 1 torr collidine atmosphere. Line 4 is the difference spectra between line 1 and 2. Line 5 is the difference spectra between line 1 and 3.



Figure S6 IR spectra of MOR (A), MOR-A (B), MOR-AF (C) and MOR-A-AF (D) after saturated adsorption of collidine at 200 °C (lines "0"), and after the subsequent desorption of collidine under vacuum and at elevated temperatures (lines "1 - 9": from 50 °C to 450 °C with 50 °C interval). During the evacuation, the adsorption bands at 1617 and 1573 cm⁻¹, assigned to collidine hydrogen-bonded to silanol groups disappear first. Correspondingly, the silanol groups (3743 cm⁻¹) are getting less and less occupied. (E) The quantification of the collidine remaining adsorbed on zeolite crystals after the heat treatment at increasing temperature under vacuum.



Figure S7 The IR spectra showing the v(OH) region of MOR-A (line 1) and MOR-A-AF (line 2). Line 3 is the difference spectra between line 1 and 2. The negative peak centered at ca. 3727 cm-1 shows clearly that MOR-A-AF contains lower number of internal silanol groups.