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Supporting Information

Characterization of acid sites on Hf-Beta zeolite by CD₃CN IR-TPD

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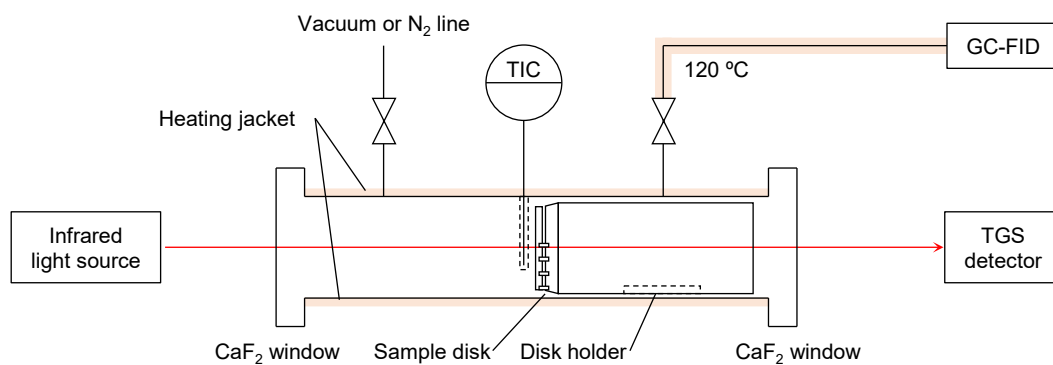


Figure S1 Schematic experimental setup for IR-TPD measurement.

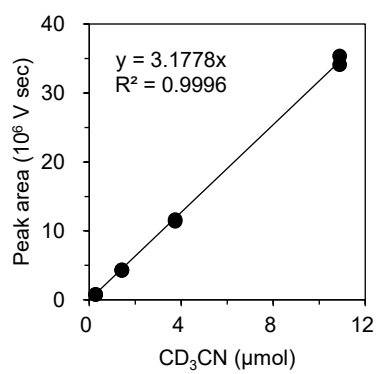


Figure S2 Calibration curve for CD₃CN on FID.

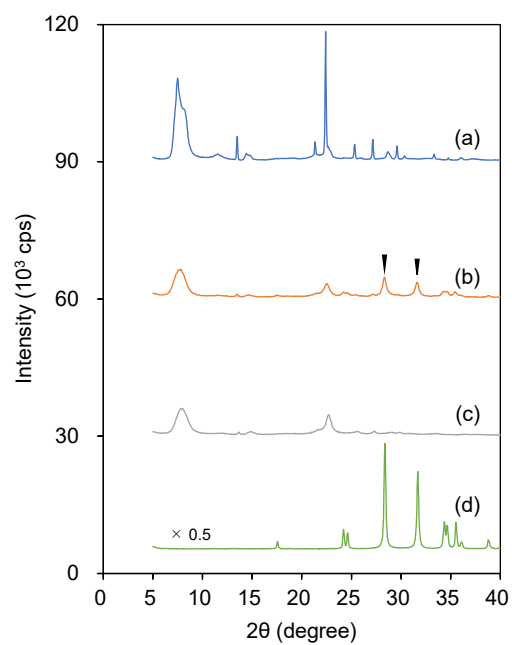


Figure S3 XRD patterns of (a) Hf-Beta-104, (b) HfO₂/Si-Beta, (c) Si-Beta, and (d) HfO₂.

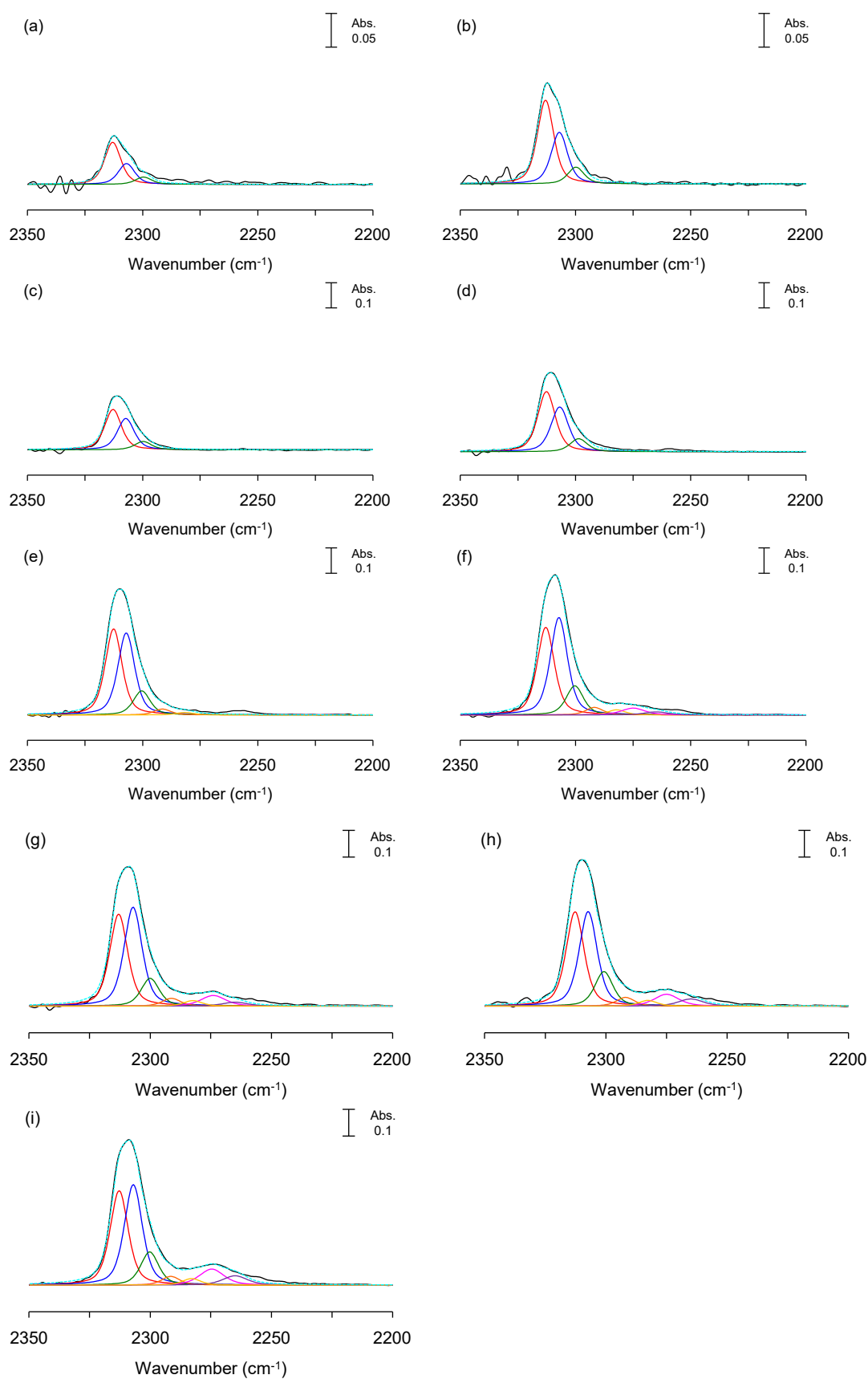


Figure S4 Curve-fitting of difference spectra for CD_3CN adsorbed on Hf-Beta-104 at dosing pressure of (a) 35, (b) 65, (c) 105, (d) 155, (e) 215, (f) 285, (g) 305, (h) 365, and (i) 370 Pa. – Raw, – Sum, – 2313 cm^{-1} , – 2307 cm^{-1} , – 2300 cm^{-1} , – 2292 cm^{-1} , – 2284 cm^{-1} , – 2275 cm^{-1} , – 2265 cm^{-1} .

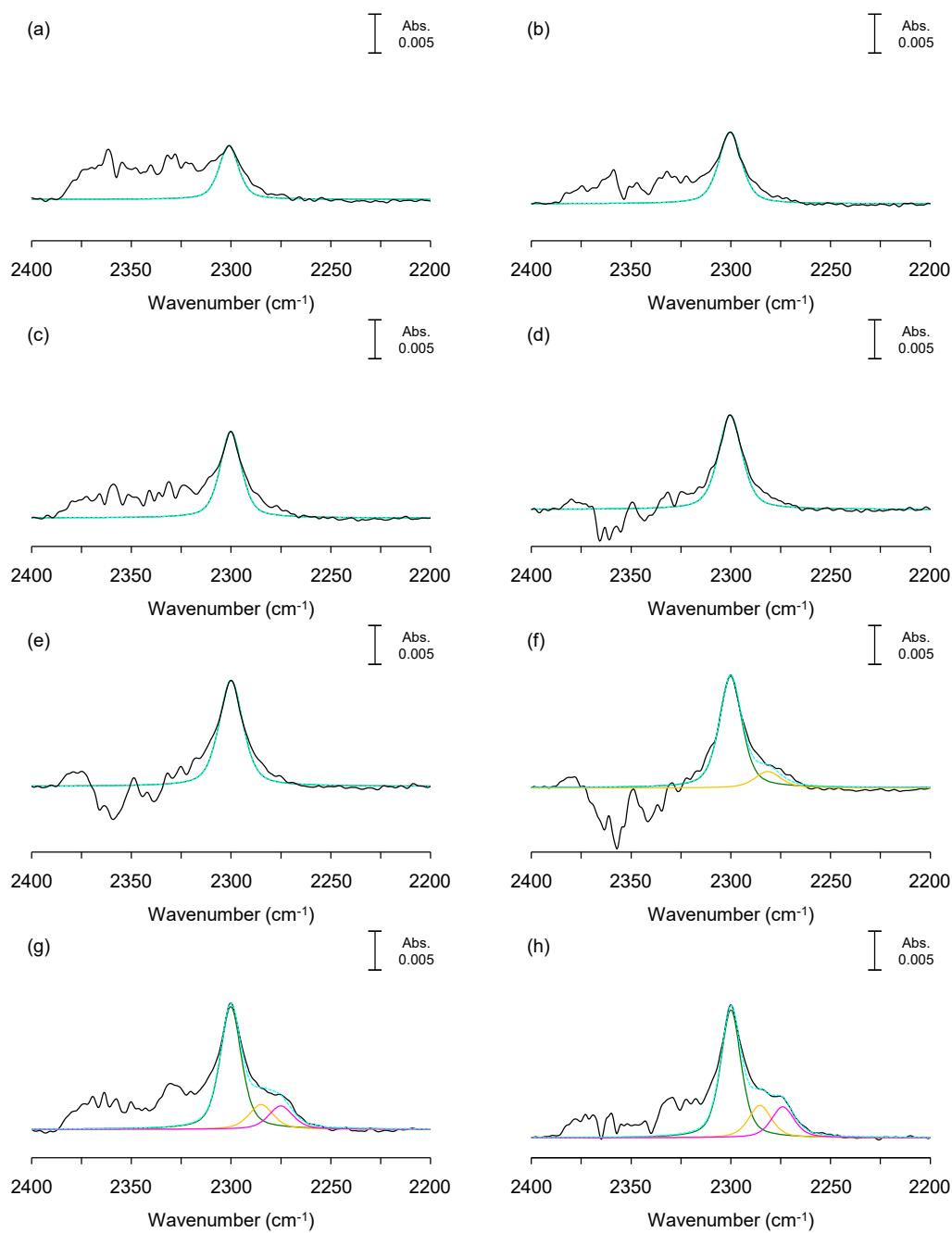


Figure S5 Curve-fitting of difference spectra for CD_3CN adsorbed on $\text{HfO}_2/\text{Si-Beta}$ at dosing pressure of (a) 10, (b) 15, (c) 19, (d) 20, (e) 20, (f) 25, (g) 35, and (h) 35 Pa. – Raw, – Sum, – 2300 cm^{-1} , – 2284 cm^{-1} , – 2275 cm^{-1} .

Considering that the absorption band at 2320 – 2380 cm^{-1} was due to ambient CO_2 on the optical path outside the cell, the fitting was performed by drawing a linear baseline from 2200 to 2400 cm^{-1} .

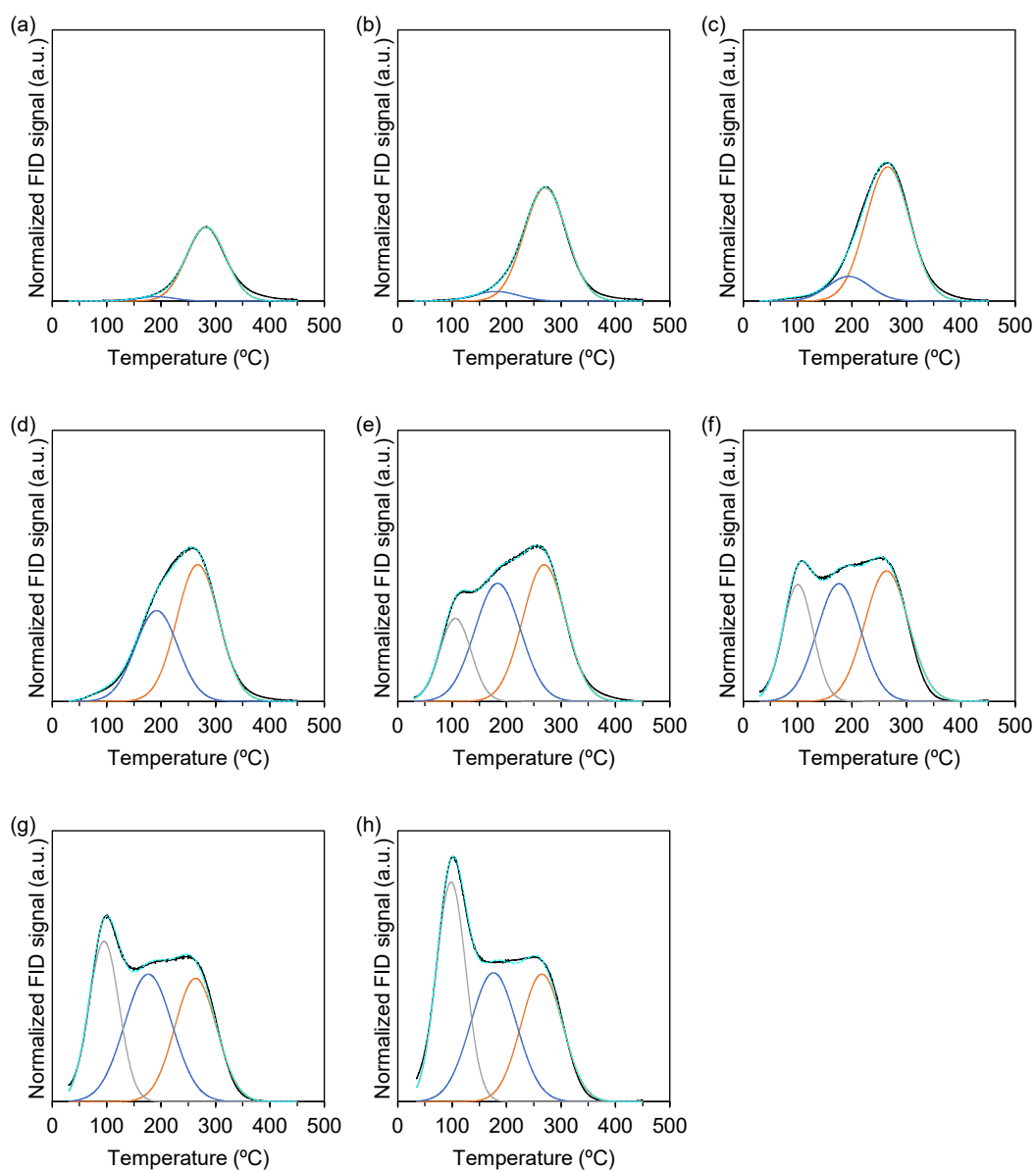


Figure S6 Curve fitting of CD_3CN -TPD profiles of Hf-Beta-104 after dosing at (a) 65, (b) 105, (c) 155, (d) 215, (e) 285, (f) 305, (g) 365, and (h) 370 Pa. – Raw, – Sum., – High temperature, – Middle temperature, – Low temperature.

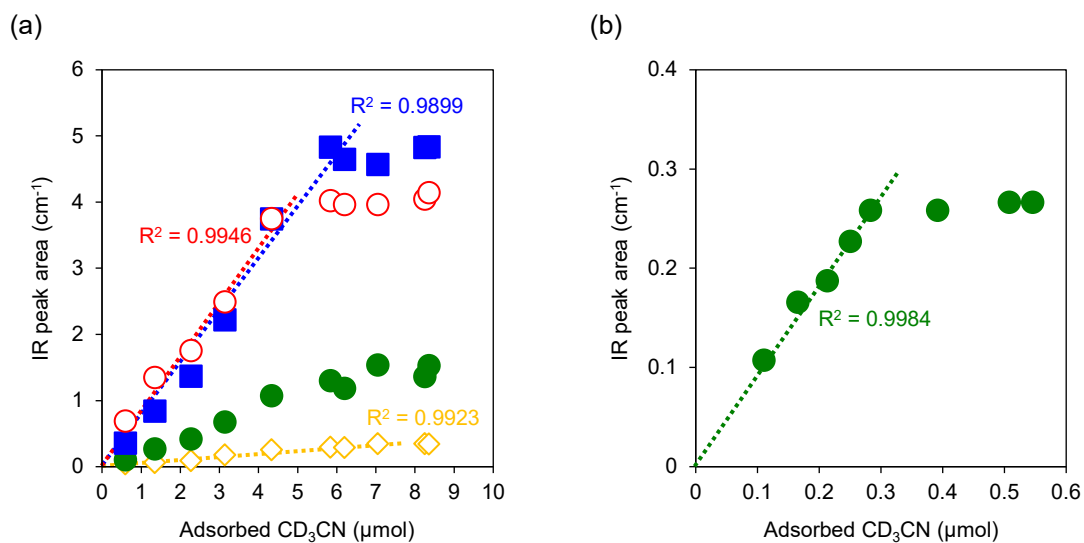


Figure S7 Relationship between IR peak area and the amount of adsorbed CD₃CN on (a) Hf-Beta-104 and (b) HfO₂/Si-Beta. 2313 cm⁻¹ (○), 2307 cm⁻¹ (■), 2300 cm⁻¹ (●), and 2284 cm⁻¹ (◇).

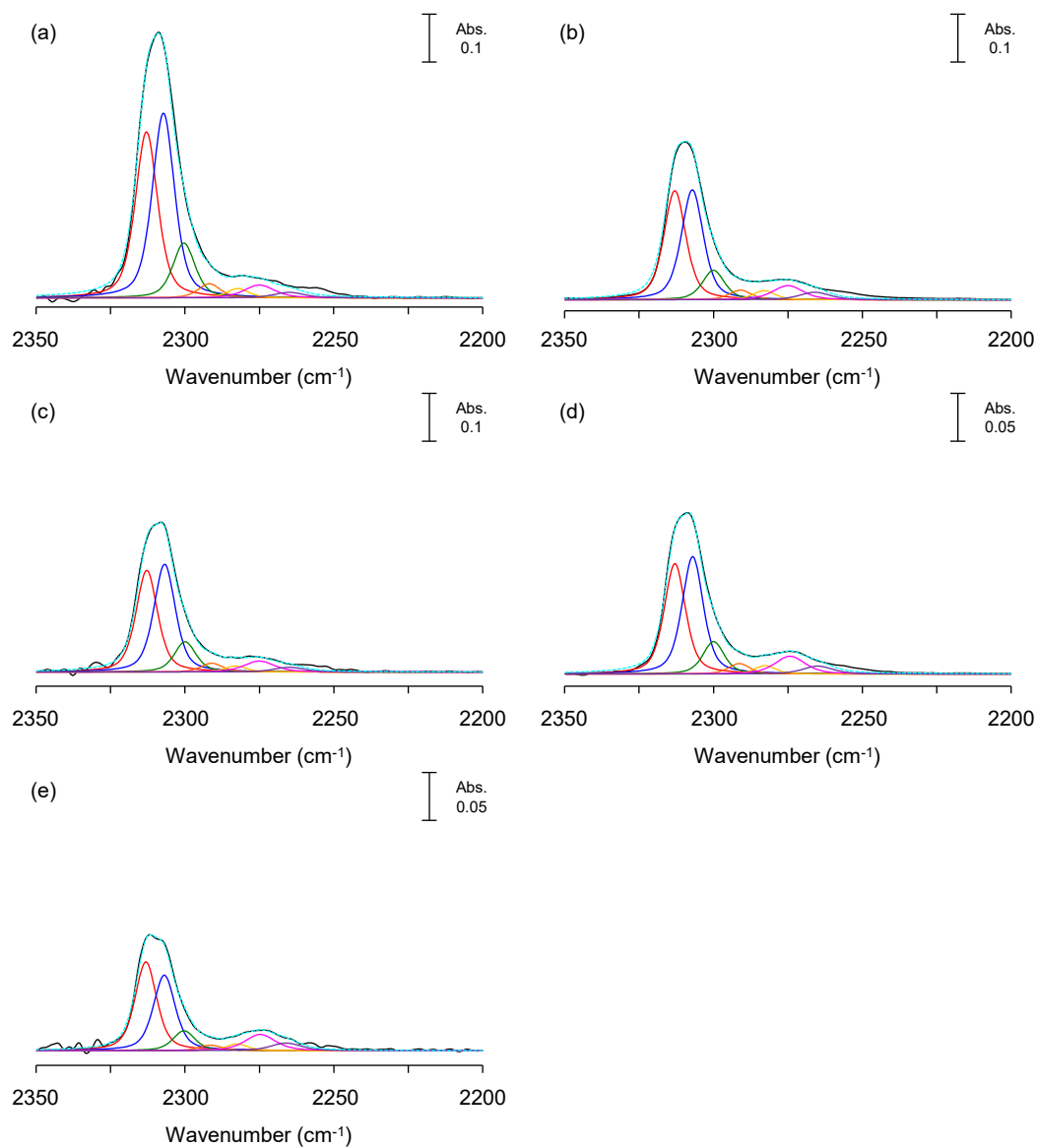


Figure S8 Curve fitting of difference spectra of CD_3CN adsorbed on (a) Hf-Beta-104, (b) Hf-Beta-130, (c) Hf-Beta-166 (d) Hf-Beta-255, and (e) Hf-Beta-475. – Raw, – Sum, – 2313 cm^{-1} , – 2307 cm^{-1} , – 2300 cm^{-1} , – 2292 cm^{-1} , – 2284 cm^{-1} , – 2275 cm^{-1} , – 2265 cm^{-1} .

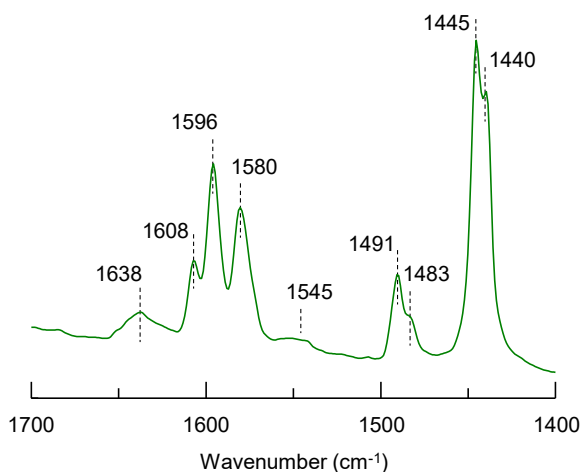


Figure S9 IR difference spectra of Hf-Beta-104 before and after dose of pyridine.

For the IR measurement of Hf-Beta-104 using pyridine as probe molecule, pyridine was dosed on the sample at 50 °C, and then, the sample was purged in nitrogen flow at 100 °C. After the sample was cooled down to 50 °C, an IR spectrum was measured.

In addition to absorption peaks of pyridine adsorbed on Lewis acid sites (1445 and 1608 cm⁻¹), other peaks attributable to protonated pyridine (1545 and 1639 cm⁻¹) and physisorbed pyridine (1440 and 1596 cm⁻¹) were also observed [S1]. The peaks at 1491 and 1580 cm⁻¹ are attributed to pyridine adsorbed on Lewis and/or Brønsted acid sites.

[S1] V.L. Sushkevich, P.A. Kots, Y.G. Kolyagin, A. V. Yakimov, A. V. Marikutsa, I.I. Ivanova, J. Phys. Chem. C, 123 (2019) 5540–5548.

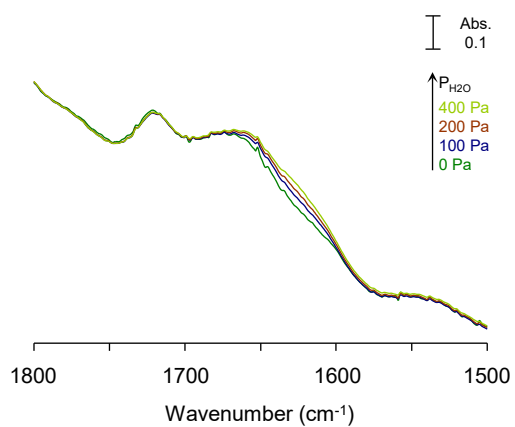


Figure S10 IR spectra upon adsorption of CD₃CN on dried or hydrated Hf-Beta-104 in the region of O-H bending vibration. Dosing pressure of CD₃CN was 455 Pa.

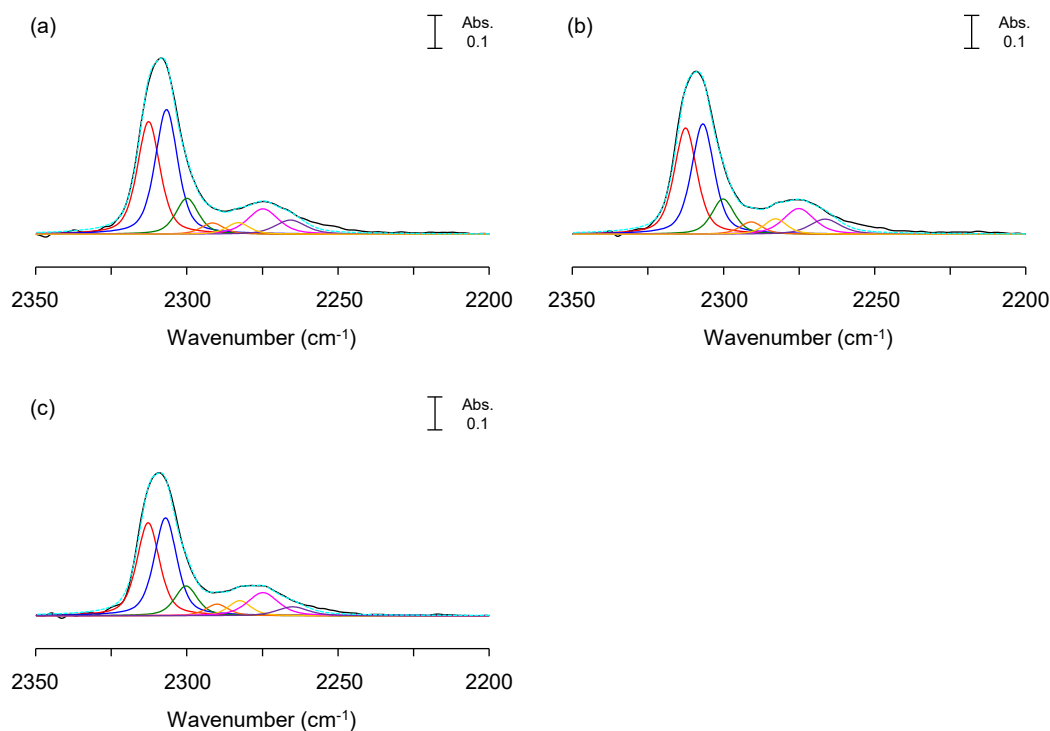


Figure S11 Curve-fitting of difference spectra for CD_3CN adsorbed on hydrated Hf-Beta-104. Dosing pressure of water vapor was (a) 100, (b) 200, and (c) 400 Pa. Dosing pressure of CD_3CN was 90 Pa. – Raw, – Sum, – 2313 cm^{-1} , – 2307 cm^{-1} , – 2300 cm^{-1} , – 2292 cm^{-1} , – 2284 cm^{-1} , – 2275 cm^{-1} , – 2265 cm^{-1} .

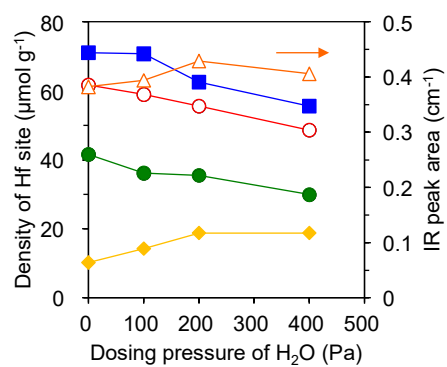


Figure S12 Influence of hydration on the density of Hf species in Hf-Beta-104 probed with CD₃CN. Dosing pressure of CD₃CN was 90 Pa. Open Hf site (○), Closed Hf site (■), Extra-framework HfO₂ (●), Hf-OH (◆), and IR peak area at 2292 cm⁻¹ for bridging hydroxy group (△).