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3 **Characterization of acid sites on Hf-Beta zeolite**

4 **by CD₃CN IR-TPD**

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16

17 **Abstract**

18 To identify Hf species and quantitatively evaluate their acid properties, combined
19 measurement of infrared (IR) and temperature-programmed desorption (TPD) with deuterated
20 acetonitrile (CD₃CN) as probe molecule was performed on Hf-Beta and HfO₂/Si-Beta. IR spectra of
21 CD₃CN adsorbed on Hf-Beta showed five types of Hf species including framework open and closed
22 Hf sites, extra-framework HfO₂, and two types of Hf species bearing hydroxy groups. IR
23 measurement showed structural change in Hf-Beta upon exposing to water vapor with generation of
24 the two types of Hf species bearing hydroxy groups. Integrated molar extinction coefficients for C≡
25 N stretching vibration of CD₃CN adsorbed on these Hf species were estimated and the number of
26 each Hf acid site was calculated. Acid strength of these Hf species was estimated from CD₃CN-TPD
27 measurement in combination with IR; the acid strength of the open and closed Hf sites, extra-
28 framework HfO₂ species, and the other Hf species was found to be strong, moderate, and weak,
29 respectively.

30

31 **Keywords**

32 CD₃CN; Hf-Beta; IR; Lewis acid; TPD

33

34 1. Introduction

35 Metallosilicate zeolites are excellent solid catalysts for various organic reactions, for which
36 isolated heterometal atoms in the zeolite framework serve as acid sites [1–3]. Since Beta framework
37 can incorporate various heterometals, zeolite Beta is commonly used as catalyst among
38 metallosilicate zeolites. In recent years, Hf-Beta, in which Hf^{4+} is incorporated in the framework of
39 zeolite Beta, has attracted great research interest. Hf-Beta has been reported to exhibit excellent
40 catalytic performance for diverse organic reactions such as Meerwein-Ponndorf-Verley (MPV)
41 reduction [4–9], aldol condensation [10–12], N-alkylation [13], sugar conversion [14–16], and ring
42 opening of epoxides [17].

43 Hf-Beta samples reported so far were commonly synthesized by the conventional
44 hydrothermal method using fluoride. Previously, we reported that in the hydrothermal synthesis of
45 Hf-Beta, Hf was more likely to form extra-framework Hf species than Sn analogue for Sn-Beta due
46 to the lower solubility of Hf in water [7]. The synthesis of Hf-Beta using post-synthesis methods in
47 which Hf precursor was immobilized on dealuminated Beta has also been reported [8,9,12,15]. For
48 example, Hf-Beta was synthesized by impregnating dealuminated zeolite Beta with hafnocene
49 dichloride [12]. This synthesis method produced a significant amount of extra-framework Hf species.
50 Thus, the type of Hf species, which include framework and extra-framework Hf species, and the
51 amount of these species are highly dependent on the synthesis method and conditions for Hf-Beta.
52 Since it is expected that these Hf species have different acid properties and catalytic consequence,
53 quantitative evaluation of Hf species and their acid properties is essential, which can deepen

54 understanding of the catalytic function of Hf-Beta and synthesize better one with higher activity.

55 Spectroscopic analysis using probe molecules is a powerful tool for the structural
56 identification and quantitative determination of active sites in metallosilicate zeolites [18–20]. By
57 means of IR using CD₃CN as probe molecule, Boronat et al. found two absorption peaks at 2316 and
58 2308 cm⁻¹ for the adsorbate on Sn-Beta, which were assigned to two types of framework Sn sites with
59 Lewis acidity, namely open and closed sites, respectively [21]. However, the structure of framework
60 Sn sites and the assignment of these absorption bands remain controversial, and several different
61 assignments have been proposed [22–24]. Harris et al. performed IR measurement using pyridine and
62 CD₃CN to individually quantify total Lewis acid sites, open sites, and closed sites in Sn-Beta [25]. It
63 has also been reported that in addition to these sites, other acid sites such as extra-framework SnO₂
64 [26,27] and bridging hydroxy groups with Brønsted acidity existed on Sn-Beta [28,29]. Spectroscopy
65 using probe molecules is also effective for the characterization of Hf-Beta, and there have been studies
66 using NMR [30,31] and IR [32]. IR measurement with CD₃CN was applied to evaluate the acid
67 properties of Hf-Beta, and the open and closed sites were quantified [32].

68 Considering the analogy between Sn-Beta and Hf-Beta, it would not be surprising if Hf-Beta
69 has the acid sites found on Sn-Beta such as extra-framework species and Brønsted-acidic hydroxy
70 groups, though there have been very limited reports on the identification and quantification of such
71 species on Hf-Beta. Iida et al. used a differential pair distribution function (PDF) method to identify
72 oligomeric extra-framework Hf species [12]. To our knowledge, such extra-framework Hf species
73 has never been confirmed nor quantified by any method other than the PDF.

IR measurement with CD₃CN as probe molecule could be a useful tool for characterization of Hf species on Hf-Beta. However, this method has not been used to identify or quantify extra-framework Hf species on Hf-Beta. In this study, we combinedly performed IR measurement with CD₃CN and CD₃CN-TPD measurement on Hf-Beta and HfO₂/Si-Beta to establish a method to quantify Hf species and estimate the acid strength of each Hf species present on Hf-Beta.

2. Experimental

2.1. Materials

Hafnium chloride (HfCl₄, 98%), tetraethylammonium hydroxide aqueous solution (TEAOH, 35 wt.%), and tetraethyl orthosilicate (TEOS, 99%) were purchased from Sigma-Aldrich. Hydrofluoric acid (HF, 46 – 48 wt.%) and nitric acid (HNO₃, 60 wt.%) were purchased from FUJIFILM Wako Pure Chemical Co. Deuterated acetonitrile (CD₃CN, 99.8% deuterated) was purchased from Cambridge Isotope Laboratories. Al-Beta (CP-814E, Si/Al = 12.5) was purchased from Zeolyst International.

2.2. Synthesis of Hf-Beta and HfO₂/Si-Beta

Hf-Beta was hydrothermally synthesized by the conventional hydrothermal method using fluoride [28]. 22.72 g of 35 wt.% TEAOH aqueous solution, 6.86 g of Milli-Q water, and specified amount of HfCl₄ were added to a 50 mL PTFE beaker. The mixture was homogenized by stirring at 60 °C for 30 min and naturally cooled to room temperature. 20.83 g of TEOS was added and then the

94 mixture was heated and stirred at 70 °C to evaporate ethanol produced by the hydrolysis of TEOS
95 and a part of water. When ethanol was considered to have completely evaporated based on the weight
96 loss, the mixture was allowed to cool to room temperature and 2.17 g of hydrofluoric acid was added
97 to form highly viscous gel. The molar composition of the obtained gel was 1.0 SiO₂: 0.0025 – 0.0125
98 HfCl₄ : 0.54 TEAOH: 0.5 HF: 8.0 H₂O. The gel was ground well by hand with a PTFE rod to obtain
99 white powder. The powder was ground with a mortar and heated at 150 °C for 21 d in a PTFE-lined
100 autoclave. The resulting solid was recovered by suction filtration, washed with ethanol and Milli-Q
101 water, dried at 60 °C overnight, and finally calcined in air at 650 °C (ramp rate, 3 °C min⁻¹) for 6 h.
102 The obtained Hf-Beta samples are designated as Hf-Beta-*x*, where *x* is Si/Hf atomic ratio determined
103 by ICP-AES.

104 HfO₂/Si-Beta was synthesized by the solid-mix method using siliceous zeolite Beta (Si-Beta)
105 as support. Si-Beta was prepared by treating 10 g of Al-Beta in 500 mL of 7.2 M HNO₃ at 80 °C for
106 24 h. The solid was recovered by suction filtration, thoroughly washed with Milli-Q water, and dried
107 at 60 °C overnight. Si/Al ratio of the resulting Si-Beta was estimated to be higher than 1000 by ICP-
108 AES, which confirmed the siliceous composition. 1 g of Si-Beta and 0.53 g of HfCl₄ were mixed with
109 a mortar and pestle in air at room temperature for 10 min. Finally, the obtained powder was calcined
110 in air at 650 °C (ramp rate, 3 °C min⁻¹) for 6 h. This sample had a nominal Si/Hf ratio of 10. Since,
111 for HfO₂/Si-Beta with a low Hf content similar to that of Hf-Beta, the amount of adsorbed CD₃CN
112 was so small that IR absorption bands of CD₃CN could not be clearly observed, HfO₂/Si-Beta with
113 such a high Hf content was used in this study.

114 **2.3. General characterization**

115 Powder XRD patterns were collected on a Bruker D2 PHASER with Cu K α radiation (30
116 kV, 10 mA) at 2θ step width of 0.02°. Nitrogen adsorption isotherms were measured on a
117 MicrotracBEL BEL-mini analyzer at -196 °C. Prior to the measurement, samples were pretreated in
118 nitrogen flow (50 mL min⁻¹) at 400 °C for 1 h. Specific surface area was calculated by the Brunauer-
119 Emmett-Teller (BET) method. Elemental analysis was performed by ICP-AES using a Shimadzu
120 ICPE-9000 analyzer. 10 mg of solid sample was added to 5 mL of 1 M KOH aqueous solution and
121 the mixture was heated at 100 °C for 30 min. The resulting solution was diluted with Milli-Q water
122 to obtain specimen for the ICP-AES measurement.

123

124 **2.4. CD₃CN IR-TPD measurement**

125 Acid properties of Hf-Beta and HfO₂/Si-Beta were investigated by CD₃CN IR-TPD, which
126 was a combination of IR measurement with CD₃CN as probe molecule and TPD of CD₃CN. Figure
127 S1 shows illustration of the equipment used in this experiment. After measuring IR spectra of CD₃CN
128 adsorbed on a sample at 30 °C, the sample was heated and the desorbed CD₃CN was detected by a
129 flame-ionization detector (FID).

130 45 mg of powder sample was pelletized to a disk 2 cm in diameter, which was set in a quartz
131 cell with CaF₂ optical windows. The sample disk was heated (10 °C min⁻¹) in vacuum and pretreated
132 at 450 °C for 1 h. After the temperature was naturally cooled to 30 °C, a spectrum of the clean sample
133 was measured. Then, CD₃CN was dosed into the cell at dosing pressure of 5 Pa. After the pressure

134 became constant, which indicated the adsorption equilibrium, a spectrum was measured. IR spectra
135 were recorded in the range of 4000 – 400 cm^{-1} with resolution of 2.00 cm^{-1} using a JASCO FT/IR-
136 4600 spectrometer.

137 After the IR measurement, the inside of the cell was evacuated to remove CD_3CN that very
138 weakly adsorbed on the sample or remained in the gas phase. It is noteworthy that CD_3CN adsorbed
139 on Hf species remained intact even after the evacuation. Then, the vacuum line was switched to a gas
140 flow line, and the sample was heated from 30 to 450 $^{\circ}\text{C}$ at a ramp rate of 10 $^{\circ}\text{C min}^{-1}$ in nitrogen flow
141 (50 mL min^{-1}). The effluent gas was continuously monitored with an online GC-FID (Shimadzu GC-
142 14B) without any column. The amount of CD_3CN desorbed was quantified from peak area of the TPD
143 profile using a pre-drawn calibration curve (Figure S2). After the TPD measurement, the sample disk
144 was left inside the cell and allowed to cool. The same procedure as above starting with the
145 pretreatment was repeated on the identical sample disk, but the dosing pressure of CD_3CN was
146 increased to higher than that in the previous experiment. Finally, at the dosing pressure where the
147 absorption peaks of CD_3CN due to adsorption on silanol and physical adsorption clearly appeared,
148 the adsorption of CD_3CN on Hf species was considered to be saturated and the measurement was
149 terminated.

150 IR spectra were analyzed using a JASCO Spectrum Manager software package. A linear
151 baseline was drawn from 2200 to 2400 cm^{-1} in the difference spectra before and after the adsorption
152 of CD_3CN . Curve fitting was performed for each deconvoluted absorption peak using Gauss-Lorentz
153 composite function (Gauss/Lorentz = 0.5/0.5) with full width at half maximum of 8 to 12 cm^{-1} .

154 Integrated molar extinction coefficient (IMEC, $\text{cm } \mu\text{mol}^{-1}$) for each absorption peak was estimated
155 from the relationship between integrated IR peak area and total amount of adsorbed CD_3CN
156 determined by the TPD measurement. The regression line was estimated by the least squares method
157 using a Microsoft Excel solver program. Based on IR peak area, density of each Hf site (d , $\mu\text{mol g}^{-1}$)
158 was quantified following the equation 1 using the obtained IMEC.

159
$$d = \frac{A}{\text{IMEC}} \times \frac{D}{W} \quad \cdots \text{eq. 1}$$

160 where A , D , and W are peak area (cm^{-1}), cross-sectional area (cm^2) and mass (g) of the sample disk,
161 respectively.

162

163 **2.5. IR measurement on hydrated Hf-Beta zeolite**

164 In order to characterize Hf sites in hydrated state, IR measurement was performed on
165 hydrated Hf-Beta. The pelletization and pretreatment of the sample were conducted in the same
166 procedure as above. After measuring a spectrum of the clean sample at 30°C , water vapor was
167 introduced into the cell at specific pressure (100, 200, and 400 Pa) to hydrate the sample. After the
168 pressure in the cell became constant, water vapor in the gas phase was evacuated and a spectrum was
169 measured. Then, CD_3CN IR-TPD measurement was performed in the same procedure as that for the
170 non-hydrated sample.

171

172 **3. Results and discussion**

173 **3.1. Structure and composition of Hf-Beta samples and $\text{HfO}_2/\text{Si-Beta}$**

Table 1 summarizes Si/Hf ratio and specific surface area of the samples. Hf-Beta samples showed specific surface area of $\sim 600 \text{ m}^2 \text{ g}^{-1}$, which is a typical value of zeolite Beta. However, HfO₂/Si-Beta showed lower specific surface area of $464 \text{ m}^2 \text{ g}^{-1}$, because a part of HfO₂ particles blocked the zeolite micropores and hindered the adsorption of nitrogen. Hf-Beta-104, which had the highest Hf content among Hf-Beta samples, showed only a diffraction pattern attributed to zeolite Beta and no diffraction line of HfO₂ or any other impurity was observed (Figure S3). On the other hand, HfO₂/Si-Beta showed clear diffraction lines of HfO₂ at 28.2° and 31.7° with other related weak diffraction lines in addition to those of zeolite Beta, indicating the presence of HfO₂.

Table 1 Hf content and specific surface area of samples.

Sample	Si/Hf ratio ^a (-)	S_{BET} ^b ($\text{m}^2 \text{ g}^{-1}$)
Hf-Beta-104	104	601
Hf-Beta-130	130	623
Hf-Beta-166	166	580
Hf-Beta-255	255	618
Hf-Beta-475	475	618
HfO ₂ /Si-Beta	10 ^c	464

^a Si/Hf atomic ratio determined by ICP-AES. ^b Specific surface area calculated by the BET method.

^c Nominal ratio.

3.2. Evaluation of acid properties of Hf-Beta-104 and HfO₂/Si-Beta by CD₃CN IR-TPD

188 Since it is expected that the higher the Hf content is, the more possibly various Hf species
189 are observed, Hf-Beta-104, which had the highest Hf content, was investigated in detail together with
190 HfO₂/Si-Beta. Figure 1a shows IR spectra for C≡N stretching vibration of CD₃CN adsorbed on Hf-
191 Beta-104 at different dosing pressure of CD₃CN. At low dosing pressure, asymmetrically shaped
192 absorption bands were observed in the range of 2290 – 2320 cm⁻¹ with absorption peaks at around
193 2313, 2307, and 2300 cm⁻¹. It was reported that the peaks at 2313 and 2307 cm⁻¹ were assigned to
194 CD₃CN adsorbed on the open and closed Hf sites with Lewis acid character in the zeolite framework,
195 respectively [32]. The intensity of these peaks increased along with the dosing pressure, and
196 simultaneously the absorbance rose up slightly in the range of 2260 – 2295 cm⁻¹. At high pressure,
197 absorption peaks for CD₃CN adsorbed on silanol and physisorbed CD₃CN appeared at 2275 and 2265
198 cm⁻¹, respectively [26,32]. Therefore, it was considered that the adsorption of CD₃CN on Hf species
199 saturated at dosing pressure of ~250 Pa.

200 Figure 1b shows spectra of CD₃CN adsorbed on HfO₂/Si-Beta. Since the amount of adsorbed
201 CD₃CN was small and the absorption bands of ambient CO₂ outside the cell were thus relatively
202 strong, the spectra are shown in the range of 2200 – 2500 cm⁻¹ so that change in the entire spectra can
203 be seen. Dose of CD₃CN to HfO₂/Si-Beta gave an absorption peak at 2300 cm⁻¹, and the peak intensity
204 became stronger along with the dosing pressure. As the dosing pressure of CD₃CN was increased
205 beyond 25 Pa, another absorption peak appeared at 2284 cm⁻¹, and the peak for CD₃CN adsorbed on
206 silanol was also observed at 2274 cm⁻¹. Considering the presence of a significant amount of HfO₂ in
207 HfO₂/Si-Beta, the peaks at 2300 and 2284 cm⁻¹ can be assigned to CD₃CN adsorbed on HfO₂. With

reference to the early reports that the absorption bands for CD₃CN adsorbed on Lewis acid sites of TiO₂ and ZrO₂ were observed at 2297 and 2300 cm⁻¹, respectively [33,34], the peak presently observed at 2300 cm⁻¹ can be assigned to CD₃CN adsorbed on Lewis acid sites of HfO₂. It should be noted that the adsorption of CD₃CN on HfO₂ in HfO₂/Si-Beta was saturated at much lower dosing pressure (~25 Pa) than that (~250 Pa) on Hf species in Hf-Beta-104. This indicated that the number of the adsorption sites for CD₃CN on HfO₂/Si-Beta was significantly smaller than those on Hf-Beta-104 due to the consumption of Hf to form HfO₂.

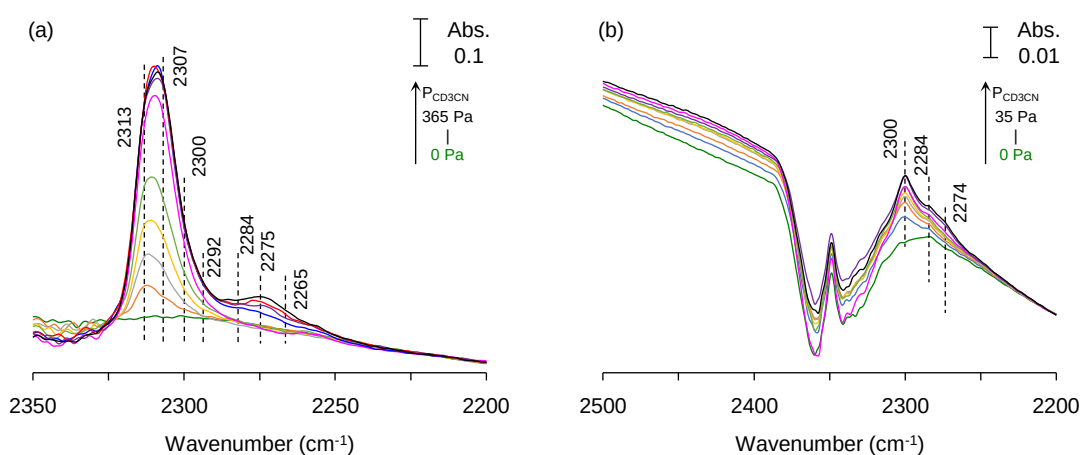
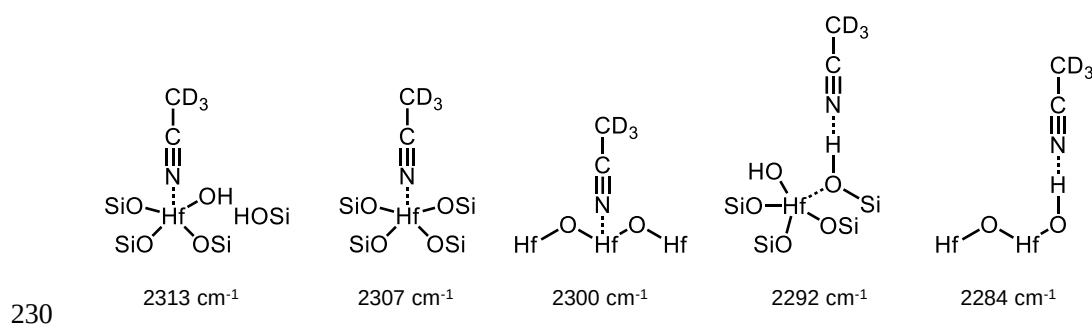


Figure 1 IR spectra of CD₃CN adsorbed on (a) Hf-Beta-104 and (b) HfO₂/Si-Beta at different dosing pressure of CD₃CN.

Based on the discussion so far, in the adsorption of CD₃CN on Hf-Beta-104, the five absorption peaks at 2313, 2307, 2300, 2292, and 2284 cm⁻¹ were considered to be derived from Hf species. Two other absorption peaks at 2275 and 2265 cm⁻¹ were due to the adsorption on silanol and physisorption, respectively. Figure 2 shows plausible structure model for adsorption of CD₃CN on these five types

224 of Hf species and wavenumber of the absorption peaks for CD₃CN adsorbed on these Hf species. As
 225 discussed above, the absorption peaks at 2313, 2307, and 2300 cm⁻¹ were assigned to CD₃CN
 226 adsorbed on the open and closed Hf sites, and HfO₂, respectively. The absorption peaks at 2292 and
 227 2284 cm⁻¹ are assigned to CD₃CN adsorbed on bridging hydroxyl group on Hf-Beta, and Hf-OH
 228 group on HfO₂, respectively. These assignments will be discussed in Sections 3.4 and 3.5.

229

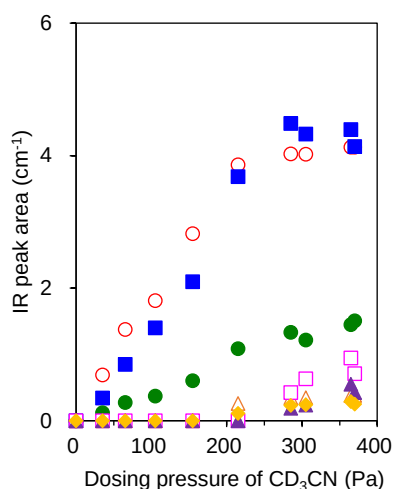


231 **Figure 2** Structure models for adsorption of CD₃CN on Hf species and wavenumber of absorption
 232 peaks for CD₃CN adsorbed on each Hf species.

233

234 The appearance of the peaks at 2300 and 2284 cm⁻¹ indicated the presence of extra-
 235 framework HfO₂ in Hf-Beta-104. No diffraction line of HfO₂ was observed in the XRD pattern of Hf-
 236 Beta-104, probably because extra-framework HfO₂ existed as fine particles (Figure S3). The
 237 difference spectra before and after the adsorption of CD₃CN on Hf-Beta-104 at each dosing pressure
 238 were curve-fitted well with the seven absorption peaks (Figure S4), and the change in each peak area
 239 is shown in Figure 3. At low dosing pressure, the main components of the spectra were the peaks at
 240 2313 and 2307 cm⁻¹, followed by the peak at 2300 cm⁻¹. After the adsorption of CD₃CN on these Hf
 241 sites was saturated at ~250 Pa, the peaks at 2292 and 2284 cm⁻¹ began to appear. Simultaneously, the

242 peaks derived from the adsorption on silanol and physisorption were observed. The difference spectra
 243 for HfO₂/Si-Beta were also curve-fitted with the three absorption peaks at 2300, 2284 and 2275 cm⁻¹
 244 (Figure S5). It was found that CD₃CN predominantly adsorbed on the Lewis acid sites on HfO₂ at
 245 low dosing pressure, and then adsorbed on Hf-OH and silanol, as the dosing pressure increased.
 246



247
 248 **Figure 3** Changes in IR peak areas of 2313 cm⁻¹ (○), 2307 cm⁻¹ (■), 2300 cm⁻¹ (●), 2292 cm⁻¹ (△),
 249 2284 cm⁻¹ (◆), 2275 cm⁻¹ (□) and 2265 cm⁻¹ (▲) for Hf-Beta-104 associated with increase in dose of
 250 CD₃CN.

251
 252 After the IR measurement at 30 °C, CD₃CN was desorbed by heating the sample disk at
 253 10 °C min⁻¹ in nitrogen flow and the effluent gas was monitored to take a CD₃CN-TPD profile. Figure
 254 4a shows CD₃CN-TPD profiles of Hf-Beta-104 taken after the adsorption of CD₃CN at different
 255 dosing pressure. At the lowest dosing pressure of 35 Pa, desorption of CD₃CN started at 200°C and
 256 completed at 400°C. According to the corresponding IR spectrum before the heating (Figures 1a and

3), this desorption peak was assigned to the desorption of CD₃CN from the open and closed Hf sites. As the dosing pressure increased, the desorption peak shifted to lower temperature, probably due to less frequency of readsorption of CD₃CN during the desorption process [35]. At high dosing pressure, the desorption started below 100 °C. In this pressure range, IR absorption peaks at 2292 and 2284 cm⁻¹ appeared, indicating that the Hf species assignable to these absorption peaks had much weaker interaction with CD₃CN than the open and closed Hf sites. Upon further increasing the dosing pressure, the desorption occurred immediately after the heating from 30 °C, which was considered to be derived from CD₃CN adsorbed on silanol and physisorbed CD₃CN.

Figure 4b shows CD₃CN-TPD profiles of HfO₂/Si-Beta taken at different dosing pressure of CD₃CN. At low dosing pressure, the desorption of CD₃CN started from 100 °C and completed at 250 °C. Extra-framework HfO₂ species present on HfO₂/Si-Beta was found to have acid sites capable of retaining CD₃CN up to ~180 °C. As the dosing pressure increased, the desorption started at lower temperature and the desorption peak shifted to the low temperature, as those for Hf-Beta-104.

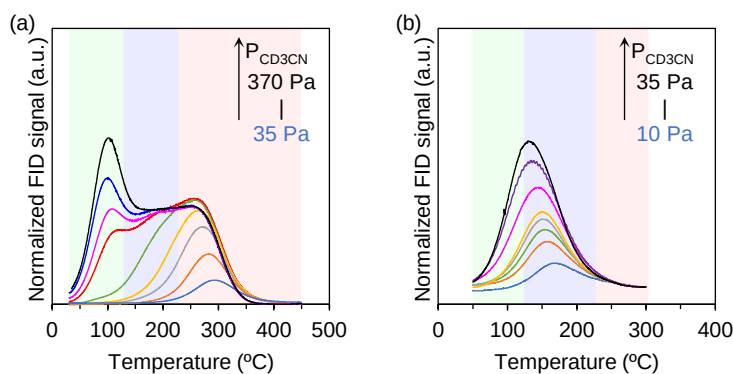
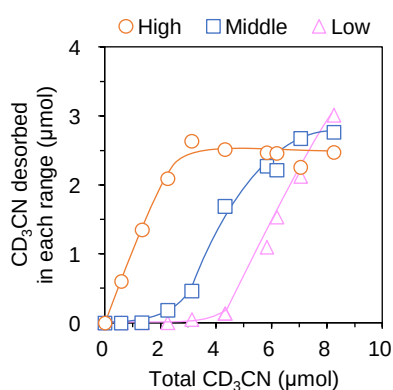


Figure 4 CD₃CN-TPD profiles of (a) Hf-Beta-104 and (b) HfO₂/Si-Beta with dosing pressure varied.

274 The CD₃CN-TPD profiles of Hf-Beta-104 were deconvoluted into three components of low-,
 275 middle-, and high-temperature desorption peaks with peak tops at around 100, 180, and 280 °C,
 276 respectively (Figure S6). The amount of CD₃CN desorbed in each temperature range with respect to
 277 the total amount is shown in Figure 5. When the total amount of CD₃CN was small, the desorption
 278 occurred mainly at high temperature. As the total amount of CD₃CN exceeded 3 μmol, the desorption
 279 at high temperature leveled off, and the desorption at low and middle temperature increased
 280 simultaneously. Considering the trends observed in the IR and TPD measurements together, it can be
 281 concluded that the desorption at high, middle, and low temperatures was attributed to of CD₃CN
 282 adsorbed on the open and closed Hf sites, extra-framework HfO₂ species, and other Hf species
 283 respectively. Therefore, the magnitude of the interaction of Hf sites with CD₃CN, i.e. acid strength,
 284 was estimated to be in the following order: open and closed Hf sites > extra-framework HfO₂ species
 285 > other Hf species.



287 **Figure 5** The amount of CD₃CN desorbed in the range of high (○), middle (□), and low (△)
 288 temperatures with respect to the total amount of CD₃CN for Hf-Beta-104.
 289

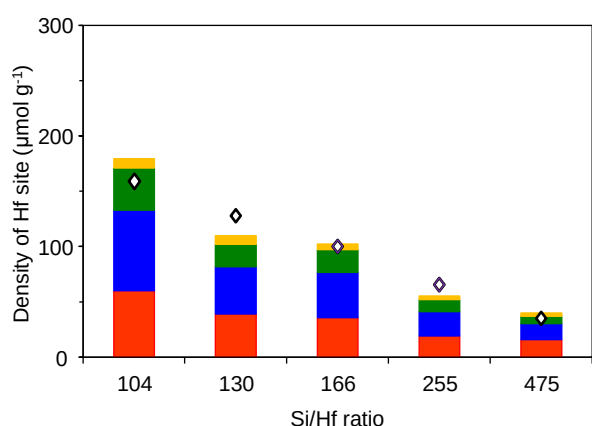
291 The desorption amount of CD₃CN was calculated from the TPD profiles using the pre-drawn
292 calibration curve and assumed to be the amount of CD₃CN adsorbed at 30 °C. There appeared linear
293 relationships between the IR peak area and the amount of adsorbed CD₃CN (Figure S7). From these
294 relationships, IMECs of the four absorption peaks derived from the Hf species (2313, 2307, 2300,
295 and 2284 cm⁻¹) were determined. Since there was no clear linear relationship between the absorption
296 peak at 2292 cm⁻¹ and the amount of CD₃CN, it was impossible to estimate the IMEC for the peak at
297 2292 cm⁻¹. The IMEC for the peak at 2300 cm⁻¹ was determined to be 2.89 ± 0.06 cm μmol⁻¹ from
298 the approximate line between the IR peak area and the amount of adsorbed CD₃CN for HfO₂/Si-Beta.
299 In the same way, the IMECs for the peaks at 2313 and 2307 cm⁻¹ were determined to be 4.53 ± 0.14
300 and 4.66 ± 0.40 cm μmol⁻¹, respectively, from the results of Hf-Beta-104. Using these values and the
301 previously reported IMEC (1.35 cm μmol⁻¹) for CD₃CN adsorbed on silanol [32], IMEC for the peak
302 at 2284 cm⁻¹ was determined to be 2.24 ± 0.13 cm μmol⁻¹.

303

304 **3.3. Acid properties of Hf-Beta with different Hf contents**

305 Hf-Beta with various Hf contents were also characterized by the CD₃CN IR-TPD technique.
306 Multiple absorption peaks of CD₃CN were observed for all the Hf-Beta samples, and their difference
307 spectra were fitted well with the seven peaks, as those for Hf-Beta-104 (Figure S8). Distribution of
308 the acid sites derived from Hf species in these Hf-Beta samples is shown in Figure 6 with the Hf
309 content determined by ICP-AES. Regardless of the Hf content, all the samples showed similar
310 distribution of the acid sites. The open and closed Hf sites, and extra-framework HfO₂ accounted for

311 approximately 35%, 40%, and 20% of the total acid sites, respectively. The rest below 10% was
 312 attributed to Hf-OH groups. The total number of Hf acid sites quantified with CD₃CN was in good
 313 agreement with the Hf content determined by ICP-AES, indicating that almost all of Hf species in
 314 Hf-Beta including extra-framework HfO₂ was exposed on the surface.

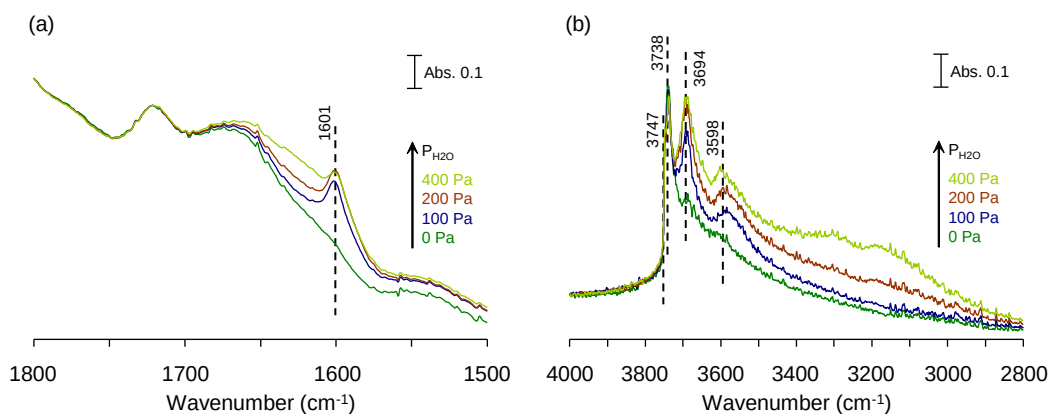


316 **Figure 6** Distribution of Hf acid sites in Hf-Beta with different Hf contents. Hf content determined
 317 by ICP-AES (◇) and the amount of open Hf site (■), closed Hf site (■), extra-framework HfO₂ species
 318 (■), and Hf-OH (■).

321 3.4. Formation of Hf species bearing hydroxy groups on Hf-Beta upon hydration

322 In order to investigate structural changes of Hf-Beta upon hydration and formation of Hf
 323 species bearing hydroxy groups, IR measurement was performed on Hf-Beta-104 pretreated with
 324 water vapor at 30 °C (Figure 7). In the IR spectrum of the sample without the water vapor pretreatment
 325 (dry sample), O-H stretching vibrations of external and internal silanol groups were observed at 3747
 326 and 3738 cm⁻¹, respectively [26]. Other weak absorption peaks were observed at 3694 and 3598 cm⁻¹

327 ¹ (Figure 7b, 0 Pa). After the sample was exposed to water vapor at dosing pressure of 100 to 400 Pa,
 328 an absorption peak due to O-H bending vibration of water appeared at 1601 cm⁻¹ and became larger
 329 as the pressure increased, confirming that water was adsorbed on the sample (Figure 7a, 100 – 400
 330 Pa). The exposure to water vapor significantly increased the intensity of the peaks at 3694 and 3598
 331 cm⁻¹, while the peaks of external and internal silanol groups at ~3750 cm⁻¹ remained intact (Figure
 332 7b, 100 – 400 Pa). As the water vapor pressure was increased, the peak intensity at 3694 and 3598
 333 cm⁻¹ slightly increased and new broad peaks appeared at around 3300 and 3200 cm⁻¹. These two new
 334 peaks are assignable to those interacting with water of the hydroxy groups originally observed at 3694
 335 and 3598 cm⁻¹, respectively. Since a part of these hydroxyl groups interacted with water, it is thought
 336 that the increase in the water vapor pressure generated more hydroxy groups than appeared.



338 **Figure 7** (a) O-H bending and (b) O-H stretching vibration region of IR spectra of Hf-Beta-104
 339 pretreated with water vapor at different dosing pressure.
 340

341
 342 Judging from the large increase caused by the dose of water vapor, it is considered that the
 343 peaks at 3694 and 3598 cm⁻¹ were assigned to stretching vibration of hydroxy groups that were formed

344 by reactions with water. The O-H stretching vibration of Sn-OH and Zr-OH were observed at ~3670
345 cm^{-1} for Sn- and Zr-Beta [29,36,37]. Based on the present results and the early reports, the peak at
346 3694 cm^{-1} was presumed to be O-H stretching vibration of Hf-OH. Since the absorption peaks derived
347 from the silanol groups did not change with the dose of water vapor, it is presumed that the hydrolysis
348 of Hf species mainly occurred on the extra-framework HfO_2 species to form Hf-OH.

349 For Al-Beta, O-H stretching vibration of the bridging hydroxy group (Al-O(H)-Si) was
350 observed at $\sim 3610 \text{ cm}^{-1}$ [38,39]. Furthermore, Sn-Beta also showed the absorption peak at 3594 cm^{-1}
351 after the hydration treatment, which was assigned to the bridging hydroxy group [29]. Referring to
352 these reports, the absorption peak at 3598 cm^{-1} in Figure 7 was analogously due to O-H stretching
353 vibration of Hf-O(H)-Si. The bridging hydroxyl group of Al-Beta is known as Brønsted acid sites. It
354 was also reported that the bridging hydroxyl group of Sn-Beta can function as Brønsted acid sites as
355 well by the IR measurement using pyridine [29]. The IR spectrum of pyridine adsorbed on Hf-Beta-
356 104 showed slight absorption peaks attributable to protonated pyridine (Figure S9), indicating that
357 the bridging hydroxyl group of Hf-Beta also functioned as Brønsted acid sites.

358

359 **3.5. Adsorption of CD_3CN on hydrated Hf-Beta**

360 Figure 8 shows IR difference spectra for adsorption of CD_3CN on Hf-Beta-104 dried or
361 pretreated with water vapor at different pressures. Large negative peaks were observed at 3694 and
362 3596 cm^{-1} for the hydrated samples, indicating that CD_3CN adsorbed on both of these two hydroxy
363 groups generated by the hydration (Figure 8a). The absorption peaks of Hf-OH and silanol interacting

with CD₃CN appeared as broadbands at 3200–3500 cm⁻¹. As the dosing pressure of water vapor increased, the amount of CD₃CN adsorbed on open and closed Hf sites decreased, though it was not remarkable (Figure 8b). This decrease indicated that water persistently adsorbed on these Hf sites even after the dose of CD₃CN, which inhibited the adsorption of CD₃CN on these Hf sites (Figure S10). In contrast, the absorption peaks at 2284 cm⁻¹ slightly increased along with the increase in the dose of water.

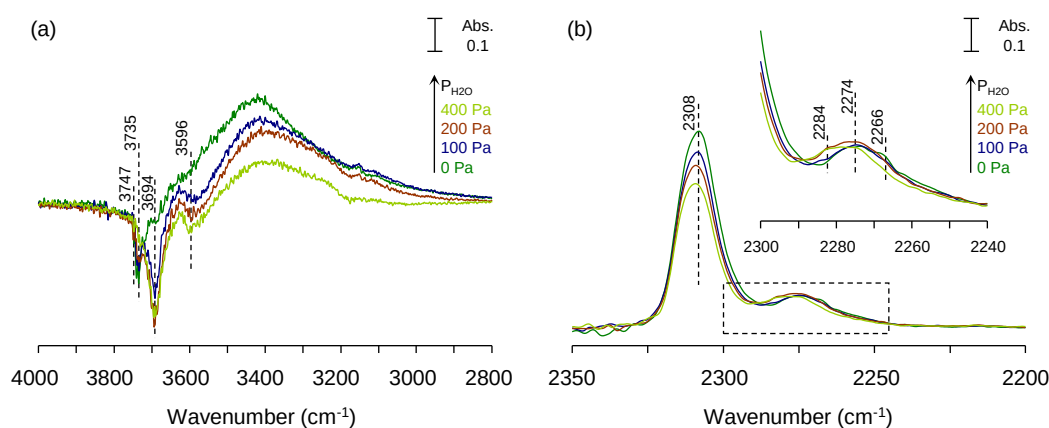


Figure 8 IR difference spectra for adsorption of CD₃CN on dry and hydrated Hf-Beta-104 in the region of (a) O-H stretching vibration and (b) C≡N stretching vibration. Dosing pressure of CD₃CN was 455 Pa.

Figure 9 shows the difference spectra for adsorption of CD₃CN on hydrated Hf-Beta-104 with the dosing pressure of CD₃CN increased. At low pressure, CD₃CN predominantly adsorbed on the open and closed Hf sites and extra-framework HfO₂, but no significant change was observed in the region of O-H stretching vibration. As the dosing pressure was increased, negative peaks appeared at 3694 and 3596 cm⁻¹, and simultaneously positive peaks appeared at 2292 and 2284 cm⁻¹. These

381 four peaks intensified with increasing the dosing pressure of CD₃CN. Particularly, the negative peak
382 at 3694 cm⁻¹ and the positive peak at 2284 cm⁻¹ intensified significantly. Judging from the link
383 between these two peaks, the peak at 2284 cm⁻¹ was attributed to CD₃CN adsorbed on Hf-OH group
384 observed at 3694 cm⁻¹. It is supposed that the peak at 2292 cm⁻¹ is assigned to CD₃CN adsorbed on
385 the bridging hydroxy groups observed at 3596 cm⁻¹. To summarize the discussion thus far, the
386 assignment of IR absorption peak for CD₃CN and IMECs for each absorption peak are shown in Table
387 2.

388 IR difference spectra for CD₃CN adsorbed on hydrated Hf-Beta-104 were well curve-fitted
389 with the aforementioned seven peaks (Figure S11) and the amount of each Hf species in the hydrated
390 sample was quantified using the above obtained IMECs (Figure S12). The amount of CD₃CN
391 adsorbed on the open and closed Hf sites was decreased due to the persistent adsorption of water. The
392 amount of CD₃CN adsorbed on extra-framework HfO₂ species was decreased due to the hydrolysis
393 to form Hf-OH group, and as the counterpart, the amount of CD₃CN adsorbed on the Hf-OH group
394 increased. The peak area at 2292 cm⁻¹ became larger upon the hydration pretreatment, due to the
395 increase in the amount of the bridging hydroxy group.

396

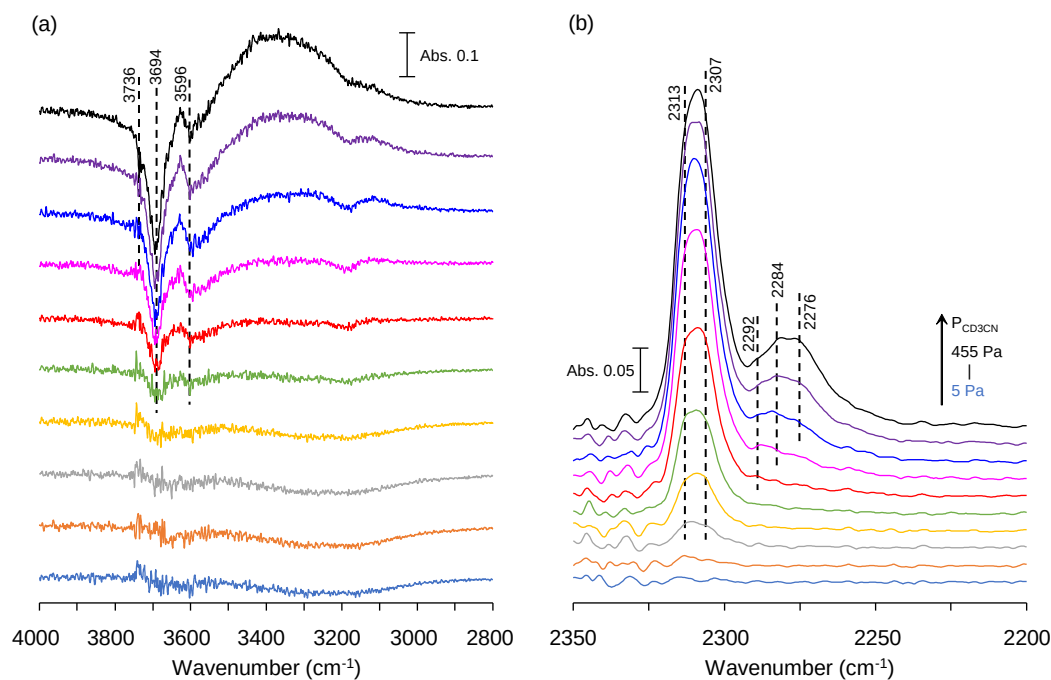


Figure 9 IR difference spectra for adsorption of CD₃CN on hydrated Hf-Beta-104 with dosing pressure of CD₃CN increased in the region of (a) O-H and (b) C≡N stretching vibration. Dosing pressure of water vapor for pretreatment was 400 Pa.

Table 2 Absorption peaks of C≡N stretching vibration and integrated molar extinction coefficients (IMECs) for CD₃CN adsorbed on acid sites in Hf-Beta.

Adsorption site	Location	Peak center (cm ⁻¹)	IMEC (cm μmol ⁻¹)
Open Hf site	Framework	2313	4.53
Closed Hf site	Framework	2307	4.66
HfO ₂	Extra-framework	2300	2.89
Bridging hydroxy	Framework	2292	n.d.
Hf-OH	Extra-framework	2284	2.24

405

406 **Conclusions**

407 CD₃CN IR-TPD measurement was performed on Hf-Beta and HfO₂/Si-Beta to identify Hf
408 species on Hf-Beta and quantify CD₃CN adsorbed on each Hf species. In the IR spectra of CD₃CN
409 adsorbed on Hf-Beta, absorption peaks derived from five types of Hf species, silanol, and physical
410 adsorption were observed. The IR measurement on hydrated Hf-Beta revealed that Hf-OH groups
411 were generated on extra-framework HfO₂. In the TPD measurement, CD₃CN adsorbed on open and
412 closed Hf sites, extra-framework HfO₂, and other sites such as Hf-OH groups desorbed at high,
413 middle, and low temperature, respectively. Based on this trend, it was found that the acid strength
414 order of Hf species was as follows; open and closed Hf sites > extra-framework HfO₂ > Hf-OH groups.
415 The IMECs for C≡N stretching vibration of CD₃CN was calculated, and the number of each type of
416 Hf acid site was estimated. Open and closed Hf sites, and extra-framework HfO₂ accounted for ~90%
417 of the total acid sites.

418

419 **Supporting Information**

420 Detailed data on experimental setup, calibration curve, XRD patterns, and IR spectra are
421 available in Supporting Information.

422

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429

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