Electronic Supplementary Information

Zeolites with isolated-framework and oligomeric-extraframework hafnium species characterized with pair distribution function analysis

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1. Experimentals

1.1 Reagents

Hafnium cyclopentadiene chloride (Hf(Cp)$_2$Cl$_2$; Sigma-Aldrich), nitric acid (60 wt%; Sigma-Aldrich), aluminosilicate *BEA zeolite (Si/Al = 12.5, CP814E*, Zeolyst), HfO$_2$ (Sigma-Aldrich), benzaldehyde (Wako Chemicals), acetone (Wako Chemicals), toluene (Wako Chemicals), tri-tert-butylbenzene (Wako Chemicals), tetraethoxyorthosilicate (TEOS; Alfa-Aesar), tetraethylammonium hydroxide (35 wt%; Sigma-Aldrich), hydrofluoric acid (48 wt%, Sigma-Aldrich), tin dimethyl dichloride (Me$_2$SnCl$_2$; Sigma-Aldrich) were used as purchased. Air (dry grade) was purchased from Airgas.

1.2 Synthesis of the catalysts

Hf-beta(post) was synthesized as follows. First, removal of framework aluminum from the aluminosilicate *BEA zeolite was performed by immersing the *BEA zeolites into nitric acid, and heating the suspension inside a Teflon*-lined steel autoclave for overnight. After collecting the solid by filtration and washing with deionized water (the product denoted as DeAl-beta), the zeolite was degassed under vacuum at 400°C for overnight. The dried zeolite was transferred and stored inside a glovebox. Into a Teflon*-lined autoclave, the degassed DeAl-beta, metal precursor (Hf(Cp)$_2$Cl$_2$ or Me$_2$SnCl$_2$), and
toluene were added, and the container was sealed inside the glovebox. The mixtures were heated at 160°C for 16 h to graft the metal precursor to the framework sites. The solid was collected by filtration, washed with hexane, and calcined in the oven at 550°C for 3 h under dry air flow (100 mL/min) after 3 h of ramping period. A second acid treatment was performed to the product after the calcination treatment following the same procedure described for removing the framework Al.

Si-beta(F), pure silica *BEA zeolite, was prepared following the procedures reported in previous works\(^1\), with ingredient molar composition of SiO\(_2\) : TEAOH : HF : H\(_2\)O = 1 : 0.5 : 0.5 : 7.5. For preparing HfO\(_x\)/Si-beta, incipient-wetness impregnation was performed with an ethanol solution containing the desired amount of HfCp\(_2\)Cl\(_2\). The dried sample was calcined at 550°C for 3 h under dry air flow (100 mL/min).

1.3 Catalyst characterization

Powder X-ray diffraction (XRD) patterns were collected using Bruker D8 diffractometer with Nickel-filtered Cu Ka radiation (\(\lambda = 1.5418 \text{ Å}\)) for a 2\(\theta\) range of 3°–50°. \(\text{N}_2\) physisorption was carried out on Quantachrome Autosorb iQ-2 automated gas sorption system. All samples were degassed under vacuum prior to use (350°C) and the measurement was conducted at liquid nitrogen temperature (-196°C).

The activity for aldol condensation between benzaldehyde and acetone was measured
using the conditions based on a previous report\(^2\). GC-FID (Shimadzu 2014) fitted with DB-1701 column (Agilent) was used for quantification of the reactant/products. Tri-tert-butylbenzene was used as an internal standard.

The high-energy X-ray Total Scattering (HEXTS) measurements were performed on powder sample in a quartz capillary at room temperature using a horizontal two-axis diffractometer at the BL04B2 high-energy X-ray diffraction beamline (SPring-8, Japan). The energy of incident X-rays was 61.43 keV (\(\lambda = 0.2018\) Å). The maximum \(Q (Q = 4\pi \sin \theta / \lambda)\), \(Q_{\text{max}}\), collected in this study was 20 Å\(^{-1}\). The obtained data were subjected to well-established analysis procedures, such as absorption, background, polarization and Compton scattering corrections, and subsequently normalized to give a Faber–Ziman total structure factor \(S(Q)^{3,4}\). These collected data were used to calculate the (reduced) pair distribution function, \(G(r)\), using the following function:

\[
G(r) = 4\pi r [\rho(r) - \rho_0] = \frac{2}{\pi} \int_{Q_{\text{min}}}^{Q_{\text{max}}} Q[S(Q) - 1] \sin(Qr) dQ,
\]

where \(\rho\) is the atomic number density.

The theoretical PDFs were calculated using PDFgui software\(^5\), and information regarding various crystal structures were taken from the following literatures; cubic\(^6\), monoclinic\(^7\), orthorhombic\(^8\) HfO\(_2\) and cassiterite\(^9\).

The following definitions were used to quantify the catalytic testing results:
Conversion [%] = moles of reactant consumed / moles of reactant fed × 100

Selectivity [%] = moles of product / moles of reactant consumed × 100
2. Theory and the calculation methods for d-PDF analysis

An unique feature of PDF is its linearity\(^{10}\), as shown in eq (1), to describe the pair distribution function, \( G(r) \), of a binary phase admixture of pure phase A and pure phase B by a linear addition of each of the pair distribution functions, \( G(r) \).

\[
G_{\text{Mixture}}(r) = x_A G_A(r) + x_B G_B(r) + x_{A-B} G_{A-B}(r) \cdots (1)
\]

Where \( x_A, x_B, \) and \( x_{A-B} \) are coefficients and \( G_{\text{Mixture}}(r), G_A(r), G_B(r), \) and \( G_{A-B}(r) \) represent the pair distribution functions describing the structure of the mixture, phase A, phase B, and the interatomic correlations between phases A and B. When the phases are totally independent (for example, having no atomic connectivity by chemical bondings), the following approximation holds\(^{11}\):

\[
G_{A-B}(r) = 0 \cdots (2)
\]

By modifying this equation as shown in Eq (3) below, and calculating the difference in the PDFs of mixture and B (as shown in the right side eq (3)), the structure of phase A can be extracted:

\[
x_A G_A(r) \equiv G_{\text{Mixture}}(r) - x_B G_B(r) \cdots (3)
\]

There are two things to be taken into account for the calculation of d-PDFs regarding heteroatom-containing zeolites.

1) For heteroatom-containing zeolites, the assumption made in eq (2) does not hold
because there is a direct connectivity between the heteroatom and the zeolite, and thereby, the PDF describing the surrounding environment of the heteroatom (for example Hf) including the interatomic correlations with the zeolite framework, $G_{Hf}(r)$, is extracted from the right side of eq (3). That is, eq (3) can be fixed to the following form.

$$x_AG_{Hf} (r) = G_{Mixture} (r) - x_BG_{Zeolite} (r) \cdots (4)$$

2) In X-ray experiments, the scattering factors are functions of wavenumber vector $Q$, and thereby, assumption that $x_B$ stays constant does not hold in the strict sense. Thereby, in this work, $x_BG_{Zeolite}(r)$ was calculated by the following Fourier transformation equation;

$$x_BG_{Zeolite}(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} Q \left[ \frac{c_B^2 \langle f_B(Q) \rangle^2}{\langle f_{Mixture}(Q) \rangle^2} F_{Zeolite}(Q) \right] \sin (Qr) dQ \cdots (5)$$

Where,

$$F_{Zeolite}(Q) = S_{Zeolite}(Q) - 1 \cdots (6)$$

c_B represents the total the atomic composition of elements in phase B (in this case zeolites) out of the whole mixture (that is the mixture of zeolite and hafnium oxide phases), and

$$\langle f_B(Q) \rangle, \langle f_{Mixture}(Q) \rangle$$ can be calculated based on the following equations.

$$\langle f_B(Q) \rangle^2 = \left( \sum_{i=1}^{B} c_i f_i \right)^2 \cdots (7)$$

$$\langle f_{Mixture}(Q) \rangle^2 = \left( \sum_{i}^{Mixture} c_i f_i \right)^2 \cdots (8)$$
Where $c_i$ represents the atomic composition of element $i$, and $f_i$ represents the X-ray scattering factor of element $i$. 
### Table S1. Results for elemental analyses of various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Hf</th>
<th>Si/Sn</th>
<th>Si/Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf-beta(post)</td>
<td>37</td>
<td>-</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Hf-beta(post)_AT</td>
<td>180</td>
<td>-</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>HfOₓ/Si-beta(F)</td>
<td>230</td>
<td>-</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Sn-beta(post)</td>
<td>-</td>
<td>59</td>
<td>&gt;1000</td>
</tr>
<tr>
<td>Sn-beta(post)_AT</td>
<td>-</td>
<td>93</td>
<td>&gt;1000</td>
</tr>
</tbody>
</table>

### Table S2. Textural properties of various catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET specific surface area [m² g⁻¹]</th>
<th>Micropore volume [cc g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al-beta</td>
<td>644</td>
<td>0.17</td>
</tr>
<tr>
<td>DeAl-beta</td>
<td>513</td>
<td>0.14</td>
</tr>
<tr>
<td>Hf-beta(post)</td>
<td>547</td>
<td>0.16</td>
</tr>
<tr>
<td>Hf-beta(post)_AT</td>
<td>577</td>
<td>0.17</td>
</tr>
<tr>
<td>Si-beta(F)</td>
<td>554</td>
<td>0.21</td>
</tr>
<tr>
<td>HfOₓ/Si-beta(F)</td>
<td>531</td>
<td>0.20</td>
</tr>
</tbody>
</table>

*Calculated using t-plot method
**Figure S1.** Crystal models of BEA and BEB zeolite polymorphs.

*BEA zeolites are obtained as an intermixture of both BEA and BEB crystal structure polymorphs. Information of the crystal structures were obtained from International Zeolite Association Structure Commission Database.

(http://www.iza-structure.org/databases/)

BEA crystal; (a = 12.66139 Å, b = 12.66139 Å, c = 26.40612Å, α=β=γ=90°)

BEB crystal; (a = 17.89654 Å, b = 17.92002 Å, c = 14.32815 Å, α=90°,β=114.803°,γ=90°)
Figure S2. \( N_2 \) adsorption desorption isotherms of zeolite samples.
Figure S3. Faber-Ziman total structure factors, $S(Q)$, of the zeolites used in this paper.
Figure S4. Comparison of the PDFs from different HfO$_2$ crystal structures.

The calculations were performed using PDFgui software$^5$. 
Figure S5. Assignment of the correlation peaks in the theoretical PDF of HfO$_2$ (monoclinic phase) made using the PDFgui software$^5$.

For example, Hf-Hf shows the probability of finding Hf-Hf distance at a given distance, $r$. Most correlations visible were found to originate from Hf-Hf or Hf-O correlations (at 2.0 and 4.4 Å) due to the relatively large X-ray scattering factor by Hf compared to O.
Figure S6. d-PDF comparison of Hf-beta(post)_AT and Sn-beta(post)_AT (top) in reference to the theoretical PDFs of $m$-HfO$_2$ and SnO$_2$ (cassiterite).

The blue dashed lines compare the peak positions in the d-PDF analysis, and with the correlations originating from $m$-HfO$_2$ in the distances between 3 ~ 4.5 Å. The black dashed lines compare the peak positions in the d-PDF analysis between Hf-beta(post)_AT and Sn-beta(post)_AT at the other distances.
**Figure S7.** DR UV-vis spectra of various *BEA zeolites with hafnium in reference to that of bulk $m$-HfO$_2$. 
References


