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Author(s)	Nakamura, Taichi; Kamiya, Yuichi; Otomo, Ryoichi
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3	A Rapid Synthesis of Hf-Beta Zeolite as Highly Active Catalyst for
4	Meerwein-Ponndorf-Verley Reduction by Controlling Water Content
5	of Precursor Gel
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7	Taichi Nakamura, <sup>1</sup> Yuichi Kamiya <sup>2</sup> , and Ryoichi Otomo <sup>2,*</sup>
8	
9	<sup>1</sup> Graduate School of Environmental Science, and <sup>2</sup> Faculty of Environmental Earth Science,
10	Hokkaido University, Kita 10 Nishi 5, Kita-ku, Sapporo 060-0810, Japan.
11	
12	*Corresponding author: Dr. Ryoichi Otomo
13	Tel: +81-11-706-2259, E-mail: otomo@ees.hokudai.ac.jp

# 1 Abstract

2	Hf-Beta is a promisingly active Lewis acid catalyst for Meerwein-Ponndorf-Verley (MPV)
3	reduction and other important organic reactions. However, the conventional hydrothermal synthesis
4	of Hf-Beta inevitably requires the troublesome procedure for hydrolysis of tetraalkoxysilane and the
5	long period to complete crystallization. In the present study, we applied a synthetic approach of
6	reducing water content of precursor gel and succeeded in considerably shortening the period for
7	crystallization of Hf-Beta using fumed silica as silicon source. By using precursor gel with H2O/SiO2
8	= 1.4 - 7.6, effect of water content of precursor gel on the crystallization of Hf-Beta, the incorporation
9	of Hf into the zeolite framework, and the catalytic performance were thoroughly investigated. Low
10	water content was favorable for accelerating the crystallization, but unfavorable for the incorporation
11	of Hf into the zeolite framework, resulting in poor catalytic activity. With the assistance of seed
12	crystal, Hf-Beta with a relatively large amount of framework Hf was obtained from the precursor gel
13	with $H_2O/SiO_2 = 6.4$ in 24 h. Hf-Beta synthesized in this way showed higher catalytic activity for
14	MPV reduction than Hf-Beta as well as Zr-, and Sn-Beta synthesized by the conventional
15	hydrothermal method.

16

# 17 Keywords

18 Hf-Beta; Lewis Acid; Metallosilicate; MPV Reduction; Zeolite

## 1 1. Introduction

2 MPV reduction is a useful reaction to produce alcohols from aldehydes or ketones under mild conditions. Traditionally, aluminum alkoxides [1-3] and metal complexes [3,4] are used as 3 homogeneous Lewis acid catalysts for MPV reduction. Various types of heterogeneous catalysts have 4 been studied for MPV reduction such as layered double hydroxides [5], metal oxides [6,7], supported 5 6 metal alkoxides [3,8], and zeolites [9-20]. Of these materials, metallosilicate Beta zeolites with \*BEA-type structure containing tetravalent heteroatoms such as Ti<sup>4+</sup>, Zr<sup>4+</sup>, Sn<sup>4+</sup>, and Hf<sup>4+</sup> have 7 8 emerged as highly active Lewis acid catalysts [10,12-20] with shape selectivity [10,12-16], tolerance 9 against water [10,14], and recyclability [14]. In the last several years, Hf-Beta has been reported to 10 show higher catalytic activity than metallosilicate analogues with Ti, Zr, and Sn for the MPV reduction of specific substrates [17-20]. 11

Almost all of Hf-Beta samples reported so far were synthesized by the conventional 12 hydrothermal method with hydrofluoric acid as mineralizing agent [17-20]. The conventional 13 synthesis method successfully gives highly crystalline Hf-Beta with high catalytic activity, whereas 14 it requires long period (several weeks) to complete the crystallization of Hf-Beta. In addition, when 15 16 silicon alkoxide such as tetraethyl orthosilicate is used as silicon source, the alcohol produced by its hydrolysis must be removed from the precursor gel. To our knowledge, there has been only one 17 alternative method, in which Hf-Beta was prepared by impregnating the Hf complex on dealuminated 18 Beta [21]. In this method, extra-framework Hf species were generated, and post-synthetic acid 19 treatment with concentrated nitric acid was required to remove them. 20

1	While there is limited variation of method for synthesis of Hf-Beta, several advanced
2	methods have been developed for short-term synthesis of the other metallosilicate Beta in simple
3	manners [22-31].For example, several groups reported the reduction of crystallization period for
4	synthesis of Sn-Beta by decreasing the water content of precursor gel [23,24,26-28,30,31]. Yakimov
5	et al. [26] reported that for synthesis of Sn-Beta with $Si/Sn = 100$ , the crystallization period was
6	reduced from 60 to 16 days by decreasing H <sub>2</sub> O/SiO <sub>2</sub> ratio in precursor gel from 6.8 to 5.6 and that
7	the decrease in the water content did not affect the chemical state of Sn in the framework of Sn-Beta.
8	Yang et al. [31] investigated in detail the crystallization profile and evolution of Lewis acid sites for
9	Sn-Beta using precursor gel with $H_2O/SiO_2 = 4.5$ and 7.5. The use of the precursor gel with lower
10	water content resulted in faster crystallization and the number of Lewis acid sites for fully crystallized
11	samples did not depend on the water content. Application of these methods to other zeolites is
12	expected to bring shorter synthesis period and simplified procedure. However, the effect of water on
13	the chemical state of heteroatoms in final products can vary from metal to metal, and the developed
14	methods cannot always be applied to other metals by simply changing the metal source.
15	In the present study, Hf-Beta was synthesized from precursor gel with different $H_2O/SiO_2$

ratios using fumed silica as silicon source. Effects of water content of precursor gel on the crystallization of zeolite and the incorporation of Hf into zeolite framework were thoroughly investigated. By using precursor gel with a low  $H_2O/SiO_2$  ratio, rapid crystallization was achieved, but the amount of Hf incorporated into the zeolite framework was only little. At the optimal  $H_2O/SiO_2$ ratio, Hf-Beta rich in framework Hf was successfully synthesized in a short period with the assistance of seed crystal. In addition, Hf-Beta synthesized in this way showed higher catalytic activity for MPV
 reduction than Hf-Beta and other metallosilicate zeolites that were synthesized by the conventional
 hydrothermal method.

4

### 5 2. Experimental

6 2.1. Materials

7 Tetraethylammonium hydroxide (TEAOH, 35 wt.% aqueous solution), hafnium chloride (HfCl<sub>4</sub>, 98 wt.%), and furfural (≥99.0%) were purchased from Sigma-Aldrich. Ammonium fluoride 8 (NH<sub>4</sub>F, 97%), hydrofluoric acid (47 wt.%), 2-propanol (98%), and o-xylene (98%) were purchased 9 10 from FUJIFILM Wako Pure Chemical. 4-Methylcyclohexanone (98%), cinnamaldehyde (≥98.0%), and acetophenone (≥98.5%) were purchased from TCI. Fumed silica Aerosil<sup>®</sup> 300 was purchased 11 from NIPPON AEROSIL. Deuterated acetonitrile (CD<sub>3</sub>CN, 99.8% deuterated) was purchased from 12 Cambridge Isotope Laboratories. Al-Beta (CP-814E with Si/Al = 12.5) was purchased from Zeolyst 13 International. 14

15

#### 16 2.2. Synthesis of Hf-Beta

Hf-Beta was synthesized by hydrothermal treatment of aqueous precursor gel, typically as follows. 0.107 g of HfCl<sub>4</sub> was added to 7.56 g of TEAOH solution in 50 mL Teflon beaker, and the resulting mixture was stirred at 60 °C for 1 h. After cooling the mixture to ambient temperature, 2.0 g of fumed silica was added with stirring. At this point, seed crystal corresponding to 1 wt. % of SiO<sub>2</sub>

1	was optionally added. The resulting suspension was further stirred at ambient temperature for 2 h.
2	Then, 0.67 g of NH <sub>4</sub> F was added to the suspension. Considering the water contained in fumed silica
3	(1.9 wt.%), the resulting gel had a molar composition of 1.0 SiO <sub>2</sub> : 0.55 TEAOH: 0.01 HfCl <sub>4</sub> : 0.55
4	NH <sub>4</sub> F: 8.7 H <sub>2</sub> O. To obtain precursor gel with lower water content, the gel was heated at 60 °C to
5	evaporate desired amount of water. The weight of the gel was measured before and after the heating,
6	and the amount of water in the final precursor gel was estimated assuming that the weight loss during
7	the heating was due to the evaporation of water. For several representative precursor gel samples, the
8	actual water content was measured by the thermogravimetric analysis, and it was confirmed that the
9	above estimation was correct. The volume of precursor gel with $H_2O/SiO_2 = 6.4$ and 1.4 was 7.5 and
10	4.6 mL, respectively. The precursor gel was transferred to a 100 mL Teflon-lined stainless-steel
11	autoclave. The crystallization was done by heating the autoclave under static conditions at 180 °C for
12	a set period. After the crystallization, the solid sample was recovered by filtration, washed with
13	ethanol and Milli-Q water, and finally dried at 60 °C overnight. The as-synthesized sample was
14	calcined in air at 650 °C for 6 h. Samples for different crystallization periods were obtained in separate
15	synthesis batches following the aforementioned procedure.
16	The seed crystal was prepared by dealumination of the commercially available Al-Beta. 10

recovered by suction filtration, washed with Milli-Q water, and dried at 60 °C overnight. Si/Al ratio

g of Al-Beta was treated in 500 mL of 7.2 mol L<sup>-1</sup> HNO<sub>3</sub> solution at 80 °C for 24 h. The solid was

19 of the dealuminated Beta (DeAl-Beta) was determined to be higher than 1000 by ICP-AES.

20

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As a comparison, Hf-, Zr-, and Sn-Beta were prepared by the conventional hydrothermal

method with hydrofluoric acid [32], and are denoted as Hf-HF, Zr-HF, and Sn-HF, respectively.
HfO<sub>2</sub>/Si-Beta was prepared by calcining the mixture of HfO<sub>2</sub> and Si-Beta, which was prepared by the
conventional hydrothermal method.

4

#### 5 2.3. Characterization

Powder XRD patterns of samples were collected on a Rigaku MiniFlex diffractometer with 6 Cu K $\alpha$  radiation (30 kV, 15 mA,  $\lambda = 0.154$  nm) at a step width of 0.02°. Nitrogen sorption isotherms 7 were measured on a MicrotracBEL BEL-mini analyzer at -196 °C. Prior to the measurement, samples 8 were pretreated in nitrogen flow (50 mL min<sup>-1</sup>) at 400 °C for 1 h. Specific surface area was calculated 9 10 by the Brunauer-Emmett-Teller (BET) method. Morphology of samples was observed by a FE-SEM using Hitachi S-4800 microscope at an acceleration voltage of 1 kV. Elemental analysis of solid 11 samples was performed by ICP-AES using a Shimadzu ICPE-9000 analyzer. 10 mg of samples were 12 added to 5 mL of 1 M KOH aqueous solution and heated at 100 °C for 30 min. The resulting solution 13 was diluted with Milli-Q water and analyzed. 14

Acid properties of samples were examined by FT-IR spectroscopy with  $CD_3CN$  as a probe molecule. FT-IR measurement was carried out on a JASCO FT/IR-4600 with a TGS detector with 64 scans and 2 cm<sup>-1</sup> resolution in the range of 4000 – 400 cm<sup>-1</sup>. A powder sample (45 mg) was pelletized to a self-supporting disk with diameter of 2 cm and placed in a quartz IR cell with CaF<sub>2</sub> optical windows. The sample disk was pretreated at 400 °C for 1 h under vacuum. After the sample was cooled to 30 °C, the first spectrum of the bare sample was recorded. A dose of CD<sub>3</sub>CN with

1	predetermined pressure of 5 Pa was introduced into the cell. After the pressure became constant, a
2	spectrum was recorded. Then, CD <sub>3</sub> CN was evacuated. This procedure was repeated with the dosing
3	pressure of CD <sub>3</sub> CN increased up to 2000 Pa. Here, difference spectra between the first spectrum and
4	the spectra after dosing CD <sub>3</sub> CN at certain pressure are shown. To compare the spectra quantitatively,
5	spectra were normalized by using absorption bands of framework vibration at $1500 - 2100$ cm <sup>-1</sup> .

#### 7 2.4. Catalytic reaction

8 Catalytic performance of samples was evaluated in MPV reduction of various ketones and 9 aldehydes such as 4-methylcyclohexanone (MCHOne), furfural, cinnamaldehyde, and acetophenone 10 with 2-propanol (2-PrOH). Typically, MPV reduction of MCHOne with 2-PrOH was conducted as 11 follows. A powder catalyst (25 mg) was added to 10 mL of 2-PrOH solution of MCHOne (0.5 mol L<sup>-</sup> <sup>1</sup>) and *o*-xylene (internal standard, 0.015 mol L<sup>-1</sup>) in a test tube. The resulting suspension was heated 12 at 70 °C with stirring for 1 h. The solid catalyst was separated by centrifugation and the supernatant 13 solution was analyzed on a Shimadzu GC-2025 gas chromatograph equipped with a frame ionization 14 detector and a capillary column (SH-Rtx-Wax, 30 m × 0.25 mm × 0.5 µm, Shimadzu). Substrate 15 16 conversion and products yield were calculated from pre-drawn calibration curves using o-xylene as an internal standard. 17

18

#### 19 **3. Results and Discussion**

#### **3.1.** Influence of Water Content of Precursor Gel on Crystallization, Hf Incorporation

#### and Catalytic Activity

Influence of water content of precursor gel on crystallization of Hf-Beta was investigated by 2 3 heating precursor gel with  $H_2O/SiO_2 = 1.4 - 7.6$  at 180 °C for 72 h. Fig. 1 shows XRD patterns of samples calcined at 650 °C. The products obtained from the precursor gel with  $H_2O/SiO_2 = 1.4 - 6.4$ 4 showed typical diffraction patterns assignable to \*BEA-type structure and no impurity phase was 5 found. From the precursor gel with  $H_2O/SiO_2 = 6.8$  and 7.6, amorphous products were obtained, 6 indicating that for the precursor gel with the high water content, crystallization did not proceed 7 8 sufficiently under the present conditions. By using the precursor gel with low water content, Hf-Beta was successfully synthesized in far shorter period than that required for the conventional method 9 10 typically using the precursor gel with  $H_2O/SiO_2 \ge 7.5$  [17-20].





12



14 The numbers in the figure represent  $H_2O/SiO_2$  ratios of precursor gel.

Fig. 2 shows the relationship between water content of precursor gel and Hf content, and catalytic activity for MPV reduction of MCHOne with 2-PrOH. Please note that the amorphous products obtained from the precursor gel with  $H_2O/SiO_2 = 6.8$  and 7.6 are excluded. The Hf content increased as the water content increased, implying that water in precursor gel played an important role in the incorporation of Hf into zeolite framework. The catalytic activity increased as the Hf content increased. It was found that the precursor gel with high water content was necessary to synthesize highly active Hf-Beta with high Hf content.



1





11 Fig. 2. Influence of water content of precursor gel on Hf content  $(\Box)$  and catalytic activity  $(\bullet)$  of Hf-



13

#### 14 3.2. Crystallization Process of Hf-Beta from Precursor Gel with H<sub>2</sub>O/SiO<sub>2</sub> = 1.4 and

15

6.4

16 The precursor gel with  $H_2O/SiO_2 = 1.4$  and 6.4, selected as low and high water content

17 system, respectively, was heated at 180 °C for different periods to follow crystallization process of

Hf-Beta. In the synthesis using the precursor gel with  $H_2O/SiO_2 = 1.4$ , the diffraction lines of the 1 (101) and (302) planes of the **\*BEA**-type structure were observed at 7.9° and 22.7°, respectively, 2 3 even at 8 h (Fig. 3a). Upon extending the period to 16 h, the diffraction line intensity increased sharply. No further change was found in the diffraction pattern with further extension to 72 h. On the other 4 hand, for samples from the precursor gel with  $H_2O/SiO_2 = 6.4$ , very weak diffraction lines first 5 appeared at 24 h, and a highly crystalline sample was finally obtained in 72 h (Fig. 3b). For both 6 systems, no crystalline impurity phase was found. Hereafter, the samples will be denoted as Hf-x-y, 7 8 where x and y represent  $H_2O/SiO_2$  ratio of precursor gel and crystallization period, respectively.

9





12 and (b) 6.4 at different crystallization periods.

13

14	Relative crystallinity of samples from the precursor gel with $H_2O/SiO_2 = 1.4$ and 6.4 were
15	calculated based on the diffraction line intensities of Hf-1.4-16 and Hf-6.4-72, respectively (Fig. 4a).

For both systems, an induction period was observed before steep increase in the relative crystallinity. A very short induction period of ~4 h was observed for  $H_2O/SiO_2 = 1.4$ , while a relatively long induction period of ~30 h was found for  $H_2O/SiO_2 = 6.4$ . When the relative crystallinity increased, there was also a difference in the slope of the curve between the two systems, and the crystallization proceeded more rapidly for  $H_2O/SiO_2 = 1.4$ . The relative crystallinity reached 90% at 16 and 72 h for  $H_2O/SiO_2 = 1.4$  and 6.4, respectively. Weight yield of the solid products was ~90% regardless of the water content of precursor gel and the crystallization period.

8





Fig. 4. Temporal changes in (a) relative crystallinity, (b) Hf content, and (c) catalytic activity for MPV reduction in course of crystallization of Hf-Beta from precursor gel with  $H_2O/SiO_2 = 1.4$  ( $\Box$ ) and 6.4 (•). *cis*-MCHOH = *cis*-4-methylcyclohexanol.

13

Fig. 4b shows variation of Hf content in the samples synthesized in both systems at different crystallization periods. Both types of precursor gel with  $H_2O/SiO_2 = 1.4$  and 6.4 were calcined without hydrothermal treatment (crystallization time 0 h), and their Hf content was 3.1 and 3.0 wt.%,

1	respectively, which were almost the same as the amount of Hf added to the precursor gel. For
2	$H_2O/SiO_2 = 1.4$ , the Hf content decreased to 1.0 wt.% immediately after the start of hydrothermal
3	treatment and did not change thereafter. For $H_2O/SiO_2 = 6.4$ , the Hf content was initially decreased
4	to 1.4 wt.%. However, the Hf content turned to increase after 42 h, which synchronized with the
5	relative crystallinity, shown in Fig. 4a. After 72 h, the Hf content reached a plateau at 1.9 wt.%.
6	Therefore, it is concluded that in the synthesis using the precursor gels with $H_2O/SiO_2 = 1.4$ and 6.4,
7	the crystallization was completed in 16 and 72 h, respectively.
8	In order to track the missing Hf that was not found in the solid samples, elemental analysis
9	was performed by ICP-AES for the solution remaining in the PTFE container after the hydrothermal
10	treatment for synthesis of Hf-1.4-72, Hf-6.4-42, and Hf-6.4-72. However, Hf was not detected in
11	these liquid samples, which implied that the missing Hf was mainly contained as unquantifiable Hf
12	species in the solid samples. To confirm this, HfO <sub>2</sub> /DeAl-Beta was prepared by calcining a mixture
13	of HfCl <sub>4</sub> and DeAl-Beta with Si/Hf = 100 at 580 °C. HfO <sub>2</sub> /DeAl-Beta showed very weak diffraction
14	lines assignable to monoclinic HfO <sub>2</sub> , and its Si/Hf ratio analyzed by ICP-AES was higher than 1000.
15	These results demonstrated that extra-framework Hf species was poorly quantified by ICP-AES.
16	Whereas, as explained above, the Hf species dispersed in the precursor gel without hydrothermal
17	treatment was quantitatively analyzed. Hence, it is considered that the missing Hf was mainly
18	contained in the solid samples as unquantifiable Hf species such as extra-framework Hf species and
19	that the Hf content determined by ICP-AES indicated the amount of Hf well dispersed in the zeolite
20	framework.

1	Yakimov et al. [26] reported that in the synthesis of Sn-Beta, the Sn content did not depend
2	on the water content of precursor gel and almost all of Sn in the precursor gel was incorporated into
3	the zeolites. In contrast, it is clearly shown that in the present synthesis of Hf-Beta, the Hf content
4	strongly depended on the water content of the precursor gel and that the high water content was
5	favorable for incorporation of Hf into the zeolite framework. The pH of the solution remaining after
6	the hydrothermal treatment for Hf-1.4-72, Hf-6.4-42, and Hf-6.4-72 ranged from 9 to 10. The
7	solubility of Hf in such weakly basic aqueous solution is one to two orders of magnitude lower than
8	that of Sn [33,34]. Considering these points, the different feature of Hf and Sn for the incorporation
9	into the zeolite framework was attributed to the difference in solubility of Hf and Sn in basic aqueous
10	solution. It is presumed that a part of Hf might precipitate during the hydrothermal treatment, resulting
11	in less incorporation into the zeolite framework. Accordingly, as the water content of precursor gel
12	increased, the amount of such precipitated Hf decreased and Hf-Beta with high Hf content crystallized.
13	For both types of precursor gel with $H_2O/SiO_2 = 1.4$ or 6.4, insufficiently crystallized
14	samples showed poor catalytic activity for the MPV reduction of MCHOne (Fig. 4c). Hf-1.4-16,
15	which was a highly crystallized sample, gave 27% yield of cis-MCHOH. Further extension of the
16	crystallization period did not change the catalytic activity of the samples synthesized from the
17	precursor gel with $H_2O/SiO_2 = 1.4$ . For the samples from the precursor gel with $H_2O/SiO_2 = 6.4$ ,
18	catalytic activity appeared with crystallization period of 42 h or longer. The activity increased as the
19	Hf content increased, and Hf-6.4-72 gave 59% yield of cis-MCHOH.
20	Focusing on geometric isomers of MCHOH, thermodynamically favorable trans isomer was

1	preferentially produced by using aluminum isopropoxide, which is a typical homogeneous catalyst
2	(Table 1, Entry 1). All of Hf-Beta gave thermodynamically unfavorable <i>cis</i> isomer as a predominant
3	product (Entries 2-4). It is known that since the formation of the <i>cis</i> isomer takes more compact
4	transition state than that for the trans one, the cis isomer is shape-selectively produced in the
5	micropores of the *BEA-type structure [35]. These results clearly showed that the MPV reduction
6	proceeded shape-selectively in the micropores of Hf-Beta samples, demonstrating that framework Hf
7	atoms were the active sites over Hf-Beta.

9 **Table 1** Hf content, specific surface area, and catalytic activity of Hf-Beta samples.

	-			-			
Enter	Samala	Hf content <sup><i>a</i></sup>	$S_{\rm BET}{}^b$	MCHOH y	yield (%)	TON <sup>c</sup>	
Entry	Entry	Sample	(wt.%)	$(m^2 g^{-1})$	cis	trans	(-)
1	$Al(^{i}Pr)_{3}$	-	-	22	41	-	
2	Hf-1.4-72	1.0	626	24	1	888	
3	Hf-4.5-72	1.6	611	38	1	864	
4	Hf-6.4-72	1.9	566	59	2	1091	

<sup>a</sup>Hf content determined by ICP-AES. <sup>b</sup>Specific surfacea area calculated by the BET method. <sup>c</sup>Turnover number
 calculated as total amount of MCHOH (mol) per amount of Hf (mol) in a catalyst.

12

Acid properties of representative Hf-Beta samples were investigated by IR spectroscopy with CD<sub>3</sub>CN as a probe molecule. From the experiments with dosing pressure of CD<sub>3</sub>CN varied, the adsorption on Lewis acid sites was found to be saturated at dosing pressure of 200 Pa (Fig. S4). Fig. 5a compares absorption bands of C=N stretching vibration of CD<sub>3</sub>CN adsorbed on Hf-1.4-72, Hf-4.5-72, and Hf-6.4-72 at the dosing pressure of 200 Pa. As in an example of Hf-6.4-72 shown in Fig. S5, these spectra were deconvoluted into four components with the peaks at 2313, 2307, 2299, and 2275

1	cm <sup>-1</sup> . Two similar peaks above 2300 cm <sup>-1</sup> have been also found in adsorption of CD <sub>3</sub> CN on Sn-Beta
2	and attributed to the adsorption on Sn atoms in different coordination environments [36,37]. With
3	reference to the reports on Sn-Beta, the two peaks above 2300 cm <sup>-1</sup> are assigned to the adsorption on
4	framework Hf with Lewis acid character [19,38]. The peak at 2299 cm <sup>-1</sup> was attributed to adsorption
5	on extra-framework Hf, as HfO <sub>2</sub> /Si-Beta mainly showed an absorption peak at 2299 cm <sup>-1</sup> (Fig. S6).
6	The peak observed at 2275 cm <sup>-1</sup> is assigned to adsorption on silanol groups [39,40].
7	The total area of the peaks at 2313 and 2307 cm <sup>-1</sup> for Hf-1.4-72, Hf-4.5-72, and Hf-6.4-72
8	was 0.9, 1.6, and 4.0 cm <sup>-1</sup> , respectively. This increasing trend indicated that as the water content of
9	precursor gel increased, a larger number of Lewis acid sites were formed. Turnover numbers per Hf
10	atom (TONs) of Hf-1.4-72 and Hf-6.4-72 were 888 and 1091, respectively (Table 1, Entries 2 and 4).
11	The larger TON for Hf-6.4-72 suggested that as the water content of precursor gel increased, the
12	proportion of Hf that acted as Lewis acid sites increased as well. This indicates that Hf was likely to
13	be incorporated into the zeolite framework and efficiently form Lewis acid sites under H2O-rich
14	conditions.
15	To trace the evolution of framework Hf during the hydrothermal treatment, Hf-6.4-42 was
16	also investigated by IR with CD <sub>3</sub> CN and compared with Hf-6.4-72 (Fig. 5b). The peaks attributed to
17	adsorption on Lewis acid sites were also observed and the total peak area of those peaks was 1.3 and
18	4.0 cm <sup>-1</sup> for Hf-6.4-42 and Hf-6.4-72, respectively. Thus, the number of Lewis acid sites was greatly
19	increased after 42 h. This increase coincided with those in the relative crystallinity and the Hf content

20 (Fig. 4a and 4b).



2

Fig. 5. FT-IR spectra of CD<sub>3</sub>CN adsorbed on Hf-Beta (a) synthesized from precursor gel with different
 water content and (b) synthesized in different crystallization periods. Dosing pressure of CD<sub>3</sub>CN was
 200 Pa.

Based on the results so far, we propose the role of water in precursor gel in the hydrothermal synthesis of Hf-Beta as Fig. 6. Generally, aqueous precursor gel separated into solid and aqueous solution during hydrothermal treatment, and metallosilicate species dissolved in the solution deposited onto the solid (nuclei) together with silicate to proceed crystallization. In the present synthesis, regardless of the water content of precursor gel, the Hf content decreased sharply at the very beginning of the hydrothermal treatment and the induction period was present before increase

1	in the relative crystallinity (Fig. 4). It is considered that because of the low solubility of Hf species in
2	weakly basic solution, a part of Hf species in the solution precipitated, which gave extra-framework
3	Hf species eventually. Since such extra-framework Hf species was unquantifiable by ICP-AES, the
4	Hf content was decreased immediately after the start of hydrothermal treatment. The induction period
5	was attributed to the period taken for nucleation enough for the following growth of nuclei.
6	When the water content of precursor gel was low ( $H_2O/SiO_2 = 1.4$ ), the precipitation was
7	significant and only a limited amount of Hf in the solution was incorporated into the zeolite
8	framework, resulting in the formation of zeolites with the low Hf content (Fig. 6a). When the water
9	content of precursor gel was high ( $H_2O/SiO_2 = 6.4$ ), Si-rich nuclei formed during the induction period
10	and then Hf species in the solution deposited onto the nuclei in the form of hafnosilicate and Hf was
11	effectively incorporated into the zeolite framework (Fig. 6b). As the water content of precursor gel
12	increased, the amount of precipitated Hf species decreased and Hf-Beta with the high Hf content
13	crystallized. Similar crystallization mechanism in which Si-rich nuclei formed first and grew with the
14	incorporation of heteroatoms was proposed for other metallosilicate zeolites [41-43].



Fig. 6. Plausible mechanism for crystallization of Hf-Beta from (a) H<sub>2</sub>O-poor or (b) H<sub>2</sub>O-rich
precursor gel.

1

# 5 3.3. Accelerated crystallization of Hf-Beta with assistance of seed crystal

6	DeAl-Beta as seed crystal (1 wt.% of SiO <sub>2</sub> ) was added to the precursor gel with $H_2O/SiO_2 =$
7	1.4 and 6.4 to accelerate the crystallization of Hf-Beta. Samples synthesized with the seed crystal are
8	designated with "-seed" at the end of their names. From the precursor gel with $H_2O/SiO_2 = 1.4$ and
9	6.4, diffraction patterns of *BEA-type structure appeared in 3 and 12 h, respectively, and the
10	induction period was significantly shortened (Figs. 7a and S7). The seed crystal promoted the

generation of nuclei during the hydrothermal treatment, so that the induction period for the nucleation was shortened. For the precursor gel with  $H_2O/SiO_2 = 6.4$ , the relative crystallinity increased sharply at 12 h, demonstrating that the growth of nuclei was accelerated by the addition of seed crystal. Even for the synthesis with seed crystal, the solid yield was ~90%, which was almost the same as that without seed.

6 When the precursor gel with  $H_2O/SiO_2 = 6.4$  was used, the Hf content decreased to 1.8 wt.% 7 in 6 h but increased after 12 h and was 2.3 wt.% after 24 h (Fig. 7b). The behavior in which the Hf 8 content decreased once and then increased with the progress of crystallization was also observed in 9 the synthesis without the addition of the seed crystal (Fig. 4b). The Hf content was slightly higher 10 when seed crystal was added. It is speculated that the seed crystal provided silicate species different 11 from that provided by fumed silica into the solution, which was prone to condense with Hf into 12 hafnosilicate, so that the amount of Hf finally incorporated into the zeolite framework increased.

For samples from the precursor gel with  $H_2O/SiO_2 = 6.4$ , catalytic activity appeared in crystallized ones after the synthesis period of 12 h (Fig. 7c), and the yield of *cis*-MCHOH reached a maximum of 79%. This activity was higher than that of Hf-HF, which was synthesized by the conventional hydrothermal method. On the other hand, for the precursor gel with  $H_2O/SiO_2 = 1.4$ , the Hf content and catalytic activity was not increased by the addition of seed crystal.

Hf-6.4-24-seed showed the absorption peaks attributed to adsorption on Lewis acid sites and silanol groups in an IR spectrum with  $CD_3CN$  (Fig. S8). The total peak area assigned to adsorption on Lewis acid sites was 5.4 cm<sup>-1</sup>. In this way, highly active Hf-Beta was successfully synthesized in 1 the very short period with the addition of seed crystal to the precursor gel with  $H_2O/SiO_2 = 6.4$ .

2



**Fig. 7.** Temporal changes in (a) relative crystallinity, (b) Hf content, and (c) catalytic activity for MPV reduction in course of crystallization of precursor gel containing seed crystal with  $H_2O/SiO_2 = 1.4$ (**a**) and 6.4 ( $\circ$ ). Relative crystallinity was calculated from intensity of the diffraction line at 22.7°, based on those of Hf-1.4-24-seed and Hf-6.4-36-seed, respectively. *cis*-MCHOH = *cis*-4methylcyclohexanol.

9

Particle morphology of representative samples was observed by SEM. Rounded octahedral particles were observed for Hf-1.4-72 (Fig. 8a), and truncated octahedral particles typical for Beta zeolite were observed for Hf-6.4-72 (Fig. 8b). The size of both samples was  $\sim 10 \,\mu\text{m}$ . Hf-1.4-12-seed had spherical particles with uneven surface (Fig. 8c). For Hf-6.4-24-seed, truncated octahedral particles were majorly formed and random-shaped particles were minorly present (Fig. 8d). The particle size of these two samples was reduced to  $\sim 1 \,\mu\text{m}$  by the addition of seed crystal. Because the seed crystal promoted the generation of nuclei, the particle size of the grown crystal was reduced. Hf6.4-72 showed much higher activity than Hf-1.4-12-seed despite its larger particle size (Fig. 4c and
7c). In addition, Hf-1.4-72 and Hf-1.4-12-seed showed similar activity despite the large differences
in particle size. These results implied that the catalytic activity was determined by the Hf content and
the nature of Hf, independent of the particle size.

5



7 **Fig. 8.** SEM images of Hf-Beta. (a) Hf-1.4-72, (b) Hf-6.4-72, (c) Hf-1.4-12-seed, and (d) Hf-6.4-24-

8 seed.

9

6

## 10 **3.4.** Catalytic performance of Hf-Beta for MPV reduction of various carbonyl 11 compounds

12 Catalytic performance of Hf-1.4-72, Hf-6.4-72, Hf-6.4-24-seed and metallosilicate zeolites

13 synthesized by the conventional hydrothermal method (Hf-, Zr- and Sn-HF) were compared in MPV

- 14 reduction of several carbonyl compounds. (Fig. 9). In addition to MCHOne, furfural, cinnamaldehyde,
- 15 and acetophenone were also used as substrates of MPV reduction. In the reaction of furfural, the
- 16 corresponding acetal was also produced in addition to furfuryl alcohol. The yield of acetal was ~8%
- 17 for any catalyst, which was almost the same as that in the reaction without a catalyst. The acetalization

proceeded in parallel with the MPV reduction regardless of catalysts, and so the acetal yield was excluded from the evaluation of catalytic activity. The corresponding ether was also produced in the reduction of cinnamaldehyde, and the total yield of cinnamyl alcohol and the ether was used as the product yield of MPV reduction. In the reaction of MCHOne and acetophenone, the corresponding alcohols were the sole products. Please note that reaction results of MCHOne shown in Fig. 9 are the results obtained by reducing the amount of catalyst from the standard conditions in order to suppress the conversion/product yields.





2	Hf-6.4-72 and Hf-6.4-24-seed gave much higher alcohol yields than Hf-1.4-72 for any
3	substrate. The higher activity of Hf-6.4-24-seed and Hf-6.4-72 was due to the larger number of Lewis
4	acid sites (Figs. 5 and S5). These two samples showed high activity for the MPV reduction of
5	cinnamaldehyde, which is a conjugated enone, as well. Acetophenone required a long reaction time
6	due to its significantly lower reactivity than other substrates, but Hf-6.4-24-seed and Hf-6.4-72 still
7	showed high activity for the reduction of acetophenone.
8	Catalytic activity of Hf-HF, Zr-HF, and Sn-HF for MPV reduction of the three substrates
9	except for MCHOne was decreased in the order of Hf-HF > Zr-HF > Sn-HF. On the whole, Hf-Beta
10	showed excellent catalytic performance for MPV reduction. Turnover numbers per metal atom
11	(TONs) for reduction of furfural of these zeolites were 840, 355, and 62, respectively (Table 2).
12	Considering that the active sites on these Beta zeolites for MPV reduction are the framework metal
13	atoms in common [12-18,20], the high TON of Hf-HF reflected the inherent high activity of Hf for
14	MPV reduction. It was reported that the catalytic activity of Ti-, Zr-, and Sn-Beta for MPV reduction
15	varied following the complex manner of electron donation/back donation between the metals and the
16	substrates, strongly depending on the types of substrates [15]. Such a complex electronic effect could
17	account for the exceptional high activity of Sn-Beta for the MPV reduction of MCHOne. Hf-6.4-24-
18	seed and Hf-6.4-72 showed similar or slightly higher activity than Hf-HF synthesized by the
19	conventional method, which demonstrated that the present method is excellent for efficiently
20	synthesizing highly active Hf-Beta with high Hf content in a short period.

Sample	Metal content <sup><i>a</i></sup>	FurOH yield <sup>b</sup>	TON <sup>c</sup>	
	(wt.%)	(%)	(-)	
Hf-1.4-72	1.0	11	381	
Hf-6.4-72	1.9	44	771	
Hf-6.4-24-seed	2.3	54	807	
Hf-HF	1.8	44	840	
Zr-HF	0.9	18	355	
Sn-HF	1.3	4	62	

2 **Table 2** Metal content and catalytic activity of metallosilicate zeolite samples.

<sup>3</sup> <sup>*a*</sup>Metal content determined by ICP-AES. <sup>*b*</sup>Yield of furfuryl alcohol. <sup>*c*</sup>Turnover number calculated as amount of

4 FurOH (mol) per amount of metal (mol) in a catalyst.

- 5
- 6

## 7 4. Conclusions

Hf-Beta samples were synthesized from precursor gel with different water content. The 8 9 lower water content allowed the fast crystallization of \*BEA-type framework. However, because of the low solubility of Hf in weakly basic solution, precipitation of Hf species was significant during 10 the hydrothermal treatment with low water content, resulting in the less incorporation of Hf into the 11 12 zeolite framework and the poor catalytic activity for MPV reduction. Thus, in order to synthesize active Hf-Beta with high Hf content, it is necessary to use precursor gel with relatively high water 13 content, but not too high. The role of water was considered to suppress precipitation of Hf species 14 and hold it in the form of hafnosilicate during the nucleation period. By using precursor gel with the 15 appropriate water content ( $H_2O/SiO_2 = 6.4$ ), highly active Hf-Beta zeolite was obtained in far shorter 16 period than that required for the conventional hydrothermal method. With the assistance of seed 17 crystal, the synthesis period was shortened to 24 h. Hf-6.4-24-seed and Hf-6.4-72 with the high Hf 18

1	content showed outstandingly high activity for the MPV reduction of several substrates and higher
2	activity than metallosilicate zeolites that were synthesized by the conventional hydrothermal method,
3	demonstrating that the present method is excellent for efficiently synthesizing highly active Hf-Beta
4	with high Hf content in a short period.
5	
6	
7	Supporting Information
8	Detailed data on characterization of samples are available in Supporting Information.
9	
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13	work was supported by Technical Division of Institute for Catalysis, Hokkaido University.
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