

## Supporting Materials

# Zeolites featuring 14×12-Ring Channels with Unique Adsorption Properties

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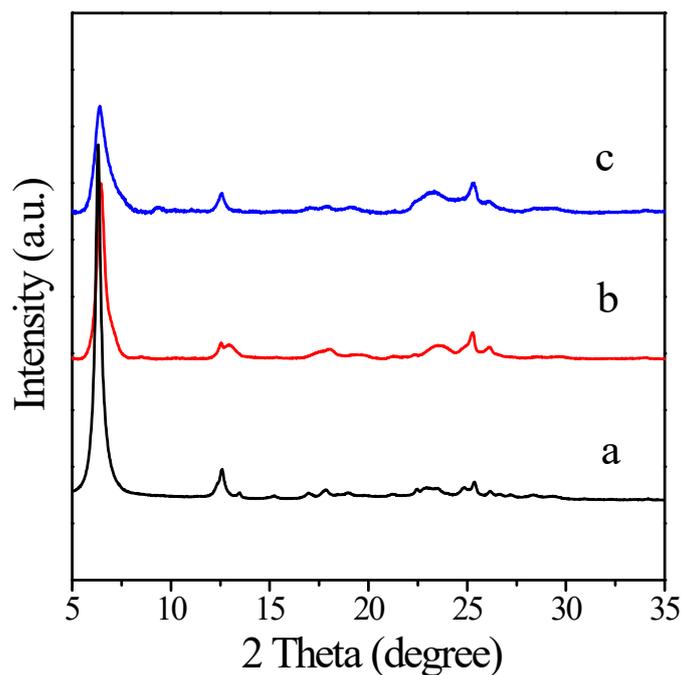
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KEYWORDS: PREFER, interlayer expansion, IEZ-FER(D4h), 4-membered ring unit

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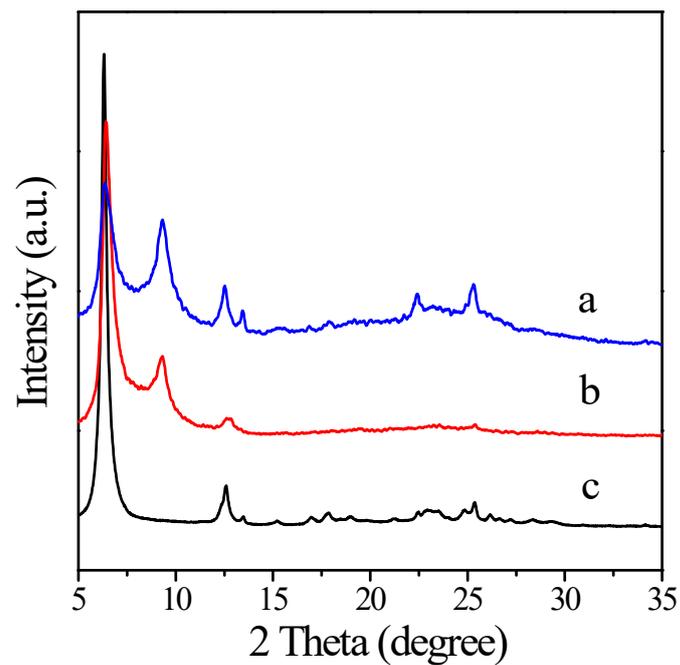
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**Figure S1.** XRD patterns of IEZ-FER(D4h) (a), IEZ-FER(Si-Si) (b), IEZ-FER(Si-O-Si) (c).

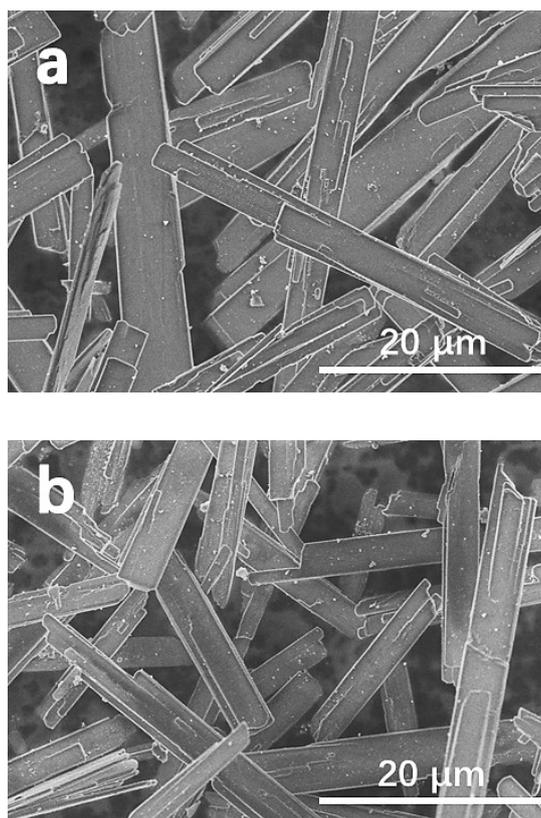
*In the preparation of IEZ-FER(Si-Si) and IEZ-FER(Si-O-Si), PREFER was silylated with 1,2-dichlorotetramethyldisilane and 1,3-dimethyltetramethoxydisiloxane under low pH conditions, respectively. Typically, 0.5 g of the PREFER was mixed with 50 mL of 1 M HNO<sub>3</sub> solution and 0.14 g 1,2-dichlorotetramethyldisilane or 0.11 g 1,3-dimethyltetramethoxydisiloxane (about 0.6 mmol). The mixture was autoclaved at 443 K for 24 h under rotating (100 rpm). The silylated sample was washed with deionized water repeatedly and dried at 373 K for 10 h*

*Both IEZ-FER(Si-Si) and IEZ-FER(Si-O-Si) showed the same layer-related diffraction in low degree region with IEZ-FER(D4h), which indicated that this strategy is universal to organosilicon sources with different structures, but the sample silylated with D4h obviously exhibited a higher structure order. It may be caused by the differences in shape, quantity, presence and matching with the silicon hydroxyl group of organosilanes after being exchanged with OSDA to enter the layer.*



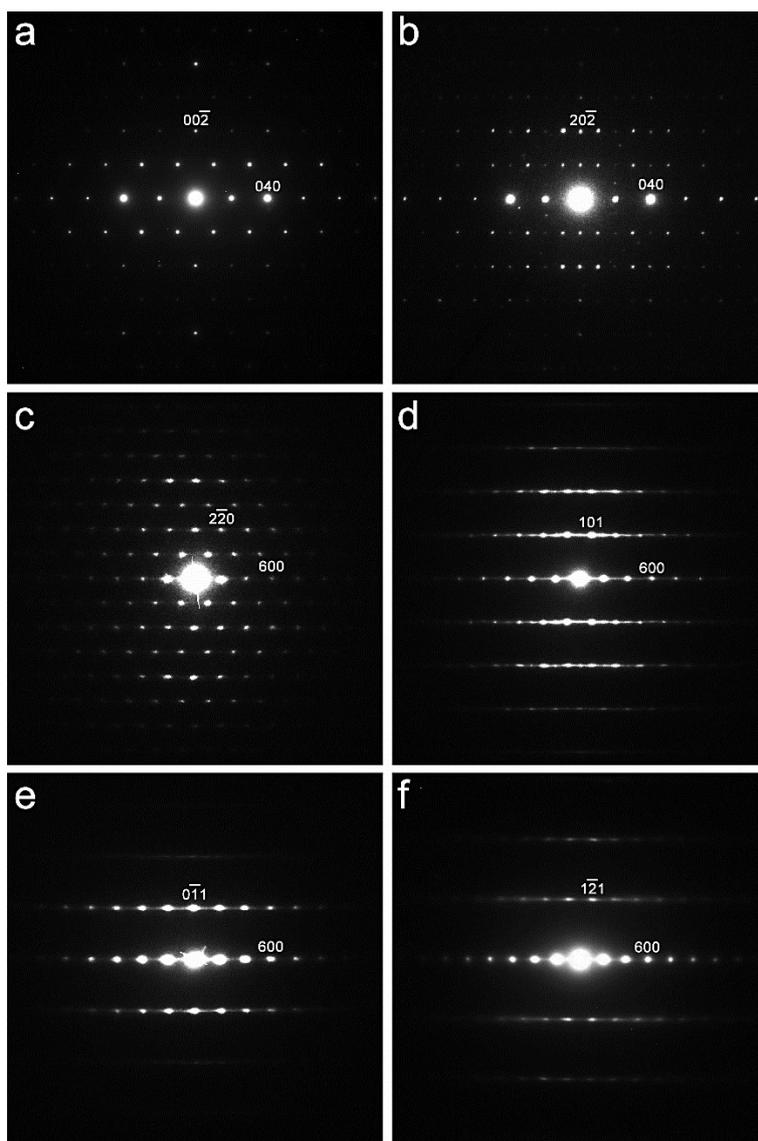
**Figure S2.** XRD patterns of IEZ-FER(D4h) synthesized at 403 K (a), 423 K (b), 443 K (c).

*The samples synthesized at 403 K and 423 K appeared the layer-related diffraction peak at a similar angle as 3D FER, which demonstrated that amount of silicon hydroxyl group of the layer could not be silylated with D4h regularly.*

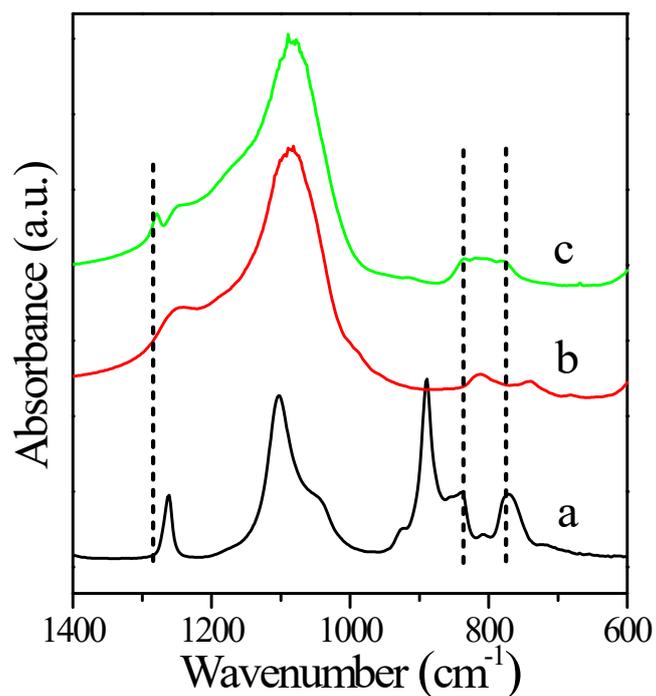


**Figure S3.** SEM images of PREFER (a), IEZ-FER(D4h) (b).

*The SEM images show that the interlayer-expanded material IEZ-FER(D4h) still preserved the sheet-like crystal morphology similar to that of pristine PREFER.*

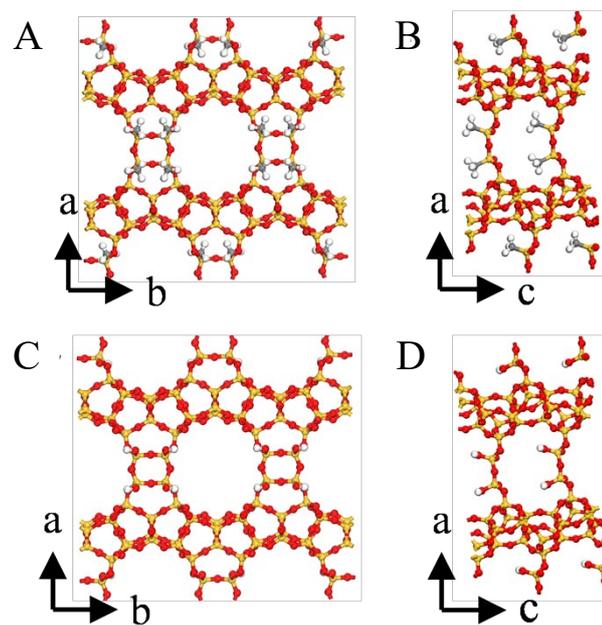


**Figure S4.** SAED patterns of IEZ-FER (D4h) taken along [100] (a), [101] (b), [001] (c), [010] (d), [011] (e) and [012] (f) directions.

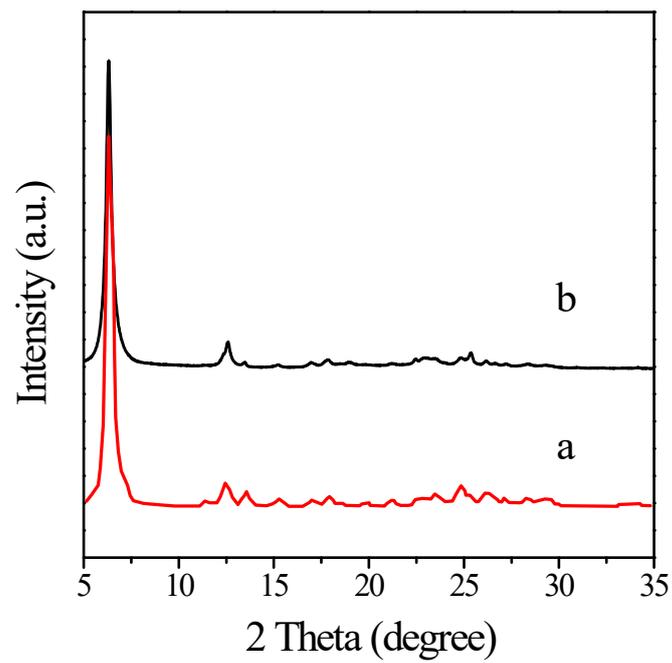


**Figure S5.** IR spectra of D4h silane (a), acid-treated PREFER in the absence of D4h (b), as-made IEZ-FER(D4h) by the silylation with 0.14 g D4h (c).

*It could not be verified that the 4MR has been inserted into the structure from the identification of the IR spectra because the characteristic absorption bands attributed to the 4MR overlap the bands (1000-1200 cm<sup>-1</sup>) arisen from the strong Si-O vibration of the framework for PREFER.*

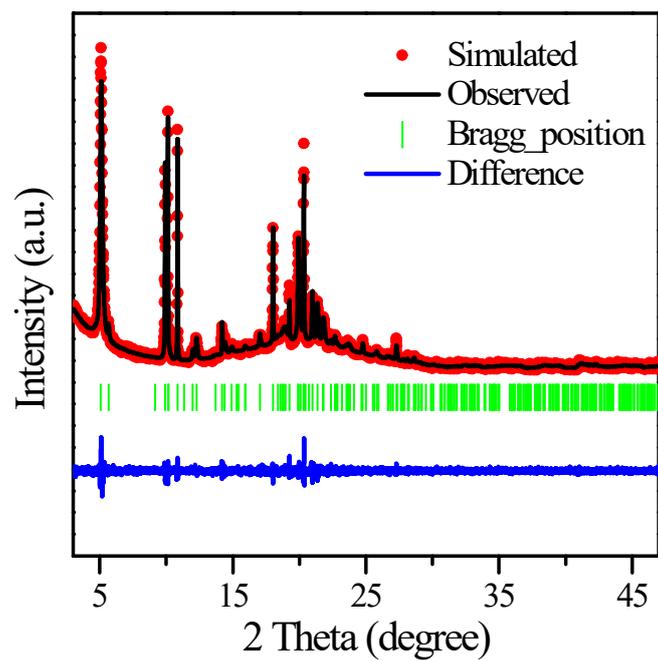


**Figure S6.** Structure model of as-made IEZ-FER(D4h) (A, B) and further calcined sample IEZ-FER(D4h-B) (C, D).

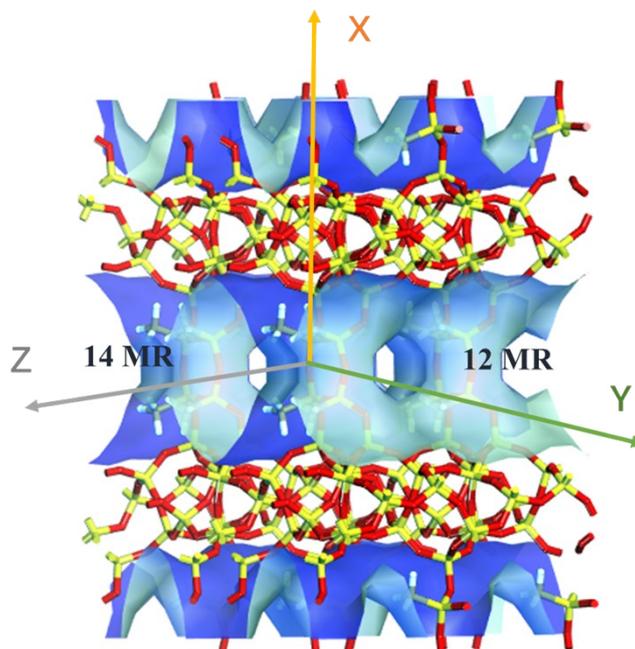


**Figure S7.** Simulated XRD pattern of ECNU-9 (a) and XRD pattern of IEZ-FER(D4h) (b).

*ECNU-9 and IEZ-FER(D4h) had analogous structure, as confirmed by the same XRD patterns.*

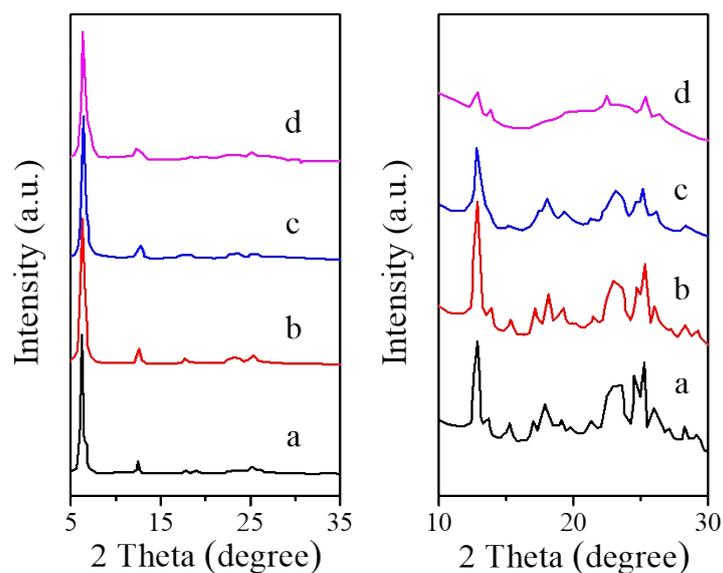


**Figure S8.** Pawley refinement of the x-ray diffraction pattern of IEZ-FER(D4h) ( $\lambda = 1.2438 \text{ \AA}$ ). (Rwp = 6.06%, Rwp(w/o bck) = 12.34%, Rp = 4.6%)



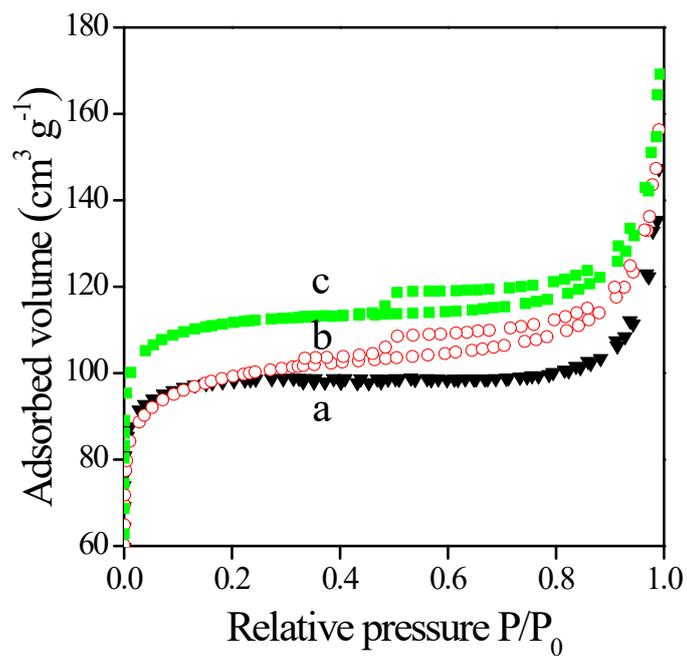
**Figure S9.** Schematic diagram of channel system for IEZ-FER(D4h).

*From its crystal structure, IEZ-FER(D4h) can be described as a two-dimensional framework comprising straight 12MR channels in one direction [010] and 14MR channels in one direction[001].*



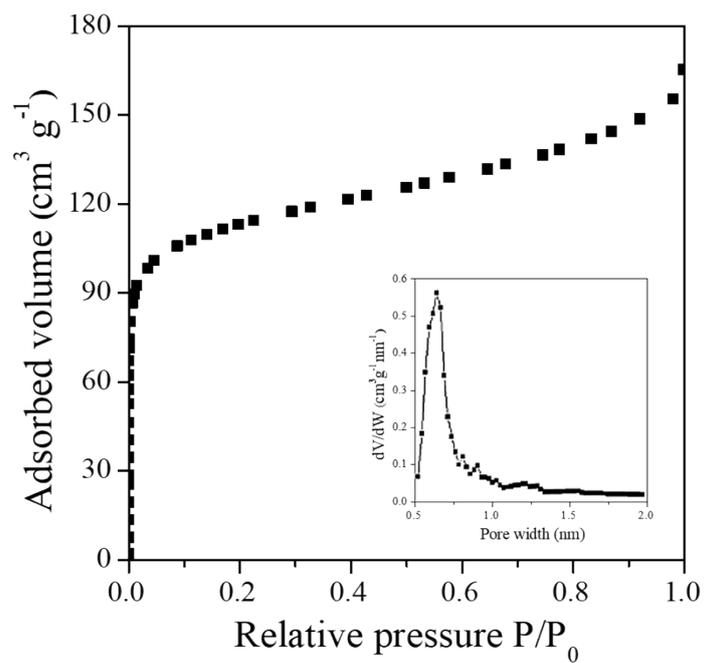
**Figure S10** XRD patterns of IEZ-FER(D4h) by the silylation with 0.14 g D4h (a), IEZ-FER(D4h) calcined at 723 K (b), IEZ-FER(D4h) calcined at 773 K (c), IEZ-FER (D4h) calcined at 823 K (d).

*XRD patterns investigated the thermal stability of IEZ-FER(D4h) after thermal treatment. No structural change was found when the temperature increased up to 723 K. Nevertheless, the temperature was higher than the 723 K, the crystal structure was gradually collapsed, and the interlayer spacing was slightly shrunk.*



**Figure S11.** Nitrogen adsorption isotherms of 3D FER(▼ a), IEZ-FER(D4h) calcined at 723 K (○ b), IEZ-FER(D4h) calcined at 823 K (■ c).

*Compared with those of 3D FER and IEZ-FER(D4h) calcined at 723 K, the material calcined at 823 K has the largest surface area and micropore volume. That was to say, the D4h was inserted into the interlayer successfully, and the methyl groups block the micropore channels.*



**Figure S12.** Argon adsorption isotherm and pore size distribution of IEZ-FER(D4h) calcined at 723 K.

*Ar gas adsorption results suggested that the average pore size of IEZ-FER(D4h) (6.0 Å), which is larger than that of 3D FER (3.9 Å).*

**Table S1.** Experimental Parameters and Pawley refinement results of IEZ-FER(D4h)

Sample	IEZ-FER(D4h-B)
condition of data collection	Room temperature data collection
diffractometer	SSRF BL14B1
sample holder	capillary
wavelength [Å]	1.2438
2 $\theta$ range [°]	3 – 48
step size [° 2 $\theta$ ]	0.01
number of points	4499
total no of reflections	279
FWHM [°]	0.015 at 2 $\theta$ = 13.5°
peak profile	Pseudo-Voigt
profile parameters	14
$a$ [Å]	28.0285(39)
$b$ [Å]	14.0921(6)
$c$ [Å]	7.4395(3)
$\alpha$ [°]= $\beta$ [°]= $\gamma$ [°]	90
space group	IMM2 (No. 44)
Rwp	6.06%
Rwp(w/o bck)	12.34%
Rp	4.6%

**Table S2.** Elemental Analysis Data for Various Materials

Sample	D4h (g)	C (%)	H (%)	N (%)	C/N ratio	n(D4h) / n([Si <sub>36</sub> O <sub>72</sub> ])
PREFER	-	13.69	3.088	2.702	5.91	-
IEZ-FER(0.07D4h)	0.07	4.4105	0.255	0.1375	37.42	1.8
IEZ-FER(0.14D4h)	0.14	4.1105	0.2385	0.077	62.28	1.9
IEZ-FER(0.28D4h)	0.28	7.177	0.7905	0.133	62.96	3.3

*The CHN elemental analyses were used to determine the D4h addition amount. The ratio of n(D4h)/n([Si<sub>36</sub>O<sub>72</sub>]) can be obtained from the amount of nitrogen, carbon and crystal-cell used for silylation. It can be found that when the D4h amount was 0.14 g, the ratio was near to the theoretical value (2.0). So, the D4h (0.14 g) was reasonable for completing the silylation.*

**Table S3.** Unit Cell Parameters of Various Materials

Sample	Unit-cell parameter (Å)	Sample	Unit-cell parameter (Å)
3DFER	a =18.6972	PREFER	a=26.3971
	b=14.0790		b=13.9954
	c=7.4800		c=7.4616
	$\alpha=\beta=\gamma=90^\circ$		$\alpha=\beta=\gamma=90^\circ$
IEZ-FER(Si)	a=24.0476	IEZ-FER(D4h)	a=28.0285
	b=14.1893		b=14.0921
	c=7.4785		c=7.4395
	$\alpha=\beta=\gamma=90^\circ$		$\alpha=\beta=\gamma=90^\circ$

**Table S4.** Relative Intensity Ratios of Q<sup>4</sup>, Q<sup>3</sup>, and T<sup>3</sup> Resonances Estimated by Deconvolution of <sup>29</sup>Si MAS NMR Spectra

Sample	Q <sup>2</sup>	Q <sup>3</sup>	Q <sup>4</sup>	T <sup>3</sup>	Q <sup>3</sup> /Q	T/(Q+T)
PREFER	-	30.82	69.18	-	30.82	-
IEZ-FER(D4h)	-	8.04	71.85	20.1	10.06	20.1
IEZ-FER(D4h) calcined at 723 K	-	8.11	73.14	18.75	-	-
IEZ-FER(D4h) calcined at 823 K	0.71	30.5	66.14	2.64	-	-

**Table S5.** Coordination Sequences and Vertex Symbols

T-atom Name	$N_1$ to $N_{10}$										Vertex Symbol
T <sub>1</sub>	4	11	20	31	48	70	92	130	162	188	[5.5(2).5.12.5.12]
T <sub>2</sub>	3	6	14	30	51	70	89	116	154	200	[4.5.12(2)]
T <sub>3</sub>	4	12	20	30	43	65	96	129	161	192	[5.5.5.5(2).5.12]
T <sub>4</sub>	4	12	20	30	43	65	96	129	161	192	[5.5.5.5(2).5.12]
T <sub>5</sub>	4	12	20	38	45	64	98	128	163	192	[5.5.5.5.5.5(2)]
T <sub>6</sub>	4	12	20	30	42	61	95	138	159	187	[5.5(2).5.5(2).14(2)]
T <sub>7</sub>	4	12	20	30	42	61	95	138	159	187	[5.5(2).5.5(2).14(2)]

**Table S6.** Mean Textural Properties of IEZ-FER(D4h)

Sample	$S_{\text{BET}}$ ( $\text{m}^2 \text{g}^{-1}$ )	$V_{\text{tot}}$ ( $\text{cm}^3 \text{g}^{-1}$ )	Pore diameter ( $\text{\AA}$ )
3D FER	375	0.224	3.9
IEZ-FER(D4h) <sup>a</sup>	378	0.239	6
IEZ-FER(D4h) <sup>b</sup>	434	0.252	-

<sup>a</sup> The material was calcined at 723 K.

<sup>b</sup> The material was calcined at 823 K.