

Supporting Information

Rational design of ZSM-5 zeolite containing a high concentration of single Fe sites capable of catalyzing the partial oxidation of methane with high turnover frequency

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1. METHODS

1.1. Sample.

1.1.1. Commercial ZSM-5. Commercial ZSM-5 zeolites purchased from TOSOH (NH₄⁺-form, Si/Al= 12.4, 820NHA; NH₄⁺-form, Si/Al= 22.0, 840NHA) and supplied by Catalysis Society of Japan (H⁺-form, Si/Al= 50.3, JRC-Z5-90H) were used as the supports to investigate the effect of the Si:Al ratio on the catalytic performance of the Fe/ZSM-5 catalysts. The accurate Si:Al ratios were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The detail was described in 1.1.7. The obtained values were adopted in this paper.

1.1.2. Dealuminated ZSM-5. Dealuminated ZSM-5 with the Si:Al ratio of 19.6 was obtained from the harsh acid treatments of the Al-rich ZSM-5 (TOSOH, 820NHA, Si/Al= 12.4).¹ 5.0 g of the Al-rich ZSM-5 zeolite was added to 6.0 M HNO₃ aqueous solution in a 300 cm³ Teflon-lined stainless-steel autoclave. The sealed autoclave was heated at 160 °C for 24 h under tumbling conditions (20 rpm) using the hydrothermal synthesis reactor developed by HIRO COMPANY. The calcined sample was ion-exchanged with 1.0 M NH₄(NO₃) aqueous solution at 80 °C for 1 hour. After the ion-exchange, the sample was well rinsed with the distilled water. This ion-exchange was repeated three times. The resulting sample was dried under vacuum at room temperature overnight. The obtained NH₄⁺-form zeolite was used for preparations of the Fe ion-exchanged zeolites as the catalyst for partial oxidation of CH₄.

1.1.3. Hydrothermal synthesis of ZSM-5. ZSM-5 with the Si:Al ratio of about 20 were hydrothermally synthesized through the previously reported procedures with slight modifications.² An aqueous solution of tetrapropylammonium hydroxide (TPAOH, TCI, 22.5wt%), Colloidal silica (Ludox HS-40, Sigma-Aldrich), aluminum nitrate nonahydrate (Wako, 98%), and sodium chloride (NaCl, Kanto chemical, 99.5%) were used as organic structure-directing agent (SDA), silica, Al, and Na sources, respectively. Two types of the starting mixtures were prepared with a molar composition of 1.0 SiO₂: 0.02 Al₂O₃: 0.25 TPAOH: 0.1 NaCl: 25 H₂O and 1.0 SiO₂: 0.02 Al₂O₃: 0.5 TPAOH: 25 H₂O. The difference between them is whether Na⁺ contains or not. The 0.5 wt% (SiO₂ base) of calcined silicate-1 was added to the starting gel as a seed crystal to promote the crystallization. The hydrothermal synthesis was conducted at 170 °C for 24 h at 30 rpm using a 100 cm³ Teflon-lined stainless steel autoclave (stirring-type hydrothermal synthesis reactor, R-100, Hiro Company, Japan). After crystallization, the solid product was collected by centrifugation, washed thoroughly with distilled water until nearly neutral, and dried at 343 K overnight. As prepared samples were calcined under air at 550 °C for 10 h to remove the organic SDA. The calcined samples were ion-exchanged with 1.0 M NH₄(NO₃) aqueous solution at 60 °C for 120 minutes. The ion-exchange treatment was repeated three times, and the resulting samples were well rinsed with the distilled water, and subsequently dried at 343 K overnight.

1.1.4. Hydrothermal synthesis of silicate-1. Silicate-1 was hydrothermally synthesized through the following procedure. First, 0.83 g NaOH and 52.06 g of 22.5 wt% tetrapropylammonium hydroxide (TPAOH: 20-25%, TCI) aqueous solution were added to 72.39 ml of distilled water in a 300-ml Teflon beaker, and the mixture was well stirred for 10 min at ambient condition. Next, 31.7 g colloidal silica was loaded into the mixture with vigorous stirring for 1 h. The synthesis solution was then transferred to a 300-ml Teflon-line stainless steel autoclave, and placed in a convection oven at 170 °C, and rotated at 15 rpm for 1 day. The sample was cooled to room temperature (RT) and collected by filtration. The sample was well rinsed and subsequently dried overnight at 80 °C. To remove the structure-directing agent, the as-synthesized zeolite was calcined in air at 500 °C overnight.

1.1.5. Preparation of iron ion-exchanged ZSM-5. 0.4–2.0 g of NH₄⁺-ion-exchanged ZSM-5 was dispersed in distilled water of 10–50 ml containing 0.001 or 0.1 M of FeSO₄•7H₂O (99.0-102.0%: Kishida) and 1.0 M of ascorbic acid (99.6%, Wako) at 80 °C for 1 h. After this, the sample was collected by centrifugation (6000 rpm) for 10 minutes, and the sample was collected. If necessary, the collected sample was re-dispersed in the Fe precursor aqueous solution containing the ascorbic acid, and the ion-exchange process was further conducted. For the rinse, the ion-exchanged sample was dispersed in 100 ml distilled water at room temperature and well mixed for 1 minute. The sample was collected by centrifugation (6000 rpm) for 10 minutes. The rinse procedures were repeated 6 times. The well-rinsed sample was dried overnight at room temperature under vacuum conditions. The samples were calcined at 500 °C for 3 h (2 °C /min) under the 10% H₂ and N₂ gas mixture flow with 100 ml min⁻¹. This reductive calcination allowed us to activate the catalyst while suppressing the aggregation of the Fe species with the generation of the bulk Fe_xO_y facilitating the undesirable side-reaction, i.e., H₂O₂ decomposition.^{4,6}

When the Fe ion exchange operation was performed on Al-free ZSM-5 (Silicate) for 6-hour, the negligible Fe loading (< 0.01 wt%) was confirmed. This is indicative that our Fe modification approach effectively leads to the Fe ion-exchange on the framework AlO₄ tetrahedra site, while suppressing the undesirable fixation of the Fe species on the outer surface of ZSM-5.

1.1.6. Preparation of iron impregnated ZSM-5 and silicate-1. 0.5 g of NH₄⁺ ion-exchanged ZSM-5 with the Si:Al ratio of 22.0 or ZSM-5 silicate-1 were dispersed in distilled water of 50 ml containing 0.1 M of FeSO₄•7H₂O (responsible for 0.44 wt% Fe loading) at 80 °C for 1 h. After this, the solvent was evaporated at 60 °C, through which the samples were collected. The collected samples were dried at room temperature under a vacuum overnight and subsequently calcined at 500 °C for 3 h (2 °C /min) under the 10% H₂ and N₂ gas mixture flow with 100 ml min⁻¹.

Compared to the Fe/ZSM-5 catalysts obtained by the ion-exchange method, the Fe/ZSM-5 catalysts obtained through the impregnation method showed by far the lowest activity (**Table S4**). There is no doubt that it is

important to apply Fe ion exchange in designing the high-performance catalyst. Therefore, in this study, we focus only on the ion-exchange approach.

1.1.7. Determination of iron loading. 5.0 ml of 47% hydrogen fluoride (HF: 46-48%, Wako) aqueous solution was added to the Fe/ZSM-5 catalyst containing Teflon bottle, where the zeolite was rapidly dissolved in the HF aqueous solution. The resulting solution was diluted to 50 mL using 0.85 M H₃BO₃ (99.5%, Wako) aqueous solution for converting the harmful HF to harmless HBF₄. The Fe content was evaluated by ICP-AES for the samples dissolved in HF aqueous solution, through which the Fe loading was calculated.

1.2. Catalytic reactivity assay toward partial oxidation of methane.

Catalytic reactivity assay was carried out based on the previously established procedures.³ 27 or 3 mg of catalysts, 10 mL of 0.5 M H₂O₂ (33-36%, Kishida) aqueous solution, and magnetic stirrer were placed in a glass vessel. It was placed in an autoclave and sealed. The reaction vessel volume was 37.36 mL. 0.8 MPa CH₄ gas was purged to the sealed reactor and flushed. This process was repeated five times. After the replacement of the air with CH₄, the CH₄ pressure was regulated to 3.0 MPa. The reactivity assay was conducted at 50 °C for 30 minutes at 1500 rpm. After the reaction, the reactor was quickly cooled with the water bath containing the ice blocks. The liquid-phase products were extracted by the syringe filter, where the catalyst was fully separated. The 700 μL of the liquid phase product as well as the 100 μL D₂O (99.9%, Wako) containing 0.02 wt% mol sodium trimethylsilylpropanesulfonate (Wako) as an internal standard were loaded to the NMR tube. The quantitative-qualitative analysis on the products was carried out the NMR measurements (Avance IIIHD, 500MHz, Bruker). The amount of unreacted H₂O₂ was quantified by the titration method with 0.1 M Ce(SO₄)₂ solution (Kishida), based on which the H₂O₂ decomposition ratio in the reaction was evaluated.

1.3. Characterization.

1.3.1. ²⁷Al MAS NMR. ²⁷Al magic angle spinning (MAS) NMR spectra of the NH₄⁺-ion-exchanged ZSM-5 catalysts were recorded at 156 MHz on a Varian 600PS solid NMR spectrometer. A 3.2 mm diameter zirconia rotor with a rotation speed of 15 kHz was selected. ²⁷Al MAS NMR spectra were acquired using 2.8 μs pulses, a 1 s recycle delay, and 256 scans. AlK(SO₄)₂·12H₂O was used as a chemical shift reference. Samples were moisture equilibrated over a saturated solution of NH₄Cl for 24 h prior to ²⁷Al MAS NMR measurements.

1.3.2. SEM. The crystal morphology was observed using a field-emission scanning electron microscope (FE-SEM; JSM-7500FA, JEOL).

1.3.3. Ultra-violet, visible (UV-Vis) diffuse reflectance (DR) spectroscopy. 10 mg of the sample was placed in an in-situ reflectance cell with a quartz window (JASCO Co., Ltd.). UV-Vis-NIR DR spectra were recorded using a JASCO V-770ICO spectrophotometer (JASCO Co., Ltd.) equipped with an integrating sphere

attachment and fiber optics. BaSO₄ was used as the reference material. The resolution and scan rate were set to 0.5 nm and 1000 nm min⁻¹, respectively.

1.3.4. X-ray absorption fine structure (XAFS) spectroscopy. The Fe K-edge XAFS spectrum including the X-ray absorption near edge structure (XANES) in the fluorescence mode was collected at BL11S2 of Aichi Synchrotron Radiation Center, Aichi & Technology Foundation, which is equipped with a double crystal Si(311) monochromator. 60 mg of the Fe ZSM-5 with the Si:Al ratio of 22.0 and the Fe loading of 0.45 wt% was pressed into pellets with a 10 mm diameter. The data analysis was performed using the Athena software included in the Demeter package.

2. Supporting data.

Table S1. Comparison of the catalytic performances of the Fe/ZSM-5 catalysts with different Si:Al ratios.

This is related to **Figure 1** in the main text. Reaction conditions: 27 mg catalyst, 3.0 MPa CH₄, 10 ml of 0.5 M H₂O₂ aqueous solution, 0.5 h reaction time, 50 °C reaction temperature.

Support	Si:Al ratio	Fe loading (wt%)	Al content (wt%)	Catalyst amount (mg)	Yield (mmol)				
					CH ₃ OH	CH ₃ OOH	HCOOH	HCHO	Total
ZSM-5 (comm.)	12.4	0.12	3.35	27	0.00	0.01	0.00	0.01	0.03
ZSM-5 (comm.)	22.0	0.12	1.95	27	0.01	0.02	0.20	0.04	0.27
ZSM-5 (comm.)	50.3	0.09	0.88	27	0.01	0.01	0.17	0.03	0.21
ZSM-5 (comm.)	19.6	0.11	2.11	27	0.01	0.017	0.21	0.03	0.26

Table S2. Comparison of the catalytic performances of the Fe/ZSM-5 catalysts with the different Fe loadings.

This is related to **Figure 2** in the main text. Reaction conditions: 27 or 3 mg catalyst, 3.0 MPa CH₄, 10 ml of 0.5 M H₂O₂ aqueous solution, 0.5 h reaction time, 50 °C reaction temperature.

Support	Si:Al ratio	Fe loading (wt%)	Al content (wt%)	Catalyst amount (mg)	Yield (mmol)				
					CH ₃ OH	CH ₃ OOH	HCOOH	HCHO	Total
ZSM-5 (comm.)	22.0	0.02	1.95	27	0.00	0.01	0.00	0.00	0.02
ZSM-5 (comm.)	22.0	0.12	1.95	27	0.01	0.02	0.20	0.04	0.27
ZSM-5 (comm.)	22.0	0.23	1.95	27	0.01	0.01	0.33	0.02	0.37
ZSM-5 (comm.)	22.0	0.35	1.95	27	0.01	0.01	0.43	0.04	0.49
ZSM-5 (comm.)	22.0	0.43	1.95	27	0.01	0.01	0.56	0.03	0.60
ZSM-5 (comm.)	22.0	0.45	1.95	27	0.01	0.01	0.56	0.03	0.60
ZSM-5 (comm.)	22.0	0.45	1.95	3	0.01	0.02	0.05	0.02	0.10

Table S3. Comparison of the catalytic performances of the Fe/ZSM-5(TPA) and Fe/ZSM-5(TPA,Na) catalysts with different Fe loadings. This is related to **Figure 6A** in the main text. Reaction conditions: 27 or 3 mg catalyst, 3.0 MPa CH₄, 10 ml of 0.5 M H₂O₂ aqueous solution, 0.5 h reaction time, 50 °C reaction temperature.

Support	Si:Al ratio	Fe loading (wt%)	Al content (wt%)	Catalyst amount (mg)	Yield (mmol)				
					CH ₃ OH	CH ₃ OOH	HCOOH	HCHO	Total
ZSM-5 (comm.)	22.0	0.12	1.95	27	0.01	0.02	0.20	0.04	0.27
ZSM-5 (comm.)	22.0	0.45	1.95	3	0.01	0.02	0.05	0.02	0.10
ZSM-5(TPA,Na)	25.8	0.14	1.68	27	0.01	0.01	0.31	0.02	0.35
ZSM-5(TPA)	23.4	0.46	1.86	3	0.01	0.01	0.13	0.03	0.19
ZSM-5(TPA)	23.4	1.11	1.86	3	0.02	0.01	0.24	0.03	0.30

Table S4. Comparison of the catalytic performances of Fe/ZSM-5(comm) prepared by the ion-exchange and impregnation methods, and Fe/Silicate-1. Reaction conditions: 27 mg catalyst, 3.0 MPa CH₄, 10 ml of 0.5 M H₂O₂ aqueous solution, 0.5 h reaction time, 50 °C reaction temperature.

Support	Si:Al ratio	Fe-fabrication approach	Fe loading (wt%)	Al content (wt%)	Catalyst amount (mg)	Yield (mmol)				
						CH ₃ OH	CH ₃ OOH	HCOOH	HCHO	Total
ZSM-5 (comm.)	22.0	Ion-exchange	0.45	1.95	27	0.01	0.01	0.56	0.03	0.60
ZSM-5 (comm.)	22.0	impregnation	0.44	1.95	27	0.02	0.02	0.24	0.03	0.30
Silicate-1	∞	impregnation	0.44	0	27	0.00	0.00	0.00	0.00	0.00

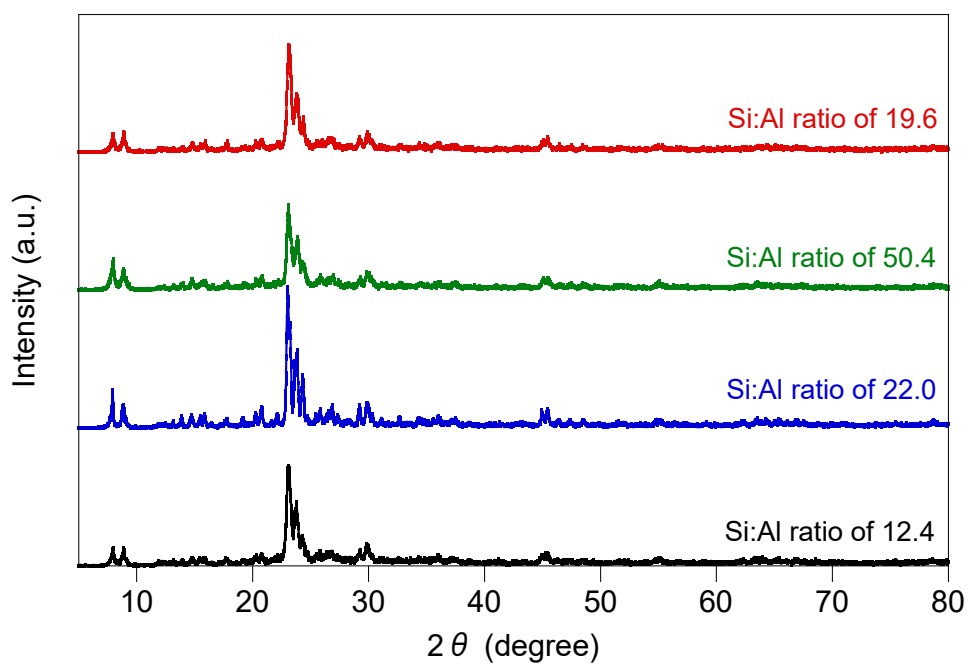


Figure S1. XRD profiles of commercial ZSM-5 zeolites with the Si:Al ratios of 12.4, 22.0, 50.3, and 19.6.

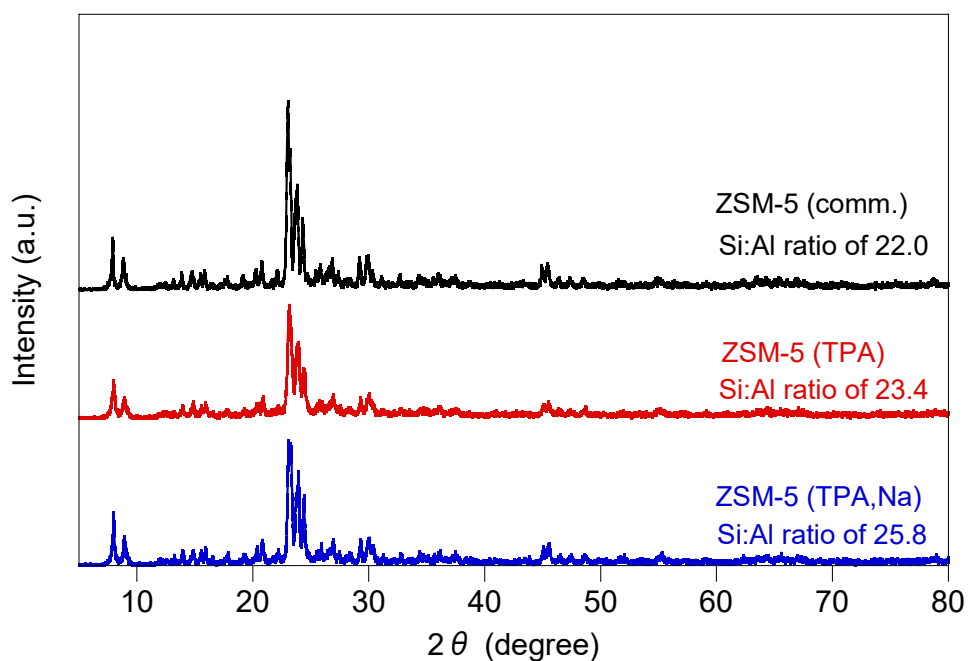


Figure S2. XRD profiles of ZSM-5(comm.), ZSM-5(TPA), and ZSM-5(TPA,Na).

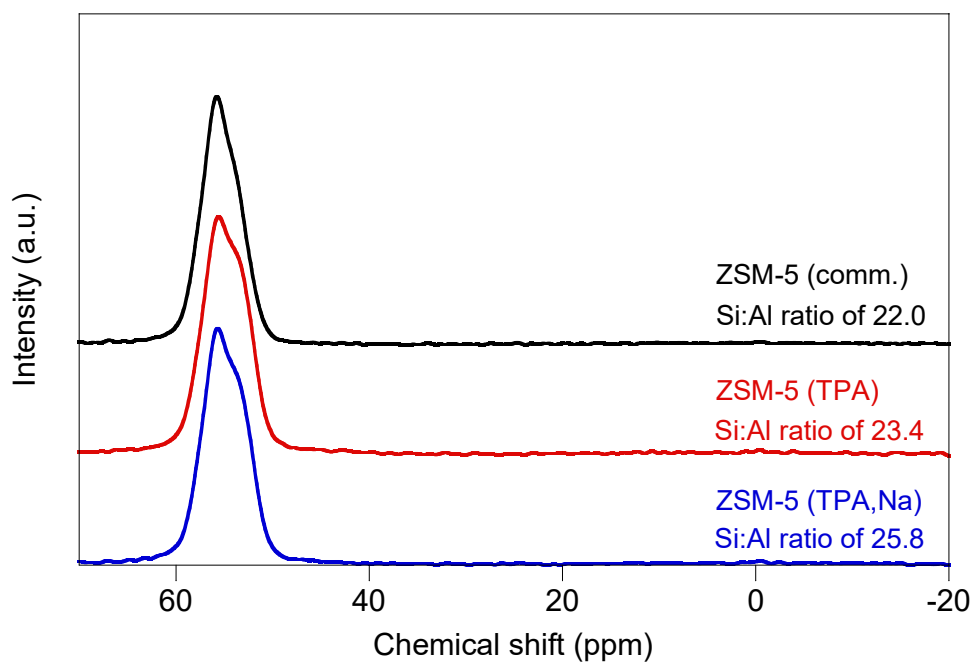


Figure S3. ^{27}Al NMR of ZSM-5(comm.), ZSM-(TPA), and ZSM-5(TPA,Na).

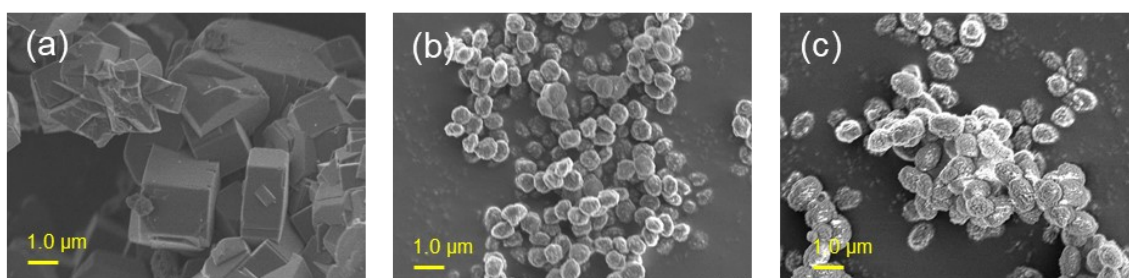


Figure S4. SEM images of (a) ZSM-5(comm.), (b) ZSM-(TPA), and (c) ZSM-5(TPA,Na).

3. Supporting references

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