

Supporting Information

Metal cation-exchanged zeolites with the location, state, and size of metal species controlled

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Synthesis of MFI[TPA] and MFI[TPA, Na]

Two types of ZSM-5 zeolites were synthesized using tetrapropylammonium hydroxide (TPAOH, Tokyo Chemical Industry (TCI) Co., 35 wt%) as an organic-structure-directing-agent (OSDA) with (MFI[TPA, Na]) or without (MFI[TPA]) Na cations. MFI[TPA] and MFI[TPA, Na] were synthesized by hydrothermal synthesis with the molar compositions of the synthetic gels of [1.0 SiO₂: 0.025 Al₂O₃: 0.5 TPAOH: 8.3 H₂O and 1.0 SiO₂: 0.025 Al₂O₃: 0.5 TPAOH: 0.1 NaCl: 8.3 H₂O], respectively. In the synthesis, tetraethylorthosilicate (TEOS, TCI Co.), aluminum nitrate nonahydrate (FUJIFILM Wako Pure Chemical Corporation, 99.9%) and sodium chloride (FUJIFILM Wako Pure Chemical Corporation, 99.5%) were used as Si, Al and Na sources, respectively. Their mother gels were stirred at 353 K for 24 h for aging the gels. Then, hydrothermally treatment was performed in an autoclave reactor at 443 K for 3 and 7 days, respectively. Both samples were calcined at 823 K to remove OSDAs.

Introduction of Rh species by ion-exchange method

The obtained MFI[TPA] and MFI[TPA, Na] samples were ion-exchanged at 353 K for 3 h twice by 2.5 M NH₄NO₃ aqueous solution to obtain NH₄⁺-form samples. Then, Rh ion-exchange was performed at 363 K in a RhCl₃ trihydrate aqueous solution (0.01 M) with stirring. In order to obtain the samples with the same Rh content, the treatment conditions were adjusted; the treatment times of Rh-MFI[TPA] and Rh-MFI[TPA, Na] were 24 and 5 h, respectively. After the filtration, the samples were calcined at 673 K for 6 h. For MFI[TPA], Si/Al, Rh/Al, and Rh content were 24, 0.029, and

0.172 wt%, respectively. For MFI[TPA, Na], Si/Al, Rh/Al, and Rh content were 22, 0.026, and 0.186 wt%, respectively.

As a control, Rh species supported samples (Rh/MFI[TPA] and Rh/MFI[TPA, Na]) were also prepared by the impregnation method using RhCl₃ trihydrate aqueous solution as a precursor. After drying water, the samples were calcined under the same conditions with the ion-exchange method.

Characterization

Structures of the synthesized samples were confirmed by X-ray diffraction (XRD) patterns (Rigaku Ultima III diffractometer, CuK α radiation, 40 kV, 40 mA). Elemental analysis was conducted by inductively coupled plasma analysis (ICP, Shimadzu ICPE-9000 spectrometer). Field-emission scanning electron microscopic (FE-SEM) images were obtained by an S-5200 microscope (Hitachi). SEM-energy dispersive X-ray spectroscopy (EDX) mapping images were conducted by an S-9000 microscope (Hitachi) with TEAMTM EDS System (EDAX). The Brunauer–Emmett–Teller (BET) specific surface areas of several samples were estimated from the adsorption branch data of nitrogen adsorption-desorption measurement using BELSORPmini (MicrotracBEL). The high-resolution ²⁷Al MAS NMR spectra of the NH⁴⁺-type **MFI** zeolites were obtained on a JEOL ECA-600 spectrometer (14.1 T) equipped with an additional 1 kW power amplifier. The chemical shift of ²⁷Al was referenced to AlNH₄(SO₄)₂·12H₂O at -0.54 ppm and samples were spun at 15 kHz by using a 4 mm ZrO₂ rotor. Diffuse reflectance UV-vis spectra were recorded by JASCO V-650 spectrometer. The absorbance of all spectra was converted to the Kubelka-Munk function. For *in-situ* IR measurement, self-supporting disks of each sample (20 mm diameter, 40 mg) were pretreated by evacuation at 773 K for 1 h to remove the adsorbed species in the quartz cell connected to a conventional closed gas-circulation system. IR spectra were measured using a JASCO FT/IR-4100 spectrometer with an MCT detector. All spectra were collected as averages of 64 scans at a resolution of 4 cm⁻¹. CO gas was introduced into the IR cell. IR spectra were measured with different introduction pressures of CO and after evacuation of gas-phase and weakly adsorbed CO species. Difference spectra shown in this paper were obtained by subtracting the background spectra from measured spectra after evacuation of gas-phase and weakly adsorbed CO species.

Oxidative reforming of methane

The oxidative reforming of methane was carried out in a fixed bed reactor. The reacted gas was analyzed by gas chromatography (GC-2014, Shimadzu) equipped with a TCD detector. Typically, 25 mg of catalysts were pretreated at 873 K for 30 min in Ar flow. The reaction was performed at 873 K with several SV values.

Calculating methods for conversion, yield, and selectivity

The conversion, yield, and selectivity were calculated by following equations Eq. S1 – S4,

$$CH_4 \text{ conversion (\%)} = \frac{n_{CO} + n_{CO_2}}{n_{CH_4} + n_{CO} + n_{CO_2}} \times 100\% \quad (\text{Eq. S1})$$

$$CO \text{ yield (\%)} = \frac{n_{CO}}{n_{CH_4} + n_{CO} + n_{CO_2}} \times 100\% \quad (\text{Eq. S2})$$

$$CO \text{ selectivity (\%)} = \frac{n_{CO}}{n_{CO} + n_{CO_2}} \times 100\% \quad (\text{Eq. S3})$$

$$CO_2 \text{ selectivity (\%)} = \frac{n_{CO_2}}{n_{CO} + n_{CO_2}} \times 100\% \quad (\text{Eq. S4})$$

where n means the amount of substance.

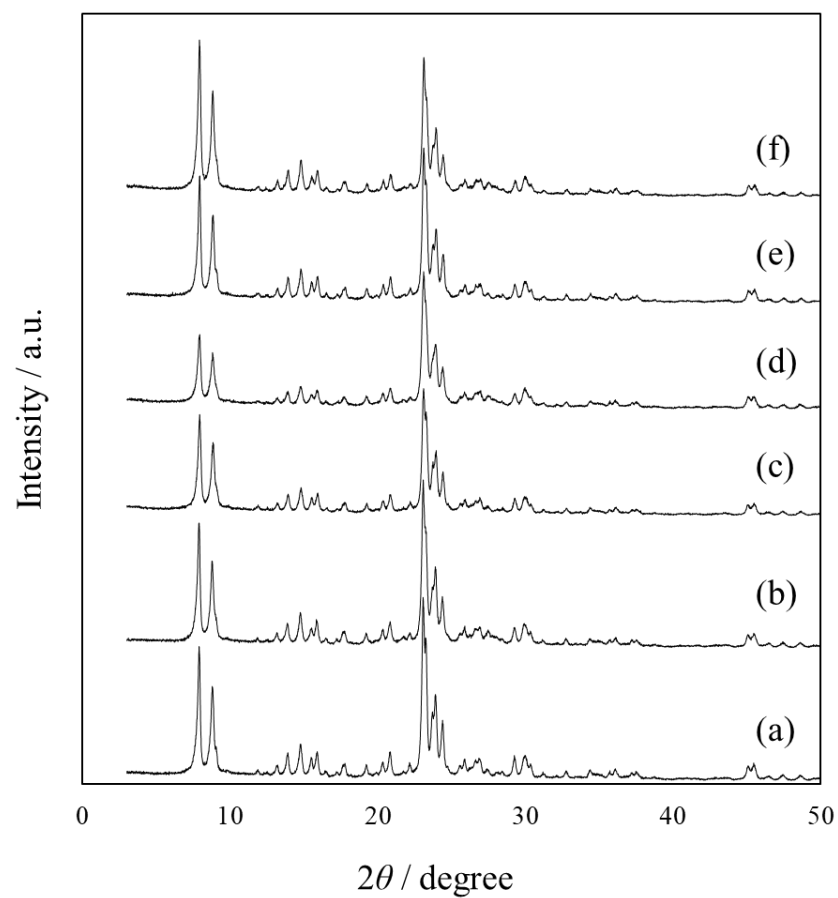


Fig. S1 XRD patterns of (a) NH_4^+ -MFI[TPA], NH_4^+ -MFI[TPA, Na], (c) Rh-MFI[TPA], (d) Rh-MFI[TPA, Na], (e) Rh/MFI[TPA], and (f) Rh/MFI[TPA, Na].

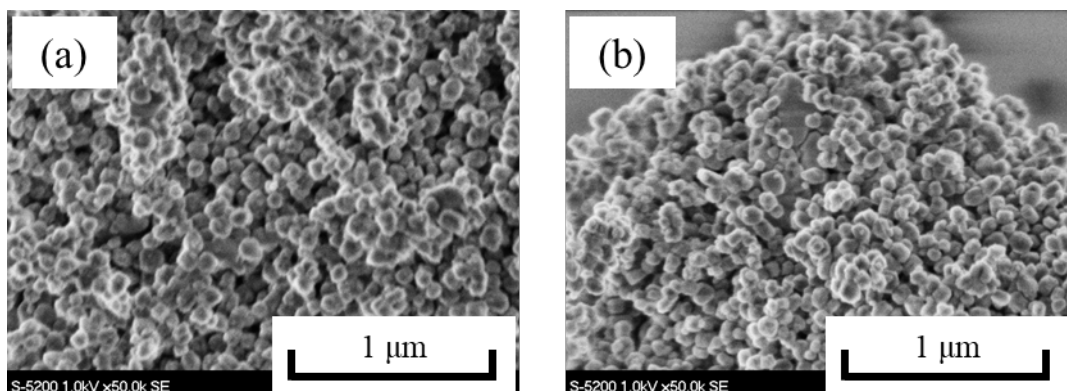


Fig. S2 SEM images of (a) NH_4^+ -MFI[TPA] and NH_4^+ -MFI[TPA, Na].

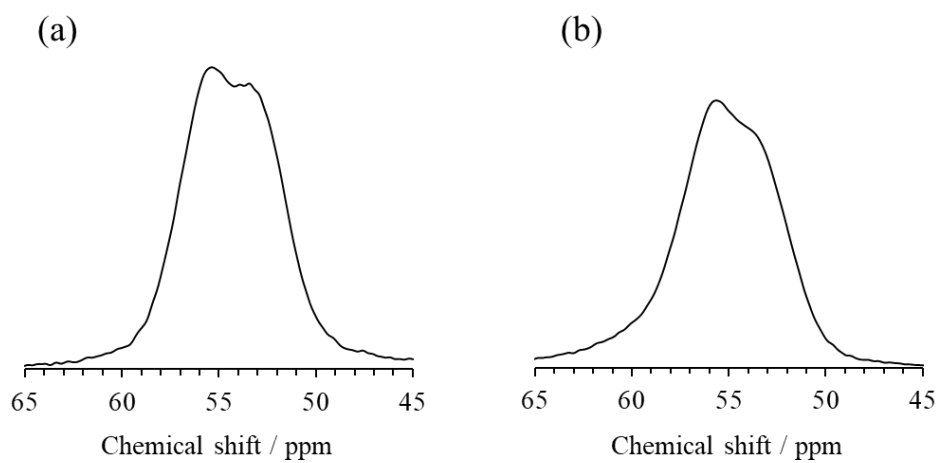


Fig. S3 ^{27}Al MAS NMR spectra of (a) NH_4^+ -MFI[TPA] and (b) NH_4^+ -MFI[TPA, Na].

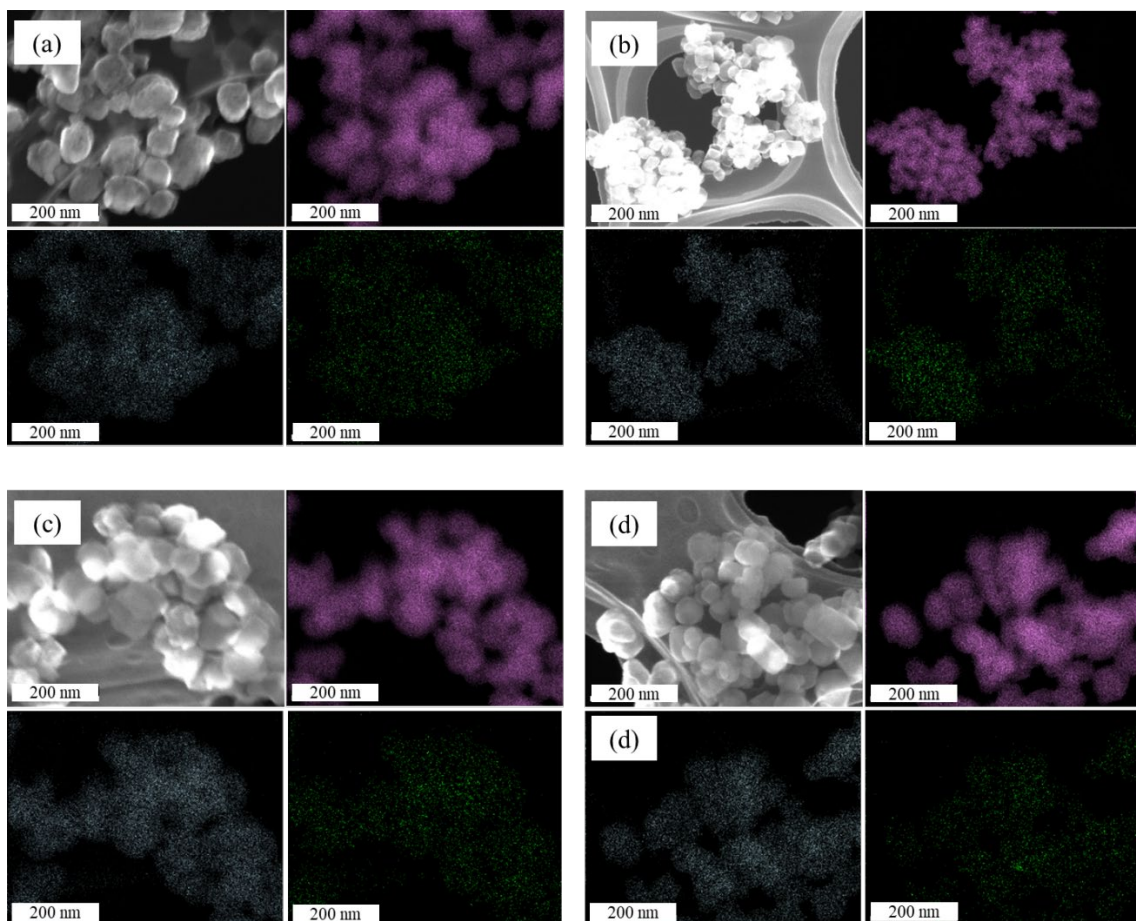


Fig. S4 SEM-EDS mapping images of Si (pink), Al (blue), and Rh (green) atoms in (a) Rh-MFI[TPA], (b) Rh-MFI[TPA, Na], (c) Rh/MFI[TPA], and (d) Rh/MFI[TPA, Na].

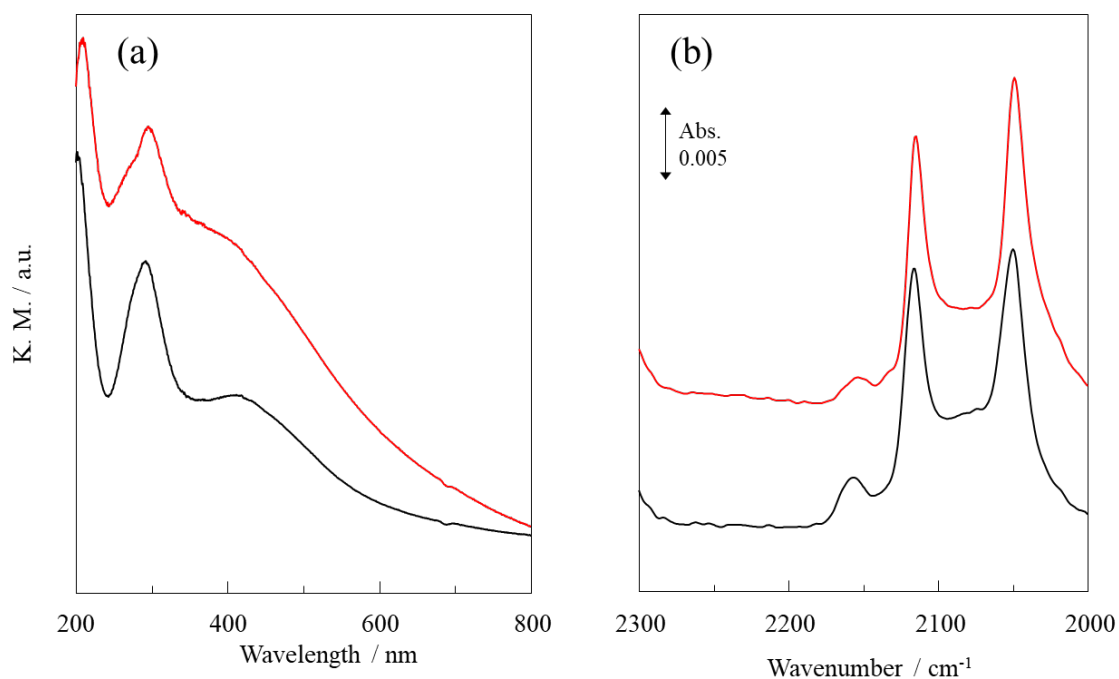


Fig. S5 (a) UV-vis spectra and (b) difference IR spectra of adsorbed CO species at 298 K; Rh/MFI[TPA] (black) and Rh/MFI[TPA, Na] (red).

Table S1 Equilibrium data for the oxidative reforming of methane under the same condition with this study.²¹

CH ₄ /O ₂ /Ar	Temperature / K	CH ₄ conversion / %	CO selectivity / %	H ₂ /CO
3.33/1.67/95	873	85	96	2.0