

Supporting Information

Highly efficient CO-assisted conversion of methane to acetic acid over Rh-encapsulated MFI zeolite prepared using RhCl₃ molten salt

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1. METHODS

Preparation of IMP_Rh/H⁺-MFI. 0.995 g of NH₄⁺-MFI (HSZ-840NHA, Si/Al= 20) with morphology and size shown in Fig. S11 was dispersed in 50 mL of distilled water, and 500 μL of a 10 g/L Rh(NO₃)₃ solution was added. The mixture was stirred at room temperature for 2 h, evaporated to dryness at 60 °C using an evaporator, and further dried overnight at 80 °C in air. The sample was reduced at 500 °C for 3 h (temperature increase rate 10 °C/min) under a 10% H₂/N₂ gas mixture (total flow rate 50 mL/min) and used for catalytic activity assay and characterization. The Rh content and Si/Al ratio were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) as 0.46 wt% and 22.0, respectively.

Preparation of RhCl₃@H⁺-MFI. NH₄⁺-MFI (HSZ-840NHA, Si/Al=20, TOSO Co., Ltd.) was calcined at 600 °C for 30 min (temperature increase rate 5 °C/min) under air, through which H⁺-MFI was obtained. 500 mg of H⁺-MFI and 9.18 mg of RhCl₃·3H₂O (FUJIFILM Wako Pure Chemicals) were well mixed with a pestle for 15 min. The mixture was transferred to a test tube and heated at 500 °C for 1 h (temperature increase rate 8 °C/min) under N₂ gas with a flow rate of 100 mL/min. After heating, the mixture was cooled to room temperature, dispersed in 50 mL of distilled water, and washed at 80 °C for 10 min with stirring. The catalyst was then centrifugated (4000 rpm, 10 min) and collected. The catalyst was again dispersed in distilled water at 80 °C, and the same washing procedure was repeated two more times. After washing, the catalyst was dried at 80 °C overnight. The Rh content and Si/Al ratio were determined by ICP-AES as 0.25 wt% and 22.0, respectively.

Catalytic Reactivity Assay. To a test tube (inner diameter 1.7 cm, length 11.5 cm), 5 mg of catalyst without any pretreatment, a magnetic stirrer, and 10 mL of distilled water were added, and the test tube was placed in a pressure-resistant reaction vessel (volume: 37.36 mL). After replacing the atmosphere within the reaction vessel with 2 bar O₂ gas five times, the reaction gases were pressurized into the tube in the order of O₂, CO, and CH₄. The purity of the reaction gases was as follows: CH₄ (Takachiho Chemical, 99.99%); O₂ (Jugo Kariya Oxygen, 99.99%); CO (Jugo Kariya Oxygen, 99.95%). The total pressure was precisely controlled from 17 to 57 bar with a pressure gauge. The reaction vessel was placed in an oil bath preheated at 150 °C, and the reaction was carried out with stirring at 1500 rpm. After the reaction, the reaction vessel was rapidly cooled with ice water for 20 min. 700 μL of the aqueous solution was collected from the system by filter syringe and placed in an NMR tube with 100 μL of 0.02 wt% 3-(trimethylsilyl)-1-propanesulfonic acid sodium salt solution as an internal standard, and ¹H NMR measurement (Avance IIIHD, 500 MHz, Bruker) was performed for the qualitative and quantitative analyses of the products (CH₃COOH, CH₃OH, HCOOH). The TOF (TOF_X) and selectivity (S_X) of each liquid phase product X (CH₃COOH, CH₃OH, or HCOOH) were calculated by the following equations

$$TOF_X (h^{-1}) = \frac{X \text{ amount (mol)}}{Rh \text{ amount (mol)} \times \text{reaction time (h)}}$$
$$S_X (\%) = \frac{X \text{ amount (mol)}}{CH_3COOH \text{ amount (mol)} + CH_3OH \text{ amount (mol)} + HCOOH \text{ amount (mol)}} \times 100$$

After the reaction, the catalyst was collected and dried at 80 °C overnight, and the catalytic reactivity assay was repeated with no additional pre-treatment. A leaching test was performed using the solution collected from the reaction system after the first reactivity assay. The amount of the Rh species eluted to the reaction solution was then analyzed by ICP.

IR Spectroscopy Using CO as a Probe Molecule. The state of Rh in the sample was investigated by DRIFT spectroscopy using CO as a probe molecule. DRIFT measurements were performed using an FT/IR-6600 (JASCO) equipped with a mercury cadmium telluride detector. The measurement range was 4000–600 cm⁻¹, the resolution was 2 cm⁻¹, and the number of integrations was 64. The sample (ca. 40 mg) was placed into the diffuse reflection cell, and the following steps were taken. First, the RhCl₃@H⁺-MFI was dehydrated at 150 °C (10 °C/min) under the flow of 100% Ar (90 mL/min) for 1 hour and then the background spectrum was collected. Next, the sample was exposed to a 0.4% CO–99.6% Ar gas mixture (total flow rate of 100 mL/min) for 10 min. After that, the atmosphere was

purged with 100% Ar (90 mL/min) for 5 min, and then CO-FTIR spectra were collected. It was confirmed that only the atmospheric CO-derived IR band disappeared during the Ar-purge processes.

XPS Spectroscopy. ESCALAB 250Xi (Thermo Fisher Scientific) with Al K α radiation from an X-ray source was used for the measurements. A carbon tape was attached to the sample holder, and an indium foil was fixed on the carbon tape. A fine groove was made on the surface of the indium foil and the sample was applied to the groove. The sample holder was placed on the apparatus and the measurement was performed. Measurements were made for 50 scans in the Rh 3d region (320–300 eV), 5 scans in the Si 2p region (110–95 eV), and 25 scans in the C 1s region (298–279 eV). The energy step size was set to 0.05 eV. XPSPEAKS41 was used for data analysis. A Shirley-type background was used. All the binding energies were calibrated using the C 1s signal as 284.8 eV. The XPS signal intensity was normalized by the area value of the Si 2p signal attributed to the surface Si species of zeolite.

Rh K-edge XAFS Spectroscopy. The Rh K-edge XAFS spectra including the X-ray absorption near edge structure (XANES) were collected at SPring-8 (BL01B1 beamline) equipped with a double crystal Si(311) monochromator. For the Rh zeolite catalysts, all measurements were made on a disk of 10 Φ in diameter in the fluorescence mode using 19-element Ge solid-state detector. XAFS spectra of reference materials (Rh foil, Rh₂O₃, and RhCl₃) were collected by the transmission mode. Athena software was used to determine the absorption edge positions, normalize XANES, perform background processing, extract EXAFS oscillations, and perform Fourier transform (FT).^[1] Fourier transformed EXAFS (FT-EXAFS) was obtained through an FT of the $k^2\chi(k)$ function in a range of 3–13 \AA^{-1} . Curve fitting analyses were performed using Artemis software. F and ϕ were obtained using FEFF6.0. Amplitude reduction factor (S_0) was calculated using Rh-foil as reference material. Wavelet transform analyses were performed using the software developed in European Synchrotron Radiation Facility.^[1-2] The $k^2\chi(k)$ functions in a range of 3–13 \AA^{-1} were wavelet transformed using a Morlet function with WT parameters of $\kappa=7$ and $\sigma=1$.

XRD. XRD measurements were performed using a Rigaku ATX-G diffractometer (Rigaku) with Cu K α radiation. Data were collected in the 2θ range of 5–50° in 0.05° steps at a continuous scan rate of 1°/min⁻¹.

DFT Cluster Calculation. The coordinate of the MFI pore was extracted from the crystallographic information file of the dehydrated MFI zeolite. The terminated parts were capped with H atoms. One Si atom located at the T7 site was replaced with an Al atom for introducing the negative charge into the zeolite structure. The [Rh(CO)₂]⁺ motif was placed in the vicinity of the framework Al atom as counter cation. All the coordinate was optimized at B3LYP/def2-TZVP, 6-31G(d) level, where def2-TZVP was used for the Rh(CO)₂ motif, whereas the 6-31G(d) basis set for the remaining atoms. The $S=0$ and 1 were considered as the possible ground electronic spin state. By comparison of the respective energies, the ground electronic structure was determined as $S=0$. The optimized geometry with a formula of Rh₁Al₁Si₁₂₇C₂H₉₂O₂₁₂ was shown in **Fig. S5**. Due to the limitation of the computational cost, the local geometry of the Rh(CO)₂ species was extracted from the optimized geometry, and used for the vibrational frequency calculation (**Fig. S6**). The energies for the symmetric and asymmetric C–O stretching vibrational modes of the [Rh(CO)₂]⁺ species were calculated at B3LYP/def2-TZVP, 6-31G(d) level and calibrated with 0.968 that was obtained from the vibrational frequency calculation of a free CO molecule at the B3LYP/def2-TZVP level. The above calculations were performed using Gaussian 16 software.^[3] Geometries were depicted using visualization for electronic and structural analysis software.^[4]

2. Supporting Data

Table S1. Best fit parameters of Rh K-edge FT-EXAFS of RhCl₃@H⁺-MFI before and after the catalytic reaction.

Sample	Scattering pair	CN	R (Å)	$\sigma^2 * 10^3$ (Å ²)	R-factor
RhCl ₃ @H ⁺ -MFI before	Rh-Cl	4.2±0.4	2.34±0.01	2.40±0.9	0.010
	Rh-Rh	1.3±0.6	2.72±0.01	3.2±2.3	
	Rh-(Cl)-Rh	2.8±1.3	3.45±0.01	7.1±2.3	
RhCl ₃ @H ⁺ -MFI after	Rh-O	3.1±0.6	2.03±0.01	6.0±2.4	0.008
	Rh-Rh	4.6±0.3	2.69±0.00	3.7±0.4	

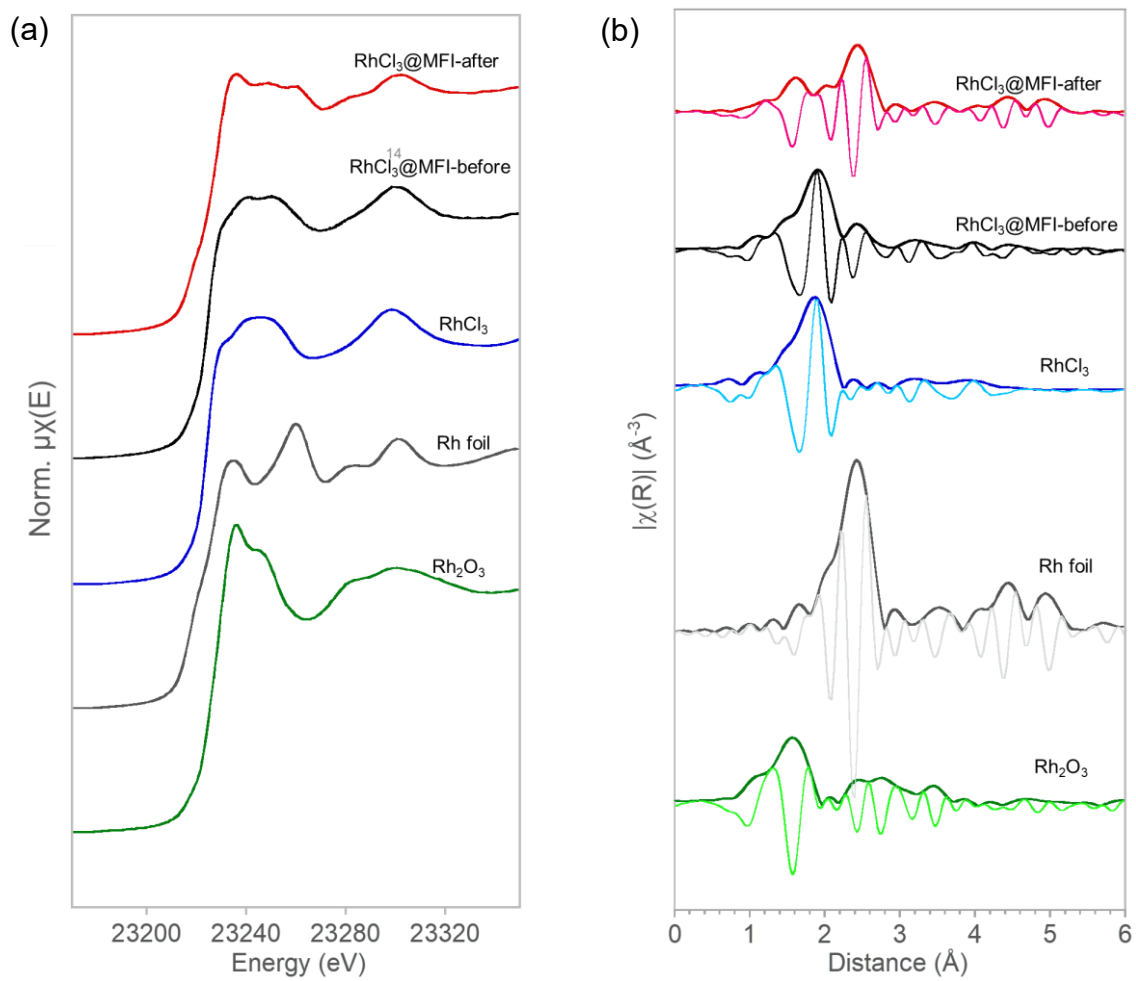


Fig. S1 Rh K-edge (a) XANES and (b) FT-EXAFS spectra of RhCl₃@MFI before and after the reaction, and reference materials: RhCl₃, Rh foil, and Rh₂O₃.

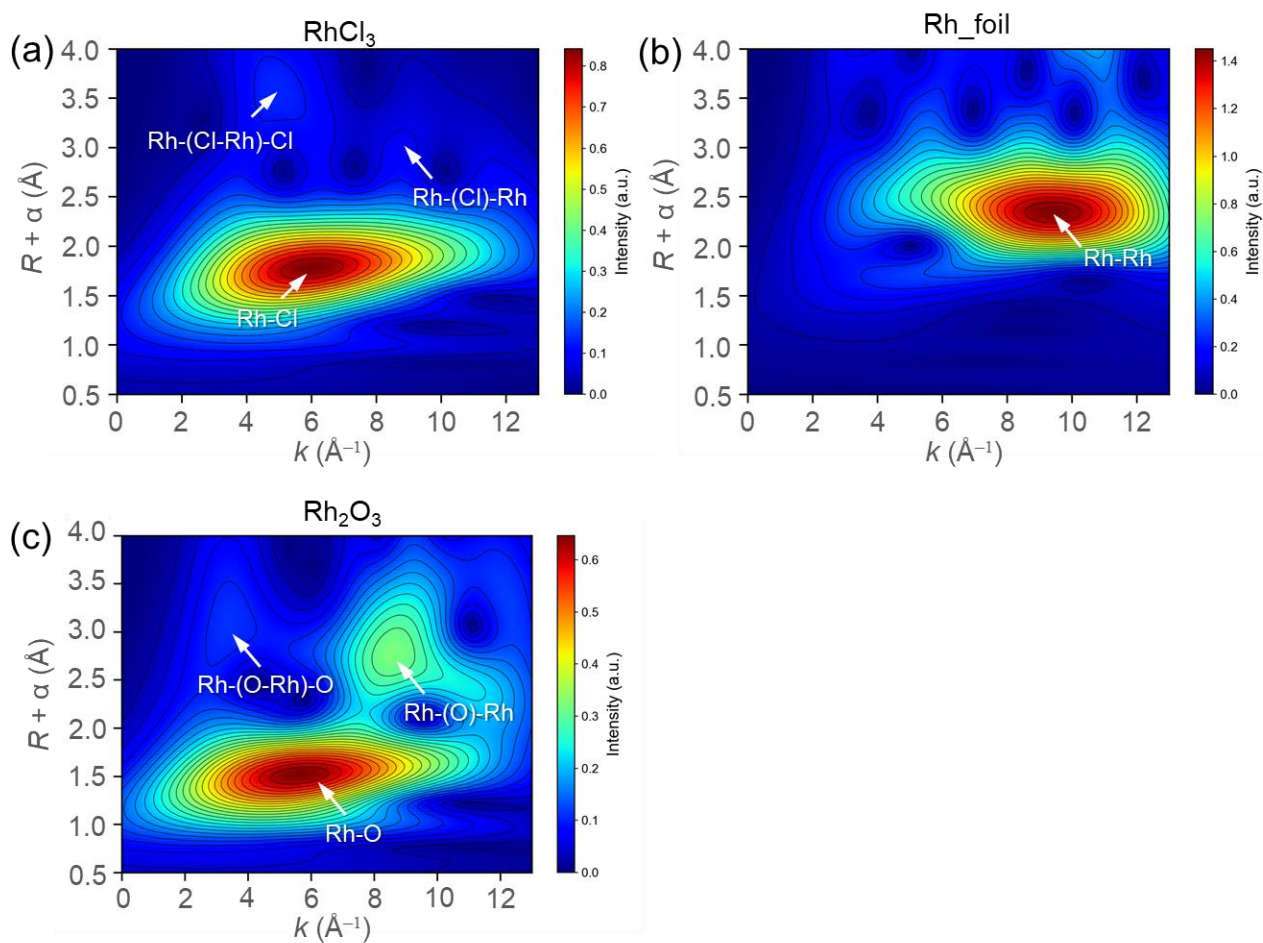


Fig. S2 WT-EXAFS of the reference materials: (a) RhCl_3 ; (b) Rh foil; (c) Rh_2O_3 .

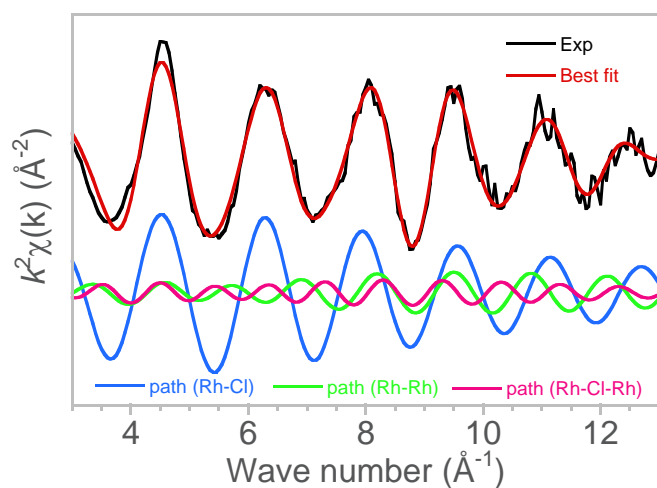


Fig. S3 Experimental and best-fit $k^2\chi(k)$ functions of Rh K-edge EXAFS of $\text{RhCl}_3@H^+$ -MFI before the catalytic reaction. The respective backscattering contributions were also given.

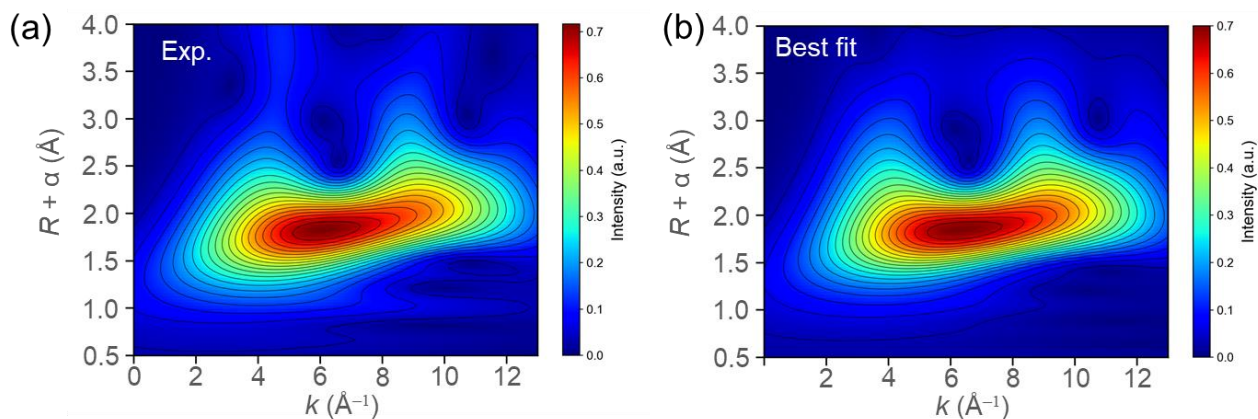


Fig. S4 WT-EXAFS of the (a) experimental and (b) best-fit $k^2\chi(k)$ functions of $\text{RhCl}_3@H^+$ -MFI before the catalytic reaction.

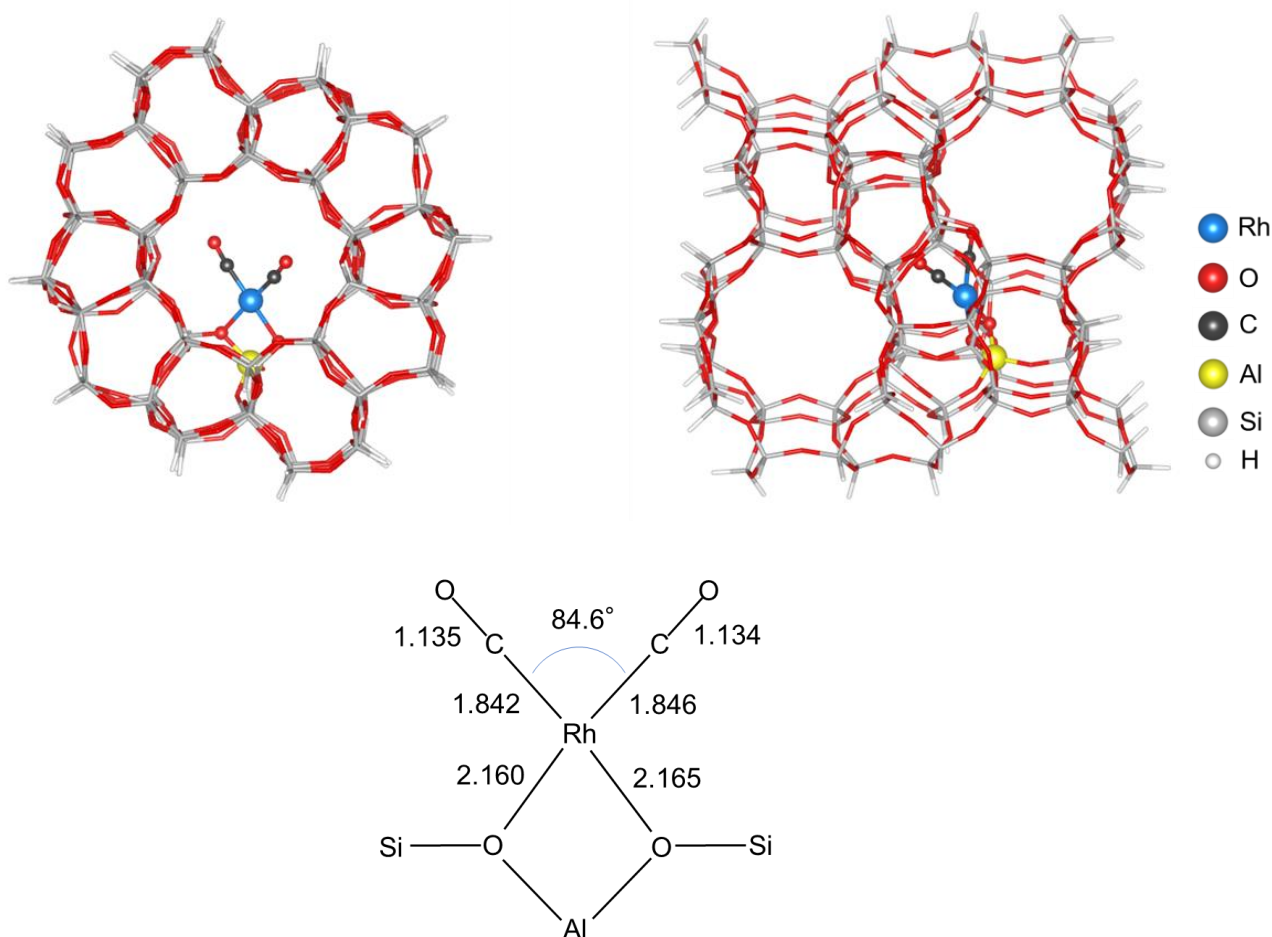


Fig. S5 Optimized DFT cluster model of the zeolite-confined $[\text{Rh}^I(\text{CO})_2]^+$ species with the formula of $\text{Rh}_1\text{Al}_1\text{Si}_{127}\text{C}_2\text{H}_{92}\text{O}_{212}$: (left) Straight channel and (right) sinusoidal channel views. A schematic view of the local structure of Rh was also given with the selected DFT parameters.

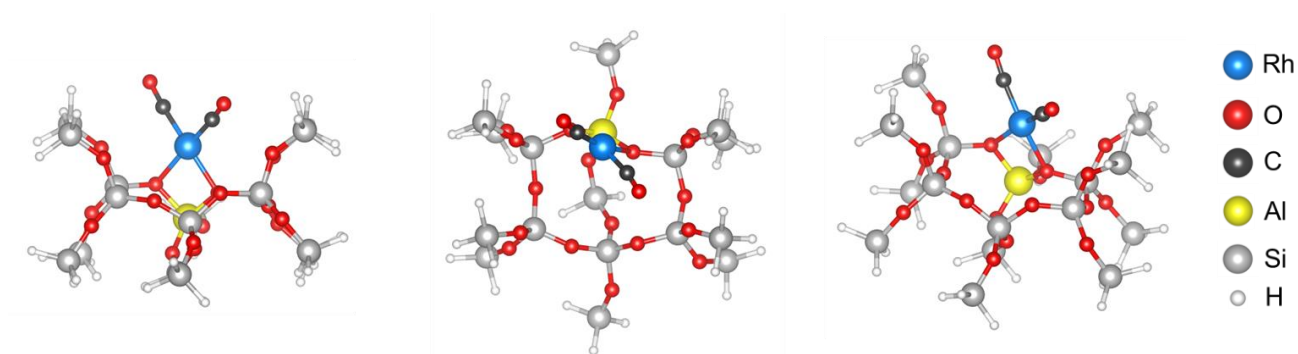


Fig. S6 DFT cluster model used for the vibrational frequency calculation of the zeolite-confined $[\text{Rh}^{\text{I}}(\text{CO})_2]^+$ species with a formula of $\text{Rh}_1\text{Al}_1\text{Si}_{16}\text{C}_2\text{H}_{32}\text{O}_{20}$. (left) front view, (middle) top view, (right) side view.

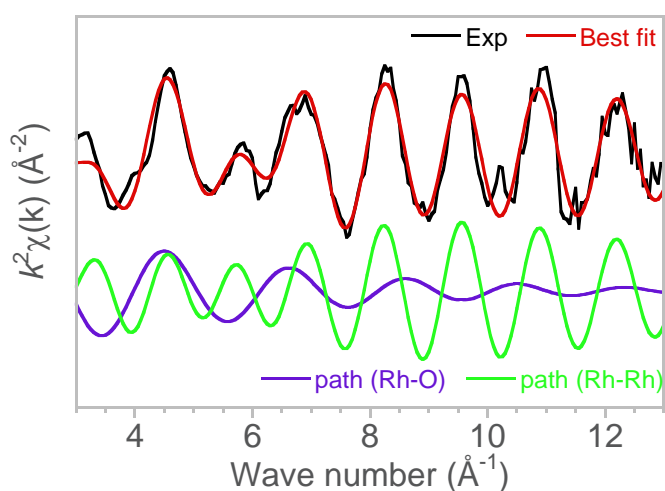


Fig. S7 (a) Experimental and best-fit $k^2\chi(k)$ functions of Rh K-edge EXAFS of $\text{RhCl}_3@H^+$ -MFI after the catalytic reaction.

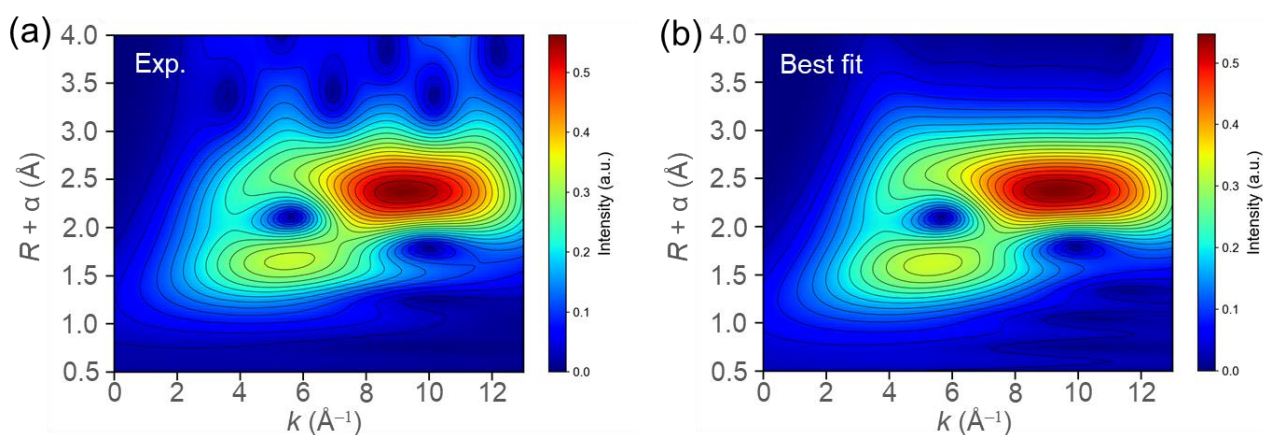


Fig. S8 WT-EXAFS of the (a) experimental and (b) best-fit $k^2\chi(k)$ functions of $\text{RhCl}_3@H^+$ -MFI after the catalytic reaction.

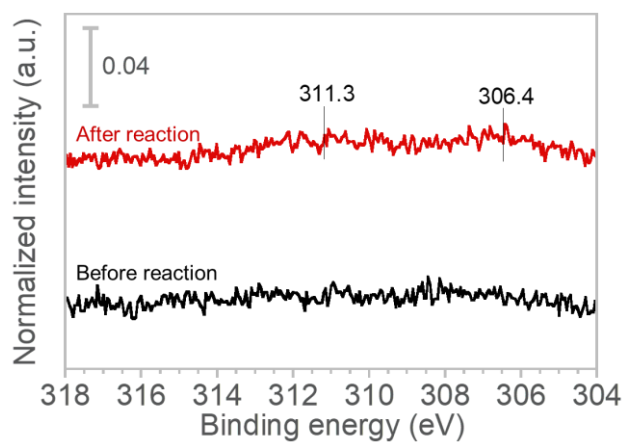


Fig. S9 Comparison of XPS spectra of $\text{RhCl}_3@H^+$ -MFI before and after the reaction.

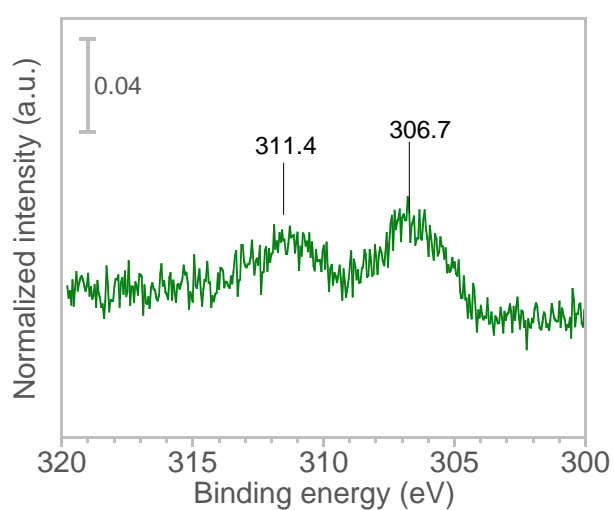


Fig. S10 XPS spectrum of the fresh IMP_Rh/H^+ -MFI.

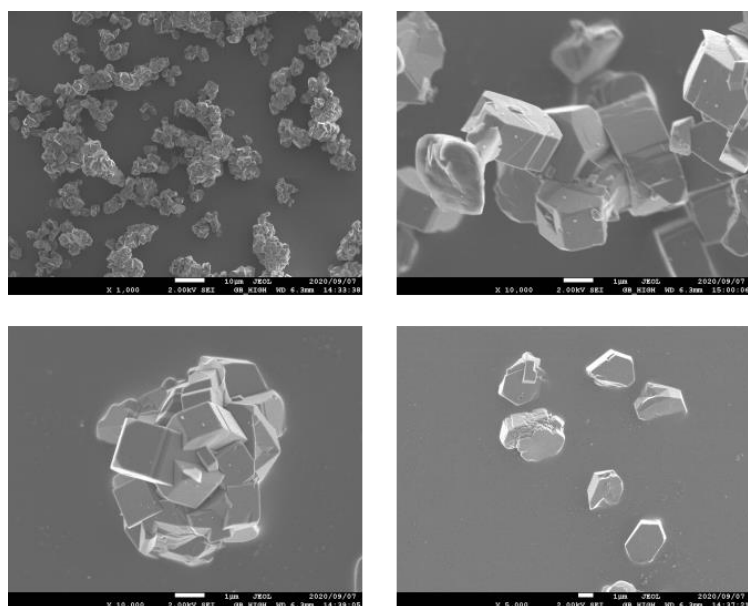


Fig. S11 SEM images of NH_4^+ -MFI used in the present study.

3. Supporting References

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