

Multi-functionality of rhodium-loaded MOR zeolite: Production of H₂ via the water gas shift reaction and its use in the formation of NH₃

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Sample preparation

The NH_4^+ -form of MOR zeolite with a Si/Al ratio of 10, denoted as $\text{NH}_4\text{-MOR}$, was supplied by Catalysis Society of Japan (JRC-Z-M20). Rh(0.6 wt%)-exchanged MOR (RhMOR) was prepared by ion-exchange of NH_4^+ -MOR (Si/Al = 10) with 0.002 M aqueous solution of RhCl_3 at 80 °C, followed by filtering, washing with distilled water (200 cm^3) three times, drying at 100 °C for 20 h, and by calcination in the air at 500 °C for 0.5 h. Rh loadings were determined by X-ray fluorescence spectroscopy (Shimadzu, EDX-700HS).

IR measurement

In situ IR measurements were carried out within transmission mode using a JASCO FT/IR-4200 spectrometer equipped with a triglycine sulfate (TGS) detector. A homemade *in situ* IR cell, set in the IR spectrometer, was connected to a conventional flow reaction system (total flow: 100 mL min^{-1}). The He flow passed through the bubbler (cooled at 0 °C) to feed H_2O into the gas mixture. The sample disk was obtained by pelletizing into a 40 mg self-supported disk and placed in the *in situ* IR cell (made by pyrex) with CaF_2 windows. IR spectra were recorded by accumulating 20 scans at a resolution of 4 cm^{-1} . The reference spectrum of the sample disk was collected under a He flow at the measuring temperature (200 °C). The gas line from the IR cell was directly connected to a homemade gas cell equipped with KBr windows to monitor the outlet gases (NO , N_2O , CO , CO_2 , and NH_3) using a JASCO FT/IR-4600 spectrometer (equipped with a TGS detector). To monitor the outlet H_2 , a mass spectrometry (BELMass, MicrotracBEL Corp.) was connected the downstream of the IR gas cell. The schematic view of the used setup is shown in **Figure S1**

Computational details

Spin-polarized density functional theory (DFT) calculations were performed using the Vienna *Ab initio* Simulation Package (VASP)^{1,2}. In particular, the projected augmented wave (PAW) method^{3,4} was employed for the Kohn–Sham equations^{5,6} with a plane-wave energy cutoff of 400 eV. The generalized gradient approximated Perdew–Burke–Ernzerhof (GGA-PBE) functional⁷ was employed to describe the electron exchange-correlation. The Brillouin zone sampling was restricted to the Γ point.⁸ Van der Waals interactions were considered using the dispersion-corrected DFT-D3 (BJ) method^{9,10}. The periodic model of the MOR

zeolite, utilized as the model zeolite for reducing computational cost for the reaction mapping, was obtained from the International Zeolite Association (IZA) database. The lattice constants of unit cell ($a = 18.2560 \text{ \AA}$, $b = 20.5340 \text{ \AA}$, $c = 15.0840 \text{ \AA}$, and $\alpha = \beta = \gamma = 90.0^\circ$) were fixed during the calculations¹¹. Among distinct T sites in the MOR framework, T4 site was applied as the Al replacement site.^{12,13} A $1 \times 1 \times 2$ of supercell was used in this study. Reaction route mapping was performed using the SC-AFIR method, as implemented in the GRRM17 program.¹⁴ A model collision energy parameter of 1000 kJ/mol was used for all calculations. Only a positive force was applied to the SC-AFIR calculations. Reactants (H_2O and CO molecules) and a Rh atom of the initial structures were considered the target atoms of the SC-AFIR algorithm. During the calculations, the positions of the atoms in the zeolite framework were fixed at the initial positions. The locally updated plane (LUP) method was used to obtain the path top (PT) points, which were subsequently re-optimized by the following intrinsic reaction coordinate (IRC) calculation to determine the transition state (TS) structures and their connectivity.¹⁵

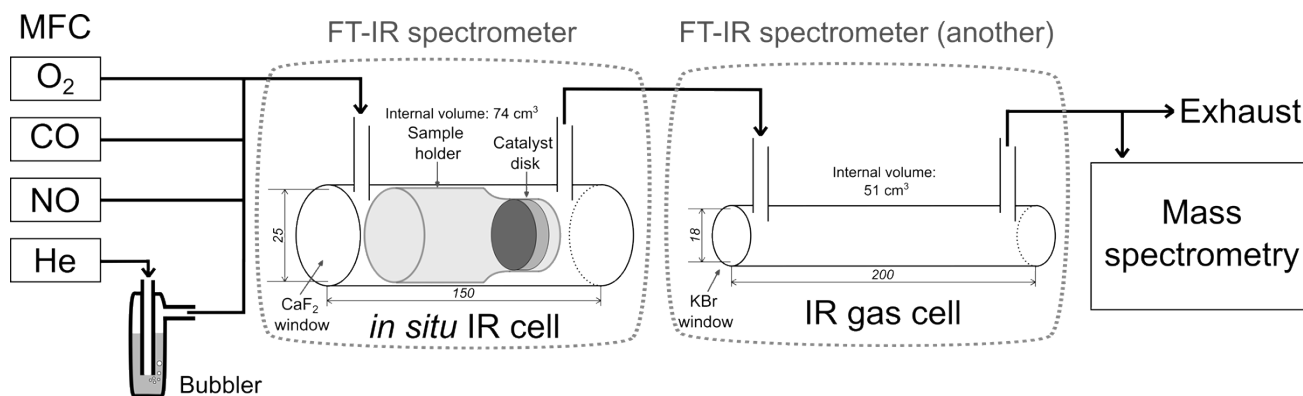


Figure S1 Schematic view of the used setup for *operando* IR measurement, including *in situ* IR cell, IR gas cell, and mass spectrometry. The inner diameter and length of the cell are provided with a unit of mm.

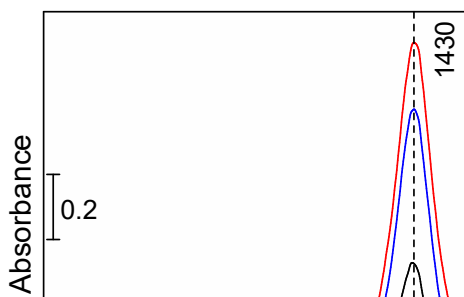


Figure S2 IR spectra during TPSR (20 °C min⁻¹) under flowing 0.1% NO + 0.5% CO + 1% H₂O over RhMOR (Figure 3).

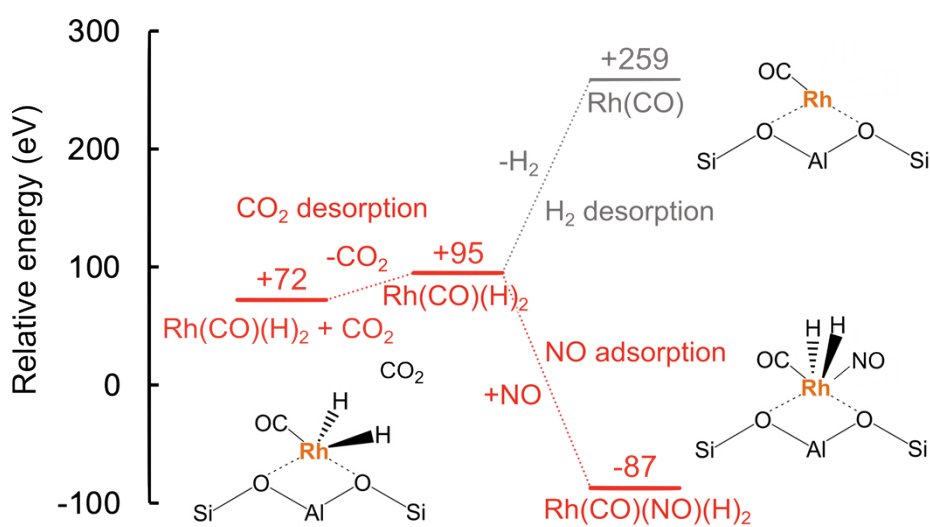


Figure S3 Energy profile for the reaction of Rh(CO)(H)₂. The reaction path shown by red and gray lines is the NO adsorption and H₂ desorption pathway, respectively. Relative energies are provided under each bar. (Unit: kJ/mol)

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