

Preferential CO oxidation in a H₂-rich stream promoted by ReO_x species attached on Pt metal particles

Yoichi Ishida ^a, Tatsuya Ebashi ^a, Shin-ichi Ito ^a, Takeshi Kubota ^a, Kimio Kunimori ^a, Keiichi Tomishige*^{a b}

Electronic supplementary information

Details of procedures in catalyst preparation

A Pt/SiO₂ catalyst was prepared by impregnating SiO₂ with an aqueous solution of Pt(NO₂)₂(NH₃)₂ (SOEKAWA CHEMICALS, Assay(Pt) 60%). The SiO₂ (CARiACT G-6 from Fuji Silysia Chemical Ltd, BET surface area, 492 m²/g) was supplied by Fuji Silysia Chemical Ltd. And this SiO₂ was used in powdery form with granule size of < 100 mesh. After the impregnation procedure and drying at 383 K for 12 h, the catalyst was calcined in air at 773 K for 3 h. Pt-ReO_x/SiO₂ was prepared by impregnating Pt/SiO₂ after the drying procedure with an aqueous solution of NH₄ReO₄ (SOEKAWA CHEMICALS, Purity 99.9%). Loading amount of Pt on the catalysts was 2%. The loading amount of Re is denoted as the molar ratio of Re/Pt in parentheses such as Pt-ReO_x/SiO₂ (Re/Pt=0.5).

Details of procedures in catalyst reaction tests

The activity tests of CO oxidation in H₂-rich stream were carried out in a fixed-bed flow reaction system at atmospheric pressure using 33 mg of the catalyst at the total flow rate of 50 cc/min (GHSV= 90,000 h⁻¹). The feed stream contained 1.0% CO, 1.25% O₂, 60% H₂, 20% CO₂, and 10% H₂O balanced with He, which denoted as the PROX+H₂O+CO₂. The CO+O₂ reaction was also tested. The feed stream contained 1.0% CO, 1.25% O₂ balanced with He. Steam was supplied to the reactor using a pump through the thin tube in the preheater. The effluent gas was analyzed using an on-line gas chromatograph (GC) system equipped with a TCD detector. In addition, the concentration at ppm level of CO in the effluent gas was determined using FID-GC equipped with methanator. Conversion of CO was calculated on the basis of CO concentration in the effluent gas. In addition, the methane concentration in the effluent gas was below the detection limit in all the cases. The selectivity of CO oxidation is defined as the ratio of O₂ consumption for the CO oxidation to total O₂ consumption, it was estimated by using CO and O₂ concentrations in the effluent gas. Furthermore, we also measured the activity of water gas shift reaction,

under 1.0% CO, 10% H₂O balanced with He. The activity in water gas shift reaction was much lower than that in the PROX+H₂O+CO₂. It is concluded that high activity in the PROX is not due to the water gas shift reaction. The activity was measured during 30 min under each reaction condition at least and severe deactivation was not observed at all.

Details of measurement of CO adsorption amount

The amount of CO chemisorption was measured in a high-vacuum system using a volumetric method. Before adsorption measurements, the catalysts were treated in H₂ at 773 K for 1 h. Subsequently, the adsorption was performed at room temperature. Gas pressure at adsorption equilibrium was about 1.1 kPa. The sample weight was about 0.15 g. The dead volume of the apparatus was about 60 cm³. Adsorption amount of CO is represented as the molar ratio to Pt and this corresponds to the number of the surface atoms assuming that the stoichiometry of adsorbed CO species to surface Pt atom is one, which can be catalytically active sites. A particle size based on the CO adsorption was calculated by the equation.

$(d / \text{nm} = 113.5/D, D$ is the dispersion calculated from the amount of CO adsorption)^[S1]

Details of the TEM observation

The catalysts after the reaction were dispersed ultrasonically in ethanol and deposited on microgrids for transmission electron microscopy (TEM) in air. After drying, the samples were observed by a transmission electron microscope (JEOL JEM 2010) with an accelerating voltage of 200 kV to measure the particle size. Figure S1 shows TEM images of the reduced Pt/SiO₂ and Pt-ReO_x/SiO₂ (Re/Pt=0.5). Metal particles are observed as dark spherical spots in S1. The average size of metal particles (d_s) was calculated using $\sum n_i d_i^3 / \sum n_i d_i^2$ (d_i , particle size; n_i , number of particles with d_i).^[S1] The average size of metal particles of the Pt/SiO₂ and Pt-ReO_x/SiO₂ (Re/Pt=0.5) was estimated to be 4.0±0.3 nm and 4.4±0.3 nm, respectively.

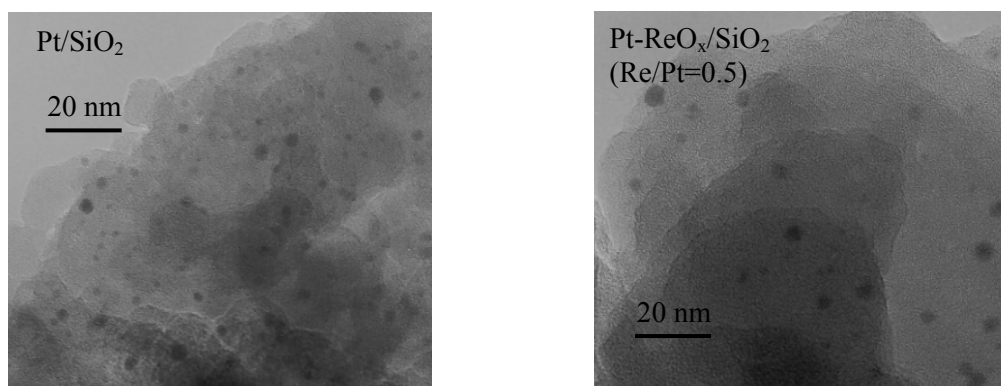


Figure S1. TEM image of Pt/SiO₂ and Pt-ReO_x/SiO₂ (Re/Pt=0.5) after the reduction at 773 K.

Details of the TPR measurement

Temperature-programmed reduction (TPR) with H₂ was performed in the fixed-bed flow reactor. The TPR profile of each sample was recorded from room temperature to 1123 K under a flow of 5.0% H₂/Ar, and the flow rate was 30 ml/min. The catalyst weight was 0.05 g. The heating rate was 10 K/min. The consumption of H₂ was monitored continuously with TCD gas chromatograph equipped with frozen acetone trap in order to remove H₂O from the effluent gas. The profiles are shown in Figure S2

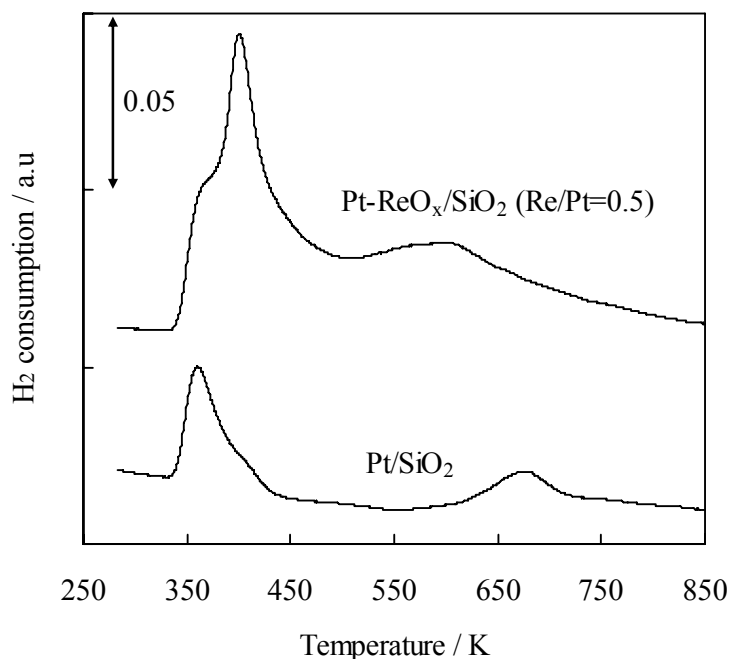


Figure S2 Results of TPR profiles of Pt/SiO₂ and Pt-ReO_x/SiO₂(Re/Pt=0.5)

Details of the X-ray absorption spectroscopic analysis

The Re *L*₃-edge and Pt *L*₃-edge extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) were measured at the BL01B1 station at SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI; Proposal No. 2008B1235). The storage ring (SPring-8) was operated at 8.0 GeV. A Si (111) single crystal was used to obtain a monochromatic X-ray beam. The monochromator was detuned to 60% maximum intensity to avoid higher harmonics in the X-ray beam. Two ion chambers filled with N₂ and 15% Ar diluted with N₂ were used as detectors of *I*₀ and *I*, respectively. The spectra of the catalysts after various pretreatment were obtained. The pretreatment of samples were reduced with hydrogen at 473-773 K for 1 h. After the pretreatment, we transferred the samples to the measurement cell without exposing the sample disk to air, using a glove box filled with nitrogen. Sample weights were almost 50 mg and the edge jump of 0.17 for Re *L*₃-edge and 0.37 for Pt *L*₃-edge. The data were collected in a transmission mode at room temperature. For EXAFS analyses, the oscillation was first extracted from EXAFS data using a spline smoothing method.^[S2] The oscillation was normalized by the edge height around 50 eV. Fourier transformation of the *k*⁰-weighted EXAFS

oscillation from k space to r space was performed to obtain a radial distribution function. The inversely Fourier-filtered data were analyzed using a curve-fitting method.^[S3, 4] The Fourier transform and Fourier filtering ranges are shown for each result. For the curve fitting analysis, the empirical phase shift and the amplitude function for the Re-O, Re-Re and Re-Pt bonds were extracted from data of NH_4ReO_4 , Re powder and Pt foil, respectively. Theoretical functions for the Re-Pt bond were calculated using the FEFF program.^[S5] The first peak in the L_3 -edge XANES is called as a white line, and the white line intensity of the Pt L_3 -edge and Re L_3 -edge XANES is known to be an informative indication of electronic state of Pt and Re; the larger white line is due to greater electron vacancy in d-orbital.^[S6] As reported previously, a relative electron deficiency and ionic valence can be determined on the basis of the white line intensity.^[S7-10] Analyses of EXAFS and XANES data were performed using a computer program (REX2000 Ver. 2.3.3; Rigaku Corp.). Figure S3 shows the Re L_3 -edge XANES and the relation between white line area and valence of Re. The valence of Re on $\text{Pt-ReO}_x/\text{SiO}_2$ (Re/Pt=0.5) reduced at various temperatures can be determined by the relation and the result are plotted in Figure 2.

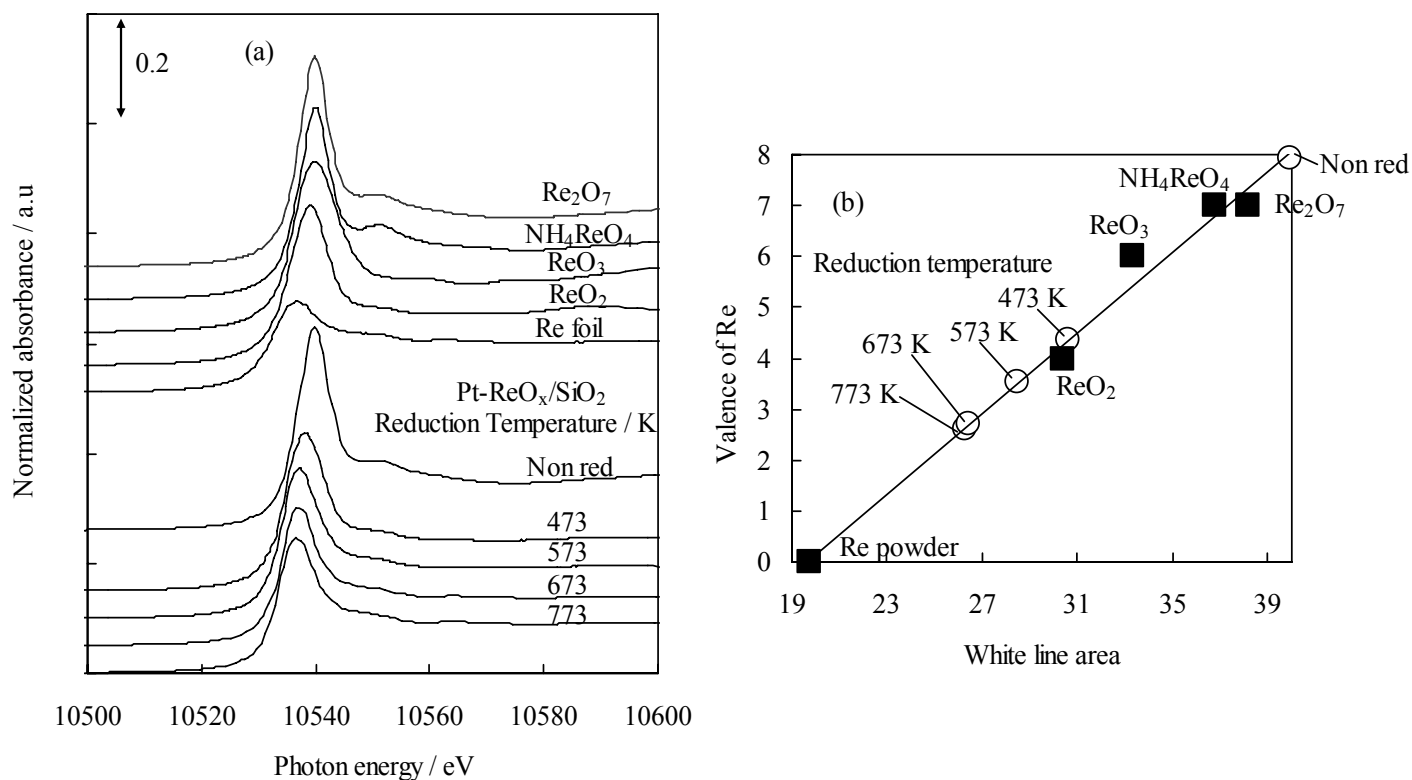


Figure S3 Results of Re L_3 -edge XANES spectra (a) and the relation between white line area and valence of Re on model compounds (■) and $\text{Pt-ReO}_x/\text{SiO}_2$ (Re/Pt=0.5) (○) (b).

Figures S4 and S5 show the Pt L_3 -edge and Re L_3 -edge EXAFS of $\text{Pt-ReO}_x/\text{SiO}_2$ (Re/Pt=0.5) after the reduction at 773 K. Generally speaking, it is difficult to distinguish between Re and Pt atoms as a scattering atom in the curve fitting analysis. However, according to the previous report,^[S11] it is possible

to overcome the difficulty by adopting the curve fitting analysis based on $k^0 \chi(k)$. Curve fitting results are listed in Table 1.

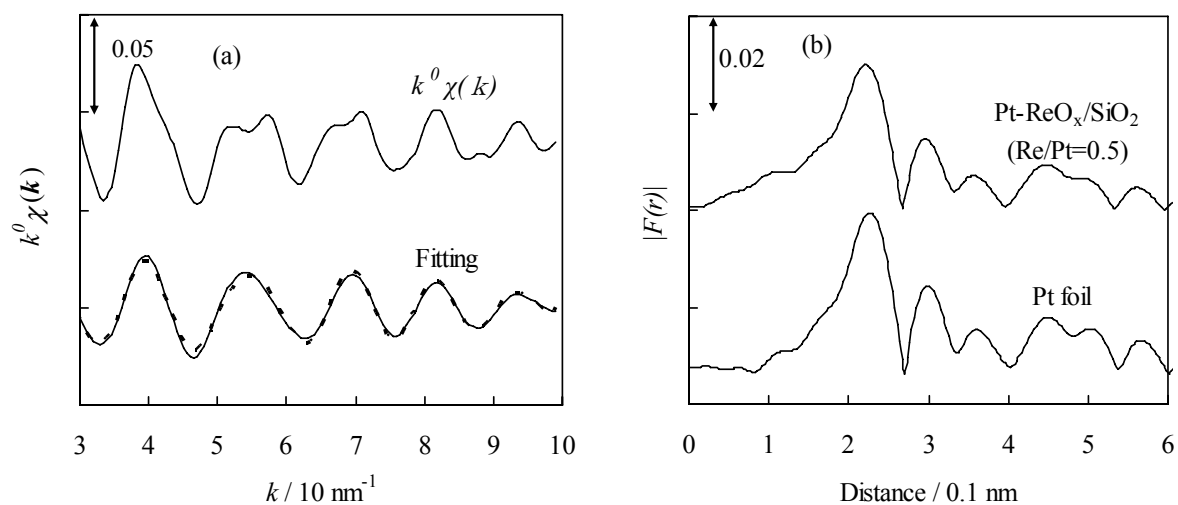


Figure S4 Results of Pt L_3 -edge EXAFS analysis of Pt-ReO_x/SiO₂(Re/Pt=0.5) after the reduction at 773 K.

(a) k^0 -weighted EXAFS oscillations and Fourier filtered EXAFS data (solid line) and calculated data (broken line), Fourier filtering range: 0.144-0.328 nm (Pt-ReO_x/SiO₂(Re/Pt=0.5)), (b) Fourier transform of k^0 -weighted Pt L_3 -edge EXAFS, FT range: 30-100 nm⁻¹ (Pt foil, Pt-ReO_x/SiO₂(Re/Pt=0.5))

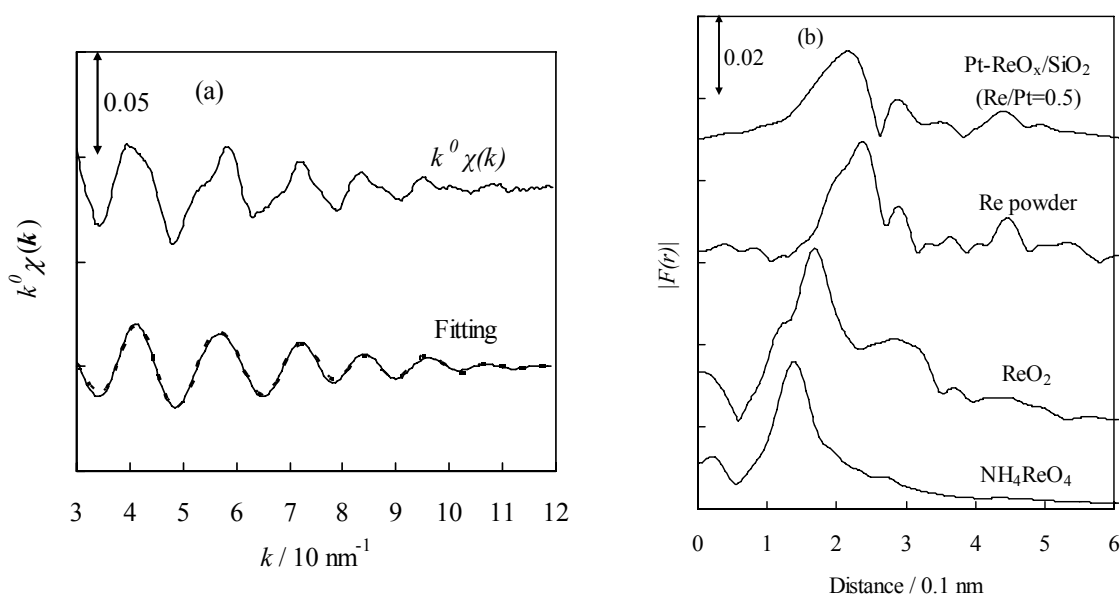


Figure S5 Results of Re L_3 -edge EXAFS analysis of Pt-ReO_x/SiO₂(Re/Pt=0.5) after the reduction at 773 K.

(a) k^0 -weighted EXAFS oscillations and Fourier filtered EXAFS data (solid line) and calculated data (dots), Fourier filtering range: 0.129-0.316 nm (Pt-ReO_x/SiO₂(Re/Pt=0.5)), (b) Fourier transform of k^0 -weighted Re L_3 -edge EXAFS, FT range : 26-120 nm⁻¹ (Re powder, ReO₂, Pt-ReO_x/SiO₂(Re/Pt=0.5)), FT range : 30-120 nm⁻¹ (NH₄ReO₄)

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