Electronic Supplementary Information

Crucial Role of Oxygen Vacancy in Molybdenum Sub-oxide that Promotes CO₂ Hydrogenation to Methanol

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Experimental Procedures

Chemicals. Hexaammonium heptamolybdate tetrahydrate ((NH₄)₆Mo₇O₂₄·4H₂O), tungsten(VI) oxide (WO₃), zinc(II) oxide (ZnO), and ruthenium(III) chloride hydrate (RuCl₃·nH₂O) were purchased from Wako Pure Chemical Industries, Ltd. Fumed silica (SiO₂), molybdenum(IV) oxide (MoO₂), cerium(IV) oxide (CeO₂), and ammonium perrhenate(VII) (NH₄ReO₄) were purchased from Sigma-Aldrich Co. Potassium tetrachloroplatinate(II) (K₂PtCl₄), disodium tetrachloroplaladate(II) (Na₂PdCl₄), copper(II) nitrate trihydrate (Cu(NO₃)₂·3H₂O), vanadium(V) oxide (V₂O₅), urea, and other commercially available chemical reagents for catalytic tests were purchased from Nacalai Tesque, Inc. α-MoO₃ was prepared by calcination of (NH₄)₆Mo₇O₂₄·4H₂O for 4 h at 500 °C in air. Nb₂O₅ (JRC-NBO-2), γ-Al₂O₃ (JRC-ALO-4), anatase TiO₂ (JRC-TIO-8), and ZrO₂ (JRC-ZRO-2) as catalyst supports were supplied from the Catalysis Society of Japan. All chemicals were used as received without further purification.

CO pulse measurement. CO pulse measurement was carried out using a BEL-METAL-1 system (MicrotracBEL Corp.) equipped with a TCD detector. A sample (ca. 50 mg) mounted in a glass vessel were pretreated in a flow of H_2 (50 mL/min) at a designated temperature (100-400 °C) for 30 min to reduce the sample, and then cooled to 50 °C. CO pulse (1% CO/He) was repeatedly injected to the vessel at 50 °C, and the adsorbed amount of CO was quantified.

Diffuse reflectance UV-vis-NIR measurement. Diffuse reflectance UV-vis-NIR spectra were measured at room temperature with a Shimadzu UV-2600 spectrophotometer equipped with an integrating sphere at room temperature. The Kubelka-Munk transformation was used to convert the measured spectra into absorption spectra.

 CO_2 adsorption measurement. CO_2 adsorption measurement was performed at 25 °C using a BELSORP-max system (MicrotracBEL Corp.). Samples were degassed at 150 °C for at least 3 h under vacuum to remove physisorbed molecules prior to each measurement.



Fig. S1 (a) Pt L3-edge X-ray absorption near edge structure (XANES) spectra and (b) the corresponding Fourier transforms of extended XAFS spectra of Pt/H_xMoO_{3-y} catalysts synthesized with varied Pt contents and several Pt references (Pt foil, K₂PtCl₄, and PtO₂).



Fig. S2 Pt 4*f* XPS spectra of unreduced Pt/MoO₃ and Pt/H_xMoO_{3-y} catalysts reduced with H₂ at different temperatures (100-300 °C).

The predominant peaks located at 74.8 and 71.5 eV are assigned to $4f_{5/2}$ and $4f_{7/2}$ orbital electrons of Pt⁰ species, respectively, while the peaks located at 75.8 and 72.5 eV are attributed to those of Pt²⁺ species. As-prepared unreduced Pt/MoO₃ dominantly exhibits the peaks attributable to Pt²⁺ species, which accounts for 95% of all Pt atoms. After H₂ reduction, the Pt/H_xMoO_{3-y} catalysts display doublet peaks which correlate well with metallic Pd⁰ species. Based on the fitting analysis, the proportion of Pt⁰ species was determined as; Pt/H_xMoO_{3-y}(100) (81%) = Pt/H_xMoO_{3-y}(200) (81%) < Pt/H_xMoO₃. (300) (86%), demonstrating that the Pt species are mostly reduced to metallic Pd⁰ nanoparticles after H₂ reduction.

Table S1	Summary o	of the resul	ts of Pt 4 <i>f</i>	XPS meas	urement
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Sample -	Atomic concentration [%]		
	Pt ⁰	Pt ²⁺	Pt ⁴⁺
Unreduced Pt/MoO ₃	0	95	5
Pt/H _x MoO _{3-y} (100)	81	19	0
$Pt/H_xMoO_{3-y}(200)$	81	19	0



Fig. S3 Relationship between the catalytic activities in the CO₂ hydrogenation and the mean surface areas of surface-exposed Pt atoms determined by CO pulse measurement for Pt/H_xMoO_{3-y} catalysts synthesized with varied Pt loadings (0.11-1.58 wt%). *Reaction conditions*: catalyst (50 mg), 1,4-dioxane (15 mL), $P_{CO2} = 1.0$ MPa, $P_{H2} = 3.0$ MPa, 200 °C, 20 h.

Pt loading [wt%]	Volume of CO adsorbed [cm ³ /g-sample]	Metal dispersion [%]	Surface area of metal [m²/g-sample]	Average diameter of metal particle [nm]
0.11	3.5×10 ⁻²	27.9	7.6×10 ⁻²	4.1
0.38	9.4×10 ⁻²	21.4	20.1×10 ⁻²	5.3
0.64	17.7×10-2	24.1	38.1×10-2	4.7
1.30	30.0×10 ⁻²	20.4	65.4×10 ⁻²	5.5
1.58	36.2×10 ⁻²	20.0	77.8×10 ⁻²	5.7

Table S2 Summary of the results of CO pulse measurement for Pt/H_xMoO_{3-y} catalysts synthesized with varied Pt loadings (0.11-1.58 wt%).



Fig. S4 GC-MS spectra of methanol produced by the hydrogenation of ${}^{13}CO_2$, ${}^{12}CO_2$ using Pt/H_xMoO_{3-y}(300) catalyst, and that of standard ${}^{12}CH_3OH$.



Fig. S5 Comparison of catalytic performance of various oxide-supported Pt catalysts in (a) the liquid-phase CO₂ hydrogenation reaction (*Reaction conditions*: catalyst (50 mg), 1,4-dioxane (15 mL), $P_{CO2} = 1.0$ MPa, $P_{H2} = 3.0$ MPa, 200 °C, 20 h) and (b) the liquid-phase CO₂ deoxygenation reaction (*Reaction conditions*: catalyst (50 mg), 1,4-dioxane (15 mL), $P_{CO2} = 1.0$ MPa, 200 °C, 20 h). Catalysts were all reduced at 300 °C for 30 min in a flow of H₂ prior to the reaction.



Fig. S6 Diffuse reflectance UV-vis-NIR spectra of MoO₃, unreduced Pt/MoO₃ and Pt/H_xMoO_{3-y}(T) catalysts reduced with H₂ at different temperatures.



Fig. S7 (a) Mo K-edge X-ray absorption near edge (XANES) spectra and (b) the corresponding Fourier transforms of extended XAFS spectra of unreduced Pt/MoO₃ and Pt/H_xMoO_{3-y}(*T*) catalysts reduced with H₂ at different temperatures and some Mo references (Mo foil, MoO₃ and MoO₂).

In Mo K-edge XANES spectra, bulk MoO₃ with an orthorhombic structure (space group *Pbnm*) exhibits a pronounced pre-edge absorption feature at 20005 eV because it is composed of distorted MoO₆ octahedra, while MoO₂ with a monoclinic structure (space group $P2_1/c$) exhibits a significantly diminished pre-edge absorption due to a fairly perfect octahedral symmetry. The shape of XANES spectra of unreduced sample is almost identical to that of MoO₃. When the catalyst is reduced at elevated temperatures, the pre-edge absorption is significantly diminished and the absorption edge position clearly shifts toward lower energy region. This result indicates a gradual transformation of Mo local structure from distorted octahedral geometry to symmetric octahedral geometry, which corresponds to the phase transition from orthorhombic MoO₃ to monoclinic H_{0.9}MoO₃ and further deep reduction to H_xMoO_{3-y} sub-oxide as confirmed by XRD.

In radial distribution functions (RDFs) obtained from extended XAFS spectra, the contiguous peaks seen at around 1.1 and 1.8 Å (phase shift uncorrected) can be attributed to the molybdenum oxo (Mo=O) species and doubly/triply coordinated O (Mo₂-O/Mo₃-O) species, while the peak at around 3.2 Å corresponds to Mo–(O)–Mo bonds.^{1, 2} The shape of RDFs of unreduced sample is almost identical to those of MoO₃.

When the reduction temperature is raised above 100 °C, the peak assignable to Mo–O bond shifts to longer interatomic distance and appears at around 1.65 Å, again confirming the phase transition from orthorhombic MoO₃ to monoclinic H_{0.9}MoO₃. When the reduction temperature is raised above 300 °C, the peak assignable to Mo–(O)–Mo bond is significantly diminished, suggesting the formation of H_xMoO_{3-y} sub-oxide possessing considerable amount of oxygen vacancies.



Fig. S8 Weight changes of the Pt/H_xMoO_{3-y}(*T*) catalysts reduced with H₂ at (a) 100 °C, (b) 200 °C, (c) 300 °C, and (d) 400 °C in a flow of either air or N₂ measured by thermogravimetric (TG) analysis.

For the Pt/H_xMoO_{3-y}(*T*) samples measured in a N₂ environment, initial weight losses seen at temperatures below 200 °C are due to the evaporation of surface adsorbed water molecules. Subsequently, they show further weight losses from 200 °C to 450 °C, which are associated with the thermal dehydration of –OH groups to form MoO_{3-x} sub-oxides (H_xMoO_{3-y} \rightarrow MoO_{3-y-x/2} + 1/2x H₂O).^{3,4} This weight loss is hardly seen for the sample possessing MoO₂ crystalline phase with smaller amount of intercalated H⁺ (Pt/H_xMoO_{3-y} (400)). In comparison, different TG profiles are observed in a flow of air due to the weight gain associated with the filling (oxidation) of oxygen vacancies with molecular O₂ to form MoO₃, in addition to the release of intercalated H⁺ as water (H_xMoO_{3-y} + O₂ \rightarrow MoO₃ + 1/2x H₂O).⁵ For the Pt/H_xMoO_{3-y}(300) sample measured in an air environment, a considerable weight gains of 4.8 wt% was observed at temperatures from 200 to 450 °C due to the presence of substantial amount of oxygen vacancy in the sample.

Based on the weight changes associated with the release of intercalated H⁺ (in N₂ environment) and the filling of V₀ (in air environment), the stoichiometric composition was determined as H_{1.76}MoO_{2.99} (100 °C reduction) \rightarrow H_{1.15}MoO_{2.72} (200 °C reduction) \rightarrow H_{0.35}MoO_{2.26} (300 °C reduction) \rightarrow H_{0.02}MoO_{1.96} (400 °C reduction) from the results of TG analysis, respectively, ascertaining a gradual reduction of intercalated H atoms and a substantial increase of oxygen vacancies at elevated reduction temperatures.



Fig. S9 CO₂ adsorption isotherms of unreduced Pt/MoO₃ and Pt/H_xMoO_{3-y}(300) measured at 25 °C.



Fig. S10 Mo 3*d* XPS spectra of Pt/H_xMoO_{3-y}(300) catalyst upon a treatment with 1.0 MPa CO₂ at 200 °C for 20 h.



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