

Supporting information

Highly Active and Durable Rh–Mo-Based Catalyst for the NO–CO–C₃H₆–O₂ Reaction Prepared by Using Hybrid Clustering

Shun Hayashi^{†,*}, Shinji Endo[‡], Hiroki Miura^{‡,§,||}, Tetsuya Shishido^{‡,§,||,*}

[†]Division of Physical Sciences, Department of Science and Engineering, National Museum of Nature and Science, Ibaraki 305–0005, Japan

[‡]Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, Tokyo 192–0397, Japan

[§]Research Center for Hydrogen Energy–Based Society, Tokyo Metropolitan University, Tokyo 192–0397, Japan

^{||}Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Kyoto 615–8520, Japan

E-mail: s-hayashi@kahaku.go.jp (SH); shishido-tetsuya@tmu.ac.jp (TS)

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1. Chemicals. (Pentamethylcyclopentadienyl)Rhodium(III) dichloride dimer was purchased from TCI. Rhodium(III) chloride, ammonium molybdate(VI) tetrahydrate, disodium molybdate(VI) dihydrate, and ammonium metavanadate were purchased from Wako Chemicals. Sodium metavanadate was obtained from Nacalai Tesque. γ -Al₂O₃ (Sumitomo Chemical, AKP-G015; JRC-ALO-8 equivalent) was supplied by the Catalysis Society of Japan. Before use, γ -Al₂O₃ was calcined under air flow at 773 K for 3 h. Deionized water (Milli-Q, >18 M Ω cm) was used in all experiments.

2. Synthesis of hybrid clusters. [(RhCp*)₄Mo₄O₁₆] was synthesized as per a literature procedure.^{S1} Na₂MoO₄·2H₂O (1.58 g, 6.53 mmol) was dissolved in water (6.4 mL), and [RhCp*Cl₂]₂ (400 mg, 0.653 mmol) was added. The mixture was then stirred for 4 h at room temperature. After the reaction, the mixture was concentrated by using a rotary evaporator and the product was extracted with dichloromethane (DCM). The DCM layer was washed with water, and the crude product was obtained by evaporating the solvent. The purified product was obtained via recrystallization from DCM/toluene. IR (KBr pellet, cm⁻¹): 924, 899, 683, 635, 576, 536. ¹H NMR (CDCl₃): 1.75 (s). ¹³C{¹H} NMR (CDCl₃): δ 9.13 (s), 90.35 (d, J_{C-Rh} = 9.5 Hz).

[(RhCp*)₄V₆O₁₉] was synthesized according to a literature procedure.^{S2} NaVO₃ (800 mg, 6.56 mmol) was added to water (20 mL) and stirred for 2 h for complete dissolution. [RhCp*Cl₂]₂ (400 mg, 0.653 mmol) was then added, and the mixture was stirred for 4 h at room temperature. After the reaction, the mixture was concentrated by using a rotary evaporator and the product was extracted with DCM. The DCM layer was washed with water, and the crude product was obtained by evaporating the solvent. The purified product was obtained via recrystallization from DCM/toluene.

IR (KBr pellet, cm⁻¹): 935, 683, 557, 488. ¹H NMR (CDCl₃): 1.94 (s). ¹³C{¹H} NMR (CDCl₃): δ 9.39 (s), 94.17 (d, J_{C-Rh} = 8.6 Hz).

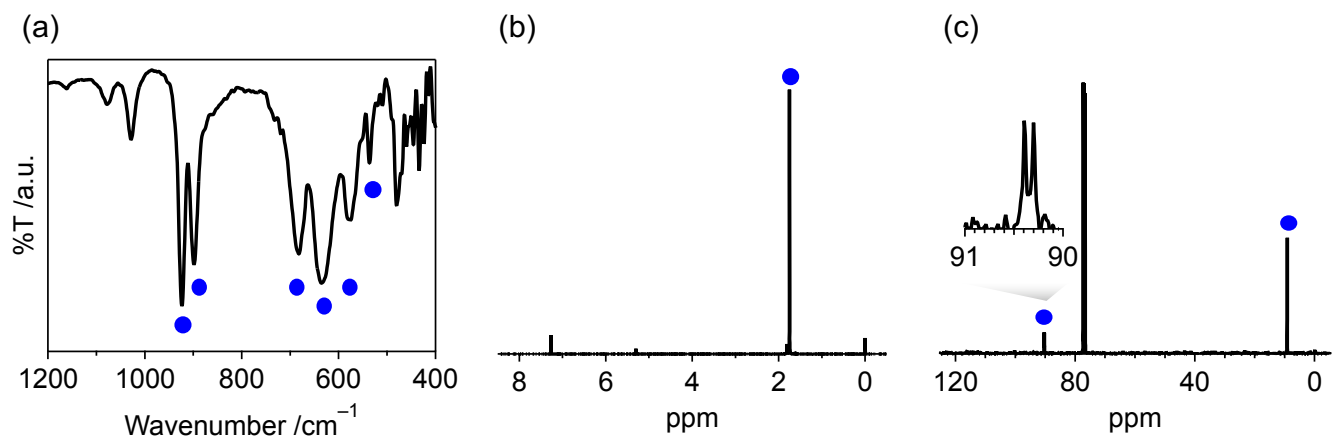


Figure S1. (a) FT-IR and (b) ^1H and (c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $[(\text{RhCp}^*)_4\text{Mo}_4\text{O}_{16}]$.

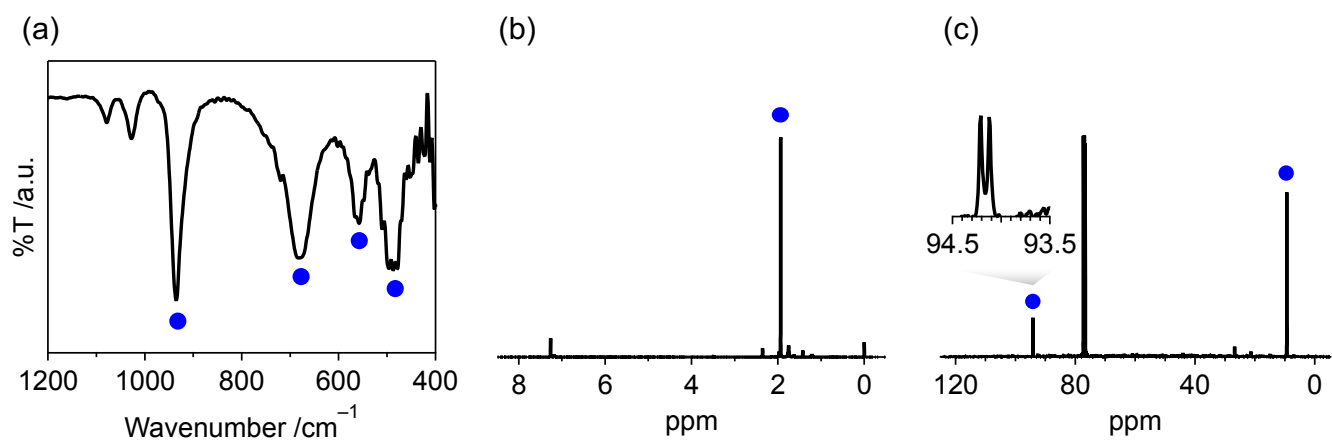


Figure S2. (a) FT-IR and (b) ^1H and (c) $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $[(\text{RhCp}^*)_4\text{V}_6\text{O}_{19}]$.

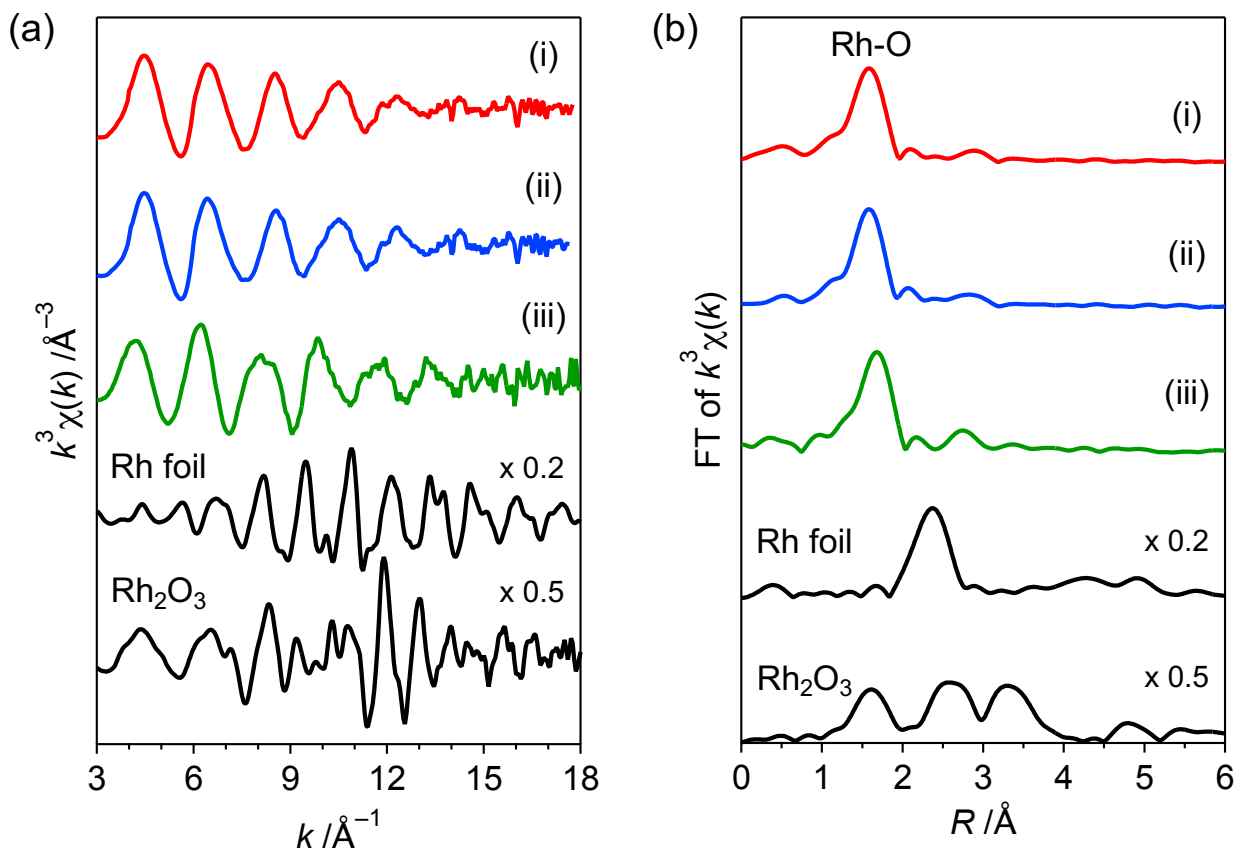


Figure S3. Rh K-edge (a) EXAFS and (b) FT-EXAFS spectra of (i) Rh₄Mo₄/Al₂O₃, (ii) Rh-Mo/Al₂O₃, and (iii) [(RhCp*)₄Mo₄O₁₆].

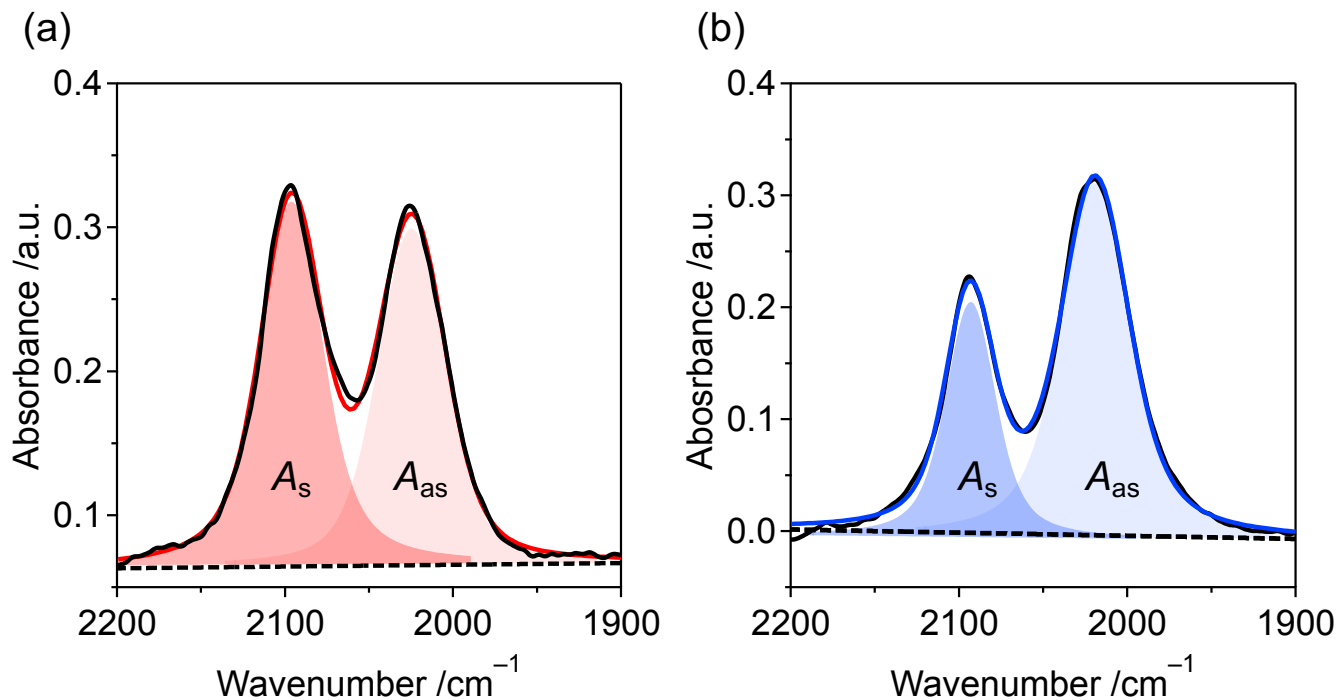
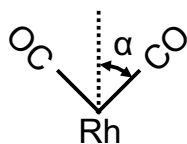


Figure S4. DRIFT spectra of adsorbed CO species on (a) Rh₄Mo₄/Al₂O₃ and (b) Rh-Mo/Al₂O₃. The spectrum was curve-fitted by applying two Voigt functions with a linear background.

Table S1. IR bands of adsorbed CO species.^a

Catalyst	ν_s / cm^{-1}	ν_a / cm^{-1}	$\nu_{\text{bridged}} / \text{cm}^{-1}$	A_{as}/A_s	$2\alpha / ^\circ$
Rh ₄ Mo ₄ /Al ₂ O ₃	2096	2026	–	0.97	89
Rh-Mo/Al ₂ O ₃	2094	2019	1849	2.18	112

$$^a \tan^2 \alpha = A_{\text{as}}/A_s$$



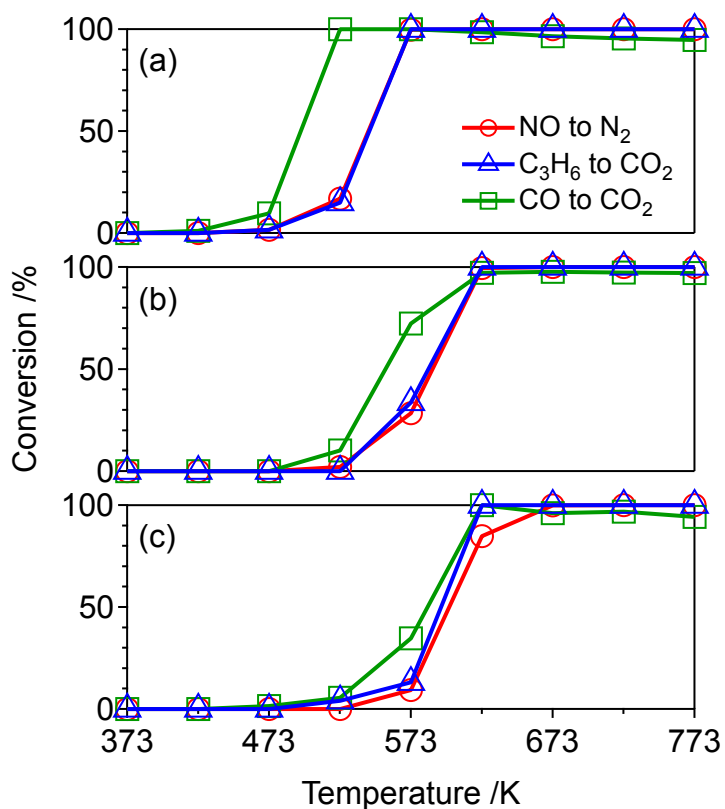


Figure S5. Conversions of NO to N₂ (red), C₃H₆ to CO₂ (blue), and CO to CO₂ (green) in the NO-CO-C₃H₆-O₂ reaction over (a) Rh₄Mo₄/Al₂O₃, (b) Rh-Mo/Al₂O, and (c) Rh/Al₂O₃.

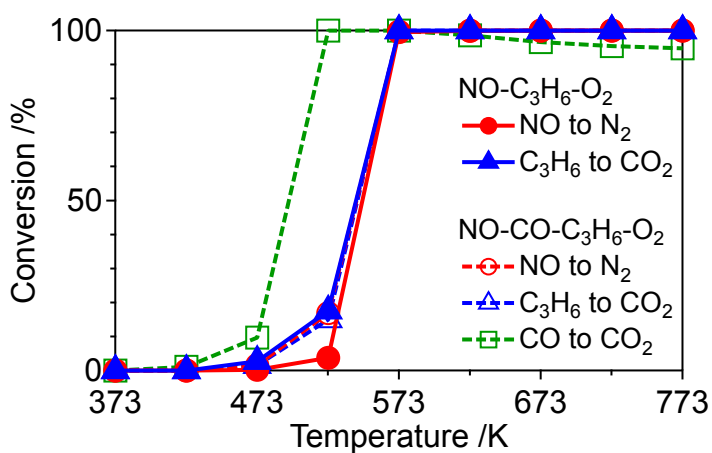


Figure S6. Conversions of NO to N₂ (red), C₃H₆ to CO₂ (blue), and CO to CO₂ (green) in NO-C₃H₆-O₂ (solid line) and NO-CO-C₃H₆-O₂ (dotted line) over Rh₄Mo₄/Al₂O₃.

Table S2. Amount of CO₂ generated under CO/He flow.

Catalyst	Temp. /K	$n_{\text{CO}_2}/\mu\text{mol}$	$n_{\text{CO}_2}/n_{\text{Rh}}$
Rh ₄ Mo ₄ /Al ₂ O ₃	473	2.56	0.13
	573	49.4	2.54
Rh-Mo/Al ₂ O ₃	473	–	–
	573	3.67	0.19
Rh/Al ₂ O ₃	473	–	–
	573	4.04	0.21

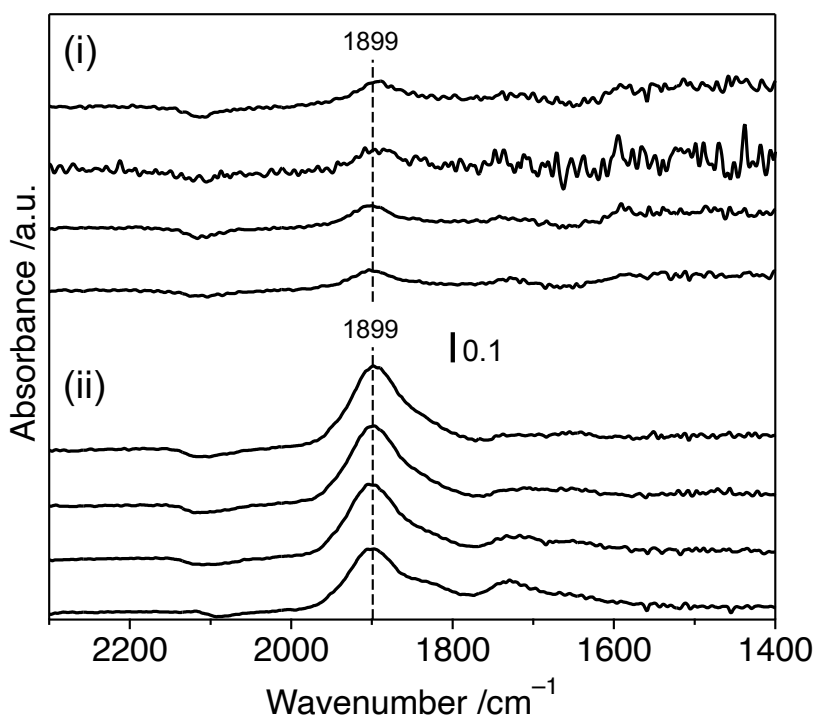


Figure S7. DRIFT spectra of adsorbed species in a flow of NO on (i) Rh₄Mo₄/Al₂O₃ and (ii) Rh-Mo/Al₂O₃. Gas composition: NO (1000 ppm) balanced with He.

Table S3. Loading amounts of Rh and Mo estimated from ICP-MS analysis.

Catalyst	Calcd. (wt%)		As-prepared (wt%)		After aging ^a (wt%)	
	Rh	Mo	Rh	Mo	Rh	Mo
Rh ₄ Mo ₄ /Al ₂ O ₃	1.00	0.93	0.94	0.92	1.03	1.00
Rh-Mo/Al ₂ O ₃	1.00	0.93	0.91	0.96	1.01	1.06

^a1273 K, 5 h, air

References

- S1. Hayashi, Y.; Toriumi, K.; Isobe, K. Novel Triple Cubane-Type Organometallic Oxide Clusters: [MCp*MoO₄]₄·nH₂O (M = Rh and Ir; Cp* = C₅Me₅; n = 2 for Rh and 0 for Ir). *J. Am. Chem. Soc.* **1988**, *110*, 3666–3668.
- S2. Hayashi, Y.; Ozawa, Y.; Isobe, K. Site-Selective Oxygen Exchange and Substitution of Organometallic Groups in an Amphiphilic Quadruple-Cubane-Type Cluster. Synthesis and Molecular Structure of [(MCp*)₄V₆O₁₉] (M = Rh, Ir). *Inorg. Chem.* **1991**, *30*, 1025–1033.