Supporting Information

γ-Alumina-Supported Pt\(_{17}\) Cluster: Controlled Loading, Geometrical Structure, and Size-Specific Catalytic Activity for Carbon Monoxide and Propylene Oxidation

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1. Additional Tables

Table S1. Curve Fitting Analysis of Pt L\(_{3}\)-edge EXAFS Data for [Pt\(_{17}\)(CO)\(_{12}\)(PPh\(_{3}\))\(_{8}\)]Cl\(_{8}\)

| Bond  | C.N. \(^{a,b}\) | R(Å) \(^{a}\) | D.W. \(^{a,c}\) | R factor (%) \(^{a}\) |
|-------|----------------|-------------|--------------|---------------------|
| Pt–C  | 1.6(4)         | 2.02(6)     | 0.008(7)     | 11.9                |
| Pt–P  | 0.5(2)         | 2.44(7)     | 0.004(3)     |                     |
| Pt–Pt | 6.9(6)         | 2.63(6)     | 0.020(10)    |                     |

The numbers in parentheses are uncertainties; 1.6(4) and 2.02(6) represent 1.6 ± 0.4 and 2.02 ± 0.06, respectively.

\(^{a}\) These values were obtained by fitting with Pt–C, Pt–P, or Pt–Pt bonds.
\(^{b}\) Coordination number
\(^{c}\) Debye–Waller factor.

Table S2. Curve Fitting Analysis of Pt L\(_{3}\)-edge EXAFS Data for Pt\(_{17}\)(CO)\(_{12}\)(PPh\(_{3}\))\(_{8}\)/γ-Al\(_{2}\)O\(_{3}\)

| Bond  | C.N. \(^{a,b}\) | R(Å) \(^{a}\) | D.W. \(^{a,c}\) | R factor (%) \(^{a}\) |
|-------|----------------|-------------|--------------|---------------------|
| Pt–C  | 1.5(2)         | 2.01(4)     | 0.003(2)     |                     |
| Pt–P  | 0.4(2)         | 2.24(6)     | 0.004(3)     | 15.0                |
| Pt–Pt | 5.0(4)         | 2.59(4)     | 0.013(6)     |                     |

The numbers in parentheses are uncertainties; 1.5(2) and 2.01(4) represent 1.5 ± 0.2 and 2.01 ± 0.04, respectively.

\(^{a}\) These values were obtained by fitting with Pt–C, Pt–P, or Pt–Pt bonds.
\(^{b}\) Coordination number
\(^{c}\) Debye–Waller factor.
Table S3. Curve Fitting Analysis of Pt L_3-edge EXAFS Data for Pt_{17}/γ-Al_2O_3

| Bond   | C.N., a,b | R(Å) a | D.W., a,c | R factor (%) a |
|--------|-----------|--------|-----------|---------------|
| Pt–C   | 3.5(3)    | 2.03(4)| 0.006(4)  | 10.0          |
| Pt–Pt  | 6.6(3)    | 2.76(3)| 0.009(4)  |               |

The numbers in parentheses are uncertainties; 3.5(3) and 2.03(4) represent 3.5 ± 0.3 and 2.03 ± 0.04, respectively.

a These values were obtained by fitting with Pt–C or Pt–Pt bonds.
b Coordination number
c Debye–Waller factor.

Table S4. Gases Used in Oxidation Reaction of CO and C_3H_6

| Reaction         | CO/C_3H_6 | O_2  | N_2  |
|------------------|-----------|------|------|
| CO oxidation     | 1%        | 0.5% | 98.5%|
| C_3H_6 oxidation | 200 ppm   | 0.5% | ~99.5%|

Table S5. Gases Used in Aging Treatment

| Atmosphere | H_2 | CO  | O_2  | H_2O | N_2  |
|------------|-----|-----|------|------|------|
| Oxidation  | 0%  | 0%  | 3%   | 10%  | 87%  |
| Reduction  | 3%  | 3%  | 0%   | 10%  | 84%  |
2. Additional Schemes

**Scheme S1.** (a) Synthesis procedure for $[\text{Pt}_{17}(\text{CO})_{12}(\text{PPh}_3)_8]\text{Cl}_n$ ($n = 1, 2$) and (b) photograph of product at each stage (i)–(vi) described in (a).\(^1\)

**Scheme S2.** Preparation procedure for honeycomb catalysts.
3. Additional Figures

**Figure S1.** Positive-ion MALDI mass spectra: (a) wide-region spectrum and (b) spectrum expanded for the main peaks. These mass spectra include the laser fragments assigned in (b). In (a), peaks other than the fragment peaks of [Pt$_{17}$(CO)$_{12}$(PPh$_3$)$_8$]Cl$_n$ are hardly observed, indicating that the product contains high-purity [Pt$_{17}$(CO)$_{12}$(PPh$_3$)$_8$]Cl$_n$.

**Figure S2.** (a)–(f) Representative HAADF-STEM images of [Pt$_{17}$(CO)$_{12}$(PPh$_3$)$_8$]Cl$_n$. 
**Figure S3.** (a)–(f) Representative HAADF-STEM images of Pt_{17}(CO)_{12}(PPh_3)_8/γ-Al_2O_3.

**Figure S4.** (a) TGA curve obtained for Pt_{17}(CO)_{12}(PPh_3)_8/γ-Al_2O_3 and (b) the gasses desorbed from the sample above 400 °C. These curves were obtained using an STA 2500 Regulus (NETZSCH) and a JMS-Q 1500GC (JEOL) at a heating rate of 5 °C/min under Ar atmosphere over the temperature range 25–900 °C. In (b), CO_2 is considered to be the product of the oxidation of the CO ligand catalyzed by Pt_{17} because this measurement was conducted under Ar atmosphere. These results imply that some of the CO remains on the supported Pt_{17} even after the calcination at 500 °C.
Figure S5. P 2p XPS spectra of (a) [Pt_{17}(CO)_{12}(PPh_3)_8]Cl_n and (b) Pt_{17}/γ-Al_2O_3.

Figure S6. (a)–(f) Representative HAADF-STEM images of Pt_{17}/γ-Al_2O_3.

Figure S7. Temperature-programmed reaction (TPR) curve monitored at m/z = 44 (CO_2) for Pt_{17}/γ-Al_2O_3 sample after air exposure. TPR analysis was performed with a Rigaku TPD type R analyzer at a heating rate of 20 °C/min under a flow of 10% O_2 diluted in He using ~100-mg samples of the catalyst powders.
Figure S8. Monitoring of the desorbed gases from Pt$_{17}$/γ-Al$_2$O$_3$ at each temperature using FT-IR spectroscopy. This experiment was conducted using FT/IR-6600 spectrometer (JASCO) with KP1000 digital program controller (CHINO) under a flow of 10% O$_2$ diluted in He. These spectra were obtained by subtracting the room-temperature spectrum from the spectrum of each temperature (100−500 °C); thus, the peaks originating from the desorbed species appear under the baseline. These spectra imply that the CO adsorbed on Pt$_{17}$/γ-Al$_2$O$_3$ is related to the CO$_2$ observed in the TPR curve (Figure S7).

Figure S9. Pt L$_3$-edge EXAFS spectra of [Pt$_{17}$(CO)$_{12}$(PPh$_3$)$_8$]Cl$_n$, Pt$_{17}$(CO)$_{12}$(PPh$_3$)$_8$/γ-Al$_2$O$_3$, and Pt$_{17}$/γ-Al$_2$O$_3$ together with those of Pt foil and PtO$_2$ for comparison.

Figure S10. Pt−Pt bond lengths of [Pt$_{17}$(CO)$_{12}$(PPh$_3$)$_8$]$^+$ (blue) and [Pt$_{17}$(CO)$_{12}$(PPh$_3$)$_8$]$^{2+}$ (red) estimated from each geometrical structure reported in our previous paper.$^1$
Figure S11. Estimation of model structures of Pt\textsubscript{17}/γ-Al\textsubscript{2}O\textsubscript{3} for bi-layered structure: (a) HAADF-STEM image, (b) method to arrange Pt atoms, and (c) proposed bi-layered structure and estimated bond lengths for this structure.

Figure S12. HAADF-STEM images of (a) Pt\textsubscript{17}/γ-Al\textsubscript{2}O\textsubscript{3} and (b) Pt\textsubscript{NP}/γ-Al\textsubscript{2}O\textsubscript{3} after aging treatment.

Figure S13. HAADF-STEM images of Pt\textsubscript{17}/γ-Al\textsubscript{2}O\textsubscript{3} loaded with a weight of 0.7 wt% Pt. The aggregation of Pt\textsubscript{17} clusters were not necessarily suppressed at this loading weight, although the size distribution is still narrow (1.40 ± 0.72 nm) compared with that of Pt\textsubscript{NP} prepared using the conventional method with lower loading weight (0.15% Pt; 3.10 ± 3.14 nm). In order to achieve the higher loading weight, we need to modify the ligand of Pt\textsubscript{17} clusters or increase the surface defects of γ-Al\textsubscript{2}O\textsubscript{3} to suppress the aggregation on the γ-Al\textsubscript{2}O\textsubscript{3} during the calcination.
4. References
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