# Supporting Information

# γ-Alumina-Supported Pt<sub>17</sub> 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<sub>3</sub>-edge EXAFS Data for [Pt<sub>17</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>8</sub>]Cl<sub>n</sub>

Bond	C.N. <i>a,b</i>	$R(Å)^a$	D.W. <i>a</i> , <i>c</i>	R factor (%) $^{a}$
Pt-C	1.6(4)	2.02(6)	0.008(7)	
Pt–P	0.5(2)	2.44(7)	0.004(3)	11.9
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  $1.6 \pm 0.4$  and  $2.02 \pm 0.06$ , respectively.

<sup>*a*</sup> These values were obtained by fitting with Pt–C, Pt–P, or Pt–Pt bonds.

<sup>b</sup> Coordination number

<sup>*c*</sup> Debye–Waller factor.

## Table S2. Curve Fitting Analysis of Pt L3-edge EXAFS Data for Pt17(CO)12(PPh3)8/7-Al2O3

Bond	C.N. <i>a,b</i>	$R(A)^{a}$	D.W. <i>a</i> , <i>c</i>	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  $1.5 \pm 0.2$  and  $2.01 \pm 0.04$ , respectively. <sup>*a*</sup> These values were obtained by fitting with Pt–C, Pt–P, or Pt–Pt bonds.

<sup>b</sup> Coordination number

<sup>c</sup> Debye–Waller factor.

Bond	C.N. <i>a,b</i>	$R(Å)^a$	D.W. <i>a</i> , <i>c</i>	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)	10.0

# Table S3. Curve Fitting Analysis of Pt L<sub>3</sub>-edge EXAFS Data for $Pt_{17}/\gamma$ -Al<sub>2</sub>O<sub>3</sub>

The numbers in parentheses are uncertainties; 3.5(3) and 2.03(4) represent  $3.5 \pm 0.3$  and  $2.03 \pm 0.04$ , respectively. <sup>*a*</sup> These values were obtained by fitting with Pt–C or Pt–Pt bonds.

<sup>b</sup> Coordination number

<sup>*c*</sup> Debye–Waller factor.

#### Table S4. Gases Used in Oxidation Reaction of CO and C<sub>3</sub>H<sub>6</sub>

Reaction	CO/C <sub>3</sub> H <sub>6</sub>	$O_2$	$N_2$	
CO oxidation	1%	0.5%	98.5%	
C <sub>3</sub> H <sub>6</sub> oxidation	200 ppm	0.5%	~99.5%	

Table S5. Gases Used in Aging Treatment

Atmosphere	H <sub>2</sub>	СО	O <sub>2</sub>	H <sub>2</sub> O	$N_2$
Oxidation	0%	0%	3%	10%	87%
Reduction	3%	3%	0%	10%	84%

## 2. Additional Schemes



**Scheme S1.** (a) Synthesis procedure for  $[Pt_{17}(CO)_{12}(PPh_3)_8]Cl_n$  (n = 1, 2) and (b) photograph of product at each stage (i)–(vi) described in (a).<sup>1</sup>



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<sub>17</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>8</sub>]Cl<sub>n</sub>.



Figure S3. (a)-(f) Representative HAADF-STEM images of Pt<sub>17</sub>(CO)<sub>12</sub>(PPh<sub>3</sub>)<sub>8</sub>/γ-Al<sub>2</sub>O<sub>3</sub>.



**Figure S4.** (a) TGA curve obtained for  $Pt_{17}(CO)_{12}(PPh_3)_8/\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> is considered to be the product of the oxidation of the CO ligand catalyzed by Pt<sub>17</sub> because this measurement was conducted under Ar atmosphere.<sup>2</sup> These results imply that some of the CO remains on the supported Pt<sub>17</sub> 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)  $Pt_{17}/\gamma$ -Al<sub>2</sub>O<sub>3</sub>.



Figure S6. (a)–(f) Representative HAADF-STEM images of Pt<sub>17</sub>/γ-Al<sub>2</sub>O<sub>3</sub>.



**Figure S7.** Temperature-programmed reaction (TPR) curve monitored at m/z = 44 (CO<sub>2</sub>) for Pt<sub>17</sub>/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> diluted in He using ~100-mg samples of the catalyst powders.



**Figure S8.** Monitoring of the desorbed gases from  $Pt_{17}/\gamma$ -Al<sub>2</sub>O<sub>3</sub> 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<sub>2</sub> 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 base line. These spectra imply that the CO adsorbed on  $Pt_{17}/\gamma$ -Al<sub>2</sub>O<sub>3</sub> is related to the CO<sub>2</sub> observed in the TPR curve (Figure S7).



**Figure S9.** Pt L<sub>3</sub>-edge EXAFS spectra of  $[Pt_{17}(CO)_{12}(PPh_3)_8]Cl_n$ ,  $Pt_{17}(CO)_{12}(PPh_3)_8/\gamma$ -Al<sub>2</sub>O<sub>3</sub>, and  $Pt_{17}/\gamma$ -Al<sub>2</sub>O<sub>3</sub> together with those of Pt foil and PtO<sub>2</sub> 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<sup>1</sup>.







Figure S12. HAADF-STEM images of (a) Pt<sub>17</sub>/γ-Al<sub>2</sub>O<sub>3</sub> and (b) Pt<sub>NP</sub>/γ-Al<sub>2</sub>O<sub>3</sub> after aging treatment.



**Figure S13.** HAADF-STEM images of  $Pt_{17}/\gamma$ -Al<sub>2</sub>O<sub>3</sub> loaded with a weight of 0.7 wt% Pt. The aggregation of  $Pt_{17}$  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  $Pt_{NP}$  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  $Pt_{17}$  clusters or increase the surface defects of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> to suppress the aggregation on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> during the calcination.

## 4. References

- 1. L. V. Nair, S. Hossain, S. Wakayama, S. Takagi, M. Yoshioka, J. Maekawa, A. Harasawa, B. Kumar, Y. Niihori, W. Kurashige and Y. Negishi, *J. Phys. Chem. C*, 2017, **121**, 11002–11009.
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