*Electronic Supplementary Information (ESI) for*

# Methane Activation with Nitric Oxide at Low Temperatures on Supported Pt Catalysts: Effects of Support

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## 1. Relationship between activity and characterization results

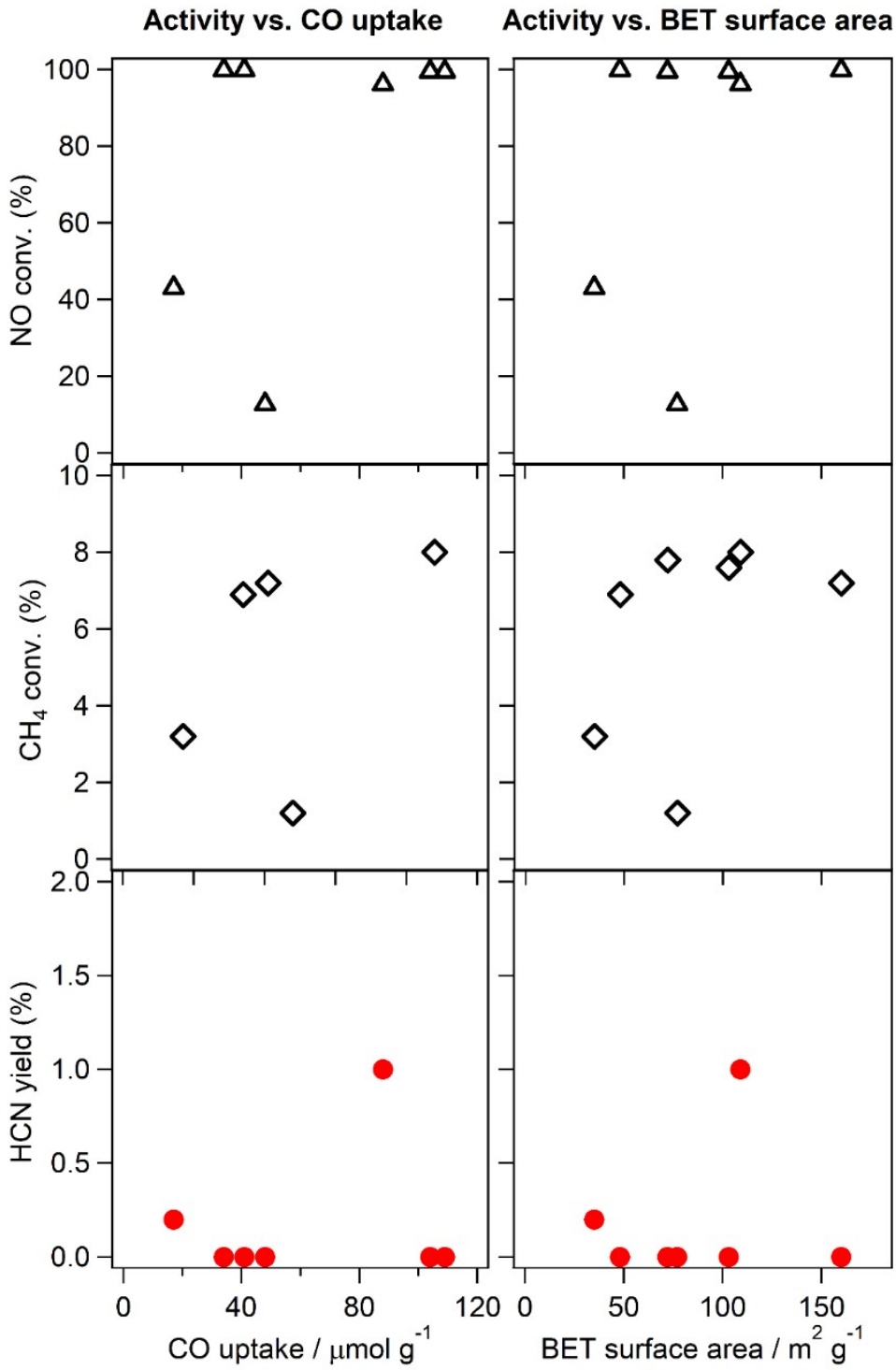


**Figure S1** Catalytic activity for $CH_4$-NO reaction at 400 °C on supported Pt catalysts as a function of CO uptake and BET surface area. Reaction conditions: Catalyst (100 mg), $CH_4$/NO/He = 13.4:1.8:84.8 = 100 mL $min^{-1}$, 0.1 MPa, GHSV = 6000 $h^{-1}$

## 2. Characterization of Pt catalysts supported on various metal oxides

### 2.1. CO adsorption and BET surface areas

**Table S1**. Characterization results of Pt catalysts supported on various metal oxides

| Support | BET surface area / $m^2\ g^{-1}$ | CO pulse | | |
|---|---|---|---|---|
| | | CO ads. / $\mu mol\ g^{-1}$ | Pt dispersion (%) | Pt particle size / nm |
| MgO | 77 | 48 | 19 | 6.0 |
| $(\theta+\gamma)$-$Al_2O_3$ | 109 | 88 | 34 | 3.3 |
| $SiO_2$ | 160 | 41 | 16 | 6.7 |
| $TiO_2$ | 48 | 34 | 13 | 8.3 |
| $Y_2O_3$ | 35 | 17 | 6.7 | 17 |
| $ZrO_2$ | 72 | 109 | 43 | 2.6 |
| $CeO_2$ | 103 | 104 | 40 | 2.8 |

## 2.2. X-ray diffraction patterns

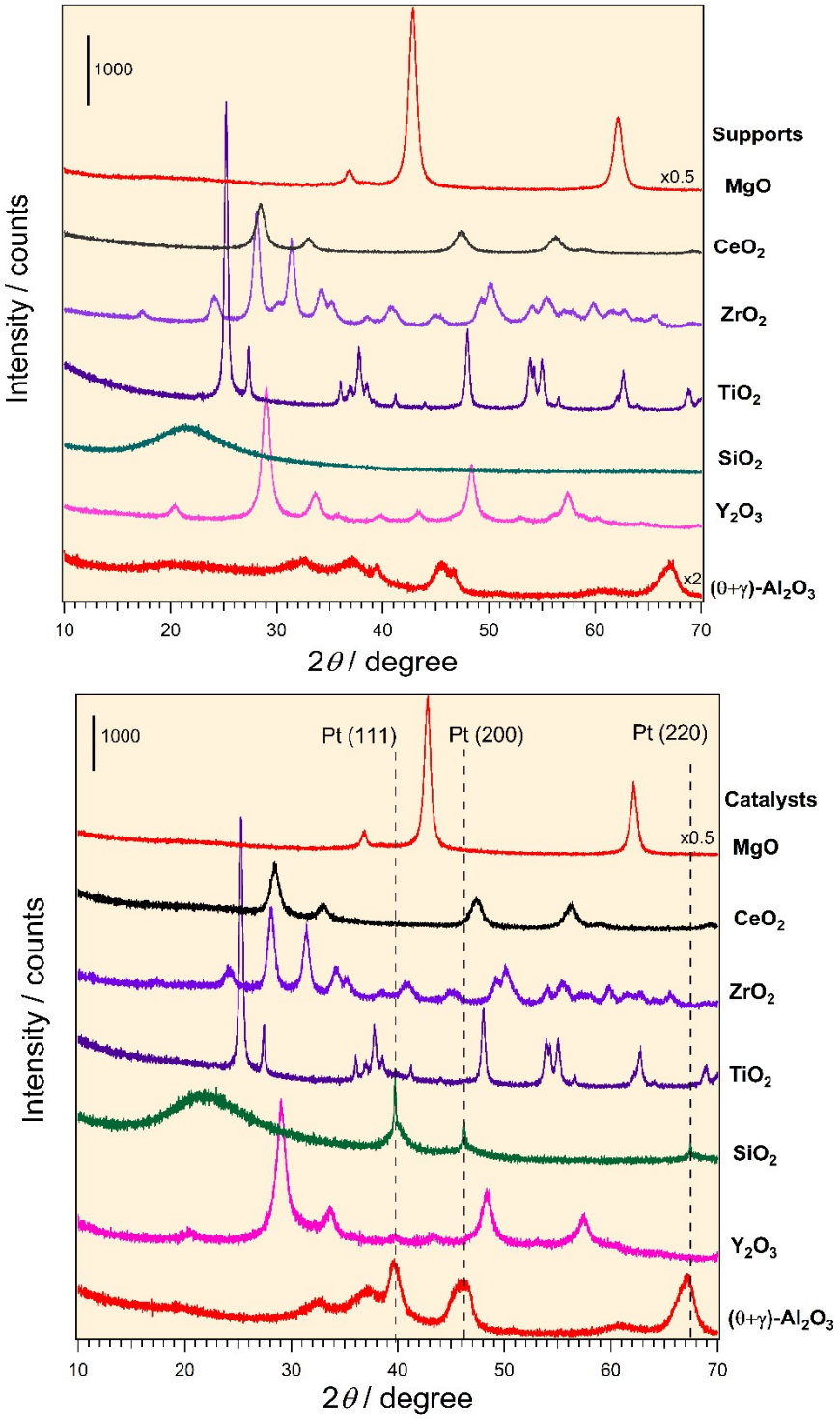


**Figure S2** X-ray diffraction patterns for the Pt catalysts on various metal oxides (top) and the bare metal oxide supports (bottom).

**Table S2** lists the powder diffraction file (PDF) numbers of the observed peaks The diffraction peaks of the supports were identified

| Sample | ICDD PDF # |
|---|---|
| MgO | 00-004-0829 |
| $CeO_2$ | Cubic $CeO_2$ (00-004-0593) |
| $ZrO_2$ | Monoclinic $ZrO_2$ (00-037-1484) |
| $TiO_2$ | Anatase (00-001-0562)<br>rutile (00-001-1292) |
| $Y_2O_3$ | Cubic $Y_2O_3$ (01-071-0049) |
| $(\theta+\gamma)$-$Al_2O_3$ | θ-$Al_2O_3$ (00-035-0121)<br>γ-$Al_2O_3$ (00-002-1420) |

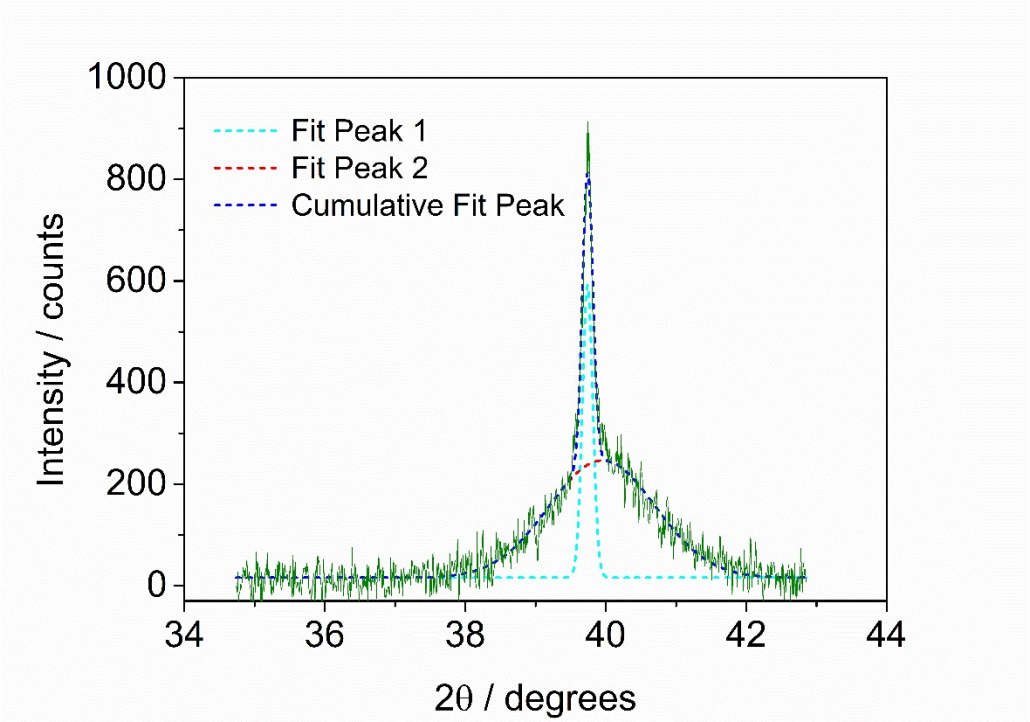


**Figure S3** XRD pattern for $Pt/SiO_2$: Deconvolution of Pt(111) reflection into two components using Gaussian function.

## 3. Characterization of Pt catalysts supported on alumina with different crystal structures

### 3.1. X-ray diffraction patterns

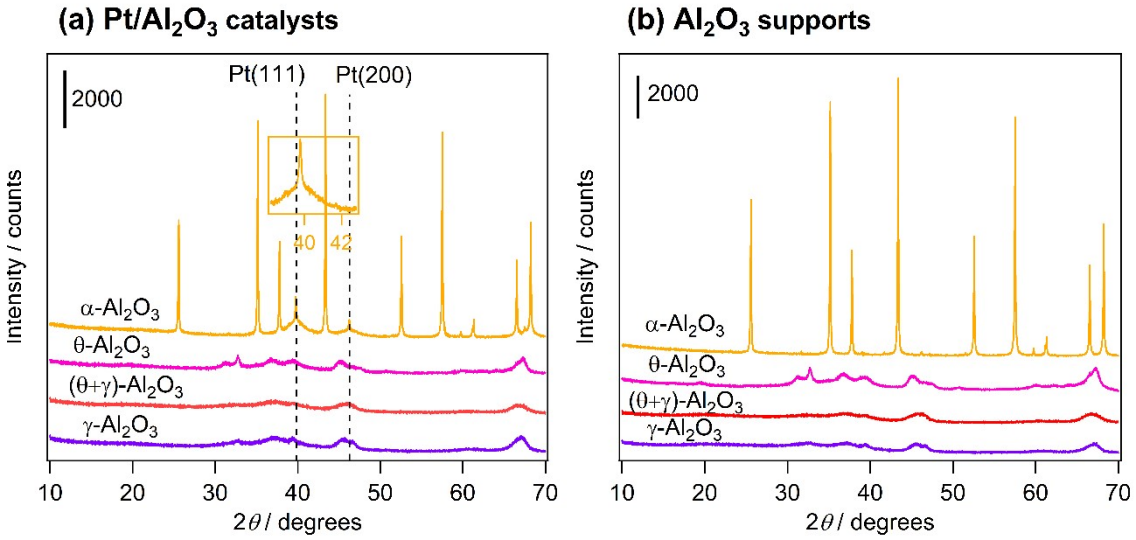


**Figure S4** X-ray diffraction patterns for the (a) Pt catalysts supported on alumina with different crystal structures and (b) the Pt-free alumina supports.

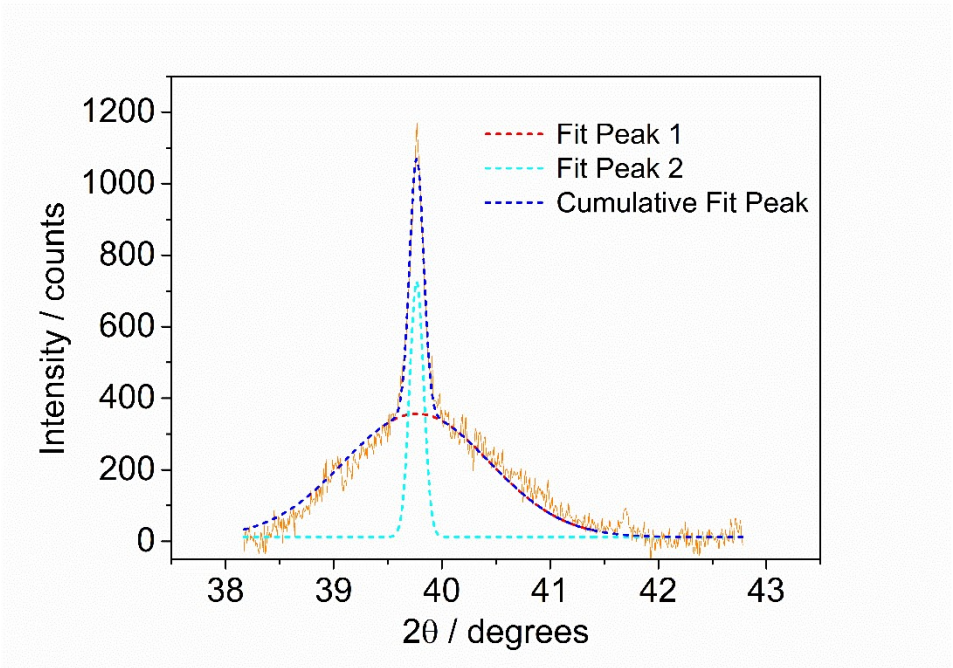


**Figure S5** XRD pattern for Pt/α-$Al_2O_3$: Deconvolution of Pt(111) reflection into two components using Gaussian function.

### 3.2. High resolution scanning electron microscope (SEM) images

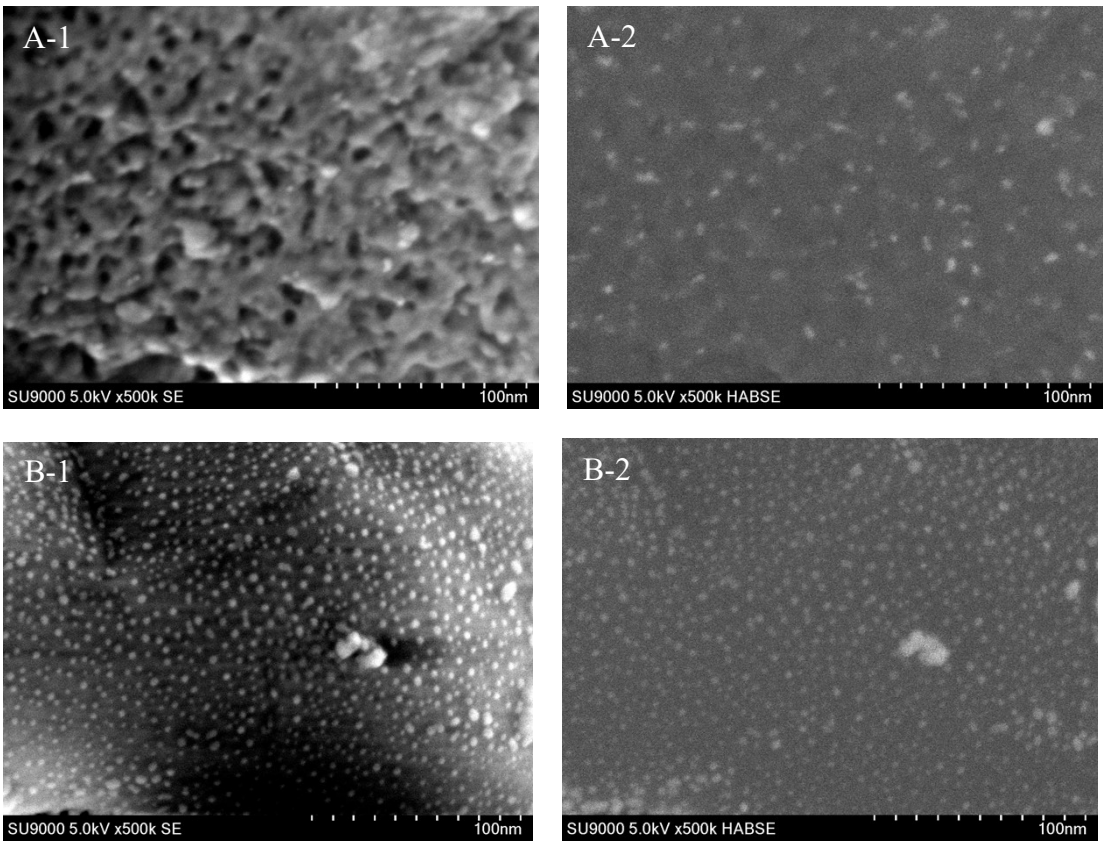


**Figure S6** SEM images of A: Pt/γ-$Al_2O_3$ and B: Pt/α-$Al_2O_3$. Numerals after A and B indicate that images are from 1: SE and 2: HABSE.

### 3.3. FT-IR spectra of adsorbed CO

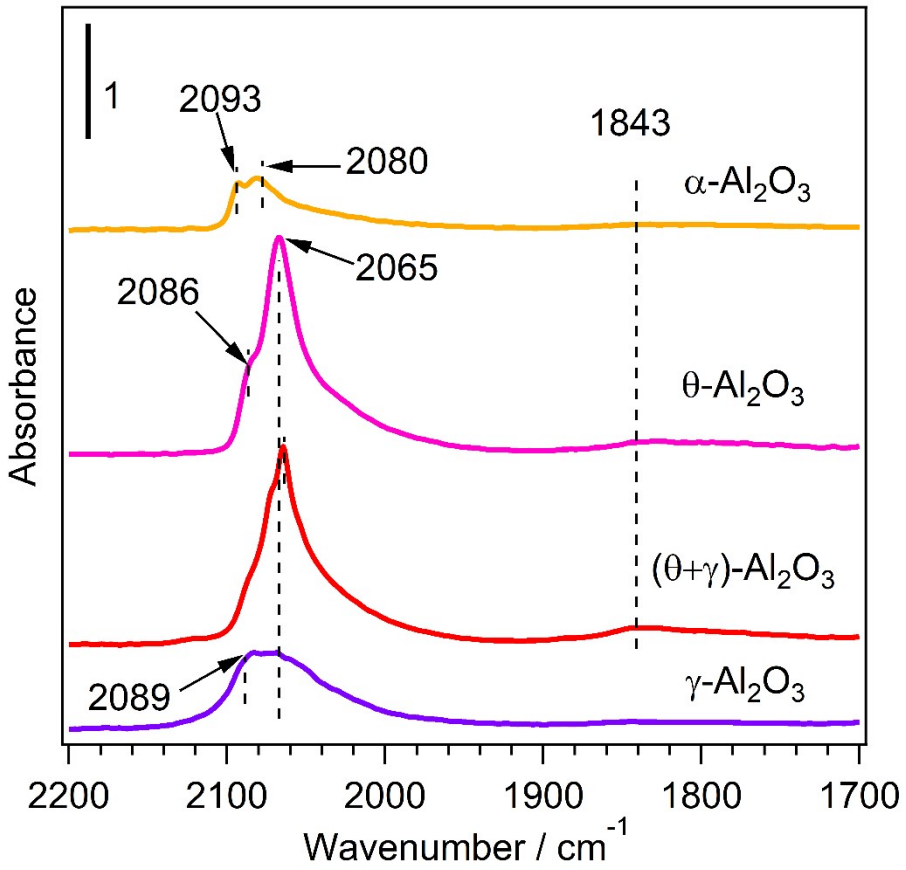


**Figure S7** FT-IR spectra of CO adsorbed at 50 °C under He flow on the Pt catalysts supported on $Al_2O_3$ with different crystal structures.

### 3.4. Pt $L_3$-edge XANES spectra of reduced catalysts

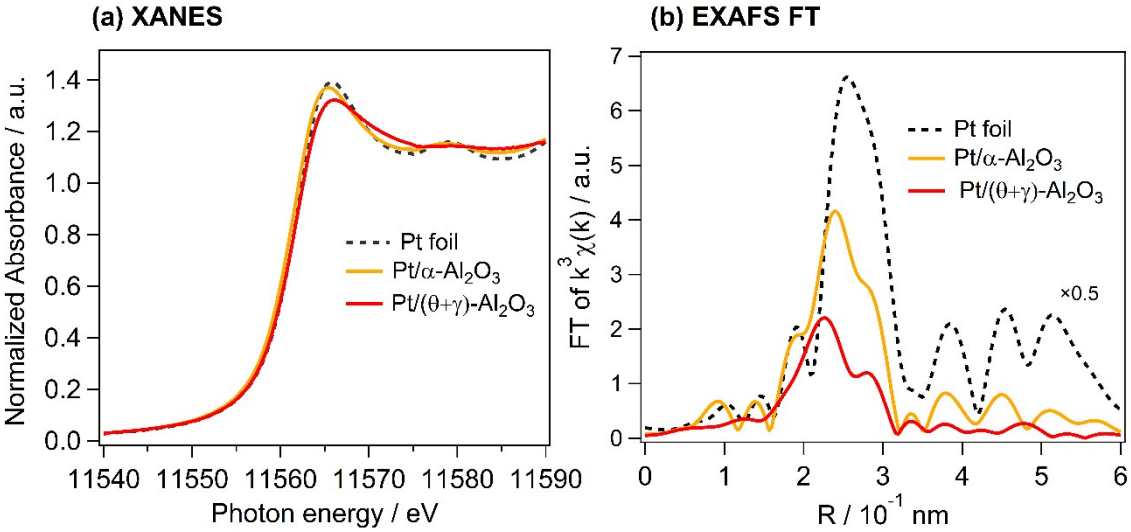


**Figure S8** (a) Normalized XANES and (b) Fourier transforms of EXAFS ($k^3\chi$(k))) spectra at the Pt $L_3$-edge for representative Pt catalysts supported on $Al_2O_3$ with different crystal structures and Pt foil. The spectra of the catalysts were obtained under in situ conditions after reduction in $H_2$ at 400 °C, purging and cooling under He to 300 °C.

## 4. *In situ* FT-IR spectroscopy of Pt catalysts supported on various metal oxides

### 4.1. Temperature-programmed desorption of adsorbed NO on the supported Pt catalysts

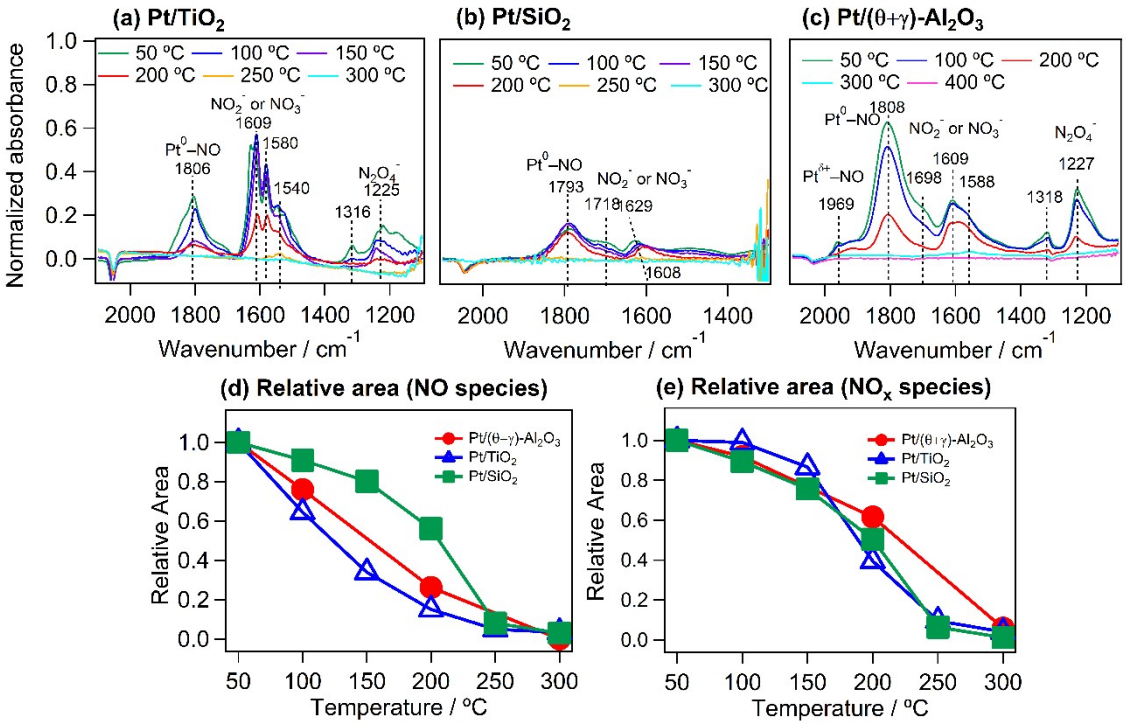


**Figure S9** In situ FT-IR spectra of NO adsorbed at 50 °C on (a) $Pt/TiO_2$, (b) $Pt/SiO_2$, and (c) $Pt/(\theta+\gamma)$-$Al_2O_3$ after treatment under a flow of He at various temperatures. Relative area of (d) NO and (e) $NO_x$ species as a function of temperature.

## 4.2. Temperature-programmed desorption of adsorbed NO on the bare supports

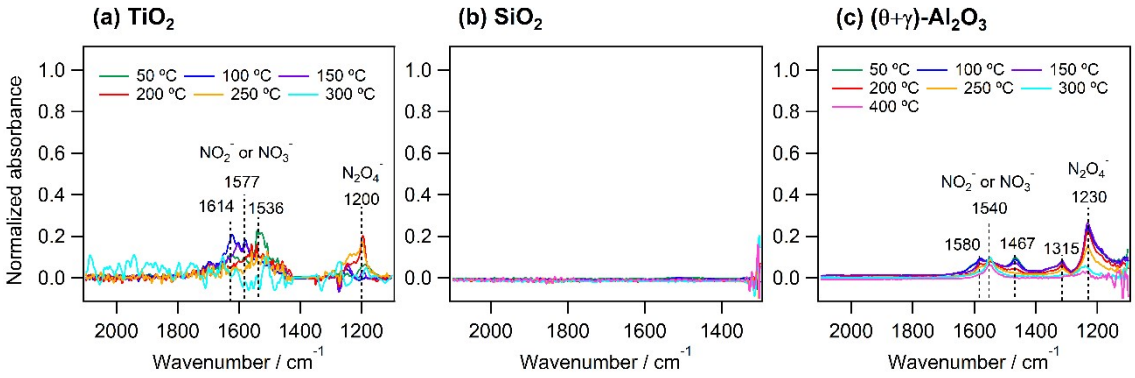


**Figure S10** In situ FT-IR spectra of NO adsorbed at 50 °C on (a) $Pt/TiO_2$, (b) $Pt/SiO_2$, and (c) $Pt/(\theta+\gamma)$-$Al_2O_3$ after treatment under a flow of He at various temperatures.

## 5. XANES spectra for Pt/(θ+γ)-$Al_2O_3$ exposed to various gases

The experiments involved passing NO and CO gases over reduced Pt/(θ+γ)-$Al_2O_3$ sample at room temperature, followed by purging under He. The experiments were conducted in a hermetically-sealed quartz flow cell with Kapton windows to prevent exposure to air. The NO concentration used was 1.8% in He and the CO concentration was 0.2% in He, which were chosen to mimic the reaction. The XANES spectra at the Pt $L_3$ edge were recorded at room temperature in transmission mode using the QXAFS technique at the BL9C beamline of the Photon Factory (PF) in the Institute of Materials Structure Science, High-Energy Accelerator Research Organization (KEK-IMSS-PF), in Tsukuba, Japan.

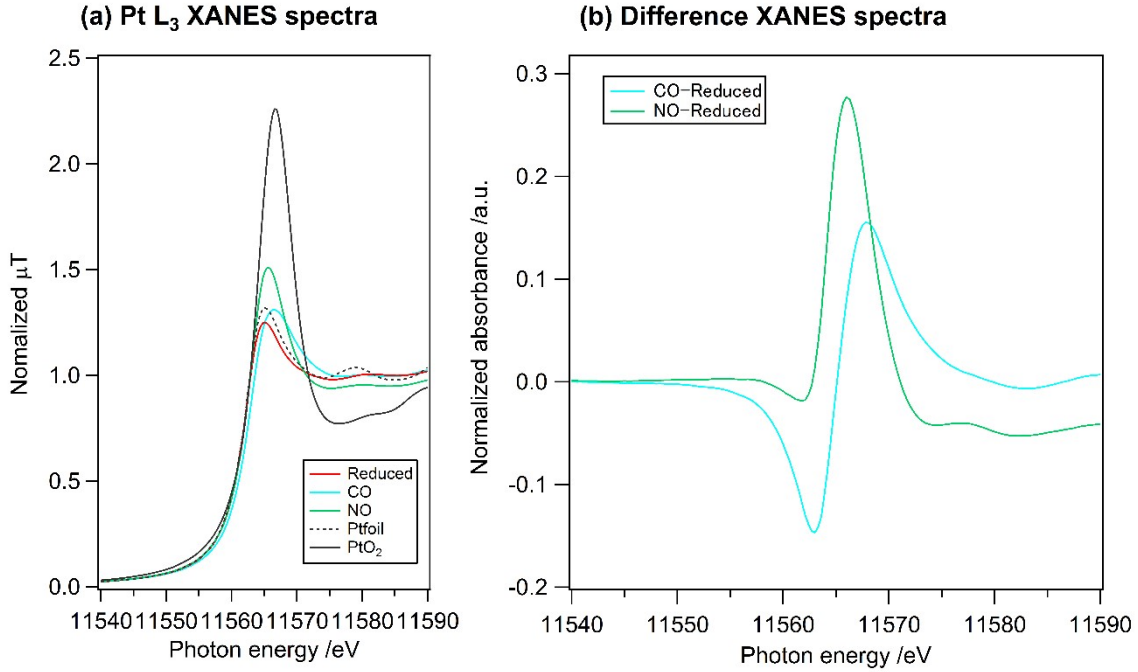


**Figure S11** (a) Pt $L_3$-edge XANES spectra for reduced Pt/(θ+γ)-$Al_2O_3$ exposed to NO and CO, and (b) difference XANES spectra after subtracting the spectrum of the reduced sample from those exposed to the various gases. The left figure also includes spectra of reference Pt foil and $PtO_2$ samples.

## 6. *In situ* XANES spectra of alumina-supported Pt catalysts

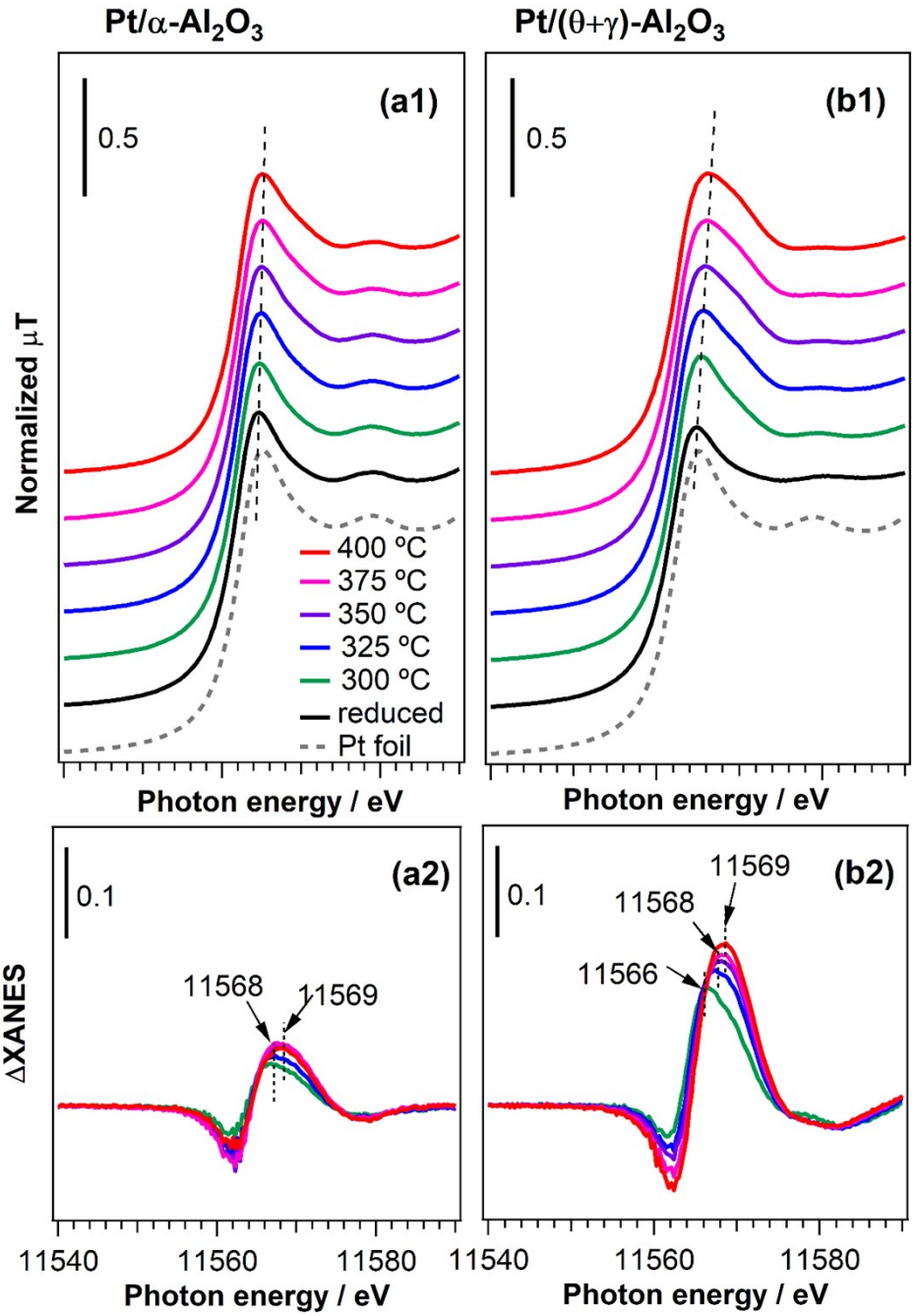


**Figure S12** (a1 and b1) Pt $L_3$-edge XANES spectra for Pt catalysts supported on (a) α-$Al_2O_3$ and (b) (θ+γ)-$Al_2O_3$ recorded *in situ* after $H_2$ reduction and at different temperatures under the 13.4%$CH_4$/1.8%NO/84.8%He mixture. (a2 and b2) Difference XANES spectra obtained by subtracting the Pt $L_3$-edge XANES spectra of the reduced catalysts from the spectra at the various temperatures.

## 7. Partial pressure dependency studies

Effect of $CH_4$ and NO partial pressure on the reaction was investigated on Pt/α-$Al_2O_3$. The experiments were carried out using 0.01 g of catalyst and at 400 °C, 101 kPa total pressure, and 100 mL $min^{-1}$ total flow rate. This condition was used to avoid complete NO conversion. The study of the effect of $CH_4$ partial pressure was carried out in a range of 1.8 to 13.4 kPa and at a fixed NO partial pressure (1.8 kPa), whereas the study of the effect of NO partial pressure was performed in a range of 0.9 to 3.6 kPa and at a fixed $CH_4$ partial pressure (13.4 kPa).

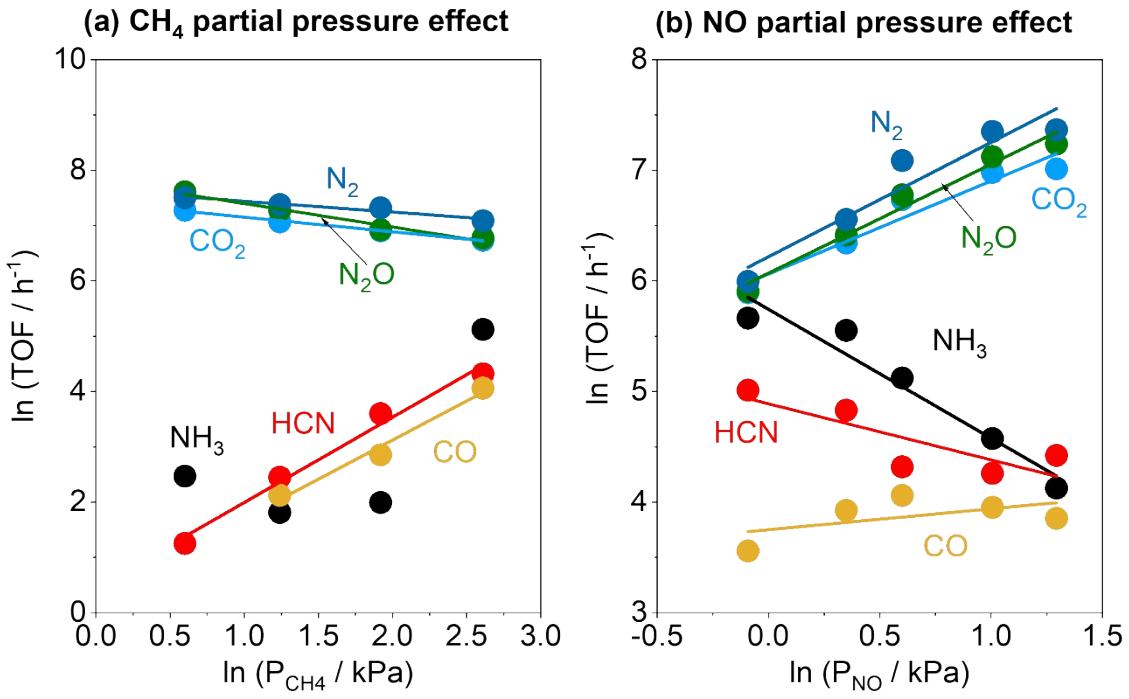


**Figure S13** Effect of (a) $CH_4$ and (b) NO partial pressures. Reaction conditions: 5wt%Pt/α-$Al_2O_3$ (10 mg), $CH_4$ = 1.8–13.4%, NO = 0.9–3.6%, 100 ml $min^{-1}$, 400 °C, 101 kPa