Electronic Supplementary Information (ESI) for

Methane Activation with Nitric Oxide at Low Temperatures on Supported Pt

Catalysts: Effects of Support

Nobuya Suganuma, † I. Tyrone Ghampson, † Hiroki Miura, †,§ Junichi Murakami, † Kyoko K. Bando, † Tetsuya Kodaira, ‡ Tatsuya Yamasaki, † Atsushi Takagaki, ‡ Tatsumi Ishihara, † Tetsuya Shishido, †,§,⁑

† Department of Applied Chemistry for Environment, Graduate School of Urban Environmental Sciences, Tokyo Metropolitan University, 1-1 Minami-osawa, Hachioji, Tokyo 192-0397, Japan.

‡ Department of Applied Chemistry, Faculty of Engineering, Kyushu University, Fukuoka 819-0395, Japan.

§ Research Center for Hydrogen Energy-Based Society, Tokyo Metropolitan University, 1-1 Minami-Osawa, Hachioji, Tokyo 192-0397, Japan

⁑ Elements Strategy Initiative for Catalysts & Batteries, Kyoto University, Goryo, Nishikyo-ku, Kyoto 615-8520, Japan

‖ Nanomaterials Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

‖‖ Research Institute for Chemical Process Technology, National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan.

‖‖‖ Division of Materials and Chemical Engineering, Faculty of Engineering, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama, Kanagawa 240-8501, Japan

*Corresponding author. Email address: shishido-tetsuya@tmu.ac.jp


Contents:

1. Relationship between activity and characterization results
2. Characterization of Pt catalysts supported on various metal oxides
3. Characterization of Pt catalysts supported on alumina with different crystal structures
4. \textit{In situ} FT-IR spectroscopy of Pt catalysts supported on various metal oxides
5. XANES spectra for Pt/(θ+γ)-Al$_2$O$_3$ exposed to various gases
6. \textit{In situ} XANES spectra of alumina-supported Pt catalysts
7. Partial pressure dependency studies
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

<table>
<thead>
<tr>
<th>Support</th>
<th>BET surface area / m² g⁻¹</th>
<th>CO pulse</th>
<th>Pt dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>77</td>
<td>48</td>
<td>19</td>
</tr>
<tr>
<td>(θ+γ)-Al₂O₃</td>
<td>109</td>
<td>88</td>
<td>34</td>
</tr>
<tr>
<td>SiO₂</td>
<td>160</td>
<td>41</td>
<td>16</td>
</tr>
<tr>
<td>TiO₂</td>
<td>48</td>
<td>34</td>
<td>13</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>35</td>
<td>17</td>
<td>6.7</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>72</td>
<td>109</td>
<td>43</td>
</tr>
<tr>
<td>CeO₂</td>
<td>103</td>
<td>104</td>
<td>40</td>
</tr>
</tbody>
</table>
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.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ICDD PDF #</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>00-004-0829</td>
</tr>
<tr>
<td>CeO₂</td>
<td>Cubic CeO₂ (00-004-0593)</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>Monoclinic ZrO₂ (00-037-1484)</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Anatase (00-001-0562)</td>
</tr>
<tr>
<td></td>
<td>Rutile (00-001-1292)</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>Cubic Y₂O₃ (01-071-0049)</td>
</tr>
<tr>
<td>(θ+γ)-Al₂O₃</td>
<td>0-Al₂O₃ (00-035-0121)</td>
</tr>
<tr>
<td></td>
<td>γ-Al₂O₃ (00-002-1420)</td>
</tr>
</tbody>
</table>

Figure S3 XRD pattern for Pt/SiO₂: 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-Al₂O₃: 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-Al₂O₃ and B: Pt/α-Al₂O₃. 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 Al₂O₃ with different crystal structures.
3.4. Pt L₃-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 L₃-edge for representative Pt catalysts supported on Al₂O₃ with different crystal structures and Pt foil. The spectra of the catalysts were obtained under in situ conditions after reduction in H₂ 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

![In situ FT-IR spectra of NO adsorbed at 50 °C on (a) Pt/TiO$_2$, (b) Pt/SiO$_2$, and (c) Pt/(θ+γ)-Al$_2$O$_3$ 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.](image)

**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/(θ+γ)-Al$_2$O$_3$ 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$_2$O$_3$ after treatment under a flow of He at various temperatures.
5. **XANES spectra for Pt/(θ+γ)-Al₂O₃ exposed to various gases**

The experiments involved passing NO and CO gases over reduced Pt/(θ+γ)-Al₂O₃ 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 L₃ 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](image)

**Figure S11** (a) Pt L₃-edge XANES spectra for reduced Pt/(θ+γ)-Al₂O₃ 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 PtO₂ 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) $\alpha$-Al$_2$O$_3$ and (b) $(\theta+\gamma)$-Al$_2$O$_3$ 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$_2$O$_3$. 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$_2$O$_3$ (10 mg), CH$_4$ = 1.8–13.4%, NO = 0.9–3.6%, 100 ml min$^{-1}$, 400 °C, 101 kPa