Supporting Information

Identification of the Structure of the Bi Promoted Pt Non-oxidative Coupling of Methane Catalyst: A Nanoscale Pt$_3$Bi Intermetallic Alloy

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Mears Criterion for External Diffusion Limitations

\[
\frac{r_{\text{obs}} \cdot \rho_{\text{cat}} \cdot R \cdot n}{k_c \cdot C} < 0.15
\]

External diffusion are negligible if

- \(r_{\text{obs}}\) - measured reaction rate, mol/(g\text{cat} \cdot s)
- \(\rho_{\text{cat}}\) - catalyst density, g/m\(^3\)
- \(R\) - catalyst pellet radius, m
- \(n\) - reaction order
- \(k_c\) - mass transfer coefficient, m/s
- \(C\) - bulk concentration

For propane dehydrogenation at 550°C for the most active catalyst 2Pt/SiO\(_2\):

\[
r_{\text{obs}} = 1.77 \cdot 10^{-5} \text{ mol/(g cat \cdot s)}, \quad \rho_{\text{cat}} = 2.65 \cdot 10^6 \text{ g/m}^3, \quad R = 4.20 \cdot 10^{-4} \text{ m}, \quad n=1, \quad k_c = 0.214 \text{ m/s}, \quad C = 0.370 \text{ mol/m}^3
\]

\[
\frac{r_{\text{obs}} \cdot \rho_{\text{cat}} \cdot R \cdot n}{k_c \cdot C} = 2.48 \cdot 10^{-3} < 0.15
\]

Weisz-Prater criterion for Internal Diffusion Limitations

\[
\psi = \frac{n + 1}{2} \cdot \frac{r_{\text{obs}} \cdot \rho_{\text{cat}} \cdot R^2}{D \cdot C} < 1
\]

Internal diffusion are negligible if

- \(\psi\) - dimensionless parameter
- \(n\) - reaction order
- \(r_{\text{obs}}\) - measured reaction rate, mol/(g\text{cat} \cdot s)
- \(\rho_{\text{cat}}\) - catalyst density, g/m\(^3\)
- \(R\) - catalyst pellet radius, m
- \(D\) - diffusion coefficient, m\(^2\)/s
C- bulk concentration

For propane dehydrogenation at 550°C for the most active catalyst 2Pt/SiO₂:

\[ n=1, \ r_{\text{obs}} = 1.77 \cdot 10^{-5} \text{ mol/(g cat \cdot s)}, \ \rho_{\text{cat}} = 2.65 \cdot 10^{6} \text{ g/m}^3, \ R = 4.20 \cdot 10^{-4} \text{ m}, \ D=1 \cdot 10^{-4} \text{ m}, \ C= 0.370 \text{ mol/m}^3 \]

\[ \Psi = \frac{n+1}{2} \cdot \frac{r_{\text{obs}} \cdot \rho_{\text{cat}} \cdot R^2}{D \cdot C} = 0.223 <1 \]

Mears Criterion for External Heat Transfer Limitations

\[ \frac{r_{\text{obs}} \cdot \rho_{\text{cat}} \cdot R \cdot E_a \cdot \Delta H}{k_g \cdot R_g \cdot T^2} < 0.15 \]

\( r_{\text{obs}} \) - measured reaction rate, mol/(g\text{cat \cdot s})

\( \rho_{\text{cat}} \) - catalyst density, g/m\(^3\)

\( R \) - catalyst pellet radius, m

\( E_a \) - activation energy, J/mol

\( \Delta H \) - reaction heat, J/mol

\( k_g \) - heat transport coefficient, J/(m\(^2\) \cdot s \cdot K)

\( R_g \) - gas constant, J/(mol \cdot K)

\( T \) - reaction temperature, K

For propane dehydrogenation at 550°C for the most active catalyst 2Pt/SiO₂:

\[ r_{\text{obs}} = 1.77 \cdot 10^{-5} \text{ mol/(g cat \cdot s)}, \ \rho_{\text{cat}} = 2.65 \cdot 10^{6} \text{ g/m}^3, \ R = 4.20 \cdot 10^{-4} \text{ m}, \ E_a= 1.20 \cdot 10^5 \text{ J/mol}, \ \Delta H= 1.29 \cdot 10^5 \text{ J/mol}, \ k_g= 1.46 \cdot 10^3 \text{ J/(m}^2\cdot\text{s} \cdot \text{K}), \ R_g= 8.31 \text{ J/(mol} \cdot \text{K}), T=823 \text{ K} \]

\[ \frac{r_{\text{obs}} \cdot \rho_{\text{cat}} \cdot R \cdot E_a \cdot \Delta H}{k_g \cdot R_g \cdot T^2} = 3.71 \cdot 10^{-2} < 0.15 \]
Figure S1. Pt L3 edge EXAFS spectra FEFF calculation: A) R space FT magnitude, B) k space, C) R space FT real part and D) R space FT imaginary part. Pt-Pt at R=2.75 Å (black), Pt-Bi at R=2.75 Å (red), Pt-Bi at R=2.80 Å (blue).
Figure S2. STEM HAADF images of A) 2Bi-2Pt/SiO₂ (2.7±0.5 nm), B) 4Bi-2Pt/SiO₂ (2.3±0.5 nm), C) 2Pt/SiO₂ (2.2±0.4 nm), D) 1Bi-2Pt/SiO₂ (2.7±0.4 nm)
Figure S3. Particle size distribution statistics of A) 2Pt/SiO$_2$ (2.2±0.6 nm), B) 1Bi-2Pt/SiO$_2$ (2.7±0.5 nm) C) 2Bi-2Pt/SiO$_2$ (2.4±0.5 nm), D) 4Bi-2Pt/SiO$_2$ (2.3±0.5 nm)
Figure S4. CO FTIR analysis of BiPt Bimetallic catalyst; CO adsorption before H\(_2\) reduction: (A) 0.8Bi1Pt/ZSM-5, (B) 1Bi2Pt/SiO\(_2\); CO adsorption after H\(_2\) reduction: (C) 0.8Bi1Pt/ZSM-5, (D) 1Bi2Pt/SiO\(_2\)
Figure S5. EXAFS comparison between 2Bi-2Pt/SiO$_2$ and 0.8Bi-1Pt/ZSM-5 (A) $k^2$-weighted $\chi(k)$ for 2Bi-2Pt/SiO$_2$ (black) and 0.8Bi-1Pt/ZSM-5 (red) (B) $k^2$-weighted Fourier transformation magnitude (dashed lines) and imaginary part (solid lines) of the EXAFS spectra for 2Bi-2Pt/SiO$_2$ (black) and 0.8Bi-1Pt/ZSM-5 (red)
Figure S6. Simulated XRD patterns (A) XRD patterns of Pt-Bi bulk alloys and experimental Pt-Bi/SiO$_2$ taken at 550 °C (X-ray energy=105.715 keV). Pt$_1$Bi$_1$ simulation (black, ICSD:9008911), Pt$_1$Bi$_2$ simulation (navy, ICSD:9012345) (B) XRD patterns of simulated tetragonal Pt$_1$Bi$_1$ (AuCu structure type) and experimental Pt-Bi/SiO$_2$ taken at 550 °C (X-ray energy=105.715 keV). Tetragonal Pt$_1$Bi$_1$ simulation (purple, Pt-Pt bond distance=2.74 Å, Pt-Bi bond distance=2.81 Å), Pt/SiO$_2$ (olive), 1Bi-2Pt/SiO$_2$ (red), 2Bi-2Pt/SiO$_2$ (blue), 4Bi-2Pt/SiO$_2$ (magenta).
Figure S7. The extracted profile of Pt M and Bi M concentration across single PtBi bimetallic nanoparticle as show inset.
### Table S1. XANES edge energy for the catalysts

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>XANES edge energy (keV)</th>
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<tbody>
<tr>
<td>2Pt/SiO₂</td>
<td>11.5640</td>
</tr>
<tr>
<td>1Bi-2Pt/SiO₂</td>
<td>11.5646</td>
</tr>
<tr>
<td>2Bi-2Pt/SiO₂</td>
<td>11.5647</td>
</tr>
<tr>
<td>4Bi-2Pt/SiO₂</td>
<td>11.5648</td>
</tr>
<tr>
<td>1Pt/ZSM-5</td>
<td>11.5640</td>
</tr>
<tr>
<td>0.1Bi-1Pt/ZSM-5</td>
<td>11.5641</td>
</tr>
<tr>
<td>0.8Bi-1Pt/ZSM-5</td>
<td>11.5646</td>
</tr>
<tr>
<td>1Bi-1Pt/ZSM-5</td>
<td>11.5646</td>
</tr>
</tbody>
</table>

### Table S2. Peaks of the XRD spectra taken at 550°C

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>(111) peak (°)</th>
<th>(200) peak (°)</th>
<th>(220) peak (°)</th>
<th>(311) peak (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Pt/SiO₂</td>
<td>2.980</td>
<td>3.430</td>
<td>4.881</td>
<td>5.712</td>
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<tr>
<td>1Bi-2Pt/SiO₂</td>
<td>2.959</td>
<td>3.404</td>
<td>4.861</td>
<td>5.680</td>
</tr>
<tr>
<td>2Bi-2Pt/SiO₂</td>
<td>2.942</td>
<td>3.378</td>
<td>4.835</td>
<td>5.650</td>
</tr>
<tr>
<td>4Bi-2Pt/SiO₂</td>
<td>2.937</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>