Superior single atom catalysts (SACs) made by flame aerosol technology: The effect Pd size on TiO$_2$ for photocatalytic NOx removal

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Flame-made Commodities @ t/h

Tires (~30 wt%)

Carbon Black ($10 B)

Inks

Paints & Photocatalysts

SiO$_2$ ($3 B$)

TiO$_2$ ($5 B$)

25 t/h, Re $10^6$

Furnace Process for Carbon Black Production

Courtesy of Cabot

Courtesy of Dupont

Flowing aid
Multi-Scale Design for Synthesis of Flame-made materials

Quantitative understanding facilitates a) Scale-up 

700 g/h SiO₂
Re = 3’000-16’000

H₂-air diffusion flame

and b) drives innovation….
Multicomponent Nanomaterials en mass
by Spray Combustion or Flame Spray Pyrolysis (FSP)

SPP1980 SPRAYSYN
NANOPARTIKELSYNTHSE
IN SPRAYFLAMMEN

A 6-year, 6M Euro program by the German NSF for 30 PhD students started in April 2017

New flame-made products @ kg/h

Biomagnetic ferrofluids:
C-coated Co
100k – 1M$/kg

Ag/SiO$_2$ → nanosilver toxicity
by ions or particles?

nano-Ag for antibacterial applications

TurboBeads®
Product #697745 → 500 mg dry powder @ $105

Flame-to-order
Nanoparticle Compositions
Phosphors for bioimaging

2 Tbj 2 Tbj 2 Tb 0.1 Eu 2 Tb 2 Tb 0.25 Eu 2 Tb 0.5 Eu 2 Tbj 1 Eu 1 Eu

SiO2-coated
SPION/Ag

Dental fillers and bone replacement

Nutrition Supplements

Conductive composites

Breath Sensors

Photocatalytic removal of NOx (NO and NO₂) [1]

Challenges
- Selectivity for NO₃⁻ (vs. NO₂)
- Minimization of Pd used

Approaches
- Maximize Pd atoms on the surface by decreasing Pd size.
- Below 1 nm, Pd dispersion becomes close to ~100%.

Prof. Kakeru Fujiwara
*currently at Yamagata University, Japan

Photocatalysts by wet-chemistry & flame synthesis

TiO₃ P25, the “gold” standard in photocatalysis, is made commercially (Evonik) for 40+ years in oxy-hydrogen flames

Pd (1wt%) photodeposition
- Commercial TiO₂, P25 (w-Pd/P25)
- FSP-made TiO₂ (w-Pd/f-TiO₂)

10 g/L of powders EtOH:H₂O (1:1)

TTIP + Pd (acac)₂ in 2-EHA+Acetonitrile

8/5 mL TTIP / L O₂
NOx removal test (ISO: 22197-1:2007)

Air (3 L/min)  
NO: 1ppm  
RH: 50%  

5 cm × 10 cm: 17 mg ± 11% of particles  

Solar simulator (AM 1.5, 100 mW/cm²)  

DI-water  

NO3⁻  

NO3⁻  

NO3⁻  

NO3⁻
Solar NO$_x$ removal activity: Preparation method

\[ \text{NO}_x \text{ removed} \Rightarrow \text{NO}_3^- \text{ formed}^{[1]} \]

\[ \text{NO}_3^- \text{ formation} = \frac{\text{(NO}_3^- \text{ formed))}}{\text{ion meter}} \times \frac{\text{total NO fed in 5 h}}{\text{total NO fed in 5 h}} \]

\[ \text{Efficiency, %} \]

\[ \text{NO}_x \text{ removal} \]

\[ \text{NO}_3^- \text{ formation} \]

\[ \text{P25} \]

\[ 51 \text{ m}^2/\text{g} \]

NO\textsubscript{x} removal activity: Pd growth

Efficiency, %

<table>
<thead>
<tr>
<th></th>
<th>NO removal</th>
<th>NO\textsuperscript{3-} formation</th>
</tr>
</thead>
<tbody>
<tr>
<td>P25</td>
<td>51 m\textsuperscript{2}/g</td>
<td></td>
</tr>
<tr>
<td>f-Pd/TiO\textsubscript{2}</td>
<td>139 m\textsuperscript{2}/g</td>
<td></td>
</tr>
<tr>
<td>Air annealed</td>
<td>90 m\textsuperscript{2}/g</td>
<td></td>
</tr>
</tbody>
</table>

Fujiwara, K.; Müller, U.; SEP., ACS Catalysis, 6, 1887 (2016)
Optimal Pd loading & conditions w.r.t. NO removal

![Chart showing NOx removal efficiency vs. air annealing temperature for different Pd loadings on TiO2. The chart includes data points for Commercial TiO2 (P25, Evonik) and Pd loadings of 1 and 3 wt%.]

- **Pd, wt%**
  - As-prepared
  - Commercial TiO2 (P25, Evonik)
  - 1
  - 3

- **Air annealing temperature, °C**
  - 200
  - 400
  - 600

- **NOx removal efficiency, %**
  - 0
  - 10
  - 20
  - 30
  - 40
  - 50
Optimal Pd loading & conditions w.r.t. NO removal

As-prepared
Commecial TiO₂ (P25, Evonik)

Air annealing temperature, °C
NOₓ removal efficiency, %

Pd, wt% (0.1, 1, 3)

Optimal Pd loading & conditions w.r.t. NO removal

Fujiwara, K.; SEP., AIChe J., 63, 139 (2017)
Comparison with other photocatalysts

\[
\text{Improvement, } \% = \frac{\eta_{\text{NO}_x}}{\eta_{\text{NO}_x} \text{ of reference TiO}_2} \times 100
\]

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Improvement over P25, %</th>
<th>Reference TiO(_2)</th>
<th>Light source</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1Pd/TiO(_2) (This work) Air annealing at 600 °C</td>
<td>917</td>
<td>P25</td>
<td>Solar simulator</td>
</tr>
<tr>
<td>[1] 1Pd/TiO(_2) (Wet precipitation)</td>
<td>121</td>
<td>P25</td>
<td>UV</td>
</tr>
<tr>
<td>[3] Plasma treated TiO(_2)</td>
<td>~250</td>
<td>ST-1</td>
<td>UV-Vis</td>
</tr>
</tbody>
</table>

Pd structure by FTIR with probing molecular (NO)

1000 ppm of NO in N₂
At 50 °C

Pd = 0%

*All catalysts are annealed in air at 600 °C for 2 h.

Pd structure by FTIR with probing molecular (NO)

1000 ppm of NO in N₂
At 50 °C

*All catalysts are annealed in air at 600 °C for 2 h.

Pd structure by FTIR with probing molecular (NO)

1Pd/TiO₂

0.1Pd/TiO₂

1000 ppm of NO in N₂
At 50 °C

Wavenumber, cm⁻¹

Pd = 1%
Pd = 0.1%
Pd = 0%

*All catalysts are annealed in air at 600 °C for 2 h.

Quantification of NO$_x$ removal by Pd atoms and clusters by DRIFTS and inclusion of BaSO$_4$ as internal standard.

TiO$_2$ containing 0.1 wt% of Pd with 50 wt.% of BaSO$_4$.
Quantification of NO$_x$ removal by Pd atoms and clusters by DRIFTS and inclusion of BaSO$_4$ as internal standard

The peak height of NO adsorption normalized to the S-O height is **linearly** proportional to the population of isolated Pd sites.
Quantification of NO$_x$ removal by Pd atoms and clusters by DRIFTS and inclusion of BaSO$_4$ as internal standard.

The peak height of normalized NO adsorption on isolated Pd sites [NO-Pd$_{iso}$] is **NOT linearly** proportional to [Pd].

10-fold increase [Pd] → only a 25 % increase in [NO-Pd$_{iso}$] peak height!!
Quantification of NO\textsubscript{x} removal by Pd atoms and clusters by DRIFTS and inclusion of BaSO\textsubscript{4} as internal standard.

TiO\textsubscript{2} containing 0.1 wt% of Pd with 50 wt.% of BaSO\textsubscript{4} and 20 min exposure to 2000 ppm NO.
So what?

isolated Pd atoms on TiO$_2$ are the DOMINANT active sites as co-catalyst for photocatalytic NO$_x$ removal similar to WGS rxn\textsuperscript{1}.

Fu Q, Saltsburg H, Flytzani-Stephanopoulos M. Science. 2003;301(5635):935-938.
Conclusions

- Closely-sized sub-nano Pd on TiO$_2$ is produced by scalable flame aerosol technology.
- Subnano Pd on TiO$_2$ is stable up to 600 °C in air.
- Pd atoms on TiO$_2$ most active for solar light NO$_x$ removal than Pd clusters & nanoparticles.
Thank you for listening!

Aletsch Glacier, Fieschalp → Riederalp → suspension bridge → Belalp Switzerland
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