Superior single atom catalysts (SACs) made by flame aerosol technology: The effect Pd size on TiO_2 for photocatalytic NOx removal

Sotiris E. Pratsinis
Particle Technology Laboratory
ETH Zürich, Switzerland

Flame-made Commodities @ t/h

Paints &
Photocatalysts

Courtesy of Dupont

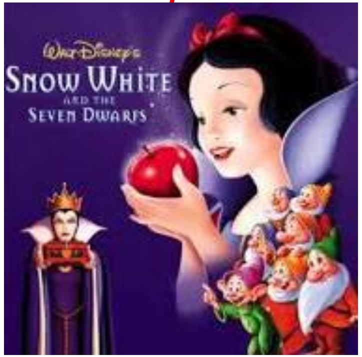
TiO_2
($5 B)

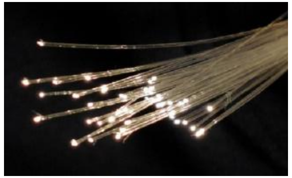
Tires (~30 wt%)

Carbon Black
($10 B)

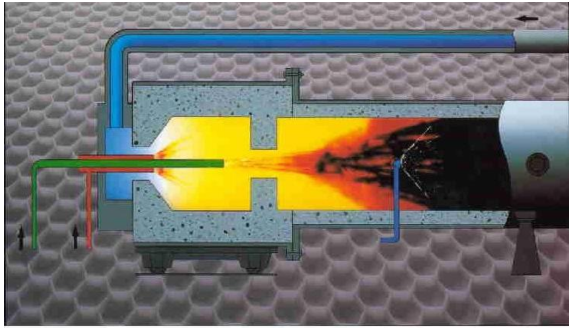
25 t/h, Re 10^6

Inks





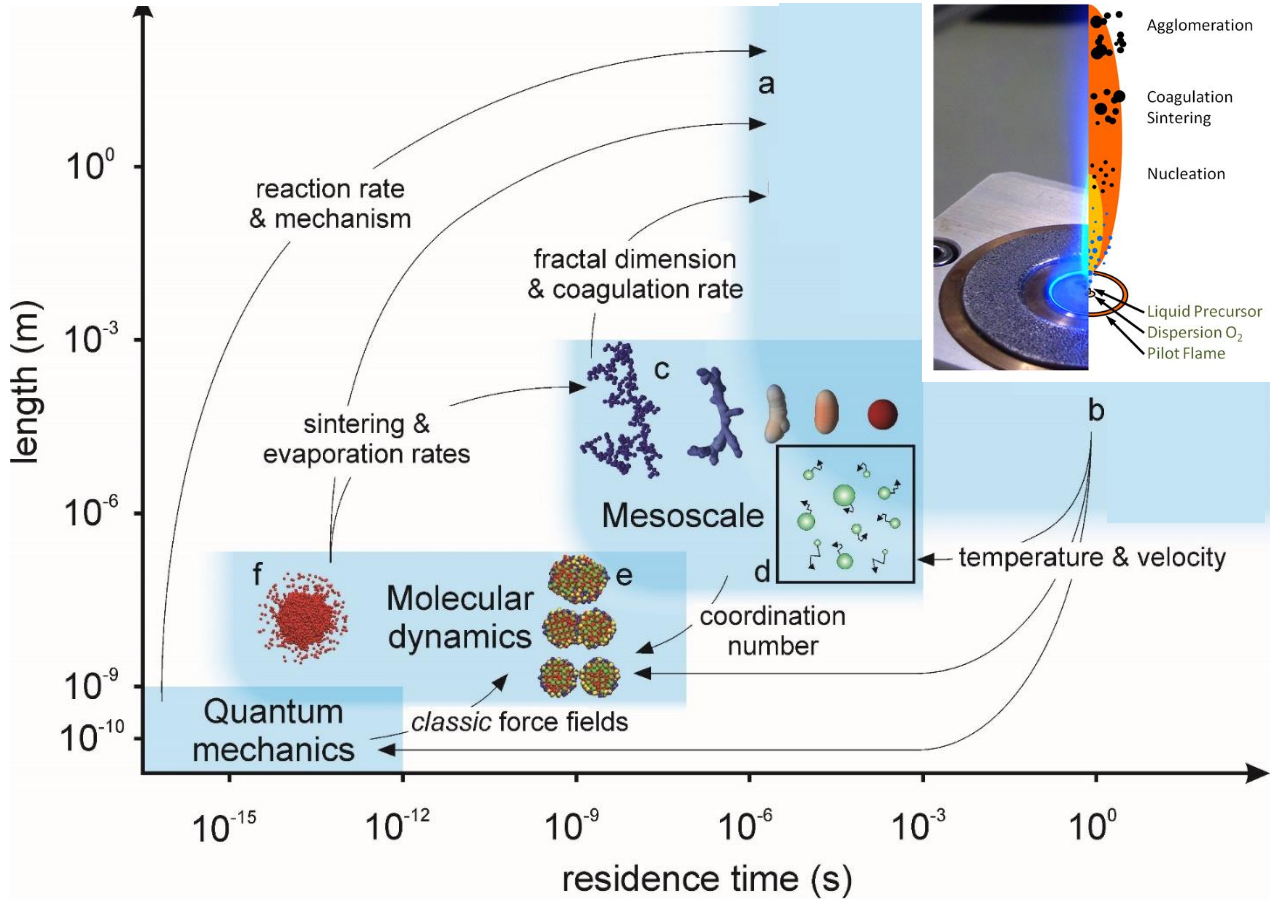
SiO_2($3 B)
Flowing aid



Furnace Process for Carbon Black Production

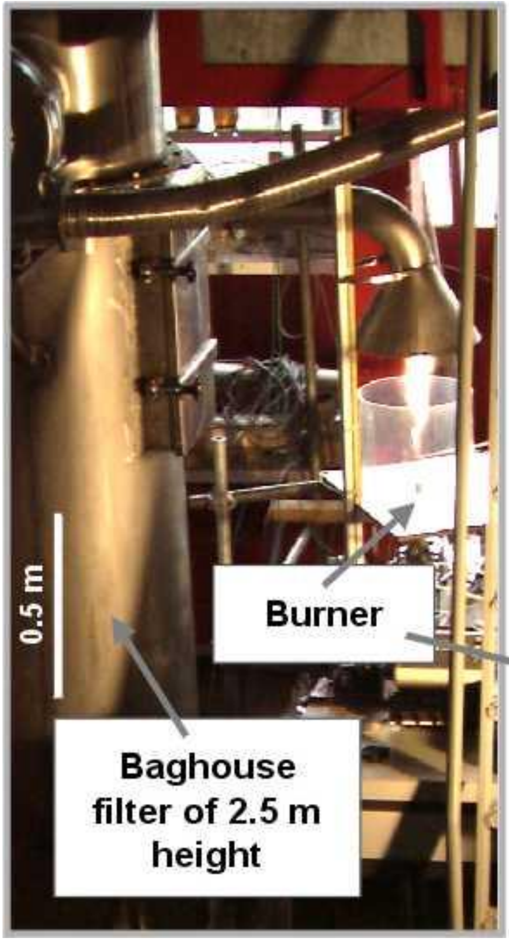
Courtesy of Cabot

Multi-Scale Design for Synthesis of Flame-made materials



Buesser, B. SEP. *Annual Rev. Chem. Biomol. Eng.*, **3**, 103 (2012).

Quantitative understanding facilitates a) Scale-up ....



700 g/h SiO_2

Re= 3’000-16’000

H_2-air diffusion flame

H. Kammler, R. Müller, O. Senn, SEP, *AIChE J.*, (2001).

and b) drives innovation….

Multicomponent Nanomaterials en mass
by Spray Combustion or Flame Spray Pyrolysis (FSP)

SPP1980
SPRAYSYN

NANOPARTIKELSYNTHESE
IN SPRAYFLAMMEN

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

HARVARD
SCHOOL OF PUBLIC HEALTH

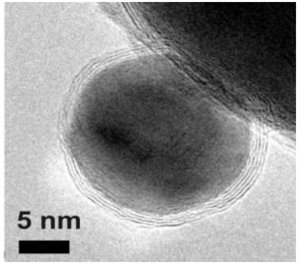
NIH – NHIR → $5M
NTU Sus Nano→ $5M

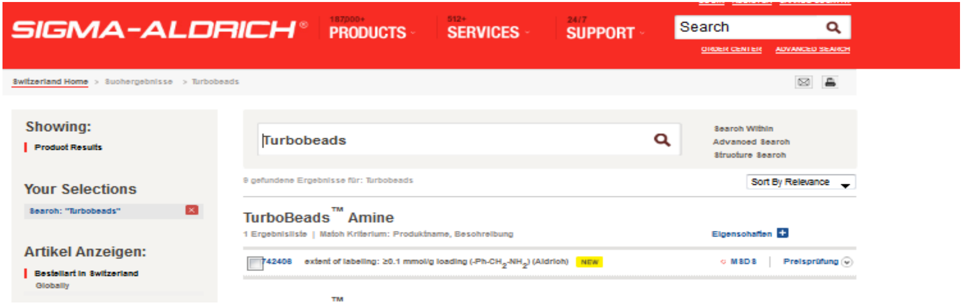
Strobel, R., Stark, W.J., Mädler, L., SEP, Baiker, A., *J. Catal.*, **213**, 296-304, (2003).
Mädler, L., Müller, R., Kammler, H., SEP, *J. Aerosol Sci.* **33**, 369-389 (2002).

New flame-made products @ kg/h

Biomagnetic ferrofluids: C-coated Co

100k – 1M$/kg





TurboBeads®

Product #697745 → 500 mg dry powder @ $105

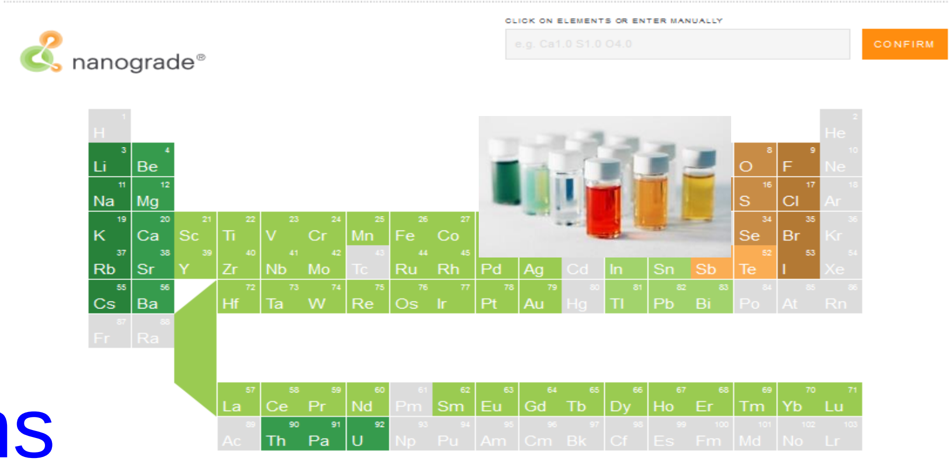
Flame-to-order

Nanoparticle Compositions

Ag/SiO_2→**nanosilver** toxicity by ions or particles?

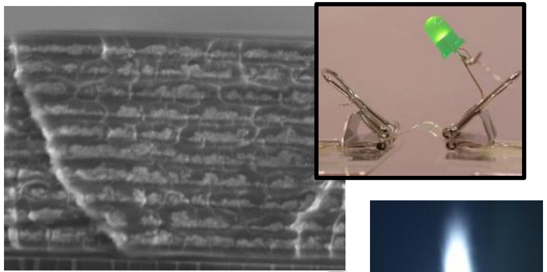
nano-Ag for antibacterial applications

HEIQ

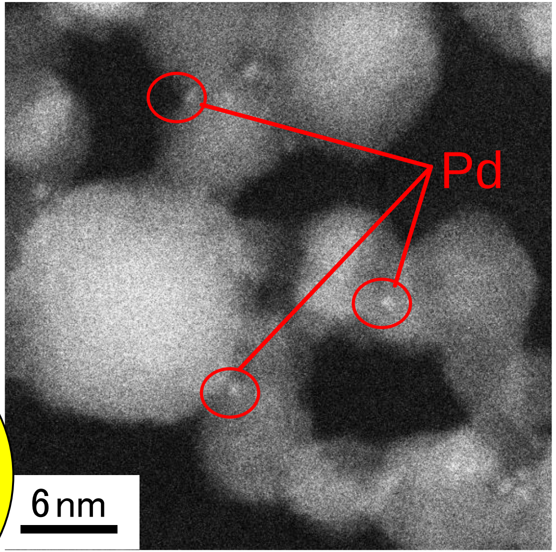


Dental fillers and bone replacement

Conductive composites



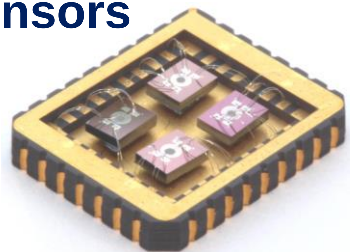
Single Atom Catalysts



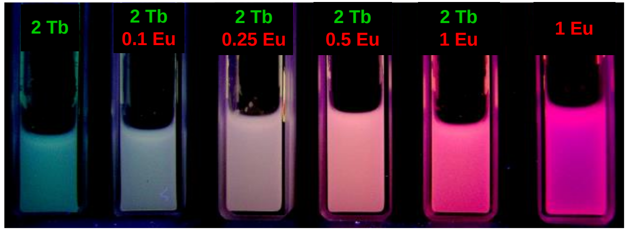
Novel flame-made functional materials

Nutrition Supplements

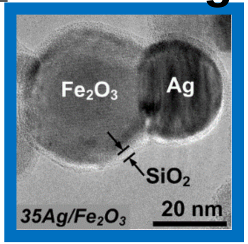
Breath Sensors



Phosphors for bioimaging

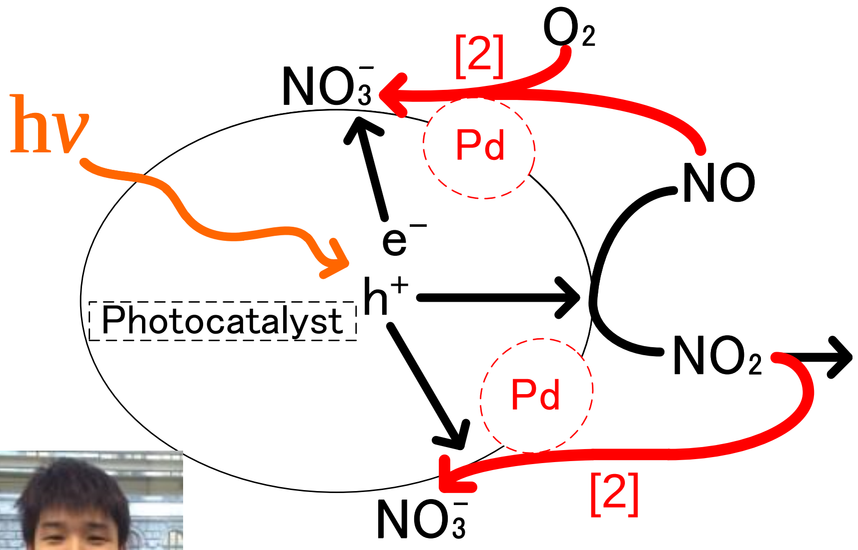


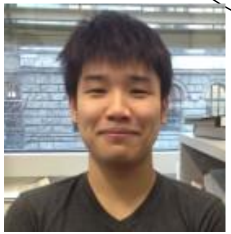
SiO_2-coated SPION/Ag



Flame aerosol synthesis of smart nanostructured materials, *J. Mater. Chem.*, **17**, 4743 (2007).

Photocatalytic removal of NOx (NO and NO_2)[1]





Prof. Kakeru Fujiwara
*currently at Yamagata University, Japan

Challenges

- Selectivity for NO_3^- (vs. NO_2)
- Minimization of Pd used

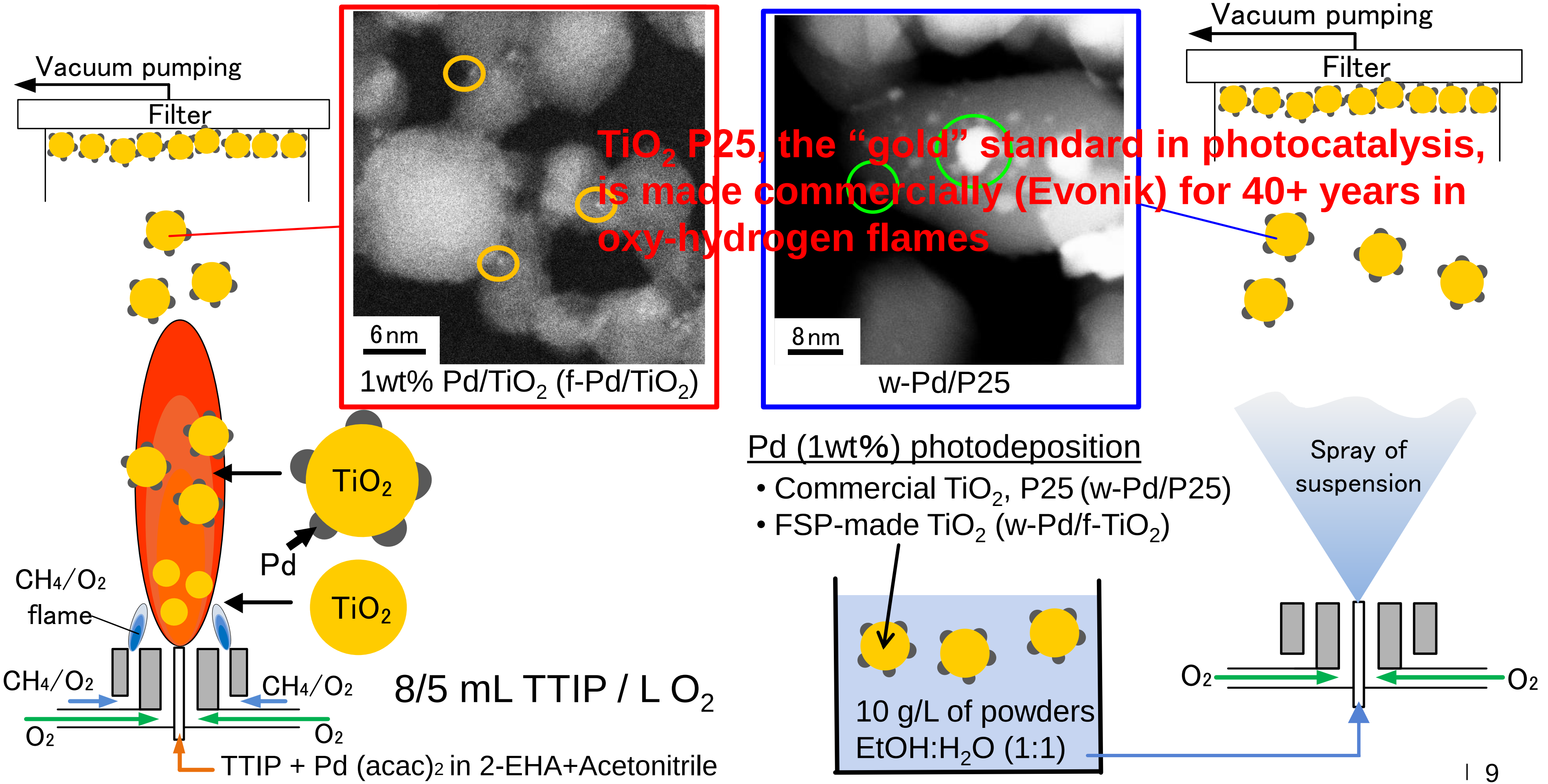
Approaches

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

[1] Dalton, J. S.; Janes, P. A.; Jones, N. G.; Nicholson, J. A.; Hallam, K. R.; Allen, G. C., *Environ. Pollut.* **2002,** *120* (2), 415-422.
[2] Wu, Z.; Sheng, Z.; Liu, Y.; Wang, H.; Tang, N.; Wang, J., *J. Hazard. Mater.* **2009,** *164* (2), 542-548.

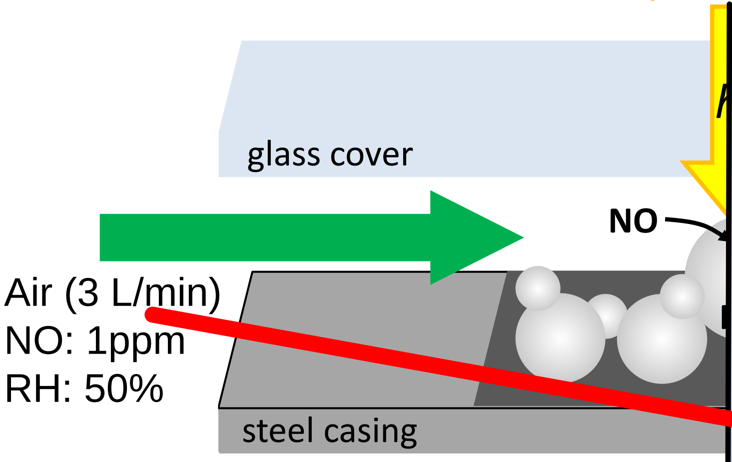
Photocatalysts by wet-chemistry & flame synthesis

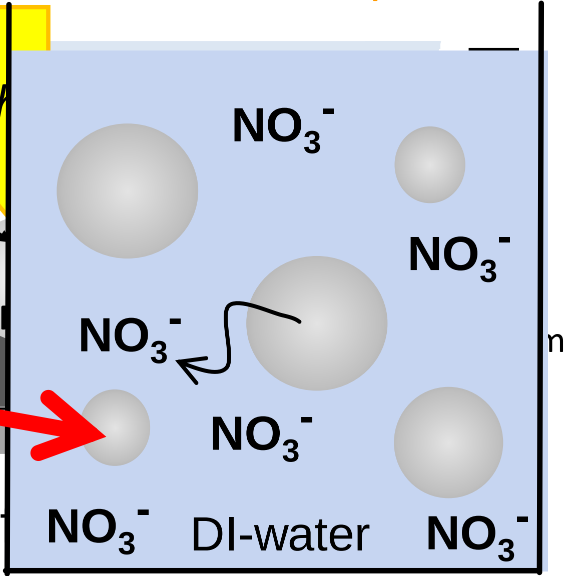
TiO_2 P25, the "gold" standard in photocatalysis, is made commercially (Evonik) for 40+ years in oxy-hydrogen flames



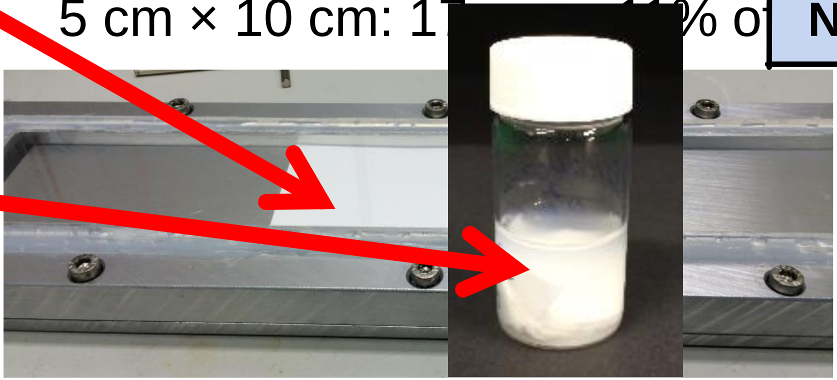
NOx removal test (ISO: 22197-1:2007)

Solar simulator (AM 1.5, 100 mW/cm^2)

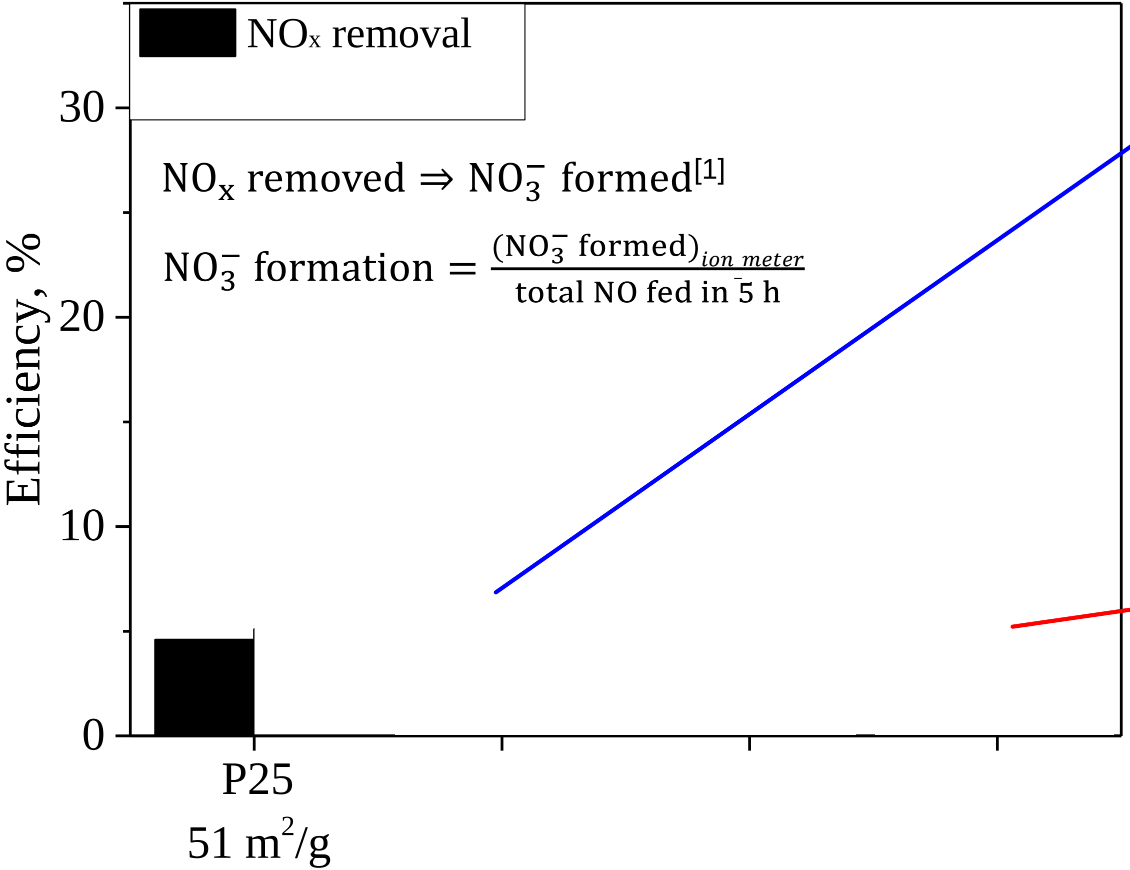




5 cm × 10 cm: 1T... % of

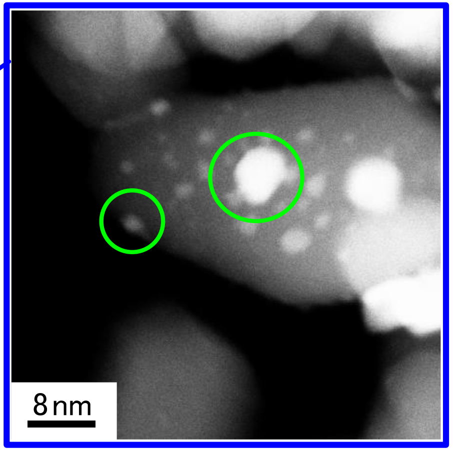


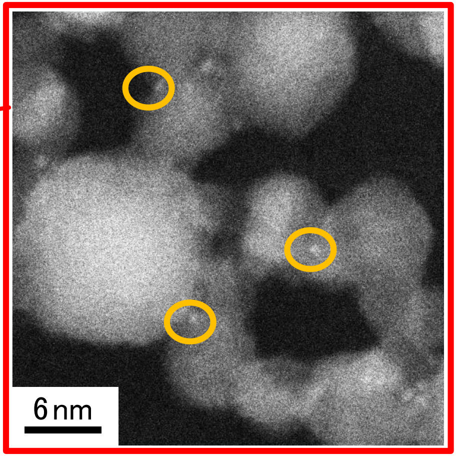
Solar NO_x removal activity: Preparation method



NO_x removed $\Rightarrow$ NO_3^- formed[1]

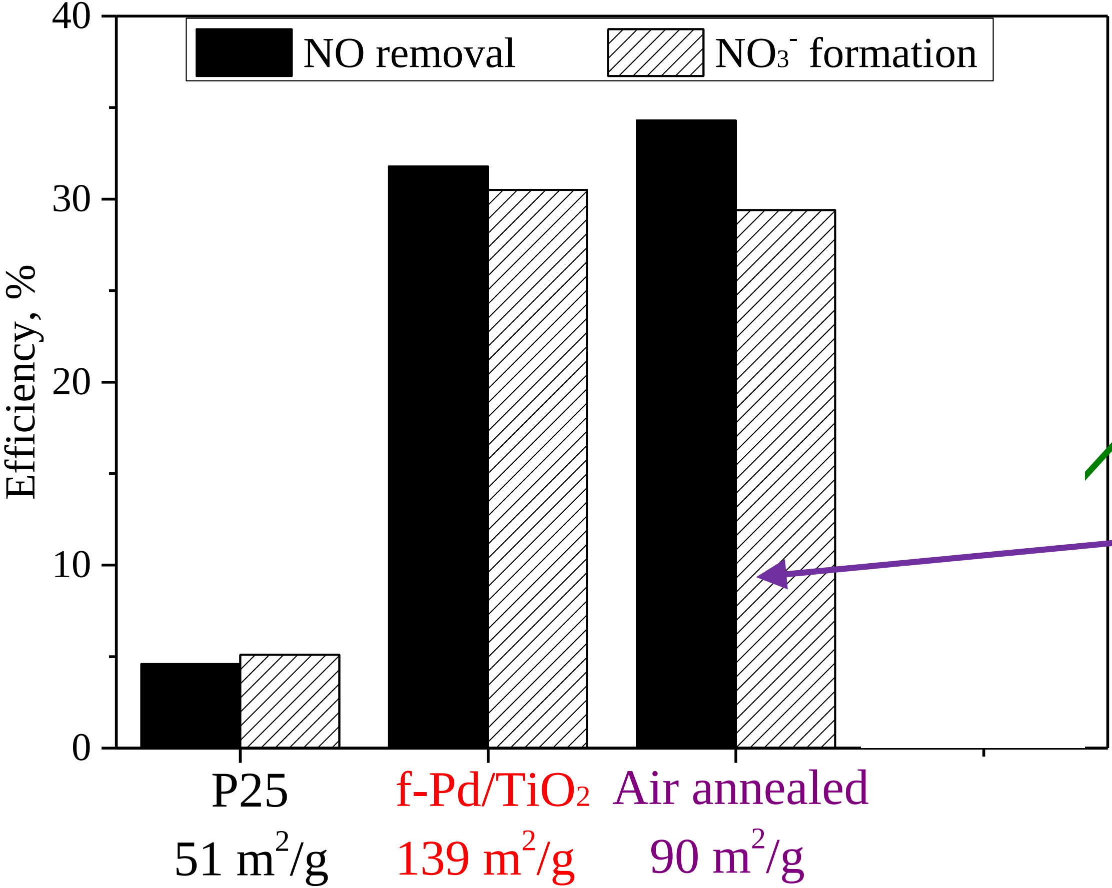
$$NO_3^- \text{ formation} = \frac{(NO_3^- \text{ formed})_{ion\ meter}}{\text{total NO fed in 5 h}}$$

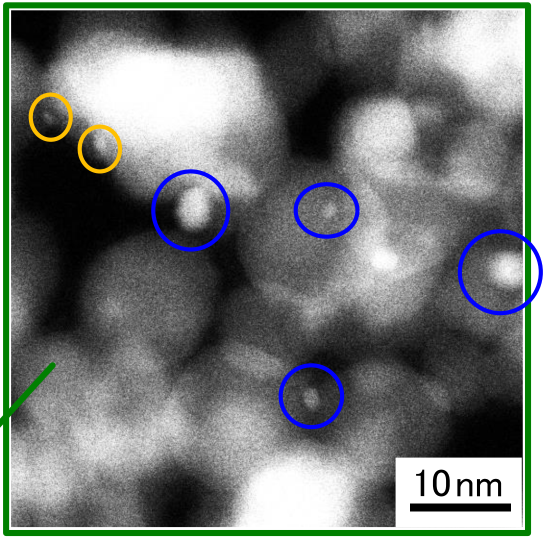


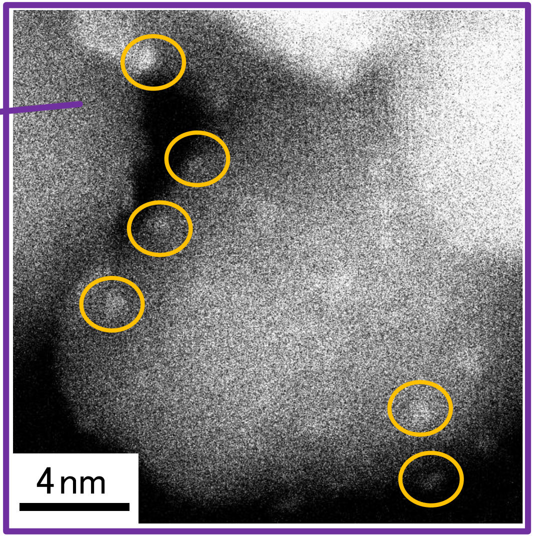


[1] Dalton, J. S.; Janes, P. A.; Jones, N. G.; Nicholson, J. A.; Hallam, K. R.; Allen, G. C., *Environ. Pollut.* **2002,** *120* (2), 415-422.

NO_x removal activity: Pd growth

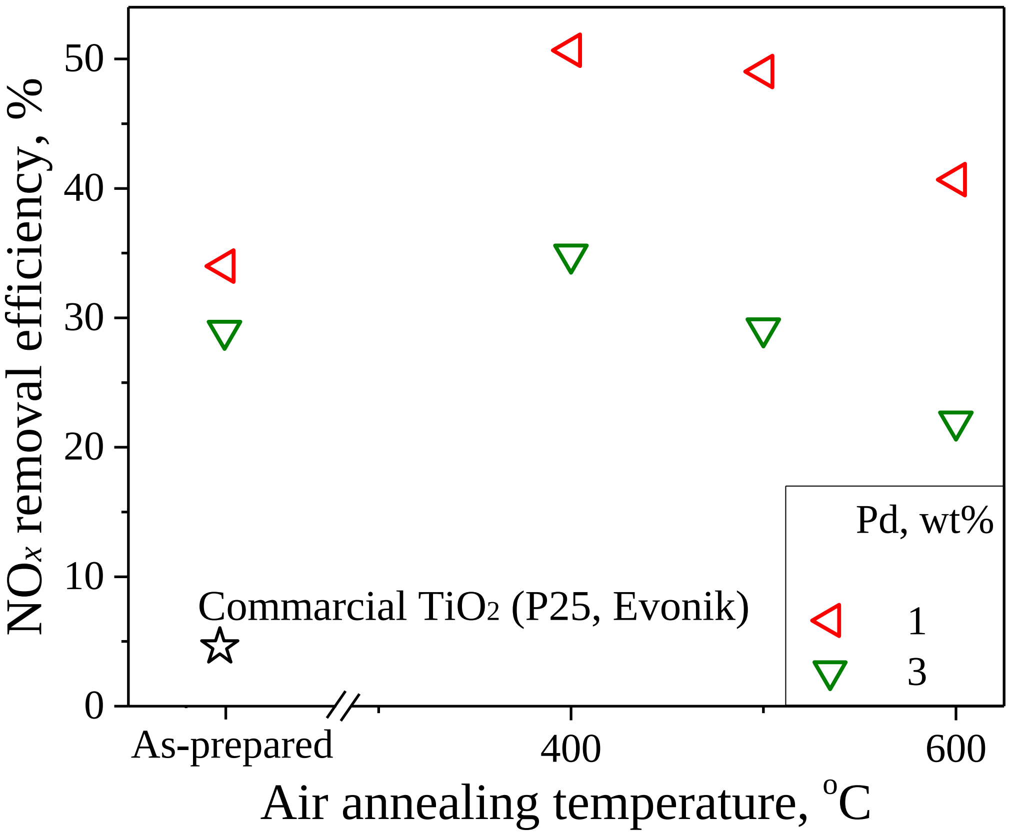


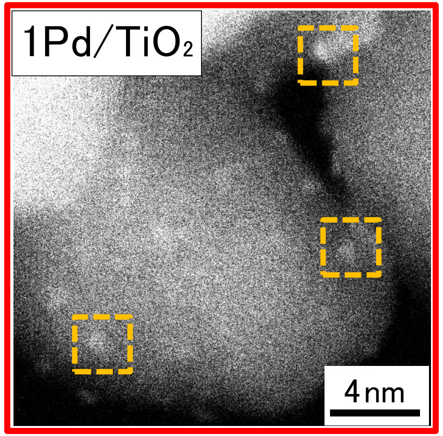


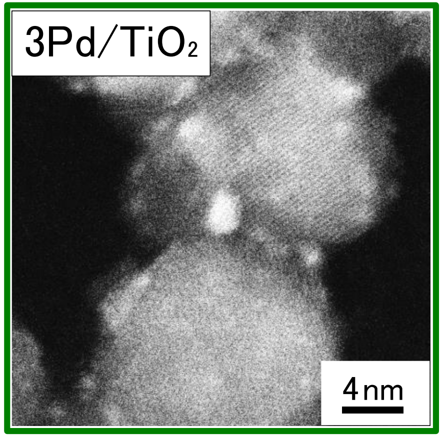


Fujiwara, K.; Müller, U.; SEP., ACS Catalysis, 6, 1887 (2016)

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







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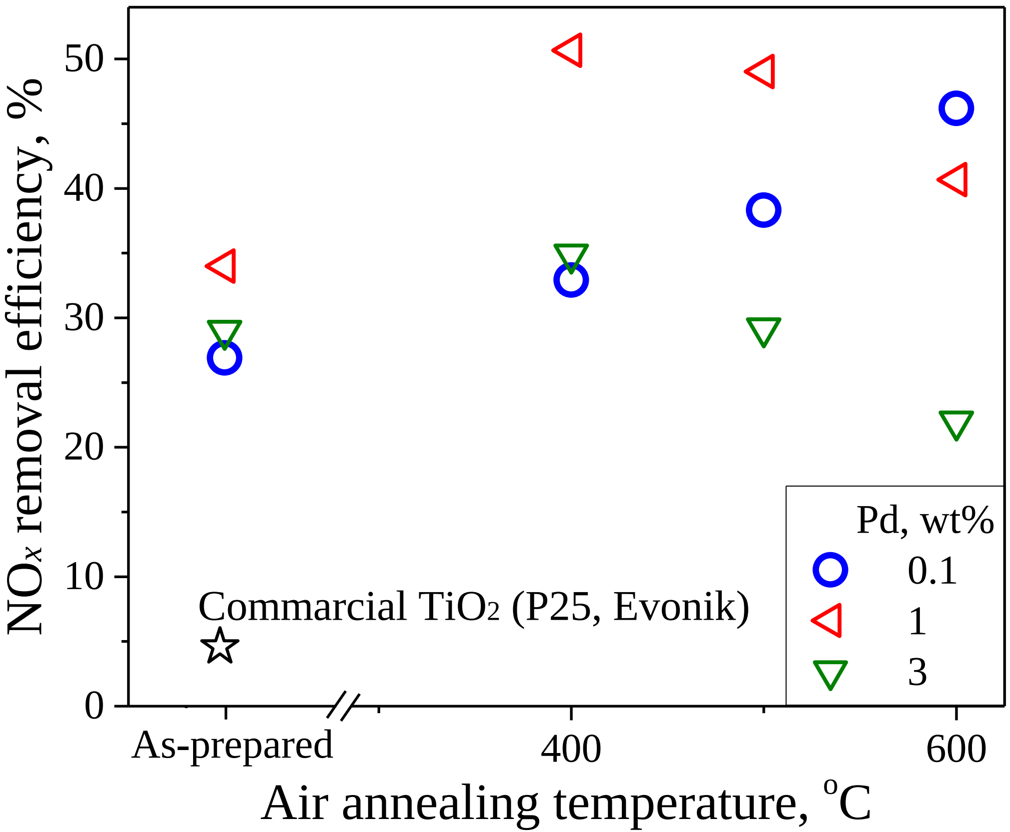
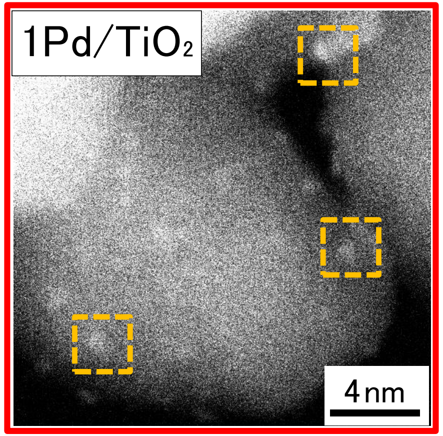
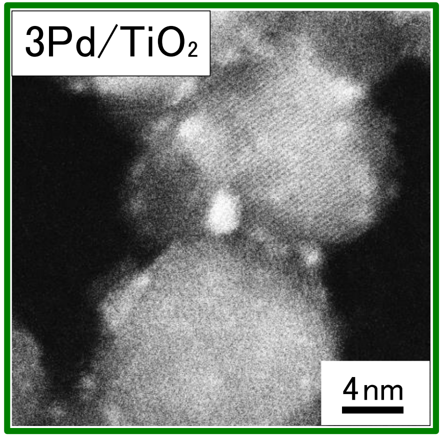
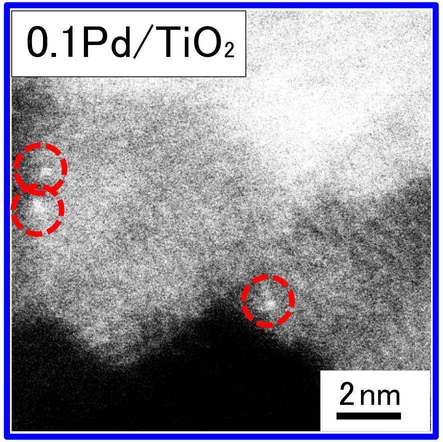








Fujiwara, K.; SEP., *AIChE J.*, **63**, 139 (2017)

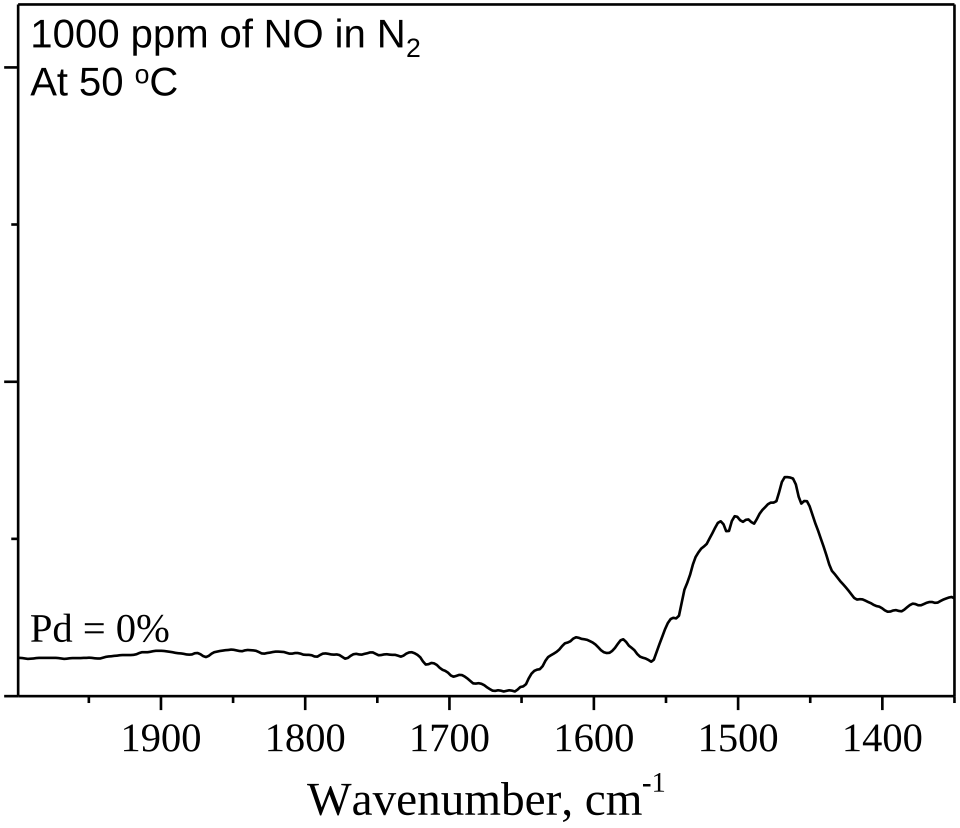
Comparison with other photocatalysts

$$\textbf{Improvement}\text{ , \%} = \frac{\eta_{NO_x}}{\eta_{NO_x}\text{ of reference TiO}_2} \times 100$$

Ref.		Improvement over P25, %	Reference TiO_2	Light source
	0.1Pd/TiO_2 (This work) Air annealing at 600 ºC	**917**	P25	Solar simulator
[1]	1Pd/TiO_2 (Wet precipitation)	121	P25	UV
[2]	Brookite TiO_2	156	P25	UV
[3]	Plasma treated TiO_2	~250	ST-1	UV-Vis

[1] Hsiao, Y.-C.; Tseng, Y.-H., *Micro & Nano Letters* **2010,** *5* (5), 317-320.
[2] Bloh, J. Z.; Folli, A.; Macphee, D. E., *RSC Advances* **2014,** *4* (86), 45726-45734.
[3] Nakamura, I.; Negishi, N.; Kutsuna, S.; Ihara, T.; Sugihara, S.; Takeuchi, K., *J. Mol. Catal. A: Chem.* **2000,** *161* (1–2), 205-212

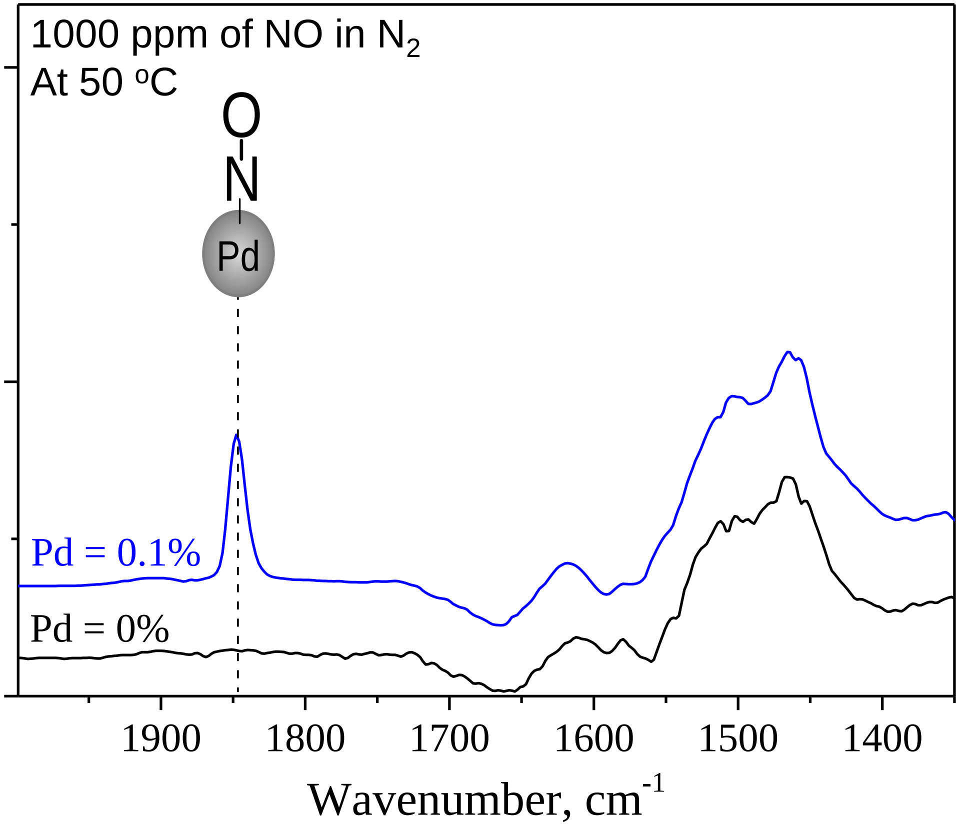
Pd structure by FTIR with probing molecular (NO)



*All catalysts are annealed in air at 600 ^oC for 2 h.

NO on Pd: Loffreda, D.; Simon, D.; Sautet, P., *J. Catal.* 2003, *213* (2), 211-225.

Pd structure by FTIR with probing molecular (NO)



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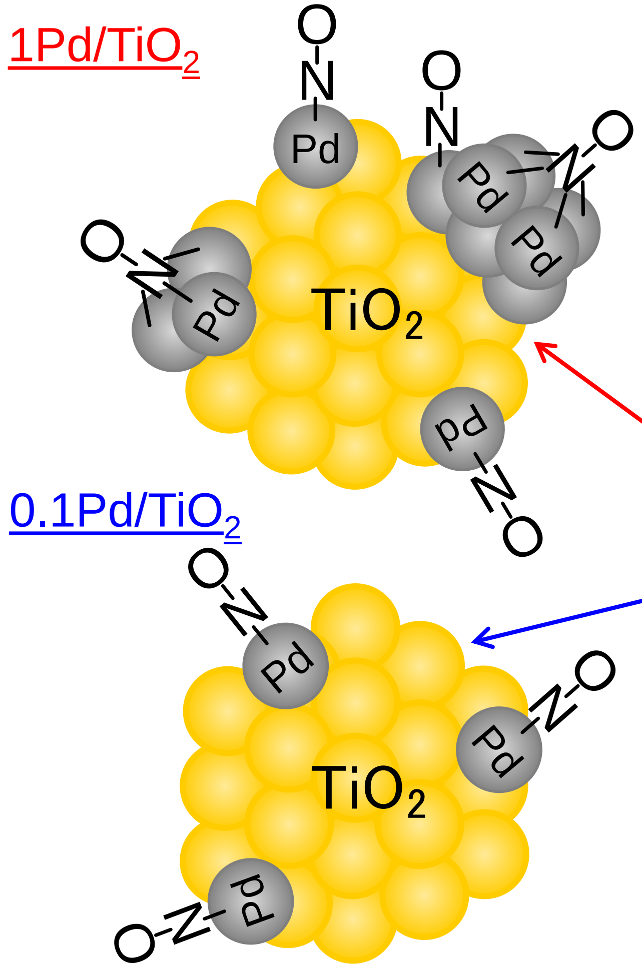

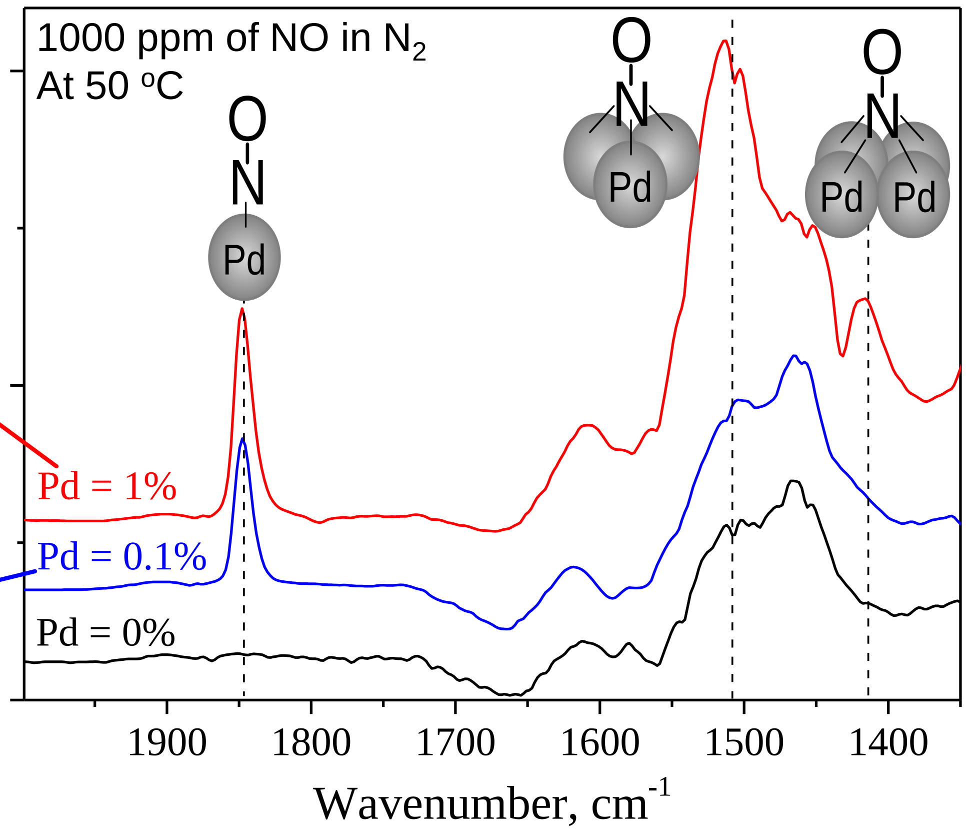

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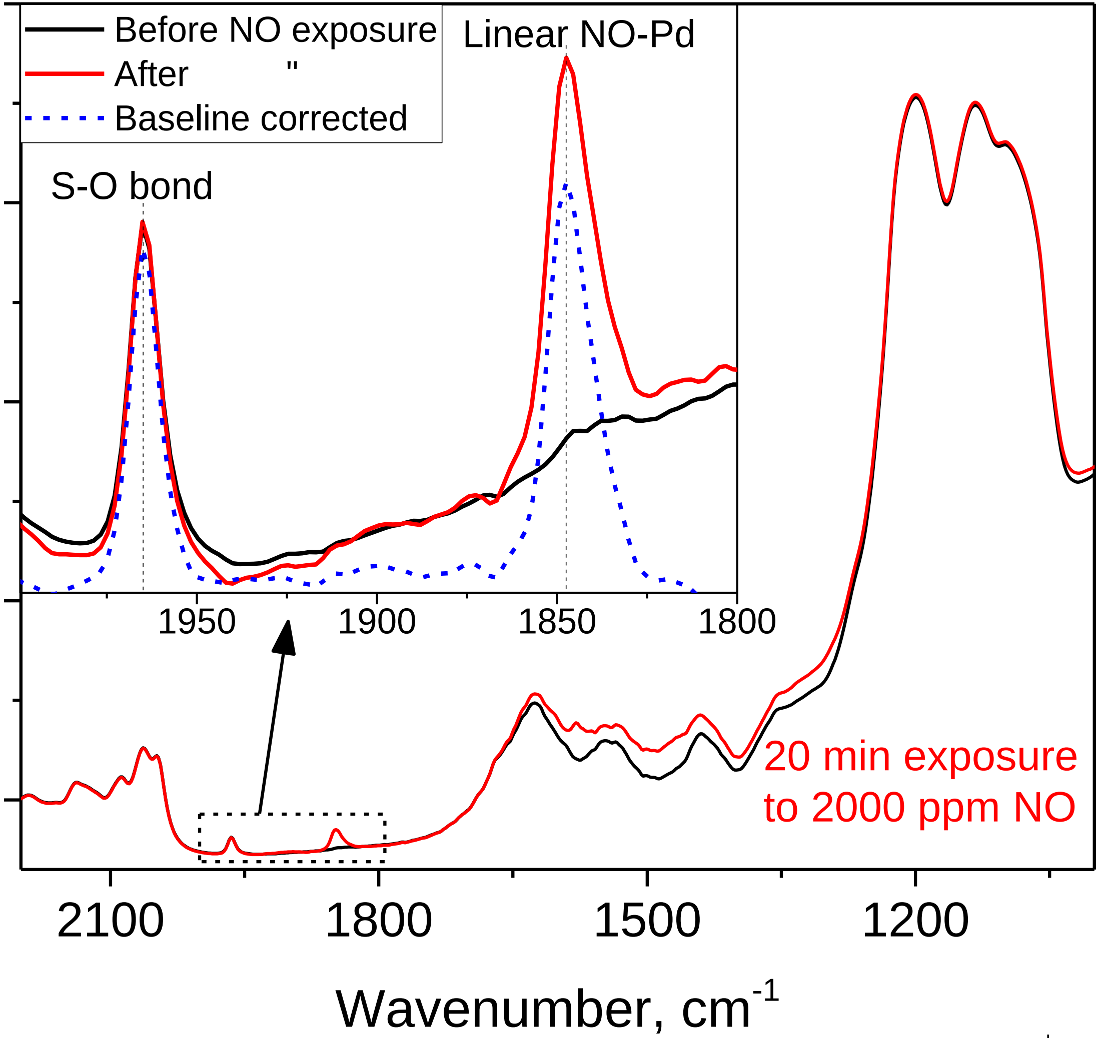
NO on Pd: Loffreda, D.; Simon, D.; Sautet, P., *J. Catal.* 2003, *213* (2), 211-225.

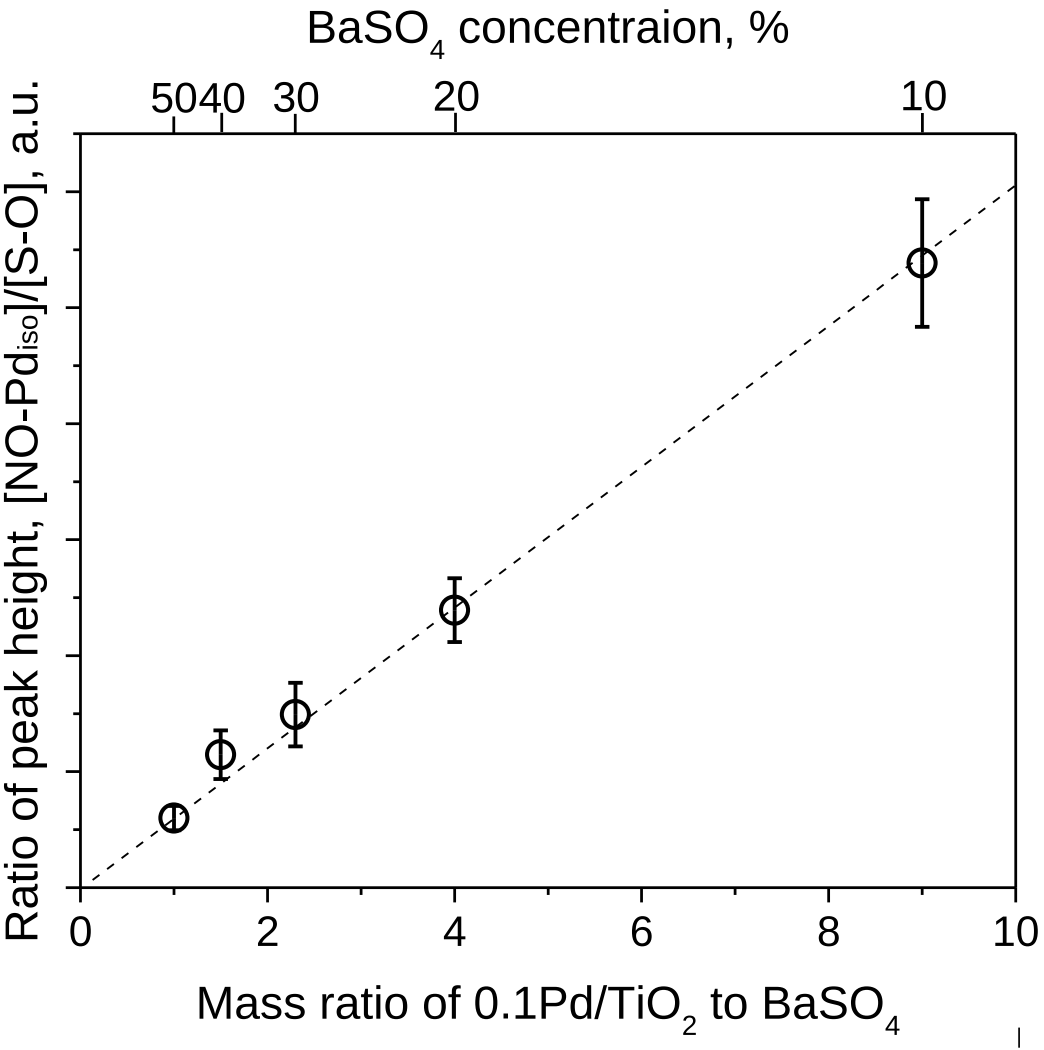
Quantification of NO_x removal by Pd atoms and clusters by DRIFTS and inclusion of $BaSO_4$ as internal standard



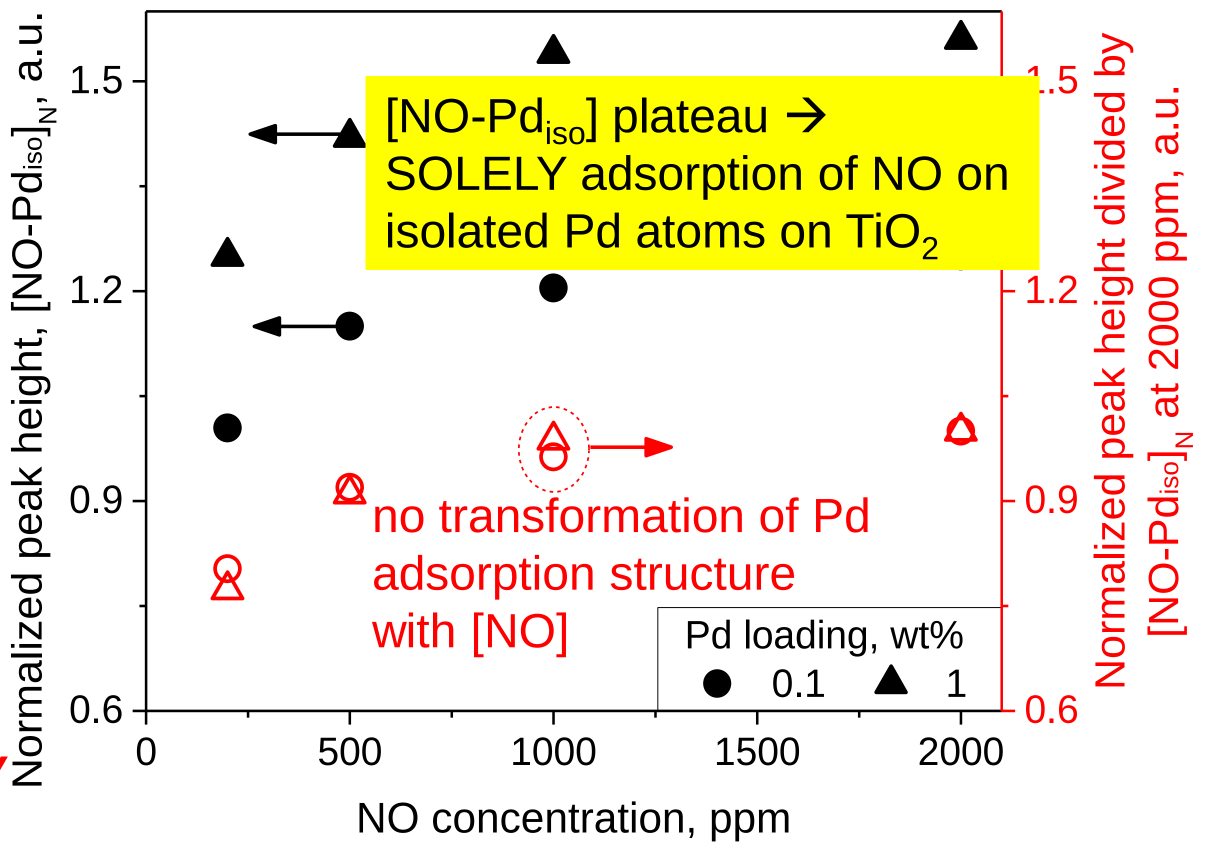
TiO_2 containing 0.1 wt% of Pd with 50 wt.% of $BaSO_4$

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



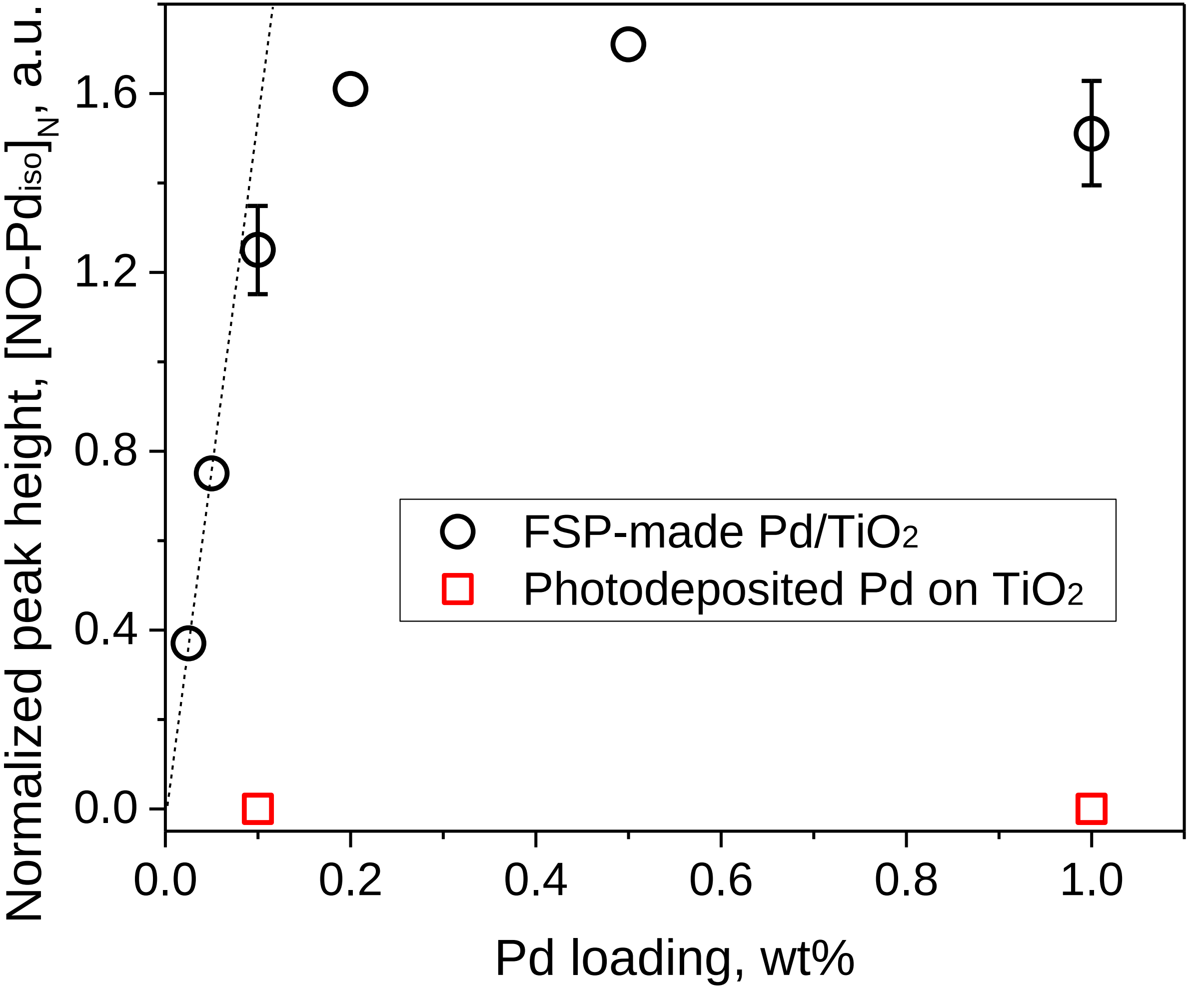
Quantification of NO_x removal by Pd atoms and clusters by DRIFTS and inclusion of $BaSO_4$ as internal standard



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!!

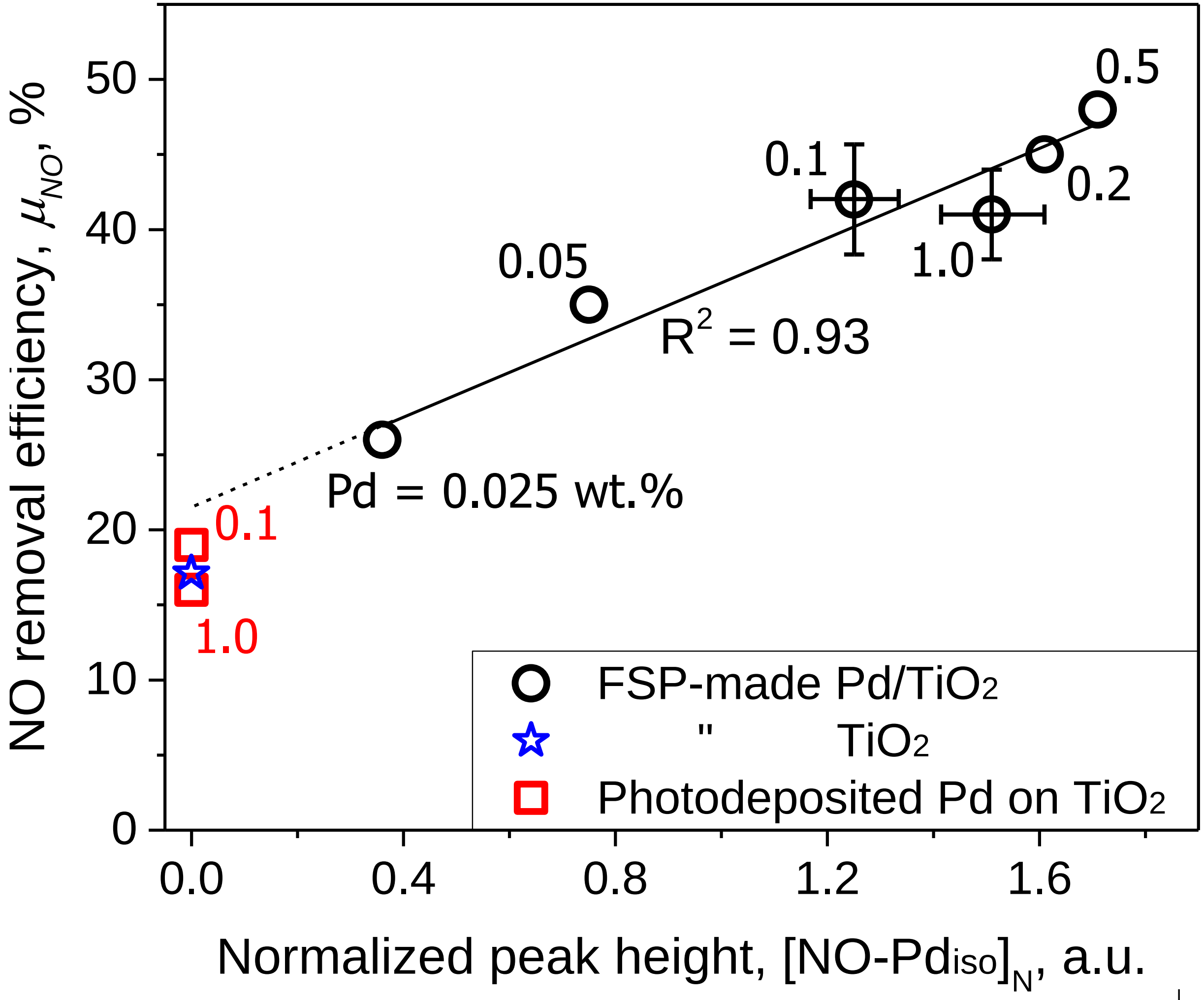
Quantification of NO_x removal by Pd atoms and clusters by DRIFTS and inclusion of $BaSO_4$ as internal standard



TiO_2 containing 0.1 wt% of Pd with 50 wt.% of $BaSO_4$ and 20 min exposure to 2000 ppm NO

So what?

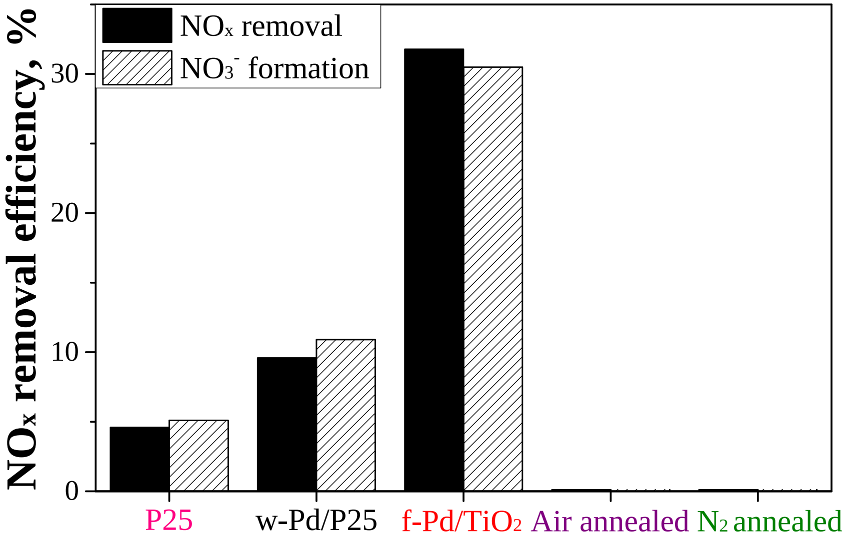
isolated Pd atoms on TiO_2 are the DOMINANT active sites as co-catalyst for photocatalytic NO_x removal similar to WGS rxn[1].

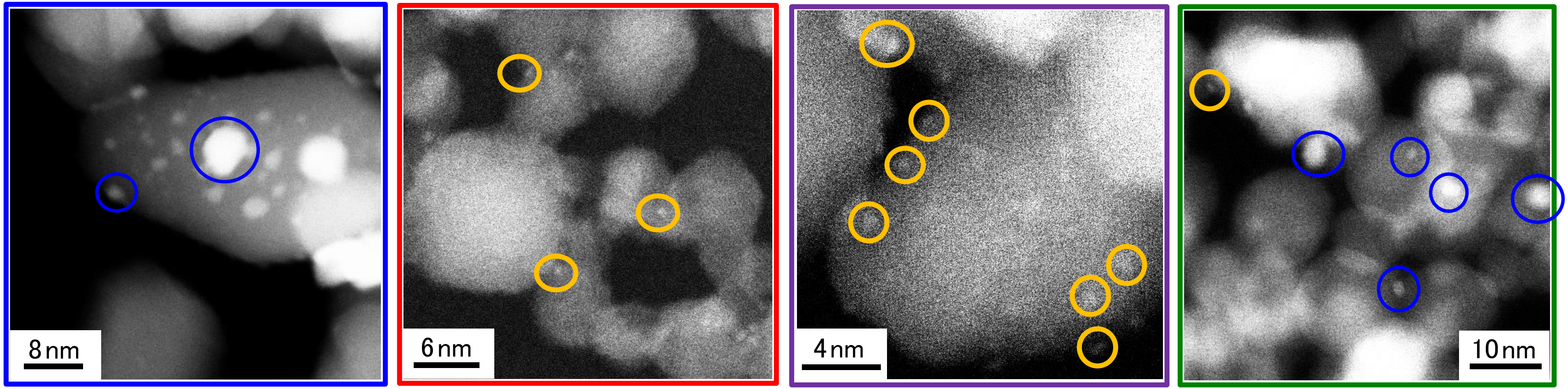


Fu Q, Saltsburg H, Flytzani-Stephanopoulos M. *Science.* 2003;301(5635):935-938.

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 ^oC in air.
- Pd atoms on TiO_2 most active for solar light NO_x removal than Pd clusters & nanoparticles





w-Pd/P25 | f-Pd/TiO_2 | air at 600 ^oC | N_2 at 400 ^oC

Thank you for listening!

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

August 25-26, 2016