Palladium subnano-clusters on TiO_2 for solar photocatalytic NO removal

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Nitrogen oxides, NO_x (NO and NO_2), are major pollutants generated by combustion. Removal of such NO_x by solar photocatalysts that requires only sunlight is quite attractive. Titanium oxide is the most widely used photocatalyst. Under light excitation, TiO_2 converts NO_x into nitrate ions (NO_3^-) but some NO is converted also into unfavorable NO_2.[1] So high conversion and selectivity for nitrate formation are essential. Sub-nanometer sized metal clusters on metal oxide supports induce high conversion and high selectivity minimizing the use of expensive noble metals on such catalysts.[2]

Here, Pd subnano-clusters on TiO_2 were prepared in one step by flame spray pyrolysis (FSP) which can be scaled up readily to yield production rates of several kg/h. The photocatalytic NO (1 ppm) removal efficiency of those Pd/TiO_2 under solar light (100 mW/cm^2) was evaluated based on ISO 22197-1:2007. The average NO_x removal (η_{NOx}) and nitrate formation (η_{NO3-}) for 5 h is defined by[3]:

$$\eta_{NOx} = \int_0^{5h} \frac{c_{NOin} - c_{NOout} + c_{NO2out}}{c_{NOin}} dt$$

$$\eta_{NO3-} = \frac{m_{NO3-}[\text{mol}]}{3[\text{L/min}] \Big/ 22.4\,[\text{L/mol}] \int_0^{300\,min} c_{NO}\,[\text{mol}]\,dt}$$

Table 1 Specific surface area (SSA) of commercial TiO_2 (c-TiO_2), FSP-made (f-TiO_2 and f-Pd/TiO_2) and wet-photodeposited Pd (w-Pd/c-TiO_2 and w-Pd/f-TiO_2) on TiO_2 and their average efficiencies of NO_x removal and NO_3^- formation in 5 h under solar-light.

Powders	SSA m^2/g	η_{NOx}, %	η_{NO3-}, %
c-TiO_2	51.1	4.6	5.1
f-TiO_2	144.1	12.9	11.9
w-Pd/c-TiO_2	49.5	9.6	10.9
w-Pd/f-TiO_2	131.4	11.9	12.2
f-Pd/TiO_2	138.7	31.8	30.5
f-Pd/TiO_2/air	89.6	34.9	29.7
f-Pd/TiO_2/N_2	135.1	25.3	21.4

As shown in Table 1, the η_{NOx} of all the catalysts is comparable with the η_{NO3-} indicating that most of converted NO becomes NO_2 and nitrate, which is consistent with photocatalytic NO removal by pure TiO_2.[1] The η_{NOx} of f-Pd/TiO_2 is 3 and 7 times higher than that of c-TiO_2 with and without photodeposited Pd on it. This activity of f-Pd/TiO_2 is higher than that of plasma-treated[4] TiO_2 was only about 2 times higher than that of commercial pure TiO_2 (ST-01). Furthermore, the η_{NOx} of f-TiO_2 is higher than that of c-TiO_2, probably due to the higher SSA but it is not improved by photodeposited Pd.

Interestingly, annealing f-Pd/TiO_2 in air at 600 ^{o}C (f-Pd/TiO_2/air) slightly improves the η_{NOx} but annealing in N_2 at 400 ^{o}C (f-Pd/TiO_2/N_2) degrades the η_{NOx}.
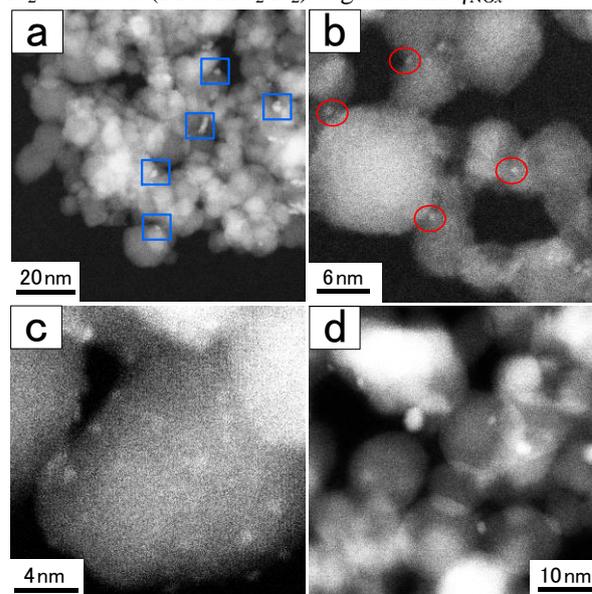

Figure 1 STEM images of (a) w-Pd/f-TiO_2, f-Pd/TiO_2, (b) as-prepared and annealed for 2 h in (c) air at 600 ^{o}C and (d) N_2 at 400 ^{o}C.

Figure 1 shows the size of photodeposited Pd (squares) on f-TiO_2 (a) to be 1-5 nm. In f-Pd/TiO_2 (b), however, there are no distinguishable Pd particles (> 1 nm) and extremely small size (~ 0.5 nm) of Pd clusters can be only observed (circles). Such Pd subnano-clusters are interacting strongly with oxygen defects on the TiO_2 surface creating an intermediate oxidation state of Pd as proven by XPS.[3] Most interestingly, after annealing in air at 600 ^{o}C for 2 hours (c), the Pd size in the f-Pd/TiO_2 powder is still in the subnano range. On the other hand, annealing that powder under N_2 at 400 ^{o}C for 2 hours (d) converts most of the as-prepared Pd subnano-clusters on TiO_2 into Pd nanoparticles (1-5 nm). Therefore, Pd subnano-clusters are critical for the remarkable photocatalytic NO_x removal under solar light.

1. Ibusuki, T.; Takeuchi, K., *J. Mol. Catal.* **1994,** *88*, 93-102.
2. Flytzani-Stephanopoulos, M.; Gates, B. C., Atomically dispersed supported metal catalysts. *Annu. Rev. Chem. Biomol. Eng.* **2012,** *3*, 545-574.
3. Fujiwara, K.; Müller, U.; Pratsinis, S. E., *ACS Catalysis* **2016**, 1887-1893.
4. Nakamura, I.; Negishi, N.; Kutsuna, S.; Ihara, T.; Sugihara, S.; Takeuchi, K., *J. Mol. Catal. A: Chem.* **2000,** *161*, 205-212.