One-step synthesis of atomically dispersed palladium on titania for NO removal

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Noble metal catalysts deposited on metal oxide supports are broadly used as heterogeneous catalysts. Size reduction of such noble metal particles is a classic way to enhance their activity with minimizing the use of expensive noble metals.[2] Recently, loading of extremely small Pd clusters (~ 0.5 nm) on TiO_2 by flame spray pyrolysis (FSP) exhibits superior photocatalytic activity for NO removal[1] and its further size reduction from the clusters to the isolated atoms have a great potential to maximize the NO_x removal activity.

Here, TiO_2 with different Pd loading (0-3%) were prepared by FSP to attain atomically dispersed Pd atoms on TiO_2. 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[1] (η_{NOx}) for 5 h is

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

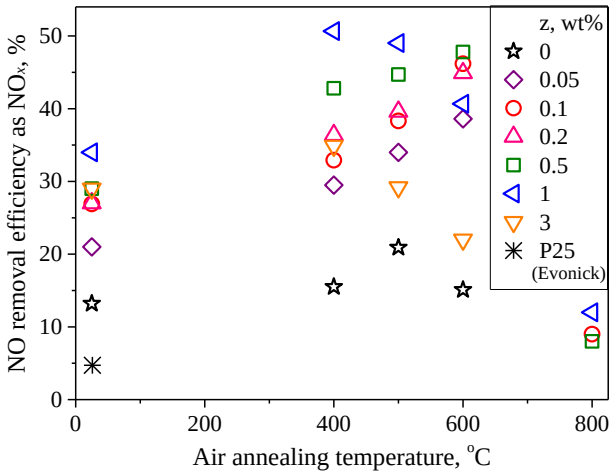

Figure 1 Solar NO removal activity as NO_x, η_{NOx}, of z Pd/TiO_2 (z = 0-3 wt%) as-prepared and annealed at different temperatures (400-600 °C) in air for 2 h.

Figure 1 shows the η_{NOx} of z Pd/TiO_2 (z = 0-3 wt%) as-prepared (25 °C) and annealed at different temperatures (400-600 °C) in air for 2 hours. Most of the removed NO_x are converted into nitrate ions that remain on the particles surface.[1] Annealing at 400 °C removes most of incomplete combustion products on the surface, which improves the η_{NOx}. By annealing at 400 °C, the η_{NOx} for z = 1 and 3% reaches maximum at 50.1% and 34.5%, respectively and gradually decreases with increasing annealing temperature. On the other hand, at z = 0.05-0.5, the η_{NOx} continuously increases up to 600 °C where the η_{NOx} reaches to comparable value for 1Pd/TiO_2 annealed at 400 °C. Interestingly, those optimal annealing temperatures for z Pd/TiO_2 are different from that of pure TiO_2 that is 500 °C. Therefore, the different Pd loading influences the characteristics of Pd that play a significant role on NO_x removal efficiency.

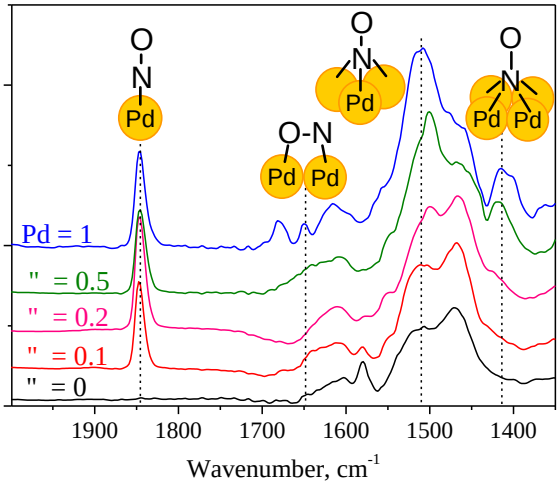

Figure 2 DRIFTS of z Pd/TiO_2 (z = 0-1 wt%) annealed in air at 600 °C for 2 h in NO (1000 ppm) in N_2 at 40 °C.

Figure 2 shows DRIFTS of NO adsorption on z Pd/TiO_2. For pure TiO_2 (Z = 0), there are several broad peaks (1581, 1554 and 1442 cm^{-1}) corresponding to nitro-nitrito complexes on TiO_2.[3] In the presence of Pd clusters[1] at Z = 1, NO adsorption[4] on single (1850 cm^{-1}) and double (1645 cm^{-1}) Pd atoms as well as at the hollows of 3- and 4-fold coordinated Pd atoms (1510 cm^{-1} and 1420 cm^{-1}) are observed. The peak intensities of adsorption sites involving multiple Pd atoms become weaker at lower z and, at z = 0.1 and 0.2, the peaks disappear. On the other hand, the peak intensity of the linear NO adsorption on single Pd atom (1850 cm^{-1}) is independent from z. If Pd atoms are isolated, the adsorption sites with multiple Pd atoms should not appear while only the one on single Pd atom does. This means the dominant presence of isolated Pd atoms at z = 0.1-0.2 while co-existence of the isolated ones and the clusters at z = 0.5-1. Since the η_{NOx} of 0.1-1Pd/TiO_2 annealed at 600 °C are comparable, the isolated Pd seems the dominant active site for photocatalytic NO removal.

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