Reduction of supported Pd nitrate catalysts by RF non-thermal plasmas

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Introduction

Non-thermal plasma based techniques have attracted significant attention for catalyst design and development [1]. Catalysts with unusual and highly advantageous catalytic properties including room temperature reduction, unusual metal particle structure and metal-support interactions, and enhanced selectivity and stability have been reported. Although the non-thermal plasma treatment is operated at room temperature, the effect lasts through high temperature calcinations and reductions. In fact, as reported earlier that both H_2 and air plasmas can reduce supported Pd nitrate catalysts. The reduction capacities of non-thermal plasma using non-reducing gases, including argon plasma and oxygen plasma, have also been reported recently [2]. The objective of this study is to obtain the fundamental understanding of the plasma reduction on supported metal catalysts for the design and development of novel heterogeneous catalysts.

Experimental

1/8" alumina and TiO_2 pellets (from Alfa Aesar) are crushed and sieved to 20-40 mesh sizes. These particles are then dried at 200°C for 12 hours followed by cooling down to room temperature in a desiccator. The resulted particles are impregnated with calculated mixed solution of palladium nitrate (Alfa), based on the incipient wetness technique. The obtained materials after drying at 120°C for 12 hours are designated as uncalcined 1%Pd/Al_2O_3 or 1%Pd/TiO_2.

Plasma treatments on uncalcined catalysts are carried out in a custom-made 360° rotating RF plasma system. 400 mtorr pressure, 130 watt output, and a continuous wave or pulsed (10ms/30ms on/off cycle) are used for H_2, Ar, and/or water plasma treatments in this study. Typically, one gram of uncalcined catalysts is loaded in the chamber for plasma treatments. Catalysts are reduced at 400°C before H_2 chemisorption for metal dispersion measurements using AMI-200 catalyst characterization (Altamira Instruments). Catalysts before and after H_2 chemisorption are analyzed by FT-IR, with a 1:10 sample to KBr ratio.

Results and Discussion

FT-IR spectra of four 1%Pd/Al_2O_3 catalysts, including the uncalcined, after H_2-Chemisorption (H_2 reduction), H_2 plasma 30 minutes and H_2 plasma 30 minutes, are shown in Figure 1. The nitrate peak of the uncalcined 1%Pd/TiO_2 is clearly at ~1385 cm^{-1} as shown in Figure 1a. After H_2 reduction at 400°C for 2 hours followed by H_2 chemisorption, the nitrate peak decreases significantly as expected, as shown in Figure 1b. However, the reduction percentage as calculated by the nitrate peak is 83% as listed in Table 1. It suggests that the nitrate group is fairly difficult to remove. H_2 plasma treatment for 30 minutes reduces the nitrate peak by 38% (Figure 1c) and 45 minutes of H_2 plasma treatment decreases 52% (Figure 1d) of the nitrate peak as compared to the uncalcined one. All three catalysts show similar Pd dispersion as listed in Table 1. The results indicate that H_2 plasma treatment is reasonably efficient for Pd nitrate reduction on Al_2O_3 support considering the treatment is at room temperature.

With TiO_2 as the support, the reduction capacity of 1%Pd nitrate can be completely removed (>99%) with 30 minutes of H_2 plasma treatment. The result suggests TiO_2 is beneficial to reduce Pd nitrate with H_2 plasma, though TiO_2 is known for stronger metal-support interaction. In addition, 30 minutes of air plasma treatment can remove 20% of nitrate peak as compared to the uncalcined 1%Pd/TiO_2.

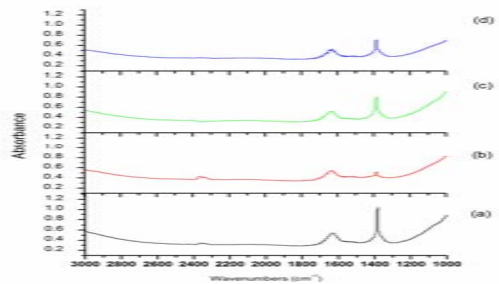

Figure 1. (a) uncalcined 1%Pd/Al_2O_3 (b) after H_2-Chemisorption (H_2 reduction), (c) After H_2 plasma treatment for 30min, (d) After H_2 plasma treatment for 45min.

Table 1. Reduction percentage and Pd dispersion

Catalyst	Treatment	Reduction (%)	Pd Dispersion (%)
1%Pd/Al_2O_3	H_2-Chemisorption	83	45.2
	H_2 plasma -30 min	38	43.8
	H_2 plasma -45 min	52	51.2
1%Pd/TiO_2	air plasma -30 min	20	NA
	H_2 plasma -30 min	>99	NA

Significance

The surprising discovery of the reduction capacity of non-thermal plasma at room temperature using traditionally non-reducing gases is an important step toward novel design and development of supported metal catalysts. It appears that Pd nitrate can be completely reduced with H_2 plasma for 30 minutes at room temperature with TiO_2 as the support while 400°C reduction in H_2 for 2 hours can only removes 83% of nitrate from the Al_2O_3 support. The reduction capacity of plasma treatment depends on treatment time, plasma gas and the support material. The support material and the plasma gas are critical for catalyst reduction and modification which are important procedures for novel catalyst design and development.

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References

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