

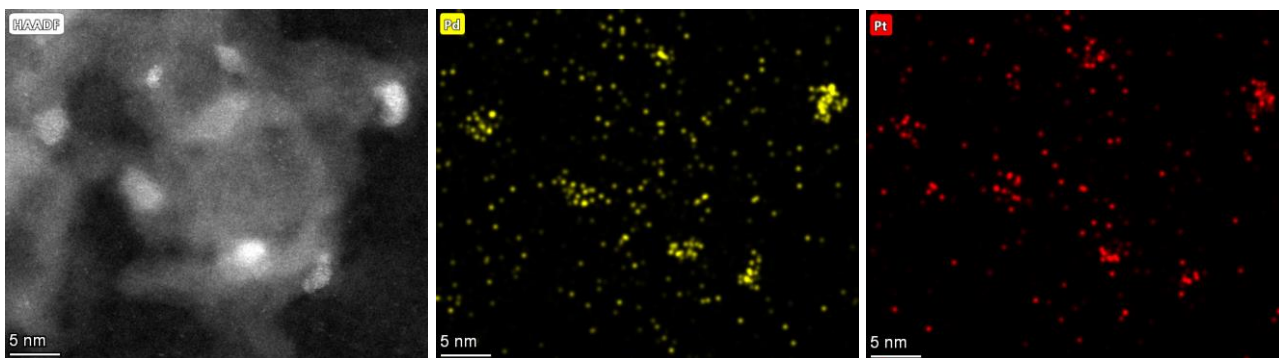
C₃H₆ and NO Oxidation over Pt/ γ -Al₂O₃ and PtPd/ γ -Al₂O₃ Prepared by Supercritical Deposition for Aftertreatment Systems of Heavy-Duty Diesel Engines

Hande Gunes¹, Deniz Şanlı Yıldız², Barkın Özener², Gökhan Hisar², Sarshad Rommel³, Mark Aindow³, Selmi Erim Bozbağ¹, Can Erkey¹

¹ Department of Chemical and Biological Engineering, Koç University, Sarıyer, 34450, Istanbul Turkey

² Ford Otosan R&D Center, Sancaktepe, 34885 Istanbul, Turkey

³ Department of Materials Science and Engineering, Institute of Material Science, University of Connecticut, Storrs, CT 06269-3136, USA



Diesel oxidation catalyst (DOC) is usually the first reactor of the aftertreatment system (ATS) of a heavy-duty diesel vehicle where toxic species such as the unburnt hydrocarbons (HC), CO and NO are oxidized to CO₂, H₂O and NO₂. Platinum group metals are used as the active metal of DOC. Among them, Pt is the mostly used metal due to its excellent oxidation performance, however, Pt is known to sinter and form large particles at high temperatures and oxidizing conditions. Addition of Pd as the secondary metal was shown to suppress the sintering of Pt particles due to ageing. Conventional techniques such as wet impregnation to prepare supported Pt and Pt-Pd catalysts often results in large particle sizes. An alternative route for the preparation of catalysts with high metal dispersion is Supercritical Deposition (SCD) which consists of the dissolution of a metal precursor in a supercritical fluid followed by the adsorption of the precursor onto support which is subsequently converted to its metal form via a variety of routes. In this study, 0.6, 1.2 and 2.1 wt. % Pt/ γ -Al₂O₃ catalyst and a bimetallic PtPd/ γ -Al₂O₃ catalyst with an overall metal loading of 1.4 wt. % and a Pt:Pd ratio of 1:1 were prepared via SCD using supercritical CO₂. Dimethyl(1,5-cyclooctadiene)platinum(II) and palladium(II) acetylacetonate were used as the metal precursors for Pt and Pd, respectively. PtPd/ γ -Al₂O₃ was prepared by simultaneous SCD of both metal precursors. After adsorption of metal precursors at 35 °C and 15.5 MPa on γ -Al₂O₃ surface, thermal treatment with flowing N₂ at 200 °C was carried out for 4 h to convert the precursors to metal nanoparticles. The catalysts were then calcined at 550 °C for 2 h. TEM images showed that the distributions of Pt and PtPd nanoparticles on the surface of γ -Al₂O₃ were extremely uniform with narrow size distributions with average nanoparticle size was around 1.0 nm for Pt catalysts and and 1.5 nm for PtPd. Bimodal nanoparticle size distributions were observed after calcination. Average particle size of 98% of the particles were around 1.0 nm for all catalysts. 2% of the nanoparticles were larger and their average nanoparticle size was around 10.0 nm for monometallic Pt catalysts and 6.5 nm for bimetallic PtPd catalyst. In PtPd/ γ -Al₂O₃ catalyst, observed nanoparticles were bimetallic mixtures of Pt and Pd without segregation. TEM images showed that bimodal particle size distribution was preserved with slightly larger average particle sizes after ageing at 800 °C for 4 h. The light-off curves of the catalysts for C₃H₆ and NO oxidation were measured in a fixed bed reactor with a feed stream representative of ATS consisting of 5% H₂O, 7% CO₂, 10% O₂ and balance being N₂. Both catalysts showed high activity for C₃H₆ and NO oxidation. Rate expressions for the disappearance of propene were developed for 2.1 wt% Pt/Al₂O₃ catalyst using rate data obtained in a differential reactor. A power law model was found to represent the data satisfactorily for the concentration ranges employed.