Sulfur tolerant bimetallic Pd-Pt catalysts for aromatics saturation of diesel and O_2-assisted H-FAME production for avoiding sulfur poisoning

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Keywords: Low-aromatics diesel, H-FAME, Noble metal catalyst, Sulfur tolerance

Diesel vehicles are core commercial vehicles in the transportation sectors, and many measures for reducing their emissions have been taken from both of the automobile and fuel sides. For EURO 5 diesel vehicles with Diesel Particulate Filter (DPF) systems, sulfur reduction of diesel (EURO 5 diesel with sulfur amounts of 10 ppm or less) will be very effective to minimize sulfur-poisoning of the exhaust gas treatment catalysts. However, aromatics reduction of diesel (total aromatics<5-10 vol%) will be more effective for EURO 4 vehicles without DPF systems, because PM amounts in the engine out gas are reported to have a positive correlation with the amounts of aromatics in diesel. Total aromatics in diesel can be successfully reduced over sulfur tolerant noble metal catalysts, which are used in the 2nd stage reactor coupled with the 1st stage HDS oriented reactor. These diesel aromatics saturation processes have been commercialized as a SynSat process and a SMDH process, etc. and contribute to the "City diesel" production. We have improved sulfur tolerance of noble metal catalysts and developed the Pd-Pt/Yb-USY-Al_2O_3 catalyst. This catalyst could reduce the total aromatics amounts to 5 vol% or less from EURO 5 diesel (S<10 ppm) as well as from EURO 3 diesel (S<500 ppm). We also confirmed its stability over 2,700 h during the aromatics saturation of EURO 3 diesel. Thermodynamic analysis using a chemical potential diagram contributed to taking improvement measures for sulfur tolerance.

Fatty Acid Methyl Ester (FAME) has been used as a diesel alternative fuel to contribute to reducing the CO_2 emission, increased energy security and promoting agricultural industry, etc., but there are concerns on FAME over B20 blend due to its

limited thermal and oxidative stability. Partially hydrogenated FAME (H-FAME) can solve these issues because of its low content of polyunsaturated FAME, e.g. about 1 wt% or less for Palm H-FAME and less than 4 wt% for Jatropha H-FAME. Oxidation stability of Palm H-FAME improved to 80 h (Rancimat) within 16 ºC of cloud point. H-FAME can be produced over Pd catalyst at the mild reaction conations, e.g. T<150 ºC, and P_{H2}<0.5 MPa, but Pd catalyst still faced S-poisoning during the low temperature hydrogenation. We have developed an innovative hydrogenation method assisted with trace amounts of coexisting oxygen for avoiding S-poisoning of Pd catalysts. Thermodynamic analysis indicated that sulfur species chemisorbed over Pd surfaces were more stable as SO_2 and its formation renewed the Pd surfaces as metallic. We confirmed the SO_2 formation experimentally during the O_2-assited hydrogenation of FAME. This O_2-assisted hydrogenation can avoid S-poisoning of noble metal catalysts, so we can expect a wide application of this method to prolong the noble metal catalyst life and to lead to cost reduction of the hydrotreating processes.