

A Near Ambient Pressure X-Ray Photoelectron Spectroscopy Study on Platinum Nanoparticles Supported on Zr-Based Metal Organic Frameworks

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Abstract : The first near ambient pressure (NAP)-XPS study of CO oxidation over Pt nanoparticles (NPs) incorporated into Zr-based UiO (UiO for Universitetet i Oslo) MOFs was carried out. For this purpose, the MOF-based Catalysts were prepared by wetness impregnation (WI-PtNPs@UiO-67) and linker design (LD-PtNPs@UiO-67) methods along with PtNPs@ZrO₂ as the control catalyst. Firstly, the as-synthesized catalysts were reduced in situ prior to the operando XPS analysis. The existence of Pt(II) species was proved in UiO-67 by observing Pt 4f core level peaks at a high binding energy of 72.6 ± 0.1 eV. However, by heating the WI-PtNPs@UiO-67 catalyst in situ to 200 °C under vacuum, the higher BE components disappear, leaving only the metallic Pt 4f doublet, confirming the formation of Pt NPs. The complete reduction of LD-PtNPs@UiO-67 is achieved at 250 °C and 1 mbar H₂. To understand the chemical state of Pt NPs in UiO-67 during catalytic turnover, we analyzed the Pt 4f region using operando NAP-XPS in the temperature-programmed measurements (100-260 °C) with reference to PtNPs@ZrO₂ catalyst. CO conversion during NAP-XPS experiments with the stoichiometric mixture shows that LD-PtNPs@UiO-67 has a better CO turnover frequency (TOF, 0.066 s⁻¹ at 260 °C) than the other two (ca. 0.055 s⁻¹). Pt 4f peaks only show one chemical species present at all temperatures, but the core level BE shifts change as a function of reaction temperature, i.e., Pt 4f peak from 71.8 eV at T < 200 °C to 71.2 eV at T > 200 °C. As this higher BE state of 71.8 eV was not observed after in situ reductions of the catalysts and only once the CO/O₂ mixture was introduced, we attribute it to the surface saturation of Pt NPs with adsorbed CO. In general, the quantitative analysis of Pt 4f data from the operando NAP-XPS experiments shows that the surface chemistry of the Pt active phase in the two PtNPs@UiO-67 catalysts is the same, comparable to that of PtNPs@ZrO₂. The observed difference in the catalytic activity can be attributed to the particle sizes of Pt NPs, as well as the dispersion of active phase in the support, which are different in the three catalysts.

Keywords : CO oxidation, heterogeneous catalysis, MOFs, Metal Organic Frameworks, NAP-XPS, Near Ambient Pressure X-ray Photoelectron Spectroscopy

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