In situ XPS study of Pt nanoparticles supported on UiO-67 MOFs for CO oxidation

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Abstract: Platinum nanoparticles (Pt NPs) supported on Zirconium-based metal-organic frameworks (MOFs, UiO-67) were prepared by the wetness impregnation and linker design methods. X-ray adsorption fine structure (XAFS) was used to study the local coordination environment, size and oxidation state of the Pt NPs in the developed MOFs based catalysts. The change in chemical state of the Pt NPs during the CO oxidation was also probed by the operando X-ray photoelectron spectroscopy (XPS) study under near ambient pressure (NAP) conditions (P_{CO} = 2 mbar and P_{O2} = 1 mbar), showing that Pt surfaces, regardless of the stabilization methods of the Pt NPs, underwent similar change from oxidation state at low temperatures (< 150 °C) to metallic state at high temperatures (> 150 °C). However, the catalysts prepared by the LD method had a higher CO conversion because of the ability of this method to produce the Pt NPs with smaller sizes and higher dispersion.

Keywords: UiO-67 MOFs, in situ NAP-XPS, CO oxidation.

1. Introduction

Metal-organic frameworks (MOFs) are porous materials formed by metal clusters connected by organic linkers. Their high specific surface area and pore volume make these materials particularly suited to incorporate metal nanoparticles (MNPs) that can exhibit catalytic activity. The role of MOFs is to serve as catalytic supports which provide stabilization of the guests under reaction conditions and also establish metal-support interactions. Recently, Zirconium-based MOFs (e.g. UiO MOFs), due to their exceptional thermal and chemical stability, have gained great attention as catalytic supports. Broadly, major approaches to stabilize the MNPs within UiO MOFs include (i) post-synthetic incorporation and (ii) in situ integration methods. Although numerous studies focused on different protocols to insert the MNPs, there are few studies elucidated the surface and structural properties of the MNPs under reaction conditions [1, 2].

In this contribution, Pt@UiO-67 catalysts were prepared by the wetness impregnation (WI) and linker design (LD) methods. The catalytic activity of the developed catalysts was compared with that of Pt NPs supported on commercial ZrO_2 supports. X-ray adsorption fine structure (XAFS) was used to observe the local coordination environment, size and oxidation state of the Pt NPs in the developed MOFs based catalysts. Additionally, the chemical state of Pt NPs was observed *in situ* in CO oxidation under near ambient pressure (NAP) conditions by X-ray photoelectron spectroscopy (XPS).

2. Experimental

For the Pt@UiO-67 catalysts prepared by the conventional WI method, $Pt(acac)_2$ precursors were used, followed by a calcination step at 200 °C under vacuum. The Pt@UiO-67 catalysts prepared by the LD method were synthesized by the standard solvothermal method in which the functionalized $PtCl_2$-bpydc linkers were replaced partially with the bpdc linkers [2].

The NAP-XPS system employed in this work is located at The University of Manchester and is equipped with a monochromated Al Kα source (hν = 1486.6 eV) and a SPECS 150 mm Phoibos 150 NAP electron energy analyzer, fitted with a three-stage, differentially pumped electrostatic lens. In order to monitor the reactivity of the catalysts under CO oxidation reaction conditions, the catalysts were exposed to a mixed gas composition of P_{CO}= 2 mbar and P_{O2}= 1 mbar while the XPS spectra are recorded *in situ* and the mass intensity of CO_2 (m/e = 44) was monitored by a mass spectrometer.

XAS experiments were carried out at core XAFS beamline B18 at diamond Light source located at Oxfordshire (UK). The XAS measurements included both the X-ray absorption near edge structure (XANES) and the extended X-ray absorption fine structure (EXAFS) regions.

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3. Results and discussion

The oxidation state of the Pt NPs during the reduction of the catalysts was observed by in situ XPS. The results showed that the Pt NPs were reduced at 250 °C under hydrogen flow and 200 °C under vacuum when the catalysts were prepared by the LD and WI methods, respectively. The local coordination of the Pt NPs in the UiO-67 frameworks were analyzed by the EXAFS spectra. For the as-synthesized catalysts by the LD method, Pt environment was completely compatible with that of Pt in the $PtCl_2$-bpydc linkers with a coordination of Pt–Cl of 2 and Pt–N of 2. After the reduction, the contributions of these two bonds reduced while new peaks were appeared at 2.2 Å and 2.6 Å, confirming the formation of the Pt metals.

The in situ XPS measurements were taken at 100 °C, 150 °C, 200 °C, 220 °C and 260 °C while the mass intensity of CO_2 (m/e = 44) was monitored by a mass spectrometer. As shown in Fig. 1, the Pt 4f spectrum at room temperature (RT) shifted slightly toward higher binding energy side (at 71.7 eV) which might be as a consequence of the existence of atomic oxygen chemisorbed on the metallic Pt NPs surfaces. By rising the temperature (>150 ºC), the Pt 4f spectrum shifted back to the lower binding energy (at 71.2 eV), indicating the metallic state of Pt NPs as the chemisorbed oxygen was consumed at the active reaction conditions.

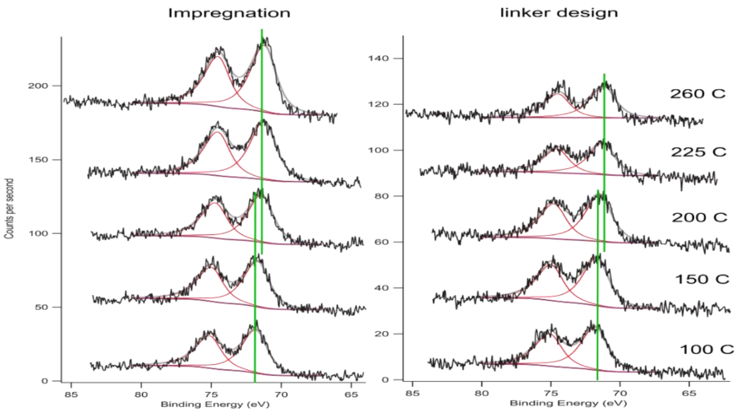

Figure 1. In-situ NAP-XPS observations of CO oxidation on Pt surfaces at different temperatures.

A comparison between the CO conversions over the developed catalysts showed that the highest catalytic activity belonged to the catalysts prepared by the LD method, resulting from the higher dispersion and smaller size of Pt NPs, proved by the CO chemisorption measurements and TEM images.

References

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