

In-situ Time-resolved Characterization of Pt-TiO₂-CeO₂ Nanocatalysts during the Water-Gas Shift Reaction

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Introduction:

CeO₂ has been studied extensively as a support for various metals such as Au [1], Cu [2], etc., where the oxygen vacancies produced are involved in the formation of active sites for the Water-Gas shift reaction. Also, Pt [3], Au [4] supported on non-stoichiometric TiO₂ could have large Water-Gas shift activity.

In this abstract, we investigate the Water-Gas shift reaction of Pt clusters supported on the mixed oxide of TiO₂ and CeO₂ using *in situ* XRD and XANES, which can probe the materials in long-range order parameters and oxidation state, respectively. In this talk, we present our recent results on this model catalyst, correlating both the reactivity and structure.

Experimental:

Pt (0.5 wt% metal) was supported on CeO₂/TiO₂ (6.6 wt% CeO₂), which is prepared by an impregnation method [5].

The *in situ* TR-XRD patterns were obtained at beamline X7B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory [1,2]. The sample (3-4 mg) was loaded into a sapphire capillary tube, which was attached to a flow system [1,2]. The capillary was heated using a small resistance heater that was wrapped around the capillary and a 1 mm chromel-alumel thermocouple placed inside the capillary was used to measure the temperature. *In situ* X-ray absorption spectra were obtained at beamlines X19A and X18B under similar conditions to the experiments at X7B, except that a kapton tube was used to load the catalyst.

The Water-Gas shift reaction was carried out isothermally at 200, 250, 300 and 350 °C, with a flow of 5% CO/He gas mixture through a water bubbler at a rate of ~10 ml/min. At each temperature, the Water-Gas shift reaction was monitored for a period of three hours.

Results and Discussions:

Water-gas shift activity is observed at 200, 250, 300 and 350 °C.

Figure 1 shows *in situ* Pt-L_{III} edge XANES spectra collected for the fresh catalyst, under operando conditions as well as after exposed to air. In the spectrum of

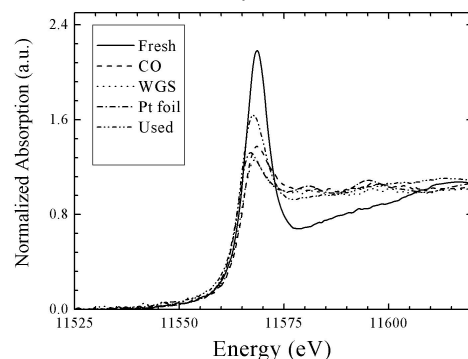


Figure 1. Pt L_{III}-edge XANES spectra of Pt-TiO₂-CeO₂ catalyst: (—) Fresh catalyst; (---) Exposed to CO at 200 °C; (·····) Water-gas shift reaction at 250 °C; (-·-·-) Pt Foil; (- - -) Used catalysts exposed to air.

the fresh catalyst, large whiteline intensity is observed, which suggests the existence of platinum oxide. The whiteline intensity decreased while the catalyst is exposed to CO at 200 °C, pointing to the reduction of platinum oxide. At 250 °C, under Water-Gas shift conditions, the whiteline intensity is very comparable with that of the Pt foil, pointing to the existence of metallic Pt in the active catalyst. Surprisingly, metallic Pt could be re-oxidized to its oxide form when exposed to air, which is also shown in figure 1 for comparison.

Figure 2 shows Ce L_{III} edge XANES spectra collected for the fresh catalyst, as well as under operando conditions. The fresh catalyst shows twin peaks, which is consistent with the reference CeO₂ powder. The peak intensity around 5728 eV increased when exposed to CO at 200 °C and indicates a substantial reduction of Ce⁴⁺ to Ce³⁺. Under Water-Gas shift conditions (250 °C), a further increase of the peak intensity is observed, pointing to the existence of a large portion of Ce³⁺ in the active catalyst.

In situ Ti K-edge XANES spectra shift to lower energy position during the Water-Gas shift compared to those of the fresh catalyst, pointing to a reduction of the Ti⁴⁺ to Ti³⁺.

Thus, the active phase during the Water-Gas shift reaction consists of Pt clusters supported on CeO_{2-x} and TiO₂.

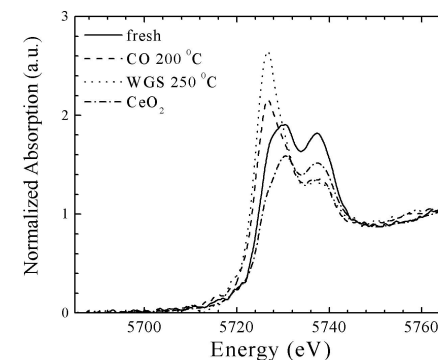


Figure 2. Ce L_{III}-edge XANES spectra of Pt-TiO₂-CeO₂ catalyst: (—) Fresh catalyst; (---) Exposed to CO at 200 °C; (·····) Water-gas shift reaction at 250 °C; (-·-·-) CeO₂ powder.

Significance:

In situ XANES techniques have shown the active phase for Pt-TiO₂-CeO₂ nanocatalysts during the Water-Gas shift reaction.

Acknowledgements:

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Reference:

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