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- fill in a separate form for each project or series of measurements.
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- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



In situ XAS studies on the local structure of isolated Pt and Au atoms in single-atom catalysts for CO oxidation

Experiment number:
CH-4348

Beamline: BM26A	Date of experiment: from: 015.07.2015 to: 18.07.2015	Date of report: <i>Received at ESRF:</i>
Shifts: 12	Local contact(s): Alessandro Longo	

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Report:

Introduction

Noble metal nanoparticles (NPs) supported on metal oxide substrates have been widely used in heterogeneous catalysis with high activities in many reactions [1]. Previously, many works have clearly demonstrated the size and components of metal NPs are crucial factor which affect the catalytic performances. On the other hand, the interface between NPs and metal oxides could also play a very important role. However, most of the metal oxide supports in previous works was focused on different components and crystal structures with irregular shapes. Very few works have investigated the crystal-plane effect in metal-oxide catalysts. Therefore, in the current work, we investigated thermal driven CO oxidation over Pt/TiO₂ with different facets ({101}, {100}, {001}) by *operando* XANES/EXAFS to understand how the crystal-plane affects the CO oxidation activity. We expect to build a relationship among crystal-plane-catalytic activity-reaction mechanisms.

Experimental

TiO₂ with different crystal facets including {101}, {100}, {001} through a hydrothermal method [2]. The Pt/TiO₂ catalysts were prepared through a impregnation method. For catalytic measurements the catalysts were pressed, crushed and sieved to obtain the fraction 0.10 – 0.20 mm.

The synchrotron XANES/EXAFS study was performed on BM26A of the ESRF. All the catalysts were placed in 1.0 mm quartz capillaries with 0.01 mm thick walls (approx. 6 mm bed length, ca.8 mg of a catalyst, sieve fraction 0.1 – 0.2 mm). The capillary was placed in the X-ray beam above a hot air blower (Oxford GSB-1300). The catalysts were pretreated from 20 to 230°C with a ramp rate of 10 K/min under flow of 4% H₂/N₂ (50 ml/min). For CO oxidation experiments, the feed composition is 1000 ppm CO and 5% O₂ in He with total gas flow 50 ml/min. The catalysts were heated from 20 to 220°C with a ramp rate of 5 K/min. X-ray absorption spectra were recorded in transmission geometry with Pt foil used as a standard.

Spectra were treated and linear combination analysis was done by using Athena software [3]. For the Fourier transform k^3 -weighing and 2.5 – 11 Å Hanning-type window was used. The relative contributions of the formed species were quantified by linear combination fitting (LCF) of XANES spectra using the Athena software in the range from -10 to 30 eV relative to the threshold energy. The energy was fixed during LCF.

Results

The amount of Pt loaded on the TiO₂ was ca. 1 wt.% estimated from the intensity of the XANES. The metallic Pt prepared from the impregnation method was already oxidized in air for all the Pt/TiO₂ samples. However, these samples are easily reduced as they can be reduced by X-ray beam in the absence of H₂ gas (Fig. 1 left). After pretreatment under 4% H₂/N₂ flow at 230°C, all the samples were fully reduced. Table 1 shows the EXAFS fitting results for the samples after the pretreatment. No Pt-O bond was observed, which is in line with the linear combination analysis results. It is worth to note that Pt-Ti bond was observed for all the samples, indicating strong interactions between Pt and TiO₂ substrates. Nevertheless, the crystal-plane has remarkably influences on the CO oxidation activity. CO oxidation activities of Pt/TiO₂ catalysts follow this order: Pt/TiO₂ {101} > Pt/TiO₂ {100} > Pt/TiO₂ {001}. The full CO conversion can be achieved over Pt/TiO₂ {101} at temperature as low as 109 °C

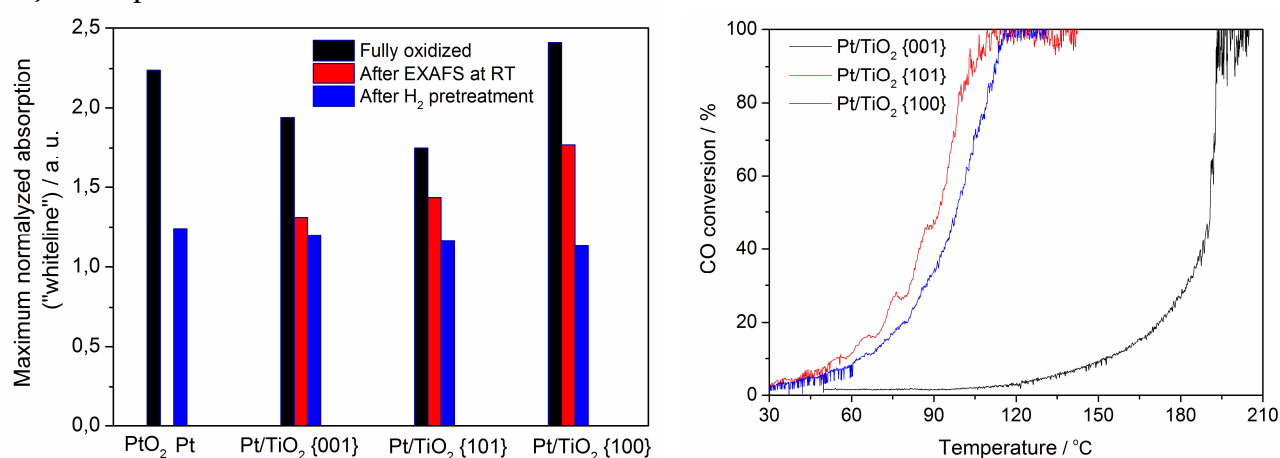


Fig.1 (left) The oxidation states of Pt on TiO₂ with different facets determined through linear combination analysis using PtO₂ and Pt as references; (right) the heating curves for CO oxidation over Pt/TiO₂ with different crystal facets.

Table 1 EXAFS fitting results for the samples after the pretreatment

Catalyst	Pt-Ti (Å)	N (Ti)	Pt-Pt (Å)	N (Pt)	σ^2 (10^{-3}Å^2)	ΔE_0 (eV)	ρ (%)
Pt/TiO ₂ {100}	2.67±0.03	1.0±0.25	2.64±0.02	2.7±0.8	7±2	1.3±1.3	3.6
Pt/TiO ₂ {001}	2.64±0.04	0.8±0.4	2.71±0.02	3.4±1.4	6±3	3.0±1.7	4.2
Pt/TiO ₂ {101}	2.68±0.02	0.8±0.2	2.67±0.001	3.1±0.7	9±1	3.1±0.9	2.4

To explore how the crystal-plane affects the CO oxidation activity, we also fitted the EXAFS data for all the samples under full CO conversion (typical shown in Fig. 2). Two interesting phenomena were observed: first of all, the different crystal-plane of TiO₂ can affect the CO adsorption ability. No Pt-C bond was observed in Pt/TiO₂ {001}, revealing that this sample has very low CO adsorption. We also performed in situ diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) measurements on these samples in our lab. In line with EXAFS results, Pt/TiO₂ {001} exhibited the lowest CO adsorption ability. Secondly, it was observed that the coordination number of Pt-Pt increased from 3.4 (before CO oxidation) to 6.7 (at full CO conversion) over Pt/TiO₂ {001}, indicating formation of Pt nanoparticles. However, Pt stays in a highly dispersed state on TiO₂ {100} and TiO₂ {101} under CO oxidation up to 220 °C. All of these results clearly demonstrated the crystal-plane effect in Pt/TiO₂ catalysts during thermal driven CO oxidation.

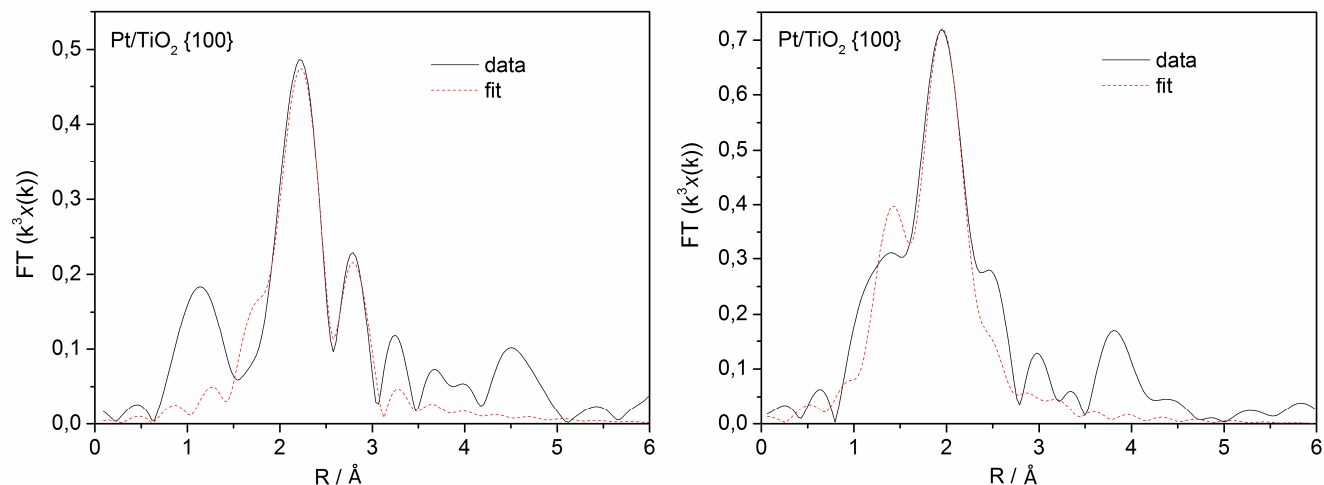


Fig.2 Representative EXAFS fit of Pt/TiO₂ {100} after pretreatment (left) and under full CO conversion (right).

Conclusions

EXAFS and XANES were used *in-situ* for the characterisation of Pt/TiO₂ with different facets including {101}, {100} and {001} under CO oxidation conditions. All of these samples exhibited strong interactions between Pt and TiO₂ substrates reflected from the formation of Pt-Ti bond. CO oxidation activities of Pt/TiO₂ catalysts follow this order: Pt/TiO₂ {101} > Pt/TiO₂ {100} > Pt/TiO₂ {001}. The low CO oxidation activity of Pt/TiO₂ {001} was ascribed to the lowest CO adsorption ability and the sintering of Pt nanoparticles. On the basis of our results, we believe that modifying the crystal plane of TiO₂ substrate is an effective route to enhance the catalytic activity of Pt/TiO₂ catalysts.

Acknowledgements

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References

1. M. Heitbaum, F. Glorius, I. Escher, *Angew. Chem. Int. Ed.* 2006, **45**, 4732.
2. L. C. Liu, X. R. Gu, Y. Cao, et al. *ACS Catal.*, **2013**, *3*, 2768.
3. B. Ravel and M. Newville, *Journal of Synchrotron Radiation*, 12 (2005) 537-541.