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	Experiment title: Operando XAS study on palladium-perovskite catalysts for applications in pollutant and greenhouse gas abatement	Experiment number: CH-2447
Beamline: BM26A	Date of experiment: from: 11/07/2007 to: 16/07/2007	Date of report: 04/02/2008
Shifts: 15	Local contact(s): S. NIKITENKO	<i>Received at ESRF:</i>

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Report:

Introduction

The use of reducible supports in the field of deNO_x reactions (elimination of NO, NO₂ and N₂O) has been largely applied for three-way catalysts [1]. Various perovskites as alternative to ceria zirconia based catalysts have shown good oxygen mobility [2] and promising catalytic properties for NO_x reduction into nitrogen [3,4]. In the case of stationary sources, the catalyst should be active at low temperature and in the presence of an excess of oxygen. Recent investigations have shown that noble metals-supported perovskite catalysts could be potentially interesting for NO_x reduction for both mobile and stationary sources running under lean conditions [3], particularly in the case of Pd/LaCoO₃ [4].

We previously report surface and structural modifications of LaCoO₃ and Pd-LaCoO₃ catalysts occurring in the course of the reaction NO+H₂ in the presence of an excess of oxygen (lean conditions). XPS experiments have been used to follow surface modifications of palladium. The increase in binding energy level of Pd 3d_{5/2} photopeak from 335.3 eV to 337.5 eV reveals the stabilisation of oxidic palladium species in a chemical environment different from that of PdO and PdO₂ [7,8]. Such changes in the catalyst in the presence of oxygen induced different catalytic properties during the reaction of NO by H₂. In the case of iron type perovskite, the presence of palladium inside the framework of a perovskite such as LaFe_{0.95}Pd_{0.05}O₃ has been suggested from ex situ XAS experiments [9].

The aim of those experiment (*Proposal CH 2447: Operando XAS study on palladium-perovskite catalysts for applications in pollutant and greenhouse gas abatement*) was to study the nature and the evolution of palladium species present in the case of cobalt-type perovskite such as Pd-LaCoO₃ catalyst in the course of the reaction of transformation of NO. This study used an *in situ* method combining X-ray absorption fine structure spectroscopy (XAFS) as well as on-line catalytic measurements by gas chromatography. Recently,

we have developed and successfully tested a new experimental cell for *in situ* and operando X-ray absorption measurements under actual running conditions for heterogeneous catalysts [10,11,12].

Experimental

We used a modified version of our catalytic cell to allow data collection in fluorescence mode in order to follow the Pd K-edge (24.350 keV) at low loading in the presence of a very absorbing support. Catalytic measurements were performed simultaneously at steady state conditions. A catalyst (Pd/Al₂O₃) was used as reference in order to follow the evolution of the palladium during *in situ* reductive/oxidizing sequences. For this catalyst, the evolution of the palladium only leads to surface palladium species since no palladium migrates inside the framework of the alumina support [13].

In the case of Pd-LaCoO₃, we reproduced similar experiments with *in situ* reductive/oxidizing thermal treatments and reactions conditions (NO(0.15%)+H₂(0.5%)+O₂(3%)+He(96.35%).

The effluents were analysed on-line using a μ GC Varian 4900 chromatograph fitted with two thermal conductivity detectors. Prior to quantification, reactants and products were separated on 5Å molecular sieve and poraplot Q columns.

Results

Reduction of the catalysts

The XANES spectra of palladium particles of the fresh samples evidenced the presence of oxidic PdO-like phase for both Pd/Al₂O₃ and Pd/LaCoO₃ catalysts (Figure 1). In the case of alumina support, the addition of hydrogen leads immediately to the reduction of palladium even at low temperature (20°C) as evidenced by strong changes in the XANES spectra. The reduction of Pd particles occurs at higher temperature on LaCoO₃ support and seems to be complete at 250°C.

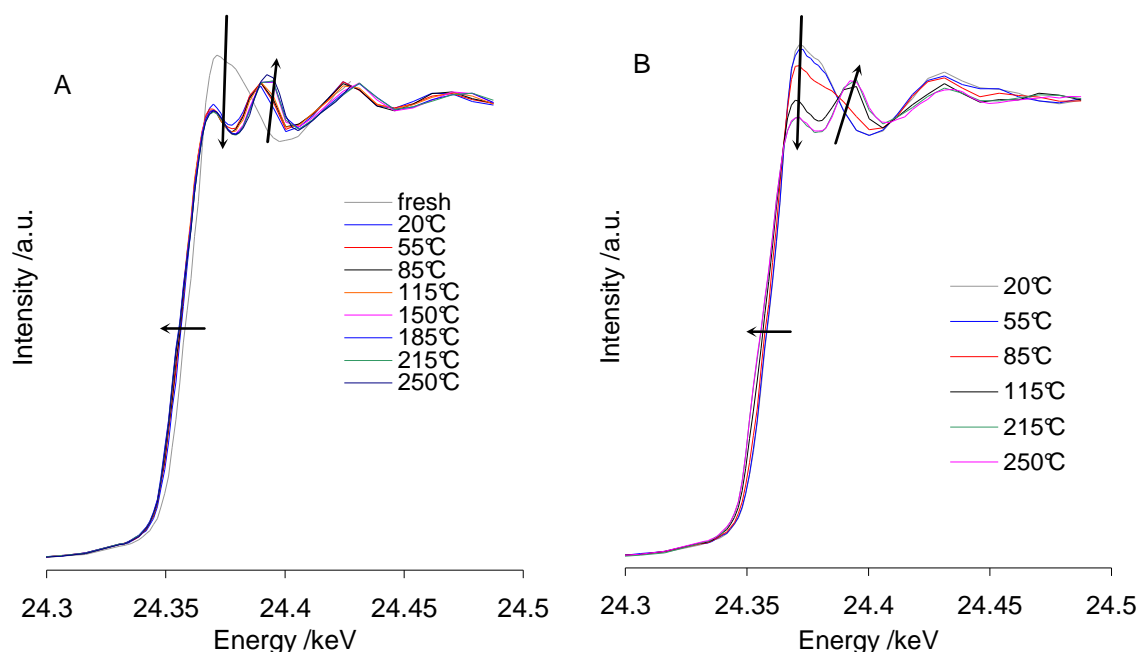


Figure 1 : XANES spectra of Pd/Al₂O₃ (A) and Pd/LaCoO₃ (B) catalysts during the *in-situ* reduction under pure H₂ (20-250°C).

The comparison of Pd K-edge EXAFS Fourier transforms evidenced changes in the coordination of palladium atoms after reduction (Figure 2).

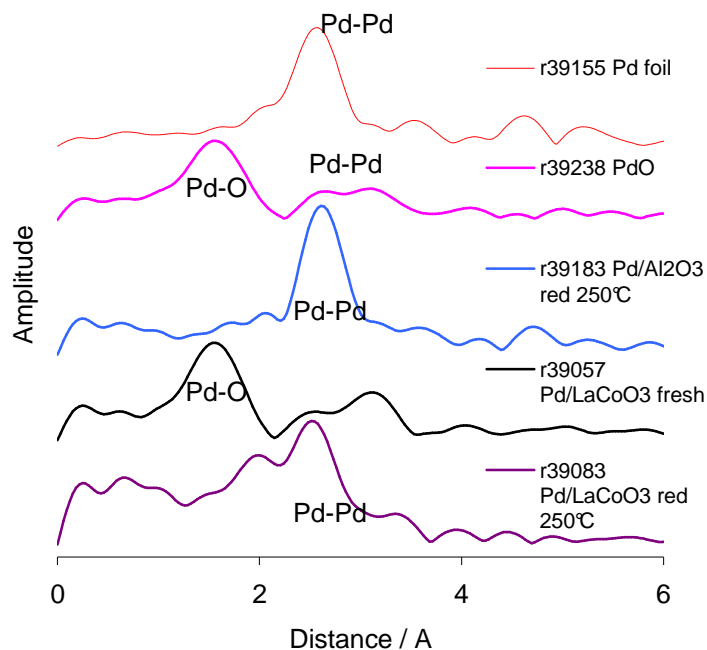


Figure 2 : Pd K-edge EXAFS Fourier transforms for Pd/Al₂O₃ and Pd/LaCoO₃ catalysts after the *in-situ* reduction under pure H₂ at 250°C, references Pd foil and PdO.

The spectra of Pd/Al₂O₃ obtained after reduction exhibit one contribution of Pd-Pd shell (0.261 nm) similar to the one observed on Pd foil (0.258 nm). On the fresh Pd/LaCoO₃, the Pd-O (0.156 nm) and Pd-Pd (0.255 and 0.311 nm) shells are characteristic of PdO phase (0.156 nm, 0.264 nm and 0.310 nm respectively). After reduction at 250°C, two contributions at 0.200 nm and 0.252 nm are observed on Pd/LaCoO₃ catalyst. The second contribution arises from Pd-Pd shell of Pd metallic particles. The first contribution with an intermediate value of distance between Pd-O and Pd-Pd has not been assigned. A similar EXAFS signal was reported in the literature for Pd black system and an additional contribution due to Pd-C at 0.207 nm was used for the fit [14].

NO+H₂+O₂ reactions on Pd/Al₂O₃ and Pd/LaCoO₃ catalysts

After the *in-situ* reduction of the catalyst under pure hydrogen at 250°C, catalysts were purged at room temperature under helium and the reaction mixture was introduced at 20°C. XANES spectra of Pd K-edge were recorded in the course of the temperature programmed experiments under 0.15%NO+0.5%H₂+3%O₂ for Pd/Al₂O₃ and Pd/LaCoO₃ (Figure 3).

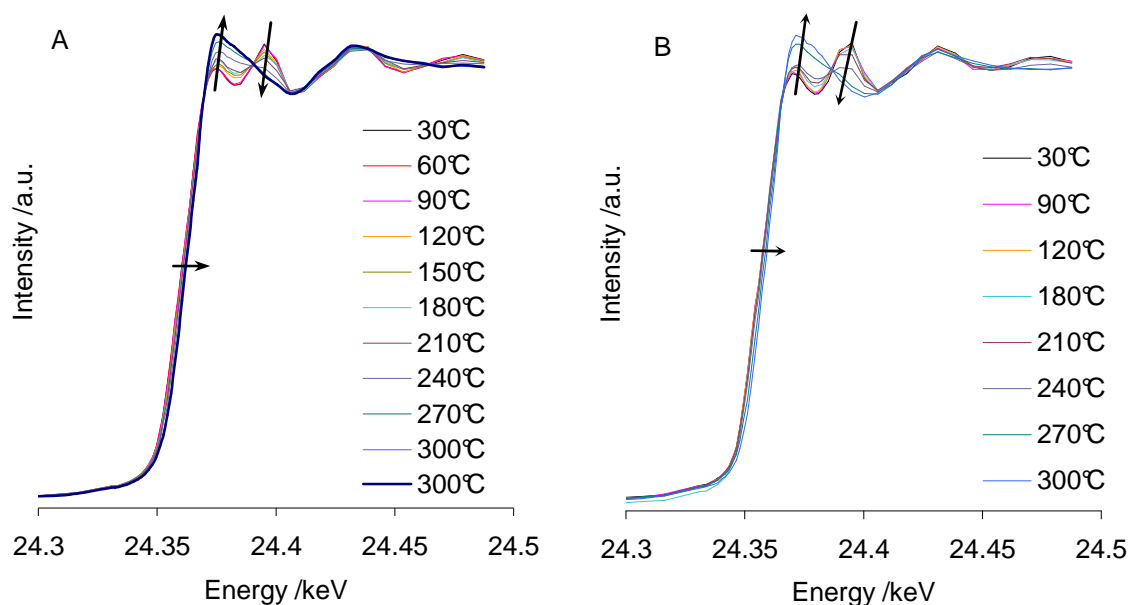


Figure 3 : XANES spectra of Pd/Al₂O₃ (A) and Pd/LaCoO₃ (B) catalysts during the *in-situ* temperature programmed reaction under 0.15% NO+0.5% H₂+3% O₂ (20-300°C).

The XANES spectra of Pd/Al₂O₃ catalyst start to change at 90°C with a shift of the K-edge energy and changes of oscillations. Such changes are observed at higher temperature for Pd/LaCoO₃ sample around 210°C showing a different behaviour of palladium particles supported on perovskite. Those results will be compared to changes in activity and selectivity [15].

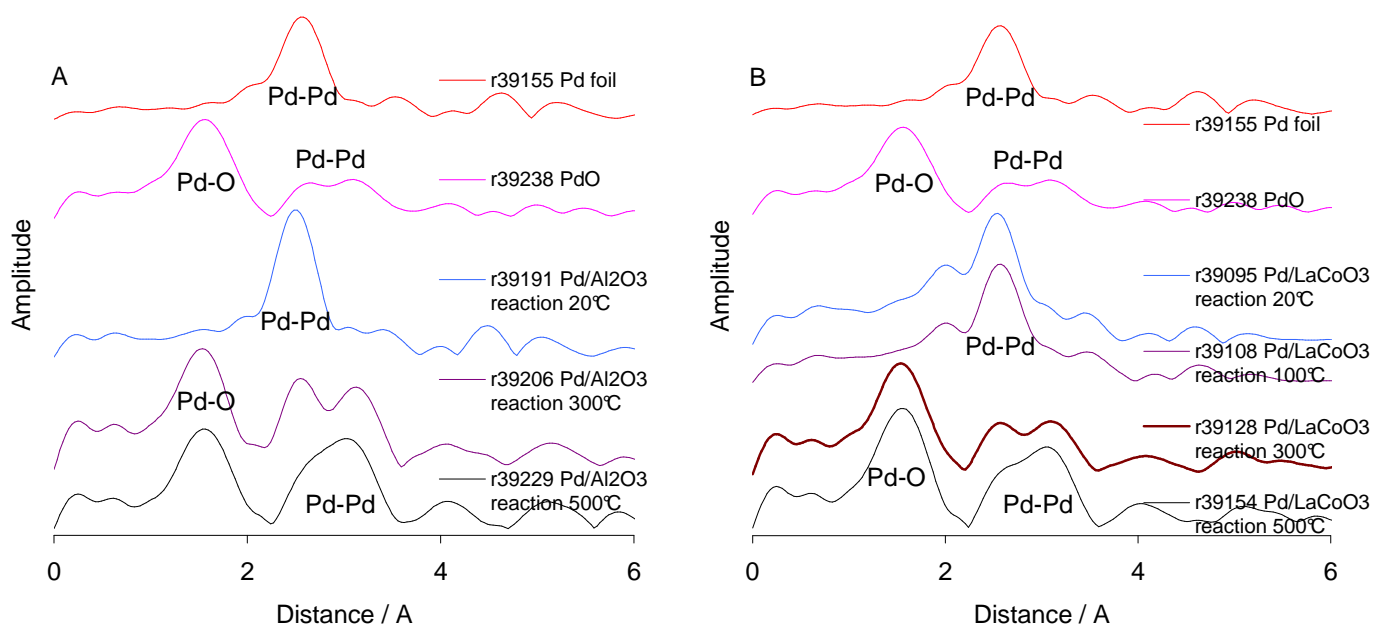


Figure 4 : Pd K-edge EXAFS Fourier transforms for Pd/Al₂O₃ (A) and Pd/LaCoO₃ (B) catalysts during the *in-situ* temperature programmed reaction under 0.15% NO+0.5% H₂+3% O₂ (20-500°C); Pd K-edge spectra were recorded at 20°C under Helium after 2h steady state for each temperature, references Pd foil and PdO.

After 2h steady state for each temperature, Pd K-edge spectra were recorded at 20°C under Helium and EXAFS Fourier transforms are presented on Figure 4. The contact of reaction mixture (0.15% NO+0.5% H₂+3% O₂) at 20°C does not change the coordination of Pd. As previously shown on XANES spectra, the increase in temperature under reaction mixture until 300°C is accompanied with the oxidation of palladium particles and the EXAFS spectra becomes similar with PdO spectra with characteristic

Pd-O and Pd-Pd bondings. After stabilisation at 500°C, the contribution assigned to Pd-Pd bondings are modified.

In the case of Pd/LaCoO₃ catalyst, an additional contribution at 0.200 nm to the classical Pd-Pd contribution of metallic Pd particles remains after the addition of reaction mixture at 20°C and 100°C. Oxidation of Pd particles is observed at 300°C and after stabilisation at 500°C, the contribution assigned to Pd-Pd bondings seem again modified.

Conclusion

The comparison of Pd/Al₂O₃ and Pd/LaCoO₃ catalysts shows the effect of an reductive support towards the properties of palladium particles. The reductive support seems to stabilize either form of the Palladium: the reduction occurs at higher temperature in a more gradual way, and in reaction conditions, the oxydation also occurs at higher temperature. A finer EXAFS analysis is being performed to determine if these properties are due to the migration of palladium atoms inside the framework of the perovskite during reaction conditions in lean conditions as it has been proposed.

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