



Experiment title: Understanding the evolution of the Pt active species in direct conversion of methane over Pt/CeO₂ by using HERFD-XANES

Experiment number:
CH-5847

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Introduction

Direct catalytic conversion of methane to olefins, aromatics and hydrogen (MTOAH process) over Pt/CeO₂ catalysts is an attractive, energy efficient route to exploit the natural gas reserves. A profound knowledge of the active site evolution and product formation pathways is key for optimizing the catalyst. The performed experiment aimed at unravelling the evolution of the Pt active species in direct conversion of CH₄ over differently prepared Pt/CeO₂ catalysts (with uniformly distributed single Pt sites synthesized by flame spray pyrolysis and with PtO_x clusters/nanoparticles synthesized by impregnation). This would allow understanding the impact of synthesis and activation conditions on the electronic structure of Pt and the nature and extent of metal-support interaction. Correlating structural parameters with the catalytic data would reveal structure-activity relationships vital for the knowledge-based catalyst development.

Experimental Section

0.5 wt.% Pt/CeO₂ catalysts were prepared by flame spray pyrolysis (FSP) and incipient wetness impregnation (IWI) from tetraammineplatinum(II) nitrate precursor and were calcined at 1000 °C in static air. For the *operando* study the catalysts were pressed and sieved to 100-200 µm sieve fraction. Catalyst samples were packed in quartz capillaries (o.d. = 1.5 mm, 0.02 mm wall thickness, ca. 4 mm bed length, ca. 14-15 mg of sample). Heating was achieved by an FMB Oxford GSD-1300 hot air blower. *Operando* measurements were performed at BM16 beamline (ESRF, Grenoble, France). X-ray beam was monochromatized using a Si (111) double crystal monochromator. A secondary emission spectrometer (Rowland geometry) using a Si (800) reflection of 12 spherically bent (1m) analyzer crystals and a position sensitive detector was used to record HERFD-XAS at Pt L₃ absorption edge (scanning incident energy with the emission spectrometer set to the maximum of the Pt L_{α1} emission line). Beam size was 0.15x0.2 (vert. x hor.) mm². The experimental procedure involved heating the as-received catalyst sample in He flow to 915 °C. After reaching the desired temperature the gas feed was replaced by 10 ml/min flow of 70%CH₄ in He for 90 min. After that the samples were cooled down in He. Concentrations of gaseous species were monitored by Pfeiffer Vacuum OmniStar GSD 320 QMS and ABB Uras 26 CO-CO₂ NDIR online gas analyzers. Ion currents recorded by the MS were normalized per

ion current of He and subtracted the average value of the background recorded in the respective gas feed but without a catalyst. HERFD-XANES spectra were measured continuously during the whole experiment. XAS data reduction was performed using Athena from the IFEFFIT software package.

Results and Discussion

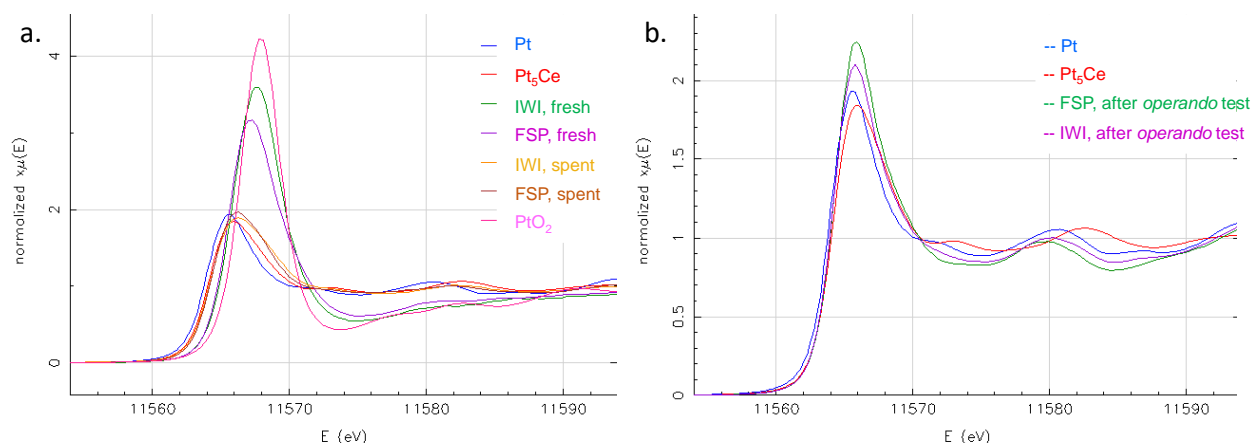


Figure 1. a.: Reference HERFD-XANES spectra as well as *ex situ* measurements of as-received (fresh) and catalysts after laboratory tests at 1000 °C in 90% CH₄/N₂. b.: Reference HERFD-XANES spectra of Pt foil and Pt₅Ce alloy as well as spectra of catalyst samples measured in He after the *operando* experiment.

Fig. 1a reports reference spectra as well as *ex situ* spectra of the studied catalysts before activation and after catalytic tests. As received catalysts show spectra resembling partially reduced platinum oxide. Spectra measured on spent catalysts demonstrate fully reduced platinum species. Moreover, EXAFS oscillations are clearly visible above the absorption edge suggesting metallic nanoparticles. Peak positions are shifted relative to the Pt foil spectrum in the same direction as the Pt₅Ce alloy spectrum and suggest Pt alloying with high (>>20%) amount of Ce. Spent IWI catalyst demonstrates shifts of spectral features to higher energies tentatively assigned to larger degree of alloying with Ce (higher Ce concentration). Fig. 1b shows comparison of HERFD-XANES spectra of catalysts measured after the *operando* experiment with Pt and Pt₅Ce reference data. Spectra of the catalysts demonstrate slightly higher white line intensity which can be assigned either to high degree but incomplete reduction of Pt or, more likely, the nanosizing effect (whereas nanoparticles in the samples tested in the laboratory are much larger). The white line in the spectra of the IWI and FSP catalysts is broader than the white line of Pt and similar to Pt₅Ce, the maximum position is also similar to that in the Pt₅Ce spectrum suggesting early stages of Pt and Ce alloying. Sintering effects are more pronounced in the spectrum of the IWI catalyst which shows lower white line intensity and features similar to bulk Pt in the EXAFS region. Hence, the trends in the catalyst structure can be reproduced in the current *operando* study.

Next, activation of catalysts by heating in He to the reaction temperature was studied. XANES spectra of both catalysts changed shape (the white line became narrower and a shoulder at 11570 eV appeared while keeping similar white line intensities. This transformation started above 100 °C and coincided with water vapor detected by MS which allows suggesting dehydration of supported Pt⁴⁺ species. Next, reduction of Pt⁴⁺ to Pt⁰ sites occurred, the transition took place between 380 and 540 °C for the FSP catalyst or sharply between 600 and 670 °C for the IWI catalyst. The spectra recorded after reduction correspond to metallic Pt nanoparticles. After reaching 915 °C and recording reference spectra in He (Figure 4, scan 318 for the FSP catalyst and scan 366 for the IWI catalyst) the methane feed was allowed into the capillary microreactor. For the FSP catalyst abundant partial oxidation (CO, H₂O) and water gas shift (CO, H₂) as well as methane coupling (ethen, propene, benzene) products were observed in the outlet gas stream (Figure 2). For the IWI catalyst very low to virtually no oxidation products were detected while the direct coupling products (H₂, higher hydrocarbons) prevailed.

After exposure to methane (Figure 3, scan 319 for the FSP catalyst and scan 367 for the IWI catalyst) the white line intensity sharply decreased at first, possibly due to overreduction of the outermost CeO₂ layer in direct contact with Pt resulting in excess electronic density on Pt sites. After approx. one hour on stream the white line intensity reached the initial value, however, with a white line shift in case of the IWI catalyst (Figure 3b). In both cases EXAFS oscillations (e.g. peak at approx. 11579 eV) observed in the CH₄ feed are shifted relative to the respective peak in He (and of Pt foil reference spectrum) at 11580 eV. This shift may point at early stages of Pt alloying with Ce, in line with the *ex situ* data and the white line shift observed for the IWI sample. Pt-Ce alloying occurs faster in the IWI catalyst, possibly due to the initially larger Pt nanoparticles.

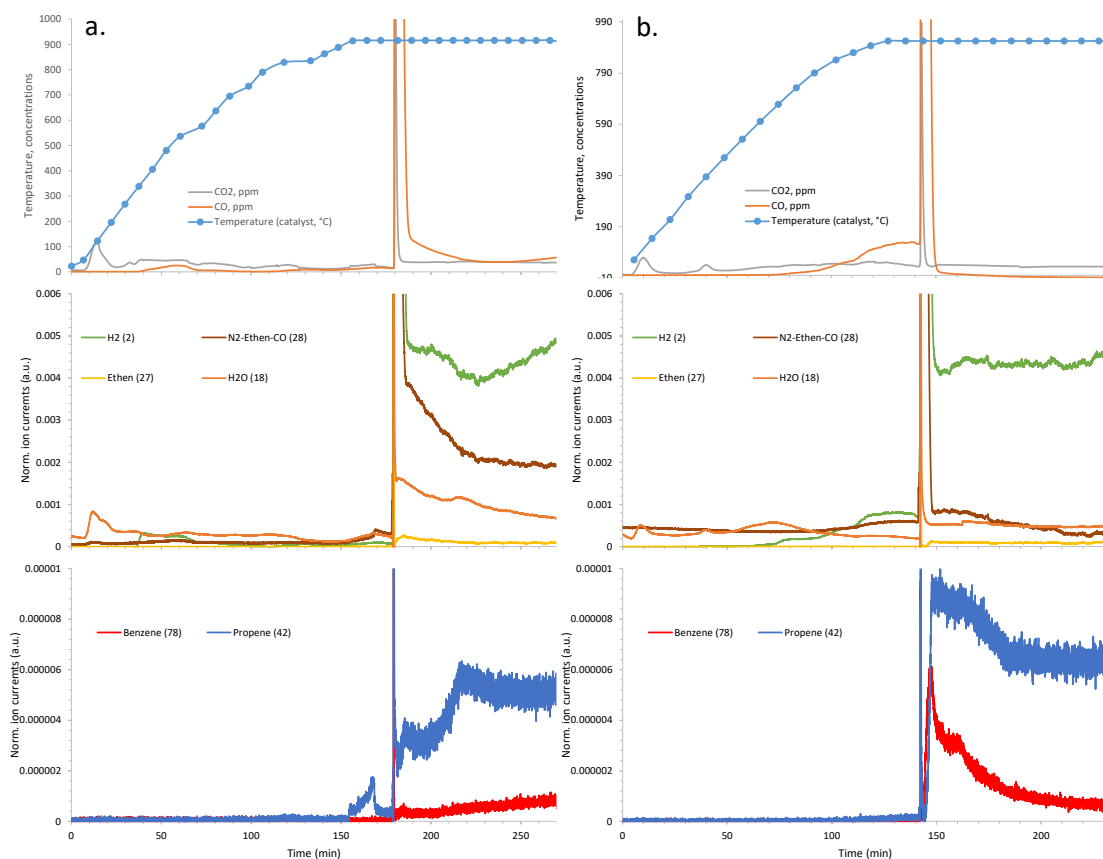


Figure 2. Temperatures and response of the CO/CO₂ NDIR detector (top), and ion currents of selected ions in the MS recorded during the operando study for FSP (a.) and IWI (b.) catalysts. The discontinuity at 140-180 min is due to switch of the gas feed from He to methane.

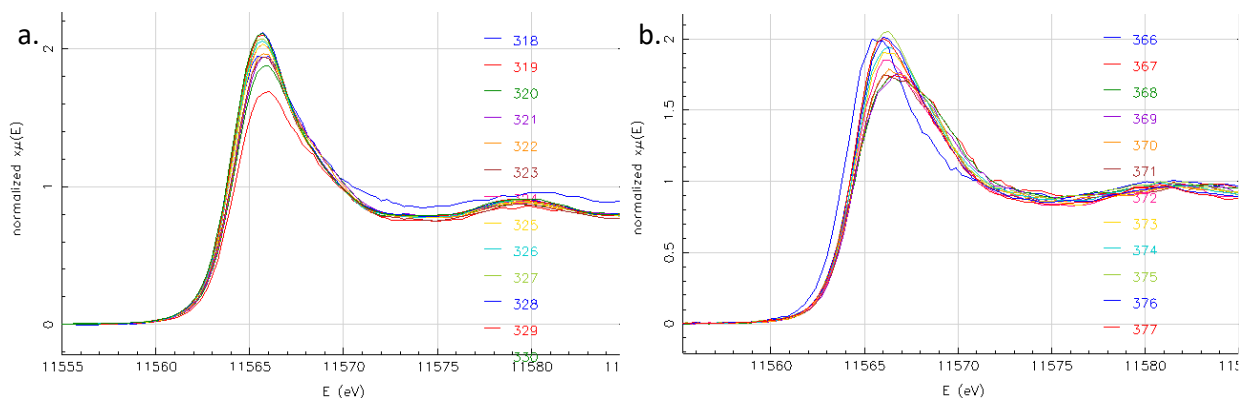


Figure 3. HERFD-XANES spectra recorded during and after the switch from He (the first scan) to methane feed over the FSP (a.) and IWI (b.) catalysts at 915 °C.

Conclusions

Operando HERFD-XANES allowed identifying several changes in the nature of Pt sites in Pt/CeO₂ catalysts for direct methane coupling during activation in He and reaction in methane at high temperature. While the end state of the catalysts after reaction was similar, synthesis route significantly influenced the dynamics of strong-metal-support interaction (SMSI) of Pt with ceria during activation and initial stages of the reaction. This resulted in much higher reducibility of highly dispersed Pt species in the FSP-synthesized material. At the same time, larger Pt nanoparticles were readily alloyed with Ce upon exposure of the IWI catalyst to the methane feed which resulted in production of the desired methane coupling products. On the contrary, transformation of the FSP catalyst during the high temperature reaction with methane was slow and accompanied by observation of undesired methane oxidation products. The conclusions are preliminary and will be confirmed via modelling.

Acknowledgements

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