



Experiment title: Investigating Rh and Pt nanoparticles formation and reactivity during reverse water gas shift and methane dry reforming by *operando* XAS

Experiment number:
CH-6269

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Names and affiliations of applicants (* indicates experimentalists):

Dr. Chiara Negri^{1*}, Dr. Cesare Atzori^{2*}, Gianluca Moroni¹, Luca Nardi^{1*}, Riccardo Colombo^{1*}, Federico Alleva^{1*}, Prof. Matteo Maestri^{1*}

1 Laboratory of Catalysis and Catalytic Processes, Department of Energy, Politecnico di Milano, Via La Masa 34, 20156, Milano, Italy

2 European Synchrotron Radiation Facility, 71 Avenue des Martyrs, CS 40220, Grenoble Cedex 9, 38043 France

Report:

Rh/Al₂O₃ and Pt/Al₂O₃ are considered active catalysts in CO₂ valorisation (e.g., Reverse Water-Gas Shift (RWGS – CO₂+H₂ ↔ CO+H₂O), Dry Reforming of Methane (DRM – CH₄+CO₂↔ CO+H₂O)).[1] Despite being largely studied,[2,3] a comprehensive picture of the structure-activity relationship at a fundamental level for these catalysts is still under way. Specifically, there is still a poor understanding of the reactions kinetic, by means of identifying the rate determining step (i.e. CO₂ activation on the catalysts surface).[4] Thus, lot of efforts in our group have been dedicated to microkinetically model the catalysts and to investigate their catalytic activity, in correlation with the catalyst structural characteristics.

The experiment CH-6269 at BM31 was aimed at investigating 4 wt.%Rh/Al₂O₃ and 4 wt.%Pt/Al₂O₃ catalysts to rationalize the catalytic behaviour observed during kinetic measurements performed in our laboratories in terms of metal oxidation state, nuclearity, structure and dimensions of the formed metal nanoparticles, reaction mechanisms, and influence of compositional gas feed parameters. In particular, we investigated by *operando* XAS and *operando* PXRD the reduction of the Rh and Pt catalysts and the consequent formation of metal nanoparticles, the surface coverage of adsorbates and the structure of the metal active sites under different operating conditions for CO₂ activation, RWGS and DRM.

X-ray Absorption Spectroscopy (XAS) data were collected using a quartz capillary with 2.5 (Rh) or 1 mm (Pt) external diameter. The catalysts were pressed and sieved, and the 75 and 106 μm fraction was selected for the measurement. Rh K- and Pt L₃-edge measurements were performed in transmission mode, employing a double-crystal Si (111) monochromator for the incident energy scan, and ionization chambers to detect incident (I₀) and transmitted (I_{1,2}) photons. An Rh or Pt metal foil was measured simultaneously using a third ionization chamber I₂, for energy calibration purposes. XAS spectra of ~ 5 min each (Rh energy range: 23070 – 24170; Pt energy range 11450 – 12600 eV; energy step = 0.5 eV; acquisition time of 70 ms/point in the whole energy range) were measured during the pretreatment in H₂ (10 Ncc/min–5% H₂/He balanced) and during RWGS (0.5-10% CO₂/0.5-10% H₂–He balanced) or MDR (1-16% CH₄/2-20% CO₂–He balanced). The gas composition from the reactor outlet has been continuously monitored by means of a mass spectrometer

Operando PXRD patterns were collected using a 45.786(1) keV monochromatic beam obtained from a sagittally focussing Si 111 double crystal monochromator. Diffracted intensities were collected by the means of a scintillation image plate detector (Dexela-Perkin Elmer 2923) having 3888x3072 pixels of 75x75 μm size whose

position calibration was made by refining it against a NIST LaB₆ standard. Integration of the images into 2D patterns was made with the software available and developed at the SNBL (Swiss Norwegian BeamLines).

We monitored Rh and Pt reduction during the H₂-pretreatment, and we observed the appearance of the typical feature of metal Rh and Pt. The spectra allowed us to evaluate the average particle size (c.a. 5 nm, for both metals). Subsequently, we exposed the reduced catalysts to the reactive gas mixture (RWGS and DRM, respectively) and we monitored CO₂ (and CH₄) conversion from MS. The spectra acquired in reaction conditions point to the stability of the investigated systems, excluding major deactivation due to sintering phenomena and C deposition in the monitored time frame. To further assess the possible formation of Rh or Pt hydrate and/or carbide in the applied experimental conditions, difference XANES spectra [5] will be calculated. This approach would contribute to shedding light on the catalysts behaviour and reaction mechanism.

Furthermore, since previous kinetic experiments have shown that CO₂ was activated by both catalysts without hydrogen aid, to better understand the nature of the observed CO₂ activation on the two active metals, XAS and PXRD experiments with 10 vol.% CO₂/He were performed. We observed that CO₂ dosage at 600°C on the Rhodium-based catalyst induced dramatic changes in the spectra and in the PXRD diffraction pattern. Specifically, we observed an almost complete oxidation of Rhodium by CO₂, with spectral features suggesting the formation of Rh⁴⁺. In parallel, the diffraction patterns highlighted the disappearance of the reflexes associated with Rh nanoparticles, indicating that in the applied experimental condition CO₂ activation promotes the disassembling of the previously formed nanoparticles. Interestingly, with both techniques we observed that when H₂ is fed after the CO₂ activation step, the oxidized Rh⁴⁺ is reduced back to Rh⁰, with the reaggregation of the nanoparticles. This unveils the reversible nature of such oxidation. On the other hand, the spectra collected on the platinum-based catalyst do not change their features upon CO₂ dosage, and Pt oxidation state is preserved during CO₂ activation. The PXRD data also confirmed the stability of the nanoparticles during the reaction. The collected data clearly highlighted a different interaction between CO₂ and the active metal phase on the two catalysts, pointing to different CO₂ activation mechanisms, also in light of the different affinity towards oxygen of Rh and Pt.

The catalysts behaviour under reaction conditions for RWGS and DRM was investigated at different temperature and reactants ratios, unveiling the different structural properties of the two catalysts.

The *operando* XAS and PXRD study we performed on BM31 is clarifying the structure of the Rh and Pt nanoparticles formed during the thermal activations, the evolution of their behaviour during the CO₂ activation and under reaction conditions and the effect of tuning the CO₂/CH₄ and CO₂/H₂ ratios on nanoparticles adsorbates surface coverage. This information is crucial to achieve a complete picture of the structure-activity relationship in Rh- and Pt-based catalysts, which is needed to develop a comprehensive structure-dependent microkinetic models and, subsequently, to optimize the catalytic processes. The possibility to follow the dynamic changes occurring at and on the metal nanoparticles under reaction conditions is allowing us to deepen the understanding of the reactive routes in metal-based catalysts for CO₂ and CH₄ activation.

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