



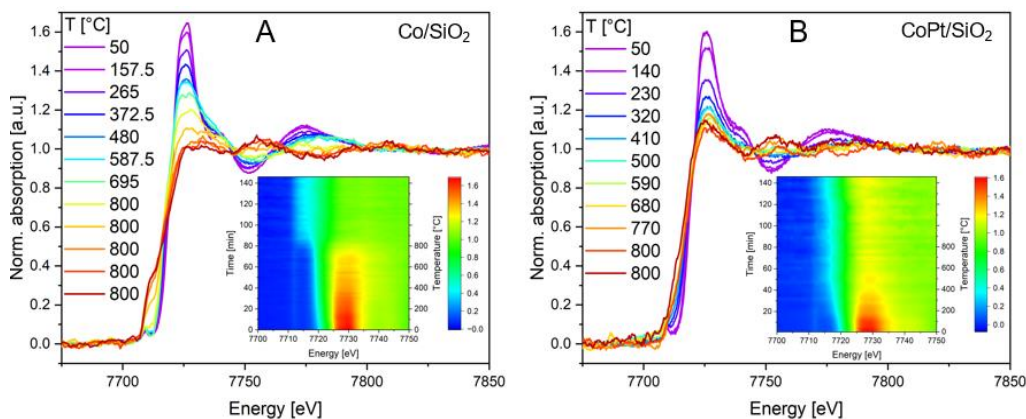
	Experiment title: Structure performance relationship in bimetallic Co-Pt based catalyst for dry reforming of methane	Experiment number: A31-1-172
Beamline: BM31	Date of experiment: from: 20 Jun 2022 to: 27 Jun 2022	Date of report: 13.02.2023
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Report:

This proposal aimed at investigating the local electronic and atomic structure of CoPt nanoparticles supported on SiO₂ under reductive pretreatment and dry reforming of methane (DRM) conditions. Aiming at elucidating structure-performance relationships and deactivation mechanisms of the Co-Pt DRM system we have developed mono- and bimetallic Co and Pt nanoparticles supported on SiO₂ (Co/SiO₂, Pt/SiO₂, CoPt/SiO₂) using strong electrostatic adsorption (SEA).¹ This method yields small particle sizes ($d_{(S)TEM} < 3$ nm) that are highly dispersed on the SiO₂ support with a metal loading of ca. 1.5-3.8 wt%. Here, we performed in situ XAS-XRD experiments on the prepared catalysts. 2-3 mg of catalyst was placed in a quartz capillary (1.5 mm OD, 0.01 mm wall thickness) between two quartz wool plugs. The capillaries were cut on both sides and glued into a U-shaped steel frame. The frame was mounted on a custom-made cell via 3/16" Swagelok connectors and aligned in such a way that the material was located ~ 5 mm above the center of a hot air blower which allowed heating of the catalyst. A set of mass flow controllers (Bronkhorst) regulated the gas flow (N₂, H₂, CO₂) through the catalyst while a gas chromatograph (compact GC4.0, Global Analyser Solutions, equipped with flame ionization and thermal conductivity detectors and a time resolution of ca. 7 minutes) analyzed the outgas. All catalysts were treated at 800 °C for 1 h (10 °C min/min) of H₂/N₂ to monitor the reduction behavior.

¹ Wong, A. et al., *Science* **2017**, 358 (6369), 1427-1430.

DRM tests were performed at 650 and 750 °C for Co/SiO₂ and CoPt/SiO₂ after they were pretreated in-situ. XAS-XRD data were collected for every metal edge interchangeably during the in-situ/operando experiments. In-situ XAS during H₂-TPR revealed differences in the reduction behavior (Figure 1). Co²⁺ species in Co/SiO₂



reduce fully to Co⁰ after 30 min at 800 °C. Co reduction is accelerated by the addition of Pt for the bimetallic system, likely due to H₂ spillover and intimacy of the two metals.¹ Cobalt reduces between 400-500 °C while Pt reduces first below 250

°C in CoPt/SiO₂. Small changes in the white line with increasing temperature are attributed to changes in the local structure of cobalt. Figure 2 A shows the XAS data of Co/SiO₂ at Co K-edge together with the Co foil and differences are attributed to the difference in particle size and crystal structure (fcc or hcp). The CoPt/SiO₂ shows an increased white line intensity compared to the monometallic Co/SiO₂ and Co. This increased intensity has been previously related to the alloying of Co with Pt leading to a charge transfer from Co to Pt and it could be the reason for the enhanced performance of the bimetallic catalyst.² Figure 2 B depicts the Fourier-transformed EXAFS of Pt/SiO₂ and CoPt/SiO₂ showing differences in radial distances and magnitudes proving the incorporation of Co into the Pt lattice. XRD (Figure 2 C) of Co/SiO₂ shows the formation of Co nanoparticles with an fcc structure of d_{XRD} = 3 nm after reduction; Pt/SiO₂ shows a broad pattern indicating nanoparticles of d_{XRD} < 2 nm. The CoPt/SiO₂ shows a shift towards larger angles due to incorporation of Co in Pt confirming the successful alloying. Finally, the operando XAS-XRD deactivation experiments of CoPt/SiO₂ showed a small increase in the white line intensity and shift of the main (111) peak towards lower angles under time on stream, which might be associated with a partial oxidation and/or dealloying, respectively. Therefore, we hypothesize that the DRM has led to a partial segregation of the CoPt alloy: on the one hand, XANES and EXAFS suggest that a great fraction of the alloy, mainly in the core, must still

exist; on the other hand, the oxidation of Co in the CoPt alloy might have led to either an Pt-richer alloy or isolated Pt islands/clusters on the surface due to dealloying.

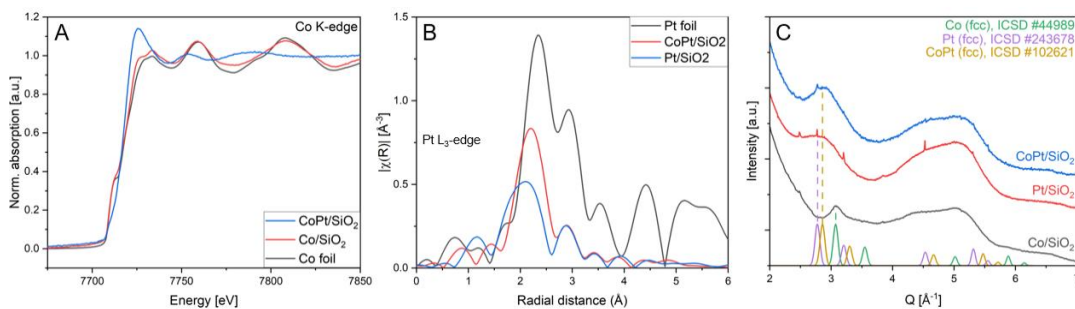


Figure 2: XAS-XRD of Co/SiO₂, Pt/SiO₂, and CoPt/SiO₂ after the pretreatment in H₂/N₂ at 800 °C for 1 h. A: Co K-edge XANES of Co foil, Co/SiO₂, CoPt/SiO₂. B: FT-EXAFS (Pt L₃-edge) of Pt foil, CoPt/SiO₂, and Pt/SiO₂. C: XRD patterns of Co/SiO₂, Pt/SiO₂, and CoPt/SiO₂ with references (the sharp peaks are due to crystalline quartz formed).

² Blanc, N. et al., *Phys. Rev. B* **2013**, 87 (15).