ESRF	**Experiment title:** M1-M2Ox-TiO2 (M1=Pt, Ni; M2=Ce, Zn) composite materials: XAS/MS study of their thermo-photo-catalytic performance in reforming reactions	**Experiment number**: CH5-381
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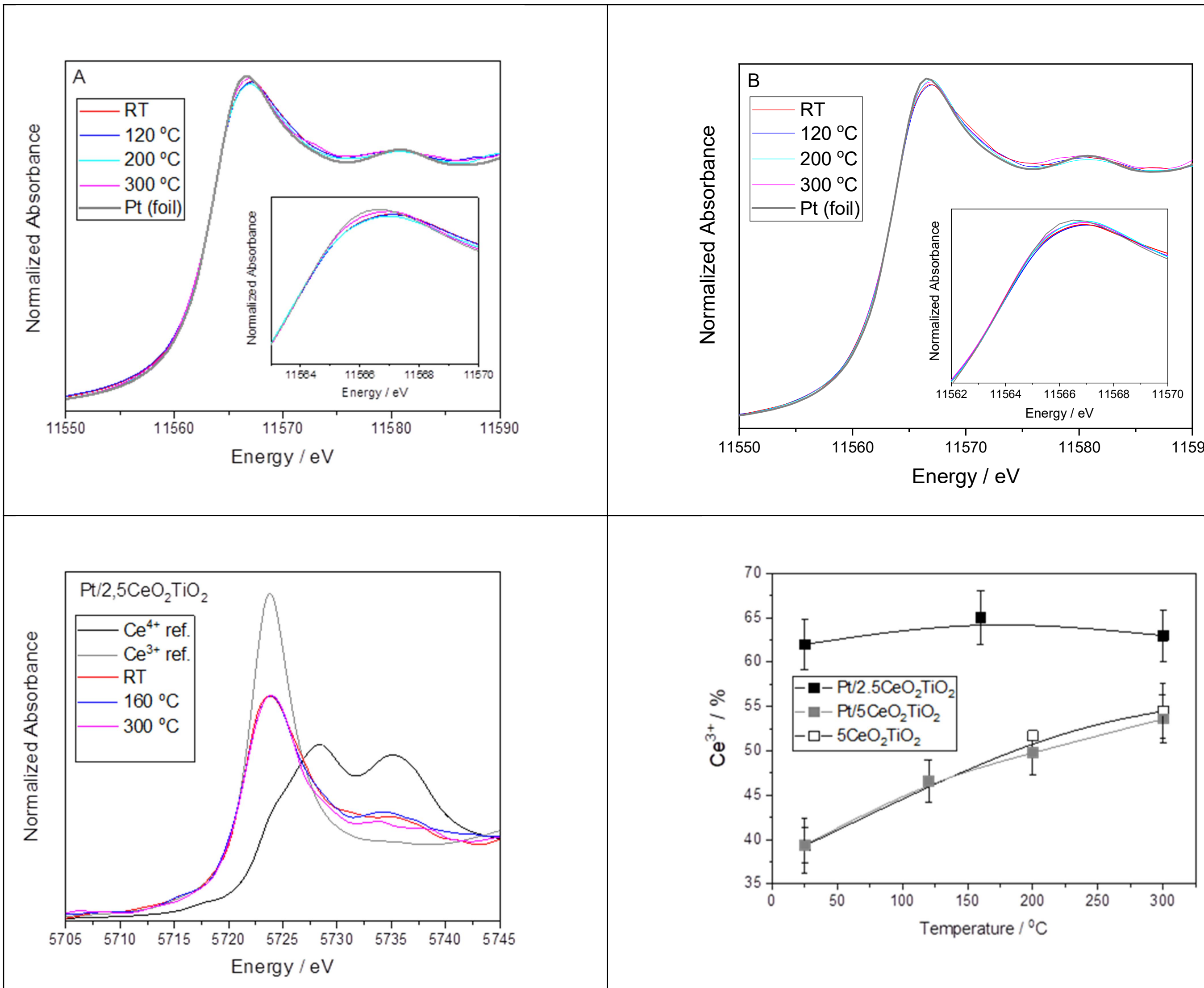
Report:

Hydrogen production from renewables such as alcohols and water is a potentially clean means for fuel generation. Currently few methods achieve this objective. Catalytic reforming is one of them but a photocatalytic (reforming) process would be a better choice owing the significantly less demanding technological (temperature, pressure) requirements and the simplicity of the concept. Moreover, the combination of light and heat energy sources is a new field of research, with important potential advantanges with respecto to the single-source energy processes.

To analyze the performance of (1 wt. %) Pt-promoted TiO_2-CeO_2 composite systems, at BM23 we carried out photocatalytic experiments using a Methanol:H_2O = 3:7 and measured XAS (XANES and EXAFS) as a function of the micro-beam position throughout the sample. Our experimental set-up is based in a low dead volume reactor able to carry out gas-phase photocatalytic reactions under continuous flow conditions. In-situ micro-beam X-ray measurements were conducted in a fluorescence mode. In parallel, we carried out the computation of the light-matter interaction at the sample holder for our systems. The intensity decay from the sample surface is obviously wavelength dependent but the samples showed rather similar profiles and an average decay of 90 % of the initial light intensity in the first 2-3 microns of the solid. The focal spot was thus selected in congruenece with this size, in order to selectively test the surface of the materials (the illuminated zone).

Photocatatytic results indicate that that optimum activity is achieved for a 2.5 mol. % of ceria. Sinergy in the combination of energy sources was demonstrated through the use of the reaction rate and quantum efficiciency observables. Suchg sinergy was tested in the 150-300 °C range. Maximum sinergistic catalytic effect (near 50 %) was observed at 240 °C. To intepret this phenomenon a XAS (together with other lab-based techniques) study was carried out. Figure 1 displays results concernining the Pt and Ce L_3-edge for selected composite and refernce samples. It also includes the fraction of Ce^{3+} species under reaction consitions (temperature, light and reactant mixture) as a function of the temperature.



Upper row: Pt L_3-edge XANES (A,B) spectra obtained under illumination as a function of reaction temperature for Pt/TiO_2 (A) and Pt/2.5CeO_2TiO_2 (B) samples.
Lower row: Ce L_3-edge XANES spectra obtained under illumination as a function of the temperature for selected samples and supportsCe reference spectra (Ce^{4+}; CeO_2 and Ce^{3+}; $CeAlO_3$) at room temperature are also presented. At the right, the figure includes a panel showing the fraction of Ce^{3+} species present on the samples as a function of the reaction temperature

XAS results demonstrates that Pt behavies rather similarly in presence and absence of ceria and not changes (both from XANES and EXAFS perspectives) were noticied as a function of the reaction temperature. Ceria however show important differences in terms of the ceria loading of the material. Low contents (equal or below 2.5 mol. %) have a rather constant behavior vs. temperature. Higher contents does not, indicating the presence of two types of Ce cations in the corresponding materials. One Ce species is directly in contact with titania and has a fixed, reduced oxidation state, while cations lacking direct contact with titania show a variable redox state. Note that they are apparently not much affect by Pt (Figure 1). The study was able to show that the presence of reduced Ce oxidation cations in contact with titania (and conrrespoding anion vacancies) optimize activity. The temperature behavior was interpreted with the help of additional techniques (mostly infrared spectroscopy). The work provided evidence that the combination of light and heat is particularly efficient in promoting the surface presence of some carboxylates (methyl-formate) with concomitant formation of hydrogen and the (further) production of hydrogen through a water gas shift type reaction.

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