EUROPEAN SYNCHROTRON RADIATION FACILITY
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	Experiment title: Why small silica supported metallic nickel nanoparticle prevent carbon formation in dry reforming catalytic conditions?	**Experiment number**: 30-02-1111
Beamline: 30B	**Date of experiment**: from: 05 April 2016 / 12 April 2016 26 April 2016 / 03 May 2016 12 May 2016 / 16 May 2016	**Date of report**:
Shifts: 18	**Local contact(s)**: O. Proux	*Received at ESRF:*

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In addition to the two published articles below, there are two papers which are currently submited :
- to Review of scientific instrument, “A new high temperature reactor for operando XAS: application for the dry reforming of methane over Ni/ZrO_2 catalyst". This work present the new operando set-up devellopped with FAME team to allow the characterization of catalyst operando.
- to ACS catalysis, “Tailor structure and reactivity of SiO_2 supported Pd-Pt catalysts pre-pared via Surface Organometallic Chemistry (SOMC)”. This work present the characterization under H_2 of Pt-Pd bimetallic nanoparticle using the previous operando set-up developed with FAME team.

Report:

1) In-operando elucidation of bimetallic CoNi nanoparticles during high-temperature CH_4/CO_2 reaction

AlSabban, B., Falivene, L., Kozlov, S.M., Aguilar-Tapia, A., Ould-Chikh, S., Hazemann, J.-L., Cavallo, L., Basset, J.-M., Takanabe, K, *Applied Catalysis B: Environmental (2017)*, 213, , 177-189

Abstract

Dry reforming of methane (DRM) proceeds via CH_4 decomposition to leave surface carbon species, followed by their removal with CO_2-derived species. Reactivity tuning for stoichiometric CH_4/CO_2 reactants was attempted by alloying the non-noble metals Co and Ni, which have high affinity with CO_2 and high activity for CH_4 decomposition, respectively. This study was focused on providing evidence of the capturing surface coverage of the reactive intermediates and the associated structural changes of the metals during DRM at high temperature using in-operando X-ray absorption spectroscopy (XAS). On the Co catalysts, the first-order effects with respect to CH_4 pressure and negative-order effects with respect to CO_2 pressure on the DRM rate are consistent with the competitive adsorption of the surface oxygen species on the same sites as the CH_4decomposition reaction. The Ni surface provides comparatively higher rates of CH_4 decomposition and the resultant DRM than the Co catalyst but leaves some deposited carbon on the catalyst surface. In contrast, the bimetallic CoNi catalyst exhibits reactivity towards the DRM but with kinetic orders resembling Co catalyst, producing negligible carbon deposition by balancing CH_4 and CO_2 activation. The in-operando X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) measurements confirmed that the Co catalyst was progressively oxidized from the surface to the bulk with reaction time, whereas CoNi and Ni remained relatively reduced during DRM. Density functional theory (DFT) calculation considering the high reaction temperature for DRM confirmed the unselective site arrangement between Co and Ni atoms in both the surface and bulk of the alloy nanoparticle (NP). The calculated heat of oxygen chemisorption became more exothermic in the order of Ni, CoNi, Co, consistent with the catalytic behavior. The comprehensive experimental and theoretical evidence provided herein clearly suggests improvement to the catalyst design protocol by selecting the appropriate composition of Co-Ni alloy.

2) Fe catalysts for methane decomposition to produce hydrogen and carbon nano materials

Zhou, L., Enakond, L.R., Harb, M., Saih, Y., Aguilar-Tapia, A., Ould-Chikh, S., Hazemann, J.-L., Li, J., Wei, N., Gary, D., Del-Gallo, P., Basset, J.-M, *Applied Catalysis B: Environmental* (2017), 208, 44-59

Abstract

Conducting catalytic methane decomposition over Fe catalysts is a green and economic route to produce H_2 without CO/CO_2 contamination. Fused 65 wt% and impregnated 20 wt% Fe catalysts were synthesized with different additives to investigate their activity, whereas showing Fe-Al_2O_3 combination as the best catalyst. Al_2O_3 is speculated to expose more Fe^0 for the selective deposition of carbon nano tubes (CNTs). A fused Fe (65 wt%)-Al_2O_3 sample was further investigated by means of H_2-TPR, in-situ XRD, HRTEM and XAS to conclude 750 °C is the optimized temperature for H_2 pre-reduction and reaction to obtain a high activity. Based on density functional theory (DFT) study, a reaction mechanism over Fe catalysts was proposed to explain the formation of graphite from unstable supersaturated iron carbides decomposition. A carbon deposition model was further proposed which explains the formation of different carbon nano materials.