Experiment Report

Proposal Code: 01-01-980

Proposal Title: Operando XAS-XRD-Raman-MS study of modified Ni/Al2O3 catalyst for CO methanation

The goal of the proposed experiment was to shed light on the structure of Ni in Ni/Al_2O_3 catalysts during activation and CO methanation in the presence of hydrocarbons in the feed. The effect of Ni content and support nature(presence or absence of SiO_2) was of specific interest. Carbon deposition will be forced by the use of ethylene (C_2H_4) added to the $CO-H_2$ feed, which is simulating real technological applications. We wanted to combine X-ray absorption spectroscopy, X-ray powder diffraction and Raman spectroscopy coupled with mass spectrometry in order to obtain information on the Ni crystallite size, valence states, local geometry of the phases and nature of carbon deposits during the various steps of the catalyst life. The results were supported by bench scale fixed-bed reactor experiments.

Firstly, the XANES spectra of Ni/Al_2O_3 catalysts pellets, with Ni loadings 1-25 wt%, were recorded at Ni K edge. The sample with 1wt% Ni loading shows similar features to $NiAl_2O_4$[1], though the white line is more intense in the sample than in the reference. For increasing Ni% the samples show more similarities with the NiO reference.

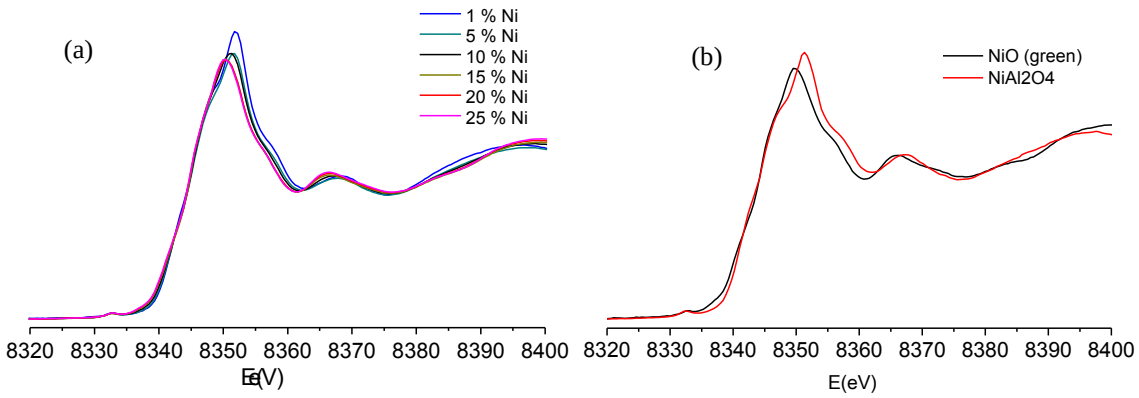

Figure 1: (a) Ni K-edge XANES spectra for all Ni/Al_2O_3 catalysts, (b) Ni K-edge XANES spectra for the NiO reference and $NiAl_2O_4$ taken from EXAFS database (http://ixs.iit.edu/database/)

[1] Jamie Y.C. Chen et al, Energy Environm. Sci., 2014, 7, 1382.

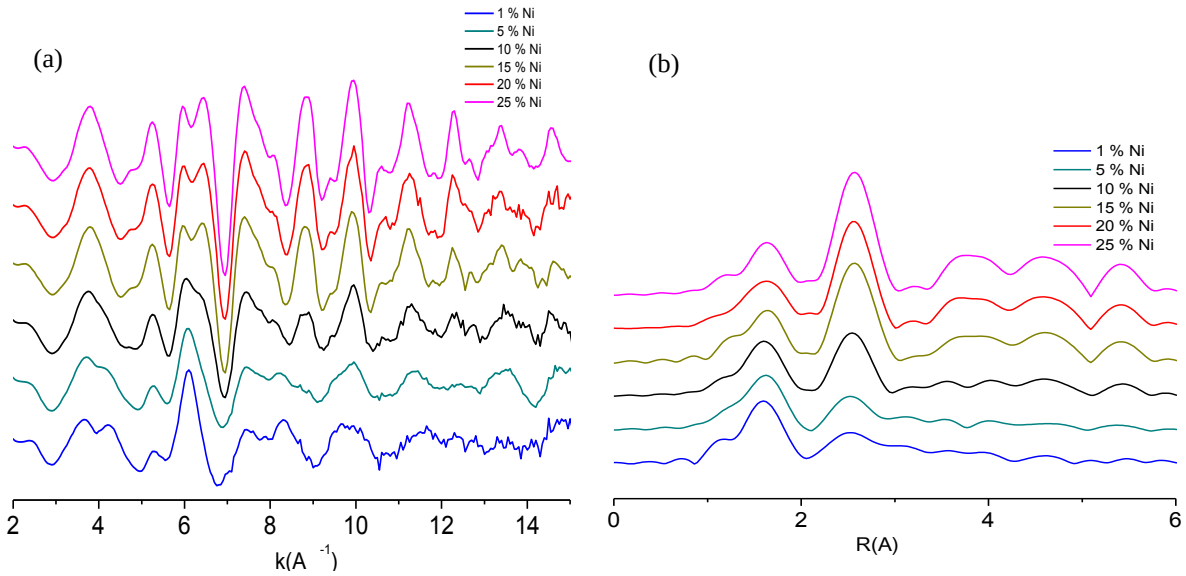

Figure 2: (a) Ni K-edge K^3-weighted EXAFS functions for all Ni/Al_2O_3 catalysts, (b) Fourier transforms (FT) of the normalized K^3-weighted EXAFS functions for all Ni/Al_2O_3 catalysts

A qualitative analysis of the FTs, in the R region between 1 and 3.3 Å shows that the 1% Ni reassembles the $NiAl_2O_4$ reference whereas the 25% Ni sample shows similar features the NiO reference. As The Ni content increases the NiO content become higher. This is consistent with the XANES description.

EXAFS Fitting,

The catalyst containing 1 wt% of Ni could be fitted using the $NiAl_2O_4$ spinel structure. The spinel structure belongs to the space group Fd3mwith cations occupying 8 tetrahedral sites (A sites), and 16 octahedral site (B sites). Thus, in $NiAl_20_4$, Ni^{+2} is present with oxygen near neighbours in both tetrahedral and octahedral coordination.

In order to simulate the spinel structure 2 Feff calculation where performed for octahedral and tetrahedral coordinated Ni. The distribution of the two cations between the tetrahedral and octahedral site is given by the fraction of each structural model.

Samples with 5, 10, 15, 20, 25% Ni, where fitted with a mixture of the spinel structure and NiO. In the fittings, in order to reduce the number of free parameters, the structural parameter for $NiAl_2O_4$ where kept constant. For the NiO phase, the DW and interatomic distances were let free and coordination numbers and E0 shift were set to the values the reference NiO. The content of phase was determined by the fittings.

At the moment is in progress the analysis of the operando experiments during activation and reaction and a publication including part of these results will be submitted in a few weeks.