Ni supported on MgFeAlO₃ as carbon resistant catalyst for methane reforming: structural and mechanistic study

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Introduction

The role of the catalyst support in syngas production from methane has been widely investigated for various reforming technologies, like steam reforming (SRM), dry reforming (DRM), partial oxidation of methane (POM) and autothermal reforming (ARM). MgAl₂O₄ has been widely investigated in literature as a suitable support material for reforming reactions due to its low cost [1]. The addition of MgO to Al₂O₃ leads to a MgAl₂O₄ spinel, which prevents the formation of inactive spinel phases by interaction between the active metals and alumina [2]. The MgAl₂O₄ spinel can effectively suppress the phase transformation to form NiAl₂O₄ and stabilizes Ni crystallites. The present study uses MgFeAlO₃ as support for Ni-based catalysts, where Fe is incorporated in the magnesium aluminate lattice, resulting in a low cost support with good redox properties, in order to control the carbon deposition during DRM at high temperature.

Materials and Methods

The Fe-K edge XANES (X-ray absorption near edge structure) and EXAFS (Extended X-ray Absorption Fine Structure) spectra of the MgFeAlO₃ support were collected at the Dutch-Belgian Beam Line (DUBBLE, BM26A) at the European Synchrotron research Facility (ESRF). The measurements were carried out in transmission mode at ambient temperature and pressures. EXAFS of the materials was measured in pellets diluted with inert boron nitride (BN) to avoid self-absorption. These spectra were measured in a closed cycle He cryostat (Oxford Instruments) at 80 K to minimize the noise contributions from the thermal Debye Waller factors. Three scans per material were energy calibrated, measured, averaged and then analyzed using GNXAS [3]. The suitability of the model is also evaluated by comparing the Fourier transform (FT) of experimental and model data to refine parameters such as coordination numbers, bond distances, Debye-Waller factors and angles from the two body and three body configurations which were defined according to the crystallographic structures used in data analysis. QXAS (Quick X-ray absorption spectroscopy) of the Ni/MgFeAlO₃ was measured in transmission at the ROCX beam line of the SOLEIL synchrotron using one oscillating monochromator over both Fe-K and Ni-K edges, by means of a macro for fast switching between edges. Approximately 5mg of as-prepared material, 50% diluted by BN, was inserted in a 2mm quartz capillary reactor and fixed by quartz wool plugs. The capillary reactor was implemented in a frame which was connected to gas feed lines.

Transient measurements were performed in a TAP-3E (Temporal Analysis of Products) reactor equipped with an Extrad Quadrupole Mass Spectrometer (QMS). The details of TAP experiments, can be found in [4]. For the experiments, 20 mg (250<d<500 µm catalyst fraction) of the as-prepared catalyst was placed in a quartz microreactor (I.D = 4mm and ~2 mm bed length), which was located between two inert beds of quartz particles with the same sieved fraction. The temperature of the catalyst was measured by a K-type thermocouple housed inside the catalytic zone.

Results and Discussion

The XANES region of the support MgFeAlO₃ (Figure 1(A)) showed reduction of Fe through a shift of edge energy position towards lower values. To unravel the structural position of Fe inside the lattice of the MgFeAlO₃, XANES simulations involving two possible sites have been performed. Fe in the fresh sample is in octahedral geometry. During the reduction process, Fe²⁺ becomes Fe³⁺, while retaining the octahedral geometry. However, a contraction of the Fe-O distance has to be taken into account. To simulate the XANES spectrum after the TPR treatment, two octahedral Fe sites were necessary: a) reduced Fe with strongly distorted and contracted Fe-O distance, b) undistorted (identical to fresh sample). A contribution of 70% for a) and 30% for b) was found, respectively.

![Figure 1: XANES spectra of (A) support MgFeAlO₃, at the Fe-K edge during H₂-TPR; XANES evolution during H₂-TPR of Ni/ MgFeAlO₃ at the (B) Fe-K edge and (C) Ni-K edge. H₂-TPR conditions: 0.2 ml/s of 5%H₂/He using a heating ramp of 10 K/min.](image)

The XANES spectra of the catalyst were recorded quasi-simultaneously at the Fe-K and Ni-K edges. XANES at the Fe-K edge (Figure 1(B)) reveals deeper reduction in comparison to the support. The edge energy shifts to lower value and the pre-edge feature (inset Figure 1(B)) also shows similarities with FeO, indicating that part of Fe could be segregated from the support to form a Ni-Fe alloy, as it was observed from in-situ XRD. Similarly, the XANES spectra at the Ni-K edge (Figure 1(C)) show reduction of NiO towards metallic Ni. Hence, addition of Ni promotes deeper reduction along with segregating Fe from the support and eventually forming a Ni-Fe alloy.

The TAP experiment revealed that DRM on Ni/MgFeAlO₃ follows a Mars-Van Krevelen mechanism where CH₄ is activated on Ni and CO₂ on the Fe sites (catalyst and support).

Significance

The redox ability of the support, with iron incorporated in the spinel lattice, is beneficial for suppressing the carbon deposition during reforming reactions.

References