

## The mechanism of carbon gasification over a Fe-Ni catalyst after methane dry reforming

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### 1. Introduction

Methane dry reforming converts two greenhouse gases into valuable chemicals, providing the attractive advantage of a H<sub>2</sub>/CO molar product ratio close to one, suitable for widespread use in many industrial processes (Fischer-Tropsch synthesis, etc). However, dry reforming technologies suffer from rapid catalyst deactivation due to carbon deposition, i.e. coke [1].

In order to inhibit or control the deactivation by carbon deposition, several methods have been examined but eventually, catalyst regeneration is required to remove all carbon species by gasification [2, 3]. Reports in literature propose different mechanisms for catalytic carbon gasification by O<sub>2</sub>, H<sub>2</sub>O, H<sub>2</sub> and CO<sub>2</sub> [1, 3]. However, the mechanisms according to which carbon species are oxidized by CO<sub>2</sub> and O<sub>2</sub> as well as the differences between both oxidation reactions await clarification. The goal of this study is to investigate the mechanisms of carbon gasification by CO<sub>2</sub> and O<sub>2</sub> over Fe-Ni supported on MgAl<sub>2</sub>O<sub>4</sub>. The deactivated and regenerated catalysts were characterized using X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and energy-dispersive X-ray spectroscopy (EDX)-STEM while the questions raised were addressed by performing X-ray diffraction (XRD) characterization of used Fe-Ni/MgAl<sub>2</sub>O<sub>4</sub> catalysts, both in situ during O<sub>2</sub>-TPO, as well as operando by coupling in situ XRD with MS. Further, a transient response technique, Temporal Analysis of Products (TAP), was used to investigate the isothermal carbon species gasification process.

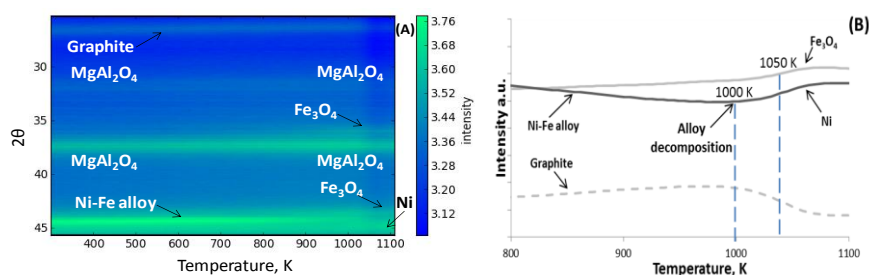
### 2. Experimental

**Operando time-resolved XRD:** The evolution of the structure during CO<sub>2</sub>- and O<sub>2</sub>-TPO was investigated with time-resolved XRD coupled with online mass spectrometry (MS, calibrated OmniStar Pfeiffer). The experiments were performed in a home-built reaction chamber with Kapton foil window housed inside a Bruker-AXS D8 Discover apparatus (Cu K $\alpha$  radiation of 0.154 nm). The setup was equipped with a linear detector covering a range of 20° in 2 $\theta$  with an angular resolution of 0.1°. A single pattern was acquired in approximately 10 s collection time.

**Temporal Analysis of Products (TAP) experiments:** Transient measurements were performed in a TAP-3E reactor (Mithra Technologies, St. Louis, USA) equipped with an Extrel Quadrupole Mass Spectrometer (QMS). For the experiments, 20 mg (250<d<500  $\mu$ m catalyst fraction) of the 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 of the same sieved fraction. The temperature of the catalyst was measured by a K-type thermocouple housed inside the catalytic zone. In addition, TAP experiments were performed with different bed configurations: a mechanical mixture of Fe-Ni catalyst and graphite, a two layers and a three layers catalyst bed ((layers of Fe-Ni catalyst and graphite, or of Fe-Ni catalyst, MgAl<sub>2</sub>O<sub>4</sub> and graphite, resp.)

### 3. Results and discussion

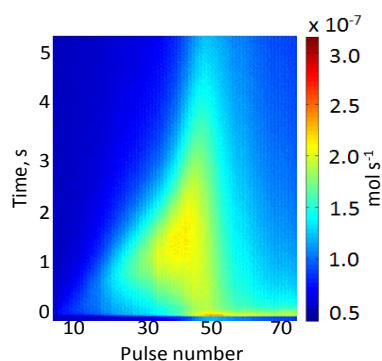
An operando experiment was performed during CO<sub>2</sub>-TPO of a used Fe-Ni catalyst (after methane dry reforming for 1 h, 1023 K, CH<sub>4</sub>/CO<sub>2</sub>/He= 1.1/1/1, total pressure of 101.3 kPa) (Fig. 1). The Fe-Ni alloy



present in the used catalyst is decomposed to metallic Ni and Fe<sub>3</sub>O<sub>4</sub> under CO<sub>2</sub> flow [4], at the same temperature at which the carbon oxidation starts.

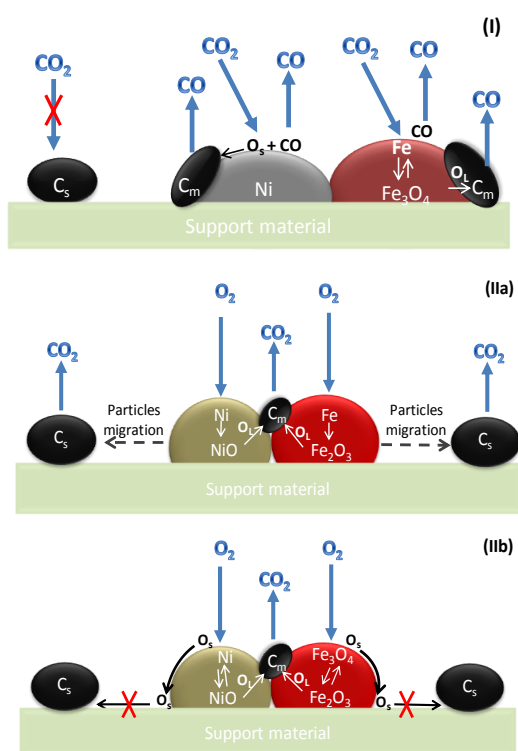
**Figure 1: Operando XRD during CO<sub>2</sub>-TPO (heating rate 20 K/min, maximum temperature 1123 K, flow rate 10 mL/s) of a used Fe-Ni catalyst (DRM for 1 h, 1023 K, CH<sub>4</sub>/CO<sub>2</sub>/He= 1.1/1/1, total pressure of 101.3 kPa):(A) 2D XRD pattern; (B) Integral intensity variation of (A) for diffraction areas 25.8-26.8° (Graphite), 35.4-36.4° (Fe<sub>3</sub>O<sub>4</sub>) and 43.7°-44.2° (Fe-Ni alloy).**

TAP experiments were applied in order to investigate the carbon gasification process by  $\text{CO}_2$  and  $\text{O}_2$  at 993 K. As a first step, the catalyst was aged by a sequence of 400  $\text{CH}_4$  pulses resulting in an “aged Fe-Ni” catalyst. Then, pulses of the oxidizing gas ( $\text{CO}_2$  or  $\text{O}_2$ ) were admitted to the reactor. Fig. 2 shows the  $\text{CO}_2$  responses as a function of  $\text{O}_2$  pulse number over the aged Fe-Ni catalyst as a 2D spectrum. An induction period was observed during first  $\text{O}_2$  pulses where  $\text{O}_2$  was completely consumed, implying that initially the active metals were oxidized. Only hereafter carbon gasification starts. Between the 10<sup>th</sup> and 50<sup>th</sup>  $\text{O}_2$  pulse, the  $\text{CO}_2$  response grew more intense, while shifting its peak maximum to higher times and acquiring a longer response tail. After the 50<sup>th</sup> pulse, the response narrowed into a sharp peak located around time = 0.2 second. The initial low  $\text{CO}_2$  intensity responses was attributed to oxidation of surface carbon. The shift in time of the  $\text{CO}_2$  peak maximum indicated however an additional route of  $\text{CO}_2$  formation



**Figure 2: 2D TAP pattern:  $\text{CO}_2$  response during  $\text{O}_2$  pulses at 993 K over aged Ni-Fe.**

possible processes: a)  $\text{CO}_2$  reversible adsorption b) migration of active particles towards deposited carbon, c) carbon bulk diffusion through the metal particle to the region where the gasification reaction takes place or d) oxygen spillover from the active metals to carbon on the support.



**Figure 3: Schematic representation of carbon species oxidation over Fe-Ni catalyst by (I):  $\text{CO}_2$  and (IIa-c):  $\text{O}_2$ ,  $C_m$ : carbon deposit on metals,  $C_s$ : carbon deposit far from metals.  $O_s$ : surface oxygen,  $O_L$ : lattice oxygen.**

## References

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## 4. Conclusions

Operando XRD and TAP experiments allowed to conclude that initially metal oxides are formed and then the carbon gasification process starts.

The major steps of carbon removal by  $\text{CO}_2$  over used Fe-Ni consist of: 1) oxidation of carbon by surface oxygen, originating from  $\text{CO}_2$  dissociation over Ni and 2) carbon oxidation through Fe oxide lattice oxygen. Direct interaction of gas phase  $\text{CO}_2$  was not observed (Fig. 3 (I)).

The mechanism of carbon species oxidation by  $\text{O}_2$  can be described by two steps: 1) oxidation of surface carbon ( $C_m$ ) through the metal oxides lattice and 2) particle migration to carbon species that were deposited far from active metals and their subsequent oxidation through lattice oxygen from the nickel and iron oxides (Fig. 3(IIa)). The analysis of TAP results after  $\text{CO}_2$  and  $\text{O}_2$  pulses over aged, reduced and oxidized Fe-Ni catalysts and from  $\text{O}_2$ -TPO over different catalyst bed configurations, showed that the contribution of oxygen spillover mechanism to carbon gasification can be considered negligible (Fig. 3 (IIb)).

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