

# Catalytic Performance of Ni-based Catalysts Supported on $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub>-TiO<sub>2</sub>-CeO<sub>2</sub> Composite Oxide for CO<sub>2</sub> Methanation

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## 1 Introduction

Increasing emissions of carbon dioxide arising from the widespread production of energy from fossil fuels is a critical matter regarding the global warming. The hydrogenation of CO<sub>2</sub> into oxygenates and/or hydrocarbons have been the most investigated reactions to obtain fuels [1]. Among several hydrogenation reactions, methanation of carbon dioxide following the Sabatier reaction is the most advantageous one regarding thermodynamics. Nickel based catalysts are the most studied materials for the latter reaction, because of their high activity and low price, but metal sintering at reaction conditions diminishes their industrial viability [2]. The type of support used for heterogeneous catalysts is an important factor to consider on solving such problems. Metal-support interactions play a role on catalyst performance in terms of the active site dispersion, activity and stability of the catalysts [3]. In this work, we focused our attention on the selection of different supports for Ni-based catalysts with constant Ni content. A series of composite oxide supported Ni-based catalysts were prepared using an impregnation-precipitation method for synthesis of the composite supports and wet impregnation technique to load Ni metal. The as-synthesized catalysts were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), N<sub>2</sub>-adsorption-desorption isotherms, temperature programmed reduction by H<sub>2</sub> (H<sub>2</sub>-TPR) and CO chemisorption.

## 2 Experimental

- I. Commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Sasol-Puralox SCCa-20/200) was impregnated with aqueous solutions of Zirconyl nitrate, Titanium (IV) isopropoxide and Cerium (III) nitrate hexahydrate salts in different ratios to get the desired percentages. 3 g of each composite support were taken and impregnated with an aqueous solution of Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with a predetermined amount of nickel to obtain a final loading of 20%Ni on the composite supports. The impregnated samples were dried in an oven at 120°C for 16 hrs and calcined at 450°C for 5 hrs. For comparison 3 g of commercial  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was taken and impregnated with 20%Ni and treated equally with the newly synthesized supports.
- II. Methanation reaction was performed at atmospheric pressure on pre-reduced catalysts in a pilot reactor with a fixed catalytic bed, 1 cm length and at space velocity of 25000 h<sup>-1</sup>. 10 mg (i.e. pre mixed with an inert) of catalyst were exposed to a CO<sub>2</sub>/H<sub>2</sub> (1:4 ratio) mixture in a temperature range of 300-400°C. Products were analyzed by on-line GC equipped with a TCD detector.

Catalysts were designed as 20%Ni/100%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> = Ni/A; 20%Ni/85%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-5% ZrO<sub>2</sub>-5% TiO<sub>2</sub>-5% CeO<sub>2</sub> = Ni/C11; 20%Ni/70%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-10% ZrO<sub>2</sub>-10% TiO<sub>2</sub>-10% CeO<sub>2</sub> = Ni/C12 and 20%Ni/55%  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-15% ZrO<sub>2</sub>-15% TiO<sub>2</sub>-15% CeO<sub>2</sub>= Ni/C13.

### 3 Results and discussion

The significant difference in XRD patterns (fig 1a) of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support and the composite oxides confirm the successful loading of the mixed oxides (ZrO<sub>2</sub>-TiO<sub>2</sub>-CeO<sub>2</sub>) in the different percentage range 5-15% for each one. It is also found that the average crystallite size of NiO, calculated from measured values using the Scherrer formula ( $d = k\lambda/B\cos\theta$ ), is increasing as the percentage of the loaded oxides increased (12 nm-16 nm).

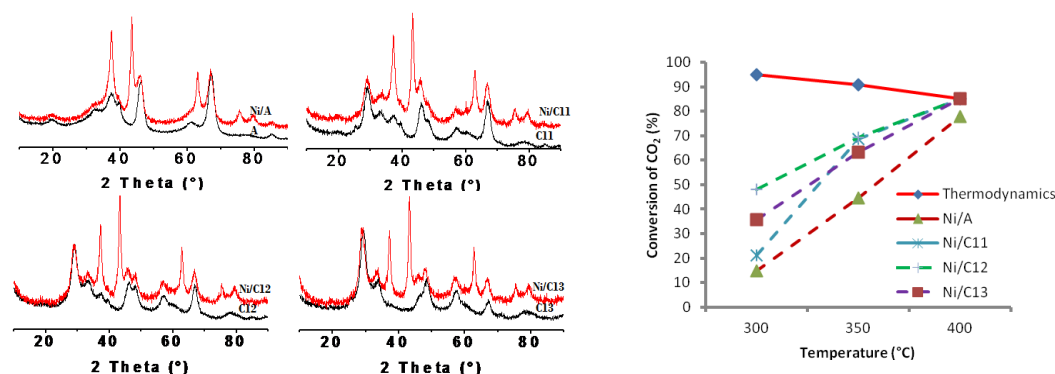


Fig. 1 (a) XRD Pattern of supports compared with the Ni/composite supported catalysts

(b) Effect of composition of the different supports on CO<sub>2</sub> conversion

Fig. 1b shows CO<sub>2</sub> conversion over supported Ni catalysts as a function of reaction temperature. CO<sub>2</sub> conversions gradually increased as the temperature was raised, and at 400°C reached the equilibrium represented by the continuous line in Fig. 1b calculated by taking CO<sub>2</sub> methanation and RWGS reactions into account. Apparently among the catalysts investigated the Ni/C12 catalyst which has 10% of each loading oxide shows better activity (69.36% conversion of CO<sub>2</sub> to CH<sub>4</sub> at 350°C). This might be mainly attributed to the fact that it is the optimum loading of the composite oxides to the conventional support ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) which influence the metal-support interaction inhibiting the incorporation of nickel species into the lattice of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, as confirmed by TPR profile. Furthermore, except for Ni/A and Ni/C13 catalysts no CO was detected at the reactor outlet in all temperature ranges.

### 4 Conclusions

Methanation of CO<sub>2</sub> has been studied over Ni-based quaternary system composite supported catalysts. Loading of composite oxides to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was found to be beneficial for the high conversion and stability of the catalysts at relatively low temperatures.

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