Tri-reforming of methane for syngas production using Ni/X-ZrO_2/$MgAl_2O_4$ catalysts (X= Ce, La, Sm and Y)

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Abstract: Nickel catalysts supported on zirconia promoted $MgAl_2O_4$ spinel were applied to tri-reforming of methane. Presence of lanthanides (Ce, La and Sm) and yttrium (Y) with ZrO_2 in the spinel showed some distinct acid-base properties, which have an influence on carbon deposition, together with nickel dispersion.

Keywords: Methane, Syngas, Spinel.

1. Introduction

Syngas (CO and H_2) is a raw material to synthetic fuels synthesis using Fischer-Tropsch processes. Steam Reforming (SRM), Dry Reforming (DRM) and Partial Oxidation (POM) of methane are the main reactions for syngas production. Tri-reforming of methane (TRM) is a combination of these reactions and the main advantages are the decrease of carbon deposition and higher energetic efficiency[1]. Zirconia as support for nickel catalysts has been studied for TRM due to its thermal stability and coke resistance[2]. Zirconia is usually associated to other elements, as lanthanides and alkaline elements due to stabilization into cubic and/or tetragonal phase[2]. Some drawbacks involving zirconia based catalysts application in reforming reactions at high temperature are the low specific surface area and particles sintering[2]. In order to avoid such limitations, zirconium compounds can be deposited on high surface area materials as $MgAl_2O_4$ spinel, which are resistant towards carbon deposition, features basicity properties. The objective of this work is to develop nickel catalyst supported on $MgAl_2O_4$ containing X-ZrO_2 (X=Ce, La, Y and Sm).

2. Experimental

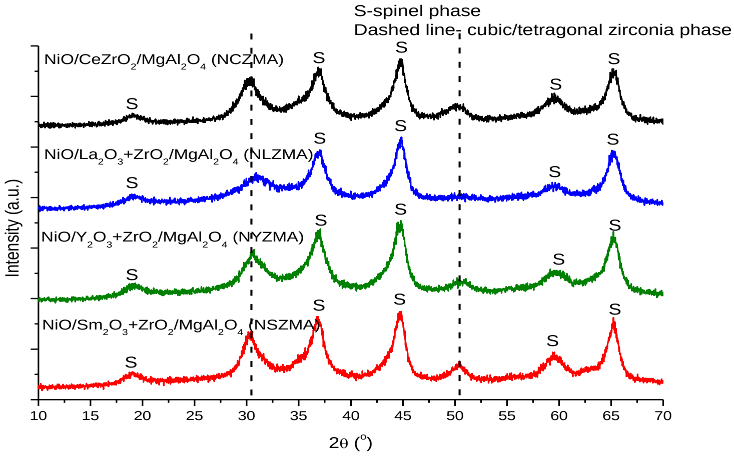
$MgAl_2O_4$ was prepared by means of P123® assisted coprecipitation technique and calcined at 750°C. The X+Zr compounds (X/Zr molar ratio of 0.25, X= Ce, La, Y and Sm) were impregnated to the support (1 mmol/g $MgAl_2O_4$) and calcined at 750°C. Nickel (10 wt.%) was introduced by incipient impregnation technique. The fresh catalysts were obtained after calcination at 750°C. TRM tests were carried out under stoichiometric conditions (CH_4:CO_2:H_2O:O_2=3:1:1:0.5 and CH_4=73.4 mL.min^{-1}) at 750°C. An amount of 85 mg of fresh catalyst was reduced *in situ* under H_2 flow at 750°C before catalytic tests.

3. Results and discussion

$MgAl_2O_4$ spinel phase is observed together with cubic/tetragonal zirconia (Figure 1). NiO was not observed as a segregated phase, suggesting the presence of highly dispersed species over the support. All catalysts presented main reduction peaks (not showed) at temperature higher than 650°C, suggesting high interaction between nickel and the spinel.

CH_4 and CO_2 conversions were practically similar among all catalysts evaluated, being around 70% and 35%, respectively. O_2 was completely converted. H_2/CO ratio was also around 2 for all catalysts, which makes syngas suitable to Fischer-Tropsch process.

Figure 1. Fresh catalysts XRD patterns.



Despite reactants conversions being similar with all catalysts, the reaction rates (Table 1) showed some differences among them. NLZMA ($Ni/La_2O_3+ZrO_2/MgAl_2O_4$) showed the highest carbon deposition rate, which can be justified by the lowest nickel dispersion and also by the lowest ratio between basic sites (B sites) that ensures carbon gasification, and the presence of Lewis acidic sites (A sites), from moderate to strong strength, that leads to CH_4 decomposition. According to Debek and cowokers[3], basic sites of strong nature make difficult the reaction between CO_2 and CH_4, enhancing the hydrocarbon decomposition. In the other hand, basic sites from weak to moderate strength would favor carbon gasification. In general, the tendency of decrease of carbon deposition followed the increase of B sites/A sites ratio, except for NCZMA ($Ni/CeZrO_2/MgAl_2O_4$), which showed the lowest carbon deposition due its highest dispersion of active phase.

Table 1. Reaction data and catalysts physical-chemical properties

Catalyst	Carbon (mmol.min^1)	Reaction rate of CH_4 ($mol_{CH4}.mol_{Ni}^{-1}.s^{-1}$)	Reaction rate of CO_2 ($mol_{CO2}.mol_{Ni}^{-1}.s^{-1}$)	Dispersion (%)	B sites/A sites*
NCZMA	0.0007	4.8	0.83	7.0	1.11
NYZMA	0.0018	5.0	0.81	5.0	1.32
NSZMA	0.0020	6.1	0.98	4.0	1.01
NLZMA	0.0048	6.4	1.0	3.5	0.85

[*] Basic sites: evaluated by CO_2-TPD and acidic sites by NH_3-TPD. The amount of Ni exposed for the reaction rates calculation were estimated using H_2-TPD.

4. Conclusions

All catalysts were active in TRM. The catalyst promoted with Ce and Zr showed the lowest carbon deposition rate, associated to the highest Ni^0 dispersion, while the presence of La and Zr lead to higher amounts of carbon accumulated on catalyst surface, not only because of the lowest dispersion of metallic phase but also because of the high concentration of Lewis acidic sites, which generated faster methane decomposition than carbon elimination by the gasifying agents.

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