

Natural Gas in Syngas Conversion over Nanosize Catalysts

L. S. Neiva^{*}, A. N. Simões^{*}, A. C. F. M. Costa^{*}, H. M. C. Andrade^{**}, M. R. Quirino^{*}, L. Gama^{*}

^{*}Academic Unit of Materials Engineering, UFCG, Campina Grande, PB, Brazil. E-mail: lsoutoneiva@yahoo.com.br

^{**}Chemical Institute, UFBA, Academic campus of Ondina, Salvador, BA, Brazil.

ABSTRACT

This work has as aim the development of Ni catalysts supported in α -Al₂O₃/Fe₂O₃, α -Al₂O₃/ZnO and α -Al₂O₃/ZrO₂ to be applied in catalytic reaction of the steam reforming of the natural gas. The catalytic supports composed by α -Al₂O₃/Fe₂O₃, α -Al₂O₃/ZnO and α -Al₂O₃/ZrO₂ were obtained by synthesis method of the combustion reaction. The catalytic supports were characterized by X-ray diffraction (XRD) and TEM. The catalytic supports were submitted to impregnation with 1.5%Ni by means humid method. After at impregnation the catalyst were submitted to catalytic test in row of seats scale. The morphologic analysis made by means TEM technique shows clusters presence formed by segregated phase over the structure of the obtained catalytic supports. The result of catalytic test showed that the catalysts developed samples in this work are efficient in the obtainment of the syngas composed by H₂ and CO with reason H₂/CO = 3.

Keywords: natural gas, syngas, catalysts doped, combustion reaction.

1 INTRODUCTION

The need to alternative energy sources in function of economic and environmental problems enabled the increase of the use of the natural gas in the world scenery, the natural gas is a natural resource not-renewable, and it is available in great quantities, it is little used in your energetic potential and has a cleaner combustion regarding the too much fossil fuels [1].

In the last years the study of alternative routes for the conversion of the methane, main component of the natural gas, in syngas (H₂ + CO) has been being very enlarged, having in mind the hydrogen production of high purity and the generation of chemical products of high aggregate values as oxygenated composed and polycarbonates, and hydrocarbons liquid free of sulfur [2]. Although the natural gas is constituted predominantly for methane, also contains an percentile certain of ethane, propane and butane, composed that are equally subject to the transformation reactions, similar to those of the methane [3].

The utilization of chemical methods for nanosize particles preparation, with physical chemical properties and

wished structural has been being the main focus of several researchers in different areas of the science and technology, due to the molecular stability and good chemical homogeneity that can be reached. These methods, also enable a good control in the particle size form and distribution and/or agglomerates. Among lots of existing chemical methods, the synthesis for combustion reaction has been being used with success for obtainment of several ceramic systems. It is an easy technique, it holds and fast to produce nanosize particles, with excellent control of the purity, chemical homogeneity and with good reproduction possibility of the post in pilot scale [4].

In this context, this work has for aim to synthesis Ni catalysts supported in α -Al₂O₃/Fe₂O₃, α -Al₂O₃/ZnO and α -Al₂O₃/ZrO₂ to be applied in catalytic reaction of the steam reforming of the natural gas.

2 EXPERIMENTAL

The catalytic supports composed by α -Al₂O₃ doped with iron oxide, zinc oxide and zirconium oxide were obtained by means synthesis method of the combustion reaction, in vitreous silica crucible as container and using the next precursors: aluminum nitrate [Al(NO₃)₃.9H₂O]; iron nitrate [Fe(NO₃)₃.9H₂O]; zinc nitrate [Zn(NO₃)₂.6H₂O]; zirconium nitrate [Zr(O(CH₂)₂CH₃)₄] and urea [CO(NH₂)₂] as fuel, all with high purity. The stoichiometric composition was calculated by means of the valencies of the components (Al³⁺, Fe³⁺, Zn²⁺ and Zr⁴⁺) and the numeric coefficients were found by the stoichiometric balancing. The concentration of dopant oxides employee in the net of the alpha-alumina was 0.05 mol of Fe₂O₃, 0.01 mol of ZnO, 0.005 mol of ZrO₂ this concentration was established in previous studies accomplished by Neiva [5]. Initially the mixture of the reagents was placed inside a muffle oven pre-heated at 500°C, where formed a viscous solution due to the dehydration of the nitrates and of the urea. The moment of ignition (combustion) occurred inside this muffle oven. The product of the combustion reaction (powder in the form of lightweight flakes and porous). The reaction combustion product, ie, the catalytic supports obtained, were passed in a sieve #325 mesh (44µm).

The synthesized catalytic supports were characterized by X-ray diffraction using a diffractometer Shimadzu (XRD 6000, with CuK α radiation, λ = 0.15418 nm) [6-7] and by

morphologic analysis by means transmission electronic microscope (TEM) Philips XL30 FEG [8].

The catalytic support were impregnated with an aqueous nickel nitrate solution (1.5% of nickel in massic percentage for each 2g of catalytic support). The suspension was evaporated at 50°C/6h and the resulting material was dried at 110°C/8h. The impregnated supports were then thermally treated in synthetic air flow (30mL/min), at 600°C/3h. After the impregnation process the catalytic activity this catalysts samples were examined in a quartz flow reactor, at atmospheric pressure and 700°C. Vapor was introduced from a saturator operating at 72°C. The rate vapor/methane was 3:1. Before reaction, the catalyst (100 mg) were treated in a He flow (50 mL.min⁻¹). A gaseous mixture of composition: 16.7 % of CH₄ in He balance. The effluents of the reaction were analyzed in a Perkin Elmer Clarus 500 gas chromatograph, operating with Carboxen 1010 (0.32mm x 30m) capillary column, and flame ionization and thermal conductivity detectors.

The obtained catalytic supports were named by codes as shown in Table 1.

Sample Code	Composition of the Structure
Cat 1	α -Al ₂ O ₃ /Fe ₂ O ₃
Cat 2	α -Al ₂ O ₃ /ZnO
Cat 3	α -Al ₂ O ₃ /ZrO ₂

Table 1: Relationship of codes of the catalytic supports obtained in this work with composition of each obtained structure respectively.

1 RESULTS

Figure 1 presents X-ray diffraction patterns of the Cat 1, Cat 2 and Cat 3 catalytic supports synthesized by combustion reaction. For the three catalytic supports Cat 1, Cat 2 and Cat 3 it can be observed in the X-ray diffraction patterns that the pure α -Al₂O₃ phase with rhombohedra structure (JCPDS 10-0173) was formed in the absence of a segregated phase. The X-ray detection limit of a substance or element belongs to 5% of the total mass of the sample, and as the dopant oxides concentration was below of this detection limit, is possible that has occurred the formation of a segregated phase, not detected by the X-ray.

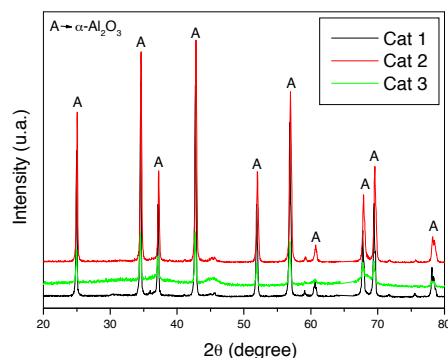


Figure 1: X-ray diffraction patterns of the Cat 1, Cat 2 and Cat 3 catalytic supports synthesized by combustion reaction.

Figure 2 shows micrographs obtained by transmission electronic microscopy (tem) for Cat 1, Cat 2 and Cat 3 catalytic supports synthesized by combustion reaction. It was possible note that the catalytic supports composed by alpha-alumina doped with iron oxide, zinc oxide and zirconium oxide presents particles agglomerates formation of 476 nm (Cat 1 sample) with clusters with a segregated phase, what probably, is formed by metallic dopants oxides. the micrograph regarding to Cat 2 catalytic support shows a agglomerated in the form of a plate and over it is possible to observe the presence of clusters of a segregated phase. The particles agglomerated in the form of a plate is a typical morphology of agglomerated of the alpha-alumina non doped [10]. The segregated phase found deposited over the agglomerated is probably composed of ZnO [5, 10, 11]. In Cat 3 sample is possible to observe a segregated phase light-colored presence deposited over dark-colored structure mostly host matrix. This light-colored phase probably is composed by the dopant oxide ZrO₂ that formed clusters of segregated phase over alpha-alumina structure. The segregated phases composed by the dopant oxides formed over alpha-alumina structure were not detected by x-ray analysis but were detected by morphologic analysis by means of tem technique.

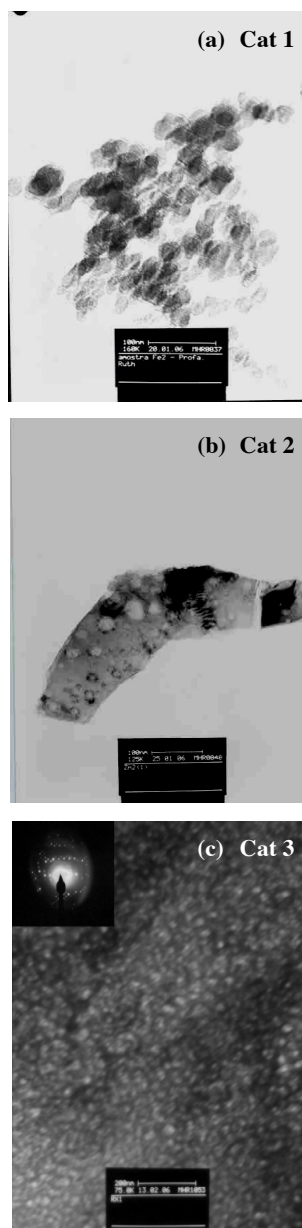


Figure 2: Micrographs obtained by TEM showing the morphologic aspect of the particles agglomerated of the Cat 1, Cat 2 and Cat 3 catalytic supports synthesized by combustion reaction.

Figure 3 presents the conversion of the methane at 700°C in function of time reaction for 1.5%Ni/Cat 1, 1.5%Ni/Cat 2 and 1.5%Ni/Cat 3 catalysts developed samples in this work.

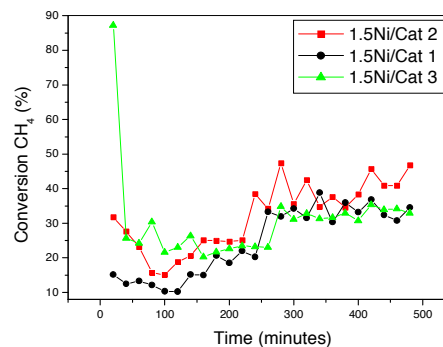


Figure 3: Conversion of the methane at 700°C in function of time of reaction for 1.5%Ni/Cat 1, 1.5%Ni/Cat 2 and 1.5%Ni/Cat 3 catalysts developed samples in this work.

In the graphic profiles representative of these catalytic activities of the samples developed in this work can be seen that the catalytic performance of these were different. In general, there was a marked decrease in CH₄ conversion early in the reaction, suggesting the occurrence of an initial rapid deactivation of catalysts in the three samples analyzed, this supposed deactivation was probably caused by the formation of coke that is substance commonly formed in processing loads consist of hydrocarbons. It is known that the presence of coke can act as an agent of poisoning the catalyst in catalytic reforming [10]. The sample named Cat 2 showed the highest percentage of conversion of CH₄ reaching the maximum value of 48% conversion on 180 minutes of reaction. Thus, it is possible affirm that among the dopant oxides employed ZnO was what led to better results by increasing the performance of the catalytic system 1.5%Ni/alpha-alumina.

In a study about nanosize particles catalytic supported by ceramics materials was concluded that the Ni/α-Al₂O₃ catalysts doped with metallic oxides, such as, Fe₂O₃, SiO₂ and CeO₂ operating in similar conditions to Ni/α-Al₂O₃ catalysts not doped, they are less prone to the structures formation the carbon base, that is, are more resistant to the coke formation and consequently presents superior catalytic activities, attributing to the dopents elements this increase in the resistance of the catalysts [11-13].

The explanation for the good performance of the 1.5%Ni/α-Al₂O₃-ZnO (1.5%Ni/Cat 2 sample) sample may be the fact the structure of it has favored the dispersion of active catalytic species in this case is nickel impregnated on the support of the sample. The literature reports a research that states that the dimension of the pore structure of the catalytic support has great influence on the performance of the catalytic system as a whole, The type and morphology of the porous structure can facilitate or hinder the interaction of the oxide of the active species with the flow of H₂ that promotes the reduction of this oxide [14].

2 CONCLUSIONS

- It is possible to synthesize catalytic supports of type α -Al₂O₃ doped with 0.05 mol of iron oxide, 0.01 mol of zinc oxide and 0.005 mol of zirconium oxide by means of the method of the combustion reaction and to obtain materials with unique phase structures composed by only α -Al₂O₃ phase.
- The morphologic characterization accomplished by MET showed the presence of the deposited clusters over particles agglomerates of the obtained doped α -Al₂O₃.
- The developed catalyst in this work showed efficient performance in the catalytic reaction of steam reforming of methane at 700°C, carrying to a good H₂/CO reason which varied about 3.
- The sample composed by 1.5%Ni deposited over alpha-alumina doped ZnO proved better catalytic activity with values higher of conversion of methane into comparison the other two samples of catalysts developed.

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