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Full Length Research Paper

NiAl2O4 a promising catalyst in theory but limited in industrial scale

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Abstract:

NiAl2O4 is a particular type of spinel phase. This material is characterized by its stability in high temperature, chemical resistance, abrasion resistance and high hardness, and it is widely used due to its unique property. In the last few years many studies showed interest in heterogeneous catalysis: oxidation of NOX, and in steam reforming (production of Hydrogen, energy of the future). All these experiments showed very good catalytic results, at the laboratory scale. Till now, no catalyst instead of Ni/Al2O3 has been able to cross the line between laboratory and insdustrial scale: we will find no response in the paper mentionned above. Therefore this article try to explain us why this spinel supported or not couldn't be use till now in industry, through the problem which occur at the ivorian refinery in August 2008 due to the presence of NiAl2O4 in the steam reforming reactor.

Keyword: NiAl2O4; spinel phase; steam reforming; refinery.

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1. Introduction

The spinels are any of a class of minerals of general formulation AB2X4 which crystallise in the cubic (isometric) crystal system, with the X anions (typically chalcogens, like oxygen and sulfur) arranged in a cubic close-packed lattice and the cations A and B occupying some or all of the octahedral and tetrahedral sites in the lattice.[1][2] Although the charges of A and B in the prototypical spinel structure are +2 and +3, respectively(A2+B3+2X2−4). NiAl2O4 is an Aluminum spinel. Spinels commonly form in high temperature processes. As a matter of fact the common uses of spinel in industry is based on deposition or spinel coatings [3], which can be used to protect base metals from oxidation or corrosion. Their superior and impressive physico-chemical properties, namely high thermal and chemical stability, high mechanical resistance, optical uniqueness, hydrophobicity and low surface acidity have been the body of comprehensive theoretical and practical studies [4-16]. All these potentialities, have lead numerous authors to essay this material in the field of catalysis.

These last decade, many research have been held in the field of catalysis. In fact, since the 1960's, we assist to a boom of development of catalyst performant and cheaper. With environmental standards that become more and more drastic, the race of the production of clean energy is on moving: we assist to the development of fuel cells, power plants and new non-polluting vehicles. . One of the least dangerous, is undoubtly hydrogen. The process to produce this molecule is SRM (Steam Reforming Methane). The catalyst (industrial) originally was Ni/Al2O3, but a lot of authors see in NiAl2O4 a promising catalyst [17-24]

It exists many different ways to synthesis NiAl2O4 catalyst. Non-supported catalyst have been made [25-29] at the beginning, then researchers have seen the importance of supported this material on alumina [30-33], some researchers try to improve the ratio Ni/Al [34], others try to improve catalyst of Ni by adding dopant [35] finally some test the catalytic activity in fixed bed flow. Their results (the last one) show that NiAl2O4 is really promising in laboratory compared to the industrial one named above [30, 31, 32, 33, 35, 36]. Since the first essay as catalyst at the beginning of 2004 [36], this material has not be tested in real condition within a reactor on going. Of course, Developing and optimizing catalysts requires extensive experimental testing because of the large number that to be evaluated [37], but, some authors [37- 38] have shown that HTCT (High Throughout Catalyst Testing) has become indispensable for catalysis research and development. It reduces time and effort to develop a catalyst by several orders of magnitude. So why in 18 years, NiAl2O4 has not be able to work under industrial conditions? Does it exists a limit to NiAl2O4 catalyst? This paper, without claiming to have the absolute truth, will attempt to enlighten the research communauty, by showing the behavior of NiAl2O4 under real operating conditions, specifically in the steam reforming reactor at SIR: in August 2008, after 8 months of working, the furnace of steam reforming methan (SRM) caught fire. Each tubes of the owen contained previously the catalyst NiO/CaAl4O7; during normal operation, the NiO supported is reduced into Ni/CaAl4O7, but as we will see below, the catalyst obtained on the damaged tubes was in fact NiAl2O4/CaAl4O7. This spinel has worked on a little short time, then, it was unactive in SRM process because it doesn't respect the endothermic reaction in the tube. Therefore steel columns had been weakened by the fire of the furnace. Through this article, we will see that, it exists a thin way to obtain the two catalyst Ni/CaL4O7 and NiAl2O4/CaL4O7 in SMR process. We will start by presenting SMR, then the condition of the synthesis of NiAl2O4 supported with characterization of the material, and finally we will conclude by showing the result of the catalytic activity of this spinel inside the tube of the furnace.

2. Experimental

2.1. Furnace description

This study was carried out in the steam reforming reactor of the Société Ivoirienne de Raffinage (SIR) shown in Figure 1. The furnace consists of 44 tubes and 11 burners per row. The feed that will be used to feed it, comes from the reformer to which it is added liquid butane and hydrogen from the PSA (Pressure Swing Adsorption - the hydrogen purification unit).

At the outlet of the reactor, hydrogen is obtained containing impurities, which will be purified in PSA.

Each tube contains a certain volume of catalyst : NiO / CaAl4O7, these catalysts based on nickel (Ni) are commonly used [39] to improve the reaction kinetics at low temperature, the reactions taking place in the steam reformer, are very endothermic [40], [41], [42]: it is an energy-intensive process. The reaction takes place from 600 ° C, under 25-30 atm, with significant yields.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \text{[Eq. 1]}$$

Methan or natural gas reforming catalysts consist of nickel oxide deposited on refractory supports, which are either calcium aluminates or oxides of magnesium and (or) aluminum. MgO and CaO present a good compromise between a low acidity which reduces the formation of coke and a good thermal stability.

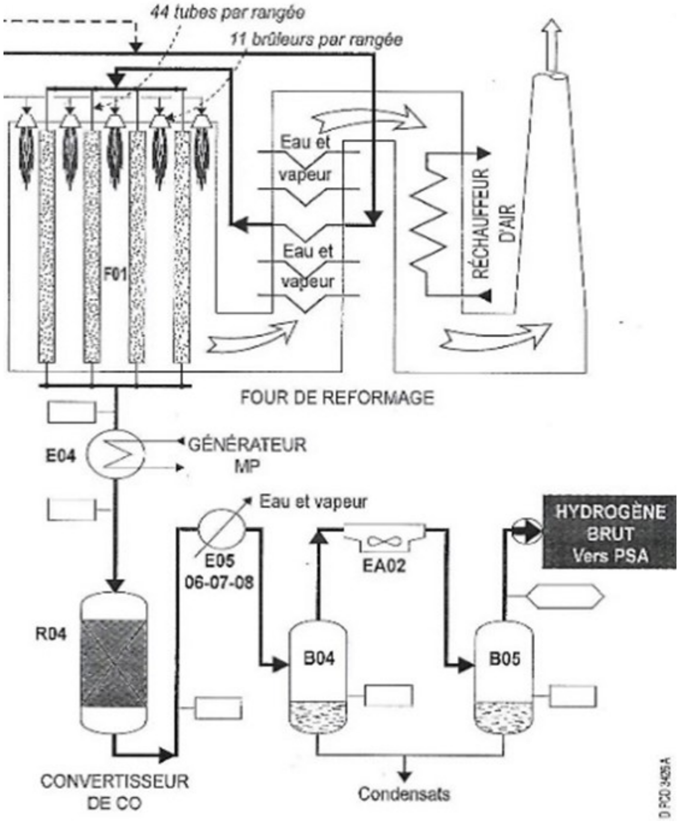

Figure 1: Steam reforming cross section at SIR

These supports are combined with alumina in the form of aluminates to increase their mechanical strength. The dispersion of nickel particles in these supports is of the order of one percent, with a particle size between 20 and 200 nm [40]. These catalysts must be activated (mechanism of sulfurization), so they will go from an oxide state to a reduced state: we can observe that the color changes, we go from a green color (due to nickel) to a black color after activation (mechanism of combustion). Ni / CaAl4O7 has two functions in the steam reforming oven tubes : (1) located at the top of the tube in order to reduces coke; and (2) located in the middle and bottom of the steam reforming oven where the activity is increased at its maximum. When the catalyst is introduced in the furnace, it is oxided. Its color is yellow green ; following the process, catalysts are activated in the furnace : in accordance with the start-up procedure recommended by the catalyst supplier – Firstly, the reactor is flushed with nitrogen (neutral gas) during the rising of the temperature, then when the target temperature is reached, the DMDS (Dimethyl disulfur) is triggered to transform the NiO / CaAl4O7 into Ni / CaAl4O7

NiO + DMDS <=> Ni + H2O + 2S+ Dimethyl. [Eq. 2]

Once this process is completed, then water vapor can then be injected into the tubes so that steam reforming can take place.

Reforming tubes are cast alloy tubes (steel - nickel), length between 10 and 15 m, their diameter varies between 80 and 130 mm and their thickness is of the order of 10 to 25 mm. They are subjected to very great stresses since they operate at high temperatures with a strong gradient (450 - 900 ° C). Their mechanical resistance strongly depends on the maximum wall temperature (i.e. the imposed heat flow). An increase in the maximum wall temperature of the tube can lead to a significant reduction in its lifespan ... They are placed inside a furnace, arranged so that each tube can "see" the flames of the tube. Burner, thus promoting thermal radiation. The furnace configuration can take three forms (Figure 2).

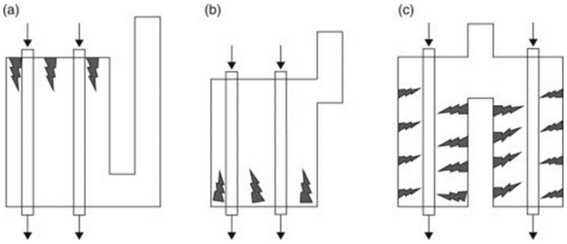

Figure 2: Configuration of Steam Reforming Furnace (a) top view (b) bottom view (c) side view [43]

To understand what happen on the furnace, we will use technics to characterize the catalysts.

For this, samples in the furnace will be collected at the refinery (old catalysts) in one side and in other side new catalysts will be taken at the Maintenance Department .They will undergo been analyzed in XRD and BET departments for analysis.

2.2. Catalyst characterization

All catalysts inside tubes, had been characterized, by multiple ways XRD, BET, and TPR. We will see below the results of these characterization.

2.2.1 X Ray Diffraction : XRD

The catalysts were analyzed by X-ray Diffraction (XRD). X-ray diffraction patterns were recorded on a BRUKKER D5005 apparatus using Kα1 radiation from copper. EVA software was used for the search for crystalline phases. Scherrer's formula was used to determine the size of the crystallites. The XRD for "standard analyzes" allows samples to be analyzed with programs adapted to each of them using fully motorized and programmable equipment. The device includes a Cu anode X-ray tube.

2.2.2. BET specific surface study

The Brunner Emlet Teller method provides information on the specific area: the surfaces of the catalyst Ni / $CaAl_4O_7$ and $NiAl_2O_4/CaAl_4O_7$ are measured by the dynamic method of physisorption of nitrogen at the temperature of liquid nitrogen.

The device used for the BET area measurement is the ASAP 2020 FROM MICROMERITICS. It is equipped with 2 pressure sensors (1000, 10 mm) which allow it to carry out mesoporosity studies of solids. The gas used for physisorption measurements is nitrogen.

2.2.3 Temperature Programmed in Reduction

Temperature Programmed Reduction is a technique used for the chemical characterization of solid materials. It is based on the reduction of the commonly used solid via a flow of hydrogen, simultaneously varying the temperature in a predetermined manner.

The device is composed of a gas system controlled by mass flow meters, an oven fitted with a thermocouple, a saturator fitted with a heating jacket, a water trap (use of zeolites or a molecular sieve), a "zero station" which allows the consumption of hydrogen to be calibrated and a thermal conductivity detector. The sample to be analyzed is placed in a quartz U-tube, itself placed in the oven where a thermocouple measures the temperature of the catalyst. In this specific case the hydrogen has been replaced by water vapor.

3. Résultats and discussion

3.1. Tube of steam reforming : state of the tube after explosion

When opening the furnace, the tubes reveal catalysts with colors varying from blue to brown. We will see explanation in the work of Benoît Marcq [44]. He demonstrated that nickel glasses could take several colors ranging from purple to green through brown depending on the degree of oxidation. Figures 5, 6, 7 and 8 show the damage to the tubes.

Horizontal opening of the tube: the catalysts have changed color, they are green or brown, depending on the degree of oxidation

Figure 5: Cross section opening of the tubes

Longitudinal opening: the catalysts have changed color green or blue-green depending on the degree of oxidation on contact with the water vapor

Figure 6: Longitudinale opening of the tube B1

Longitudinal opening: the catalysts have changed color green or blue-green depending on the degree of oxidation on contact with the water vapor.

Figure 7: Longitudinal opening of the tube P3

Longitudinal opening: the catalysts have taken a brown-orange color: this color results from the degree of oxidation of the catalysts in contact with the water vapor

Figure 8: Longitudinal opening of the tube D4

Figure 9 shows us the color difference between the catalyst present in the uncracked part and in the cracked part.

Figure 9: Ni / $CaAl_4O_7$ catalyst in the uncracked part (left) and cracked part (right)

3.2. Textural properties

After the tubes, we will analyze the textural properties of the catalyst.

3.2.1. XRD results

Figures 10, 11 and 12 show us the composition of the catalyst before and after the operation of the steam reforming furnace

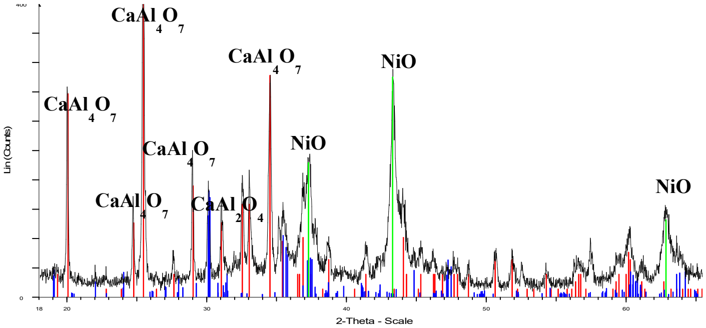

Figure 10: Diffractogram of the NiO / $CaAl_4O_7$ catalyst before the operation of Furnace 86F01

The diffractogram (Figure 10) shows us that the main active phase is NiO (green), the most intense lines being located at 2θ = 37 °, 43 ° (111) and 64 °. The majority phase of the support being an assembly of $CaAl_4O_7$ and $CaAl_4O_2$ (calcium aluminate).

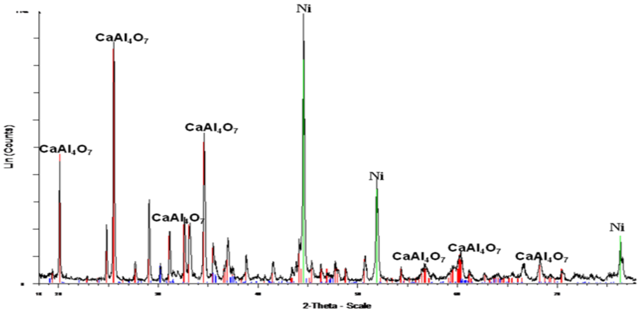

Figure 11: Diffractogram of the black catalyst after 8 months on working.

The diffractogram (Figure 11) shows three characteristic lines of Ni, the main one at 2θ = 44 ° (111). Regarding the support we always have $CaAl_4O_7$ or $CaAl_2O_4$. But we can note a decrease in the intensity of the $CaAl_2O_4$ peaks in favor of that of $CaAl_4O_7$. In addition, the intensity of the peaks shows that the Ni sintered, that means that large particles of Ni were formed.

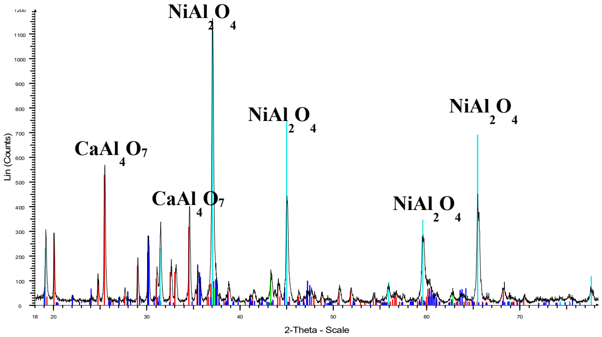

Figure 12: Diffractogram of the blue or green catalyst after 8 months on working.

This diffractogram (Figure 12) showed several phases : 1) the active phase which is not Ni but a mixture of NiAl2O4 and NiO (high intensity peaks). 2) There is no trace of Ni, but we can see traces of NiO. 3) Regarding the support, we see a predominance of CaAl4O7 and a decrease in the intensity of the CaAl2O4 phase.NiAl2O4 (majority phase) belongs to the family of spinels AB2O4 [45]. Hyun-Seog Roh et al [45] have shown that this phase is inactive in catalysis but has very interesting optical properties. The catalyst of the rugged areas changed color and especially crystallographic structure, the catalyst adopted the structure of a spinel NiAl2O4. Figure 13 representing this glass, shows the existence of traces of NiO as we could see on the XRD (peak of NiO).

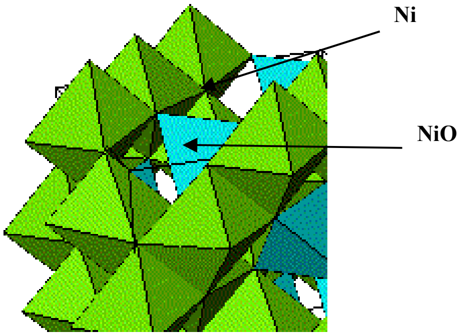

Figure 13: Spinel structure of NiAl2O4

This crystal is formed at high temperature, beginning of crystallization around 800 ° C and end of crystallization between 1000 ° C and 1200 ° C [46], [47]. However, according the intensity of the peaks, we can only say that this phase is terminal.

All authors agree that NiAl2O4 can only be formed from NiO [47] in an oxidizing atmosphere when the oxygen content in nickel oxide is insufficient. There is then a strong interaction between Ni and alumina [45 - 47]. Moreover, Trichardson et al [48] have shown that at high temperature the equilibrium of equation 3 was strongly shifted in direction 1.

$$NiO_{(s)} + H_{2(g)}(2) \Leftrightarrow (1)Ni_{(s)} + H_2O_{(g)} \quad \text{[Eq. 3]}$$

In the reduced state, thermodynamics do not allow to return to the NiO form. The diffractogram of the blue or green catalyst shows the presence of NiO, but in no case of Ni, likewise the diffractogram of the catalyst which has not undergone any gray-black damage does not in any way show the presence of NiO (in case NiO would not have been reduced). Therefore we can affirm that the catalyst underwent this strong oxidation at the start of operation before it was reduced, or again in the NiO form (this corroborates the data from the Foxboro table indicating water vapor for a long period of time. Steps).

3.2.2. BET specific surface results

We haven't information on the dispersion of the active phase, so we performed a BET analysis on the oxide catalyst in order to get an idea of the specific surface. The starting specific surface is around 300m2 /g.

Regarding blue or green catalyst, we obtain a BET surface area of around 13m2 / g. We deduced that the catalyst coming from the damaged tubes has a low porosity, and that the active phase is poorly dispersed: the catalyst has changed texture on its surface. Indeed, from an amorphous phase with a large specific surface area, we have moved on to a crystallized phase with a low specific surface area.

3.2.3. Reduced Programmed Temperature Results

Reduced Programmed Temperature has been held by the supplier ; the figures below (Figures 14 and 15) showed of the NiO / $CaAl_4O_7$ catalyst at different temperature : depending on the colors, we can see that the catalyst takes on a color varying from green to blue. (1) and (2) corresponds to the position of the catalyst inside the furnace. It seems that the different colors correspond exactly to those found on the catalysts of the tubes.

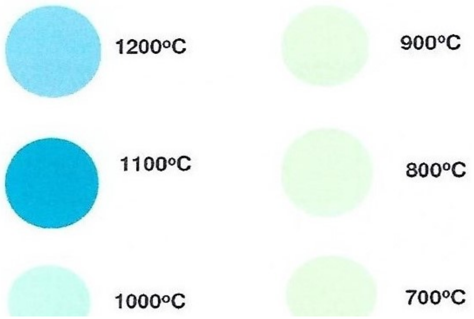

Figure 14: Effect of reduction under water vapor of the NiO/$CaAl_4O_7$ catalyst (1)

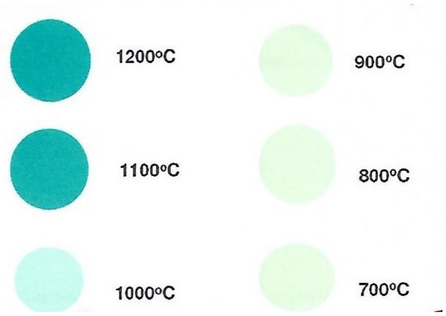

Figure 15: Effect of reduction under water vapor of the NiO/$CaAl_4O_7$ catalyst (1)

The TPR as well as the chromatic diagram of NiAl2O4 [49] shows that the more pronounced the oxidation is, the color will vary from blue to brown-orange with increasing temperature. It is deduced from this that the catalyst supposed to be activated has indeed undergone oxidation at high temperature.

4. Conclusion

This article shows us that with advanced characterization method, such as XRD, Temperature Programmed Reduction, BET, we were able to obtain scientific information explaining why the steam reforming furnace caught fire in August 2008 : the catalyst in amorphous state inside the oven, supposed to carry out the reformation of methan into H2, in reality could not be active in the sense that we no longer had Ni/CaAl4O7, but rather a spinel, NiAl2O4 (a glass) at the catalyst surface. This assertion had be corroborated by the data registered by the control system, which had shown that the catalyst was during a long time under steam. Then, the consequences of the formation of this glass have been catastrophic for the furnace in the sense that, we already not have endothermic reaction, and the tubes had suffered local overheated which led to their rupture at the places where the catalysts were deactivated [50]. All these elements allow us to affirm that, catalysts are a living memory for refinery processes. Thus, this paper, present us an industrial performance of the catalyst NiAl2O4/CaAl2O7 on a steam reforming reactor : undoubtly this material is inactive. Beyond the scientific aspect that has been demonstrated here, it should be noted that university research can be a real added value for a refinery in general. Therefore, this article opens the way for a future collaboration University/SIR for the smooth running of catalysts.

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