

Development of Ceramic Support for Methane Reformer from Alkali Aluminosilicates

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ABSTRACT

This work deals with the microstructural evolution during sintering of ceramic catalysts composed of silica and alumina due to the addition of oxide fluxing agents in order to obtain methane reformers. The catalysts were prepared by sintering the aluminosilicate ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) system with alkaline oxides. Samples of silica, alumina and sodium, calcium, potassium and magnesium oxides ($45\mu\text{m}$) were used. The samples were added to silica in fractions of 10%wt according to a fractionated factorial design $2^{(5-2)}$, and mixed and homogenized in a laboratory eccentric mill (alumina grinders, 5min). The formulations were dried (110°C , 24h) and then analyzed by optical dilatometry ($10^\circ\text{C}/\text{min}$). It is clearly perceived the influence of sodium and potassium oxides in the sintering temperatures and rates, with significant reduction of the temperature of initiation of sintering. It is possible to correlate the content of each oxide with the maximum rate of sintering, enabling to optimize the systems from the results of the factorial design.

Keywords: ceramic reformer, fuel cells, catalyst, aluminosilicate, alkali oxides

1 INTRODUCTION

This work deals with the initial development of a ceramic reformer based on alkali metal aluminosilicates coated with nickel for the generation of hydrogen from biogas (methane). The main goal was to study the microstructural evolution during sintering of ceramic catalysts composed of silica and alumina due to the addition of oxide fluxing agents in order to obtain methane reformers. The understanding of the microstructural evolution of silicon-aluminum ceramics with the addition of alkaline oxides and its correlation with the resulting physical-mechanical properties can reduce the time and temperature for the sintering of the ceramic reformer. The catalysts were prepared by sintering the aluminosilicate ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) system with alkaline oxides.

The conversion of methane into higher value-added products has acquired economic importance due to the existence of innumerable natural gas reserves and renewable sources of methane gas [1,2]. There are two methods to

convert methane: Direct and Indirect Method. The Direct Method refers to the reaction of the gas with O_2 or another oxidizing agent in order to obtain the desired product in one step. In the Indirect Method the gas is converted into the desired product in a two-step process: first it is converted into syngas, a mixture of H_2 and CO by reforming or partial oxidation of methane and after the synthesis gas is converted into the desired product. The conventional method for converting natural gas into synthesis gas is the catalytic reforming of methane with steam. This process allows for greater catalyst life because there is no coke formation as a product, which disables nickel catalysts [2-5].

The process of hydrocarbon reforming into hydrogen began with the refining of petroleum. In 1978, Karin and Metwally published a study analyzing the thermal reforming (1400K to 3000K) of water vapor/methane at a pressure between 0.5 atm and 10 atm in a 1/5 mixture of steam/methane. According to these results, the reaction is favored at temperatures above 1800K reaching equilibrium in 10 seconds. This process was not sensitive to the pressure of the gas supply. The addition of oxygen to the mixture, about 5 vol%, has little effect on the process yield, but significantly reduces the required temperature. A decade later, Nazarov and coworkers introduced a project to use the nuclear reactor coolant in the process of natural gas reforming, exploiting the transferred heat to cause the methane reforming [3,5].

That same year, Rosen presented a paper on the thermodynamic analysis of the methane reform process by steam (steam-methane-reforming - SMR). This analysis showed that the main energy loss occurs due to heat transfer through the large temperature difference caused by the irreversibility of the process. However, high temperatures were still required for the process. In 2001, Kodama [1] presented the results of the reform of methane in molten carbonate salts. Particles of metal (Ni, Cu W, Fe, or K) supported on alumina were tested. This composition significantly reduces the operating temperature of the system. Currently, several architectures of catalysts are found in the literature. The use of catalyst dispersed on alumina (Al_2O_3) is described by Santos [5], which examined the effect of adding alkaline earth metals (Mg or Ca) in the catalytic process. He noted an increase in catalyst

efficiency with reduced operating temperature given by the presence of alkaline earth metal [1-5].

Therefore, this work involves the construction of a catalyst comprising an aluminosilicate ceramic support ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) with the addition of calcium, magnesium, potassium and sodium oxides (CaO , MgO , K_2O and Na_2O , respectively). The catalytic system is composed of nickel supported on aluminosilicate ($\text{Al}_2\text{O}_3\cdot\text{SiO}_2$) added with the cited oxides.

The system to be mounted is a pipe made of a porous structure of aluminosilicates in which heated air flows. The catalyst will be plated in the aluminosilicate structure in the form of nickel nitrate. Under this scheme, methane and water vapor are added to the system by heating, which produces carbon dioxide and hydrogen. The gas formed is complexed and eliminated, allowing the formation of hydrogen with a purity suitable for use. The development of this project will enable the production of hydrogen, which can be used to power a fuel cell to generate electricity. This application allows the development of an economically viable alternative for replacing the conventional method of service of electricity to rural properties.

2 MATERIALS AND METHODS

Silica, alumina and calcium, sodium, magnesium and potassium carbonates were used as raw materials in this work. Carbonates were all calcined at their respective temperatures of decarbonation to obtain the pure oxides, which were then kept in airtight containers to avoid contact with humidity. Eight formulations with five factors were used according a mixture design experiment. The factors used were alumina, lime, potash, soda and magnesia, all added at 10 wt% on silica. The formulations were made according the mixture design (table 1), and the mixtures were homogenized in an eccentric mill (dry-milling, alumina balls, 100g, 30min) and pressed (25MPa, 9 wt% moisture) into small cylinders ($\varphi = 2\text{mm}$, $h = 2\text{mm}$) for testing by optical dilatometry (MISURA, $10^\circ\text{C}/\text{min}$).

Form.	Al_2O_3	CaO	MgO	Na_2O	K_2O	$T_{\text{sint}} (^\circ\text{C})$
1	0	0	0	10	10	920
2	10	0	0	0	10	1075
3	0	10	0	0	10	980
4	10	10	0	10	0	1062
5	0	0	10	10	0	950
6	10	0	10	0	10	995
7	0	10	10	0	0	1020
8	10	10	10	10	10	880

Table 1. Mixture design showing the sintering temperature of the system as a function of oxide addition on silica.

To confirm the chemical composition of the formulations, samples of all formulations were analyzed by X-ray fluorescence (XRF, Philips PW2400, melted sample). It should be noted that in the experimental design (Table 1) test 8 is the central point of the experiment.

3 RESULTS AND DISCUSSION

The chemical analysis of the formulations is shown in Table 2. In this, one can see variations in chemical composition in relation to the experimental design, which can be explained by experimental error associated with the technique of X-ray fluorescence, because some oxides are more easily detected than others by this technique. It was considered that variations in the chemical analysis do not reflect gross variations in the formulations, but deviations of analysis.

Form.	SiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O
1	88.0	0	0	0	5.7	6.3
2	85.0	7.4	0	0	0	7.6
3	84.8	0	8.0	0	0	7.2
4	78.0	9.4	7.3	0	5.3	0
5	84.9	0	0	8.4	6.7	0
6	81.0	7.1	0	7.0	0	4.9
7	82.9	0	8.9	8.2	0	0
8	72.4	7.5	5.2	6.2	4.3	4.4

Table 2. Chemical analysis of the formulations, including silica.

Table 3 shows the analysis of variance (ANOVA) for the temperature of maximum sintering rate (T_{sint} , Table 2) for the mixture design. The analysis shows a strong linear dependence of the factors, with a high statistical significance ($p=0.007$, i.e., $\alpha=99.3\%$) and an excellent fit to the linear model ($R^2\sim 1$).

Model	SS	df	MS	F	p	R^2
effect	31770	5	6354	152.1	0.007	0.997
error	83.5	2	41.8			
total	31854	7	4551			

Table 3. ANOVA for the temperature of maximum sintering rate of the studied system ($^\circ\text{C}$).

Figures 1 to 4 show the graphs of the contours for the temperature of maximum sintering rate of the studied system.

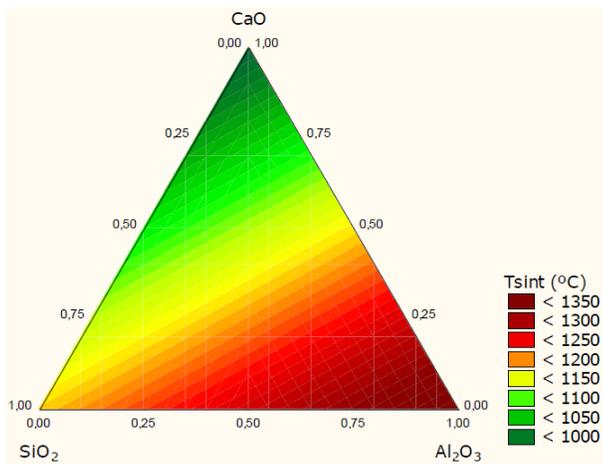


Figure 1: Contour for the temperature of maximum sintering rate of the aluminosilicate system as a function of CaO addition.

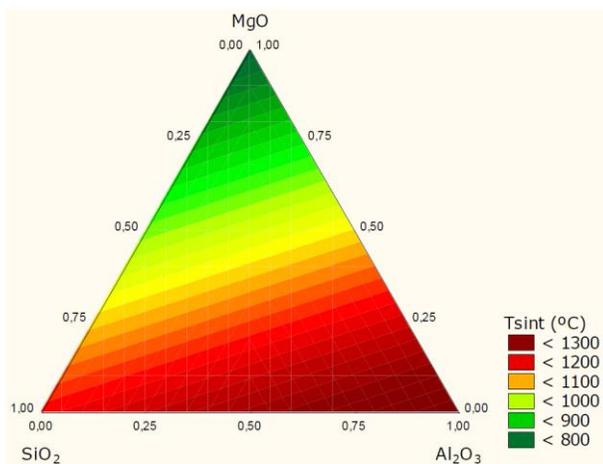


Figure 2: Contour for the temperature of maximum sintering rate of the aluminosilicate system as a function of MgO addition.

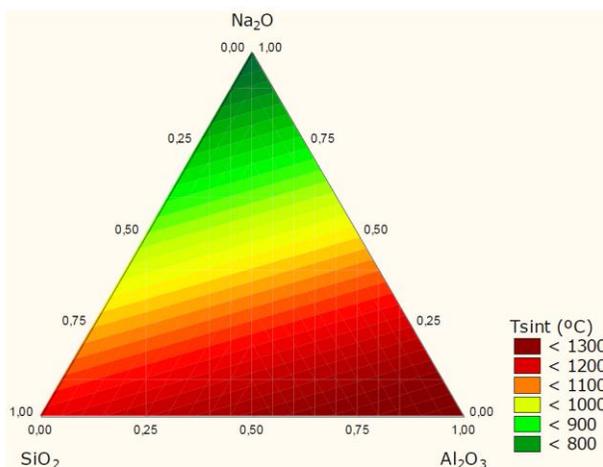


Figure 3: Contour for the temperature of maximum sintering rate of the aluminosilicate system as a function of Na₂O addition.

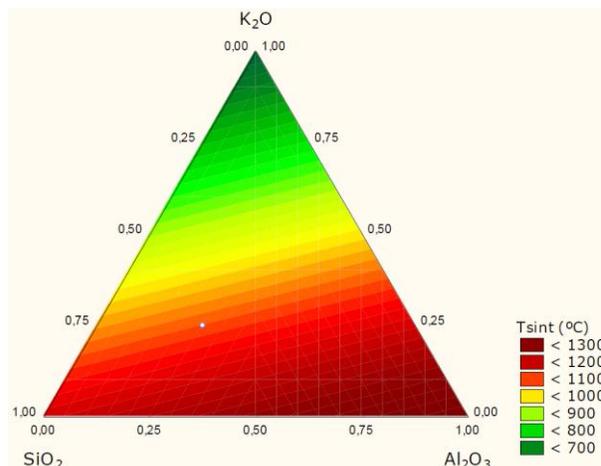


Figure 4: Contour for the temperature of maximum sintering rate of the aluminosilicate system as a function of K₂O addition.

As can be seen by the contours of Figure 1 to 4, alumina is the oxide which results in higher temperatures of maximum rate of sintering, making the most refractory ceramics, as expected. The calcium oxide is a flux less efficient in reducing the temperature of maximum rate of sintering, or in other words, has fewer tendencies to reduce the rate of sintering.

Moreover, in this study, the sodium and potassium oxides were the most effective in reducing the temperature of maximum rate of sintering, and this property is measured as the first derivative of the onset of the sintering curves obtained by optical dilatometry.

Equation 1 shows the relationship between the temperature of maximum rate of sintering and content of each oxide studied.

$$T_{sint} = 1171x_{SiO_2} + 1360x_{Al_2O_3} + 968x_{CaO} + 764x_{MgO} + 708x_{Na_2O} + 615x_{K_2O} \quad (1)$$

Figure 5 shows the SEM image of the formulation 1 (10 wt% Na₂O and 10 wt% K₂O addition on silica), the lowest temperature of maximum sintering rate (besides the central point, formulation 8). The microstructure presents open pores connected with each other, forming a “net” of pores, suitable for a catalyst support.

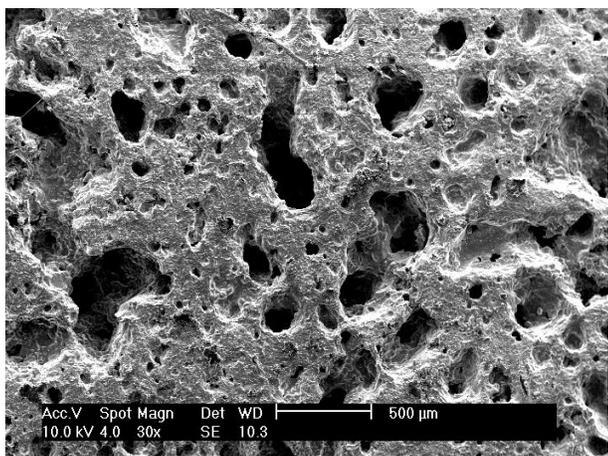


Figure 5: SEM image of composition with 10 wt% Na₂O and 10 wt% K₂O addition on silica.

On the other hand, Figure 6 shows the SEM image of the formulation 2 (10 wt% Al₂O₃ and 10 wt% K₂O addition on silica), the highest temperature of maximum sintering rate. The microstructure shows that the ceramic is not dense, i.e., it is not totally sintered yet. Probably the mechanical resistance of this formulation will not allow its use as a catalyst support.

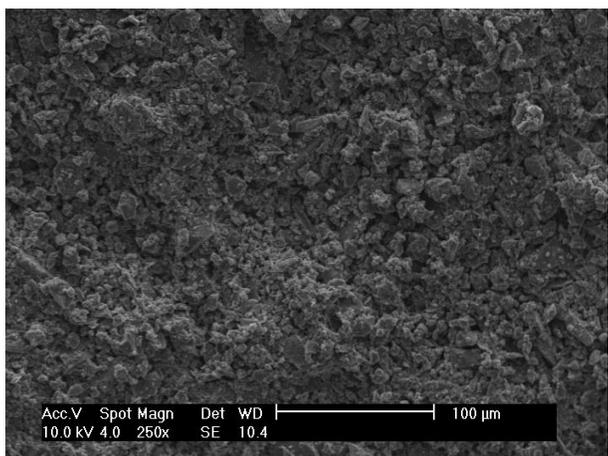


Figure 6: SEM image of composition with 10 wt% Na₂O and 10 wt% K₂O addition on silica.

4 CONCLUSION

In this work the technique of mixture design was used to verify the influence of alkaline and earth alkaline oxides added as fluxes on silica and alumina. Several studies have shown the influence of alkaline oxides in the sintering of aluminosilicate ceramics, but treating them individually.

Considering the 10 wt% oxide addition on silica used in this study, alumina tends to increase the temperature of maximum rate of sintering, while the calcium, magnesium, sodium and potassium oxides, in that order, tends to diminish it.

The microstructural analysis show that the formulation with Na₂O and K₂O addition forms a porous ceramic body with open pores connected with each other, forming a “net” of pores, suitable for a catalyst support.

The continuity of the project is to determine the microstructural evolution of this system by X-ray diffraction and electron microscopy, with quantification of the phases by Rietveld technique. Finally, the best catalyst supports will be plated with zinc and its catalytic capacity will be determined regarding its ability as a methane reformer.

REFERENCES

- [1] Z. Chen, Y. Yan, S.S.E.H. Elnashaie, Novel circulating fast fluidized-bed membrane reformer for efficient production of hydrogen from steam reforming of methane, *Chemical Engineering Science* 58 (19) 4335-4349, 2003.
- [2] K.S. Patel, A.K. Sunol, Dynamic behaviour of methane heat exchange reformer for residential fuel cell power generation system, *Journal of Power Sources* 161 (1) 503-512, 2006.
- [3] P. Ferreira-Aparicio, M. Benito, K. Kouachi, S. Menad, Catalysis in membrane reformers: a high-performance catalytic system for hydrogen production from methane, *Journal of Catalysis* 231 (2) 331-343, 2005.
- [4] A.L.Y. Tonkovich, B. Yang, S.T. Perry, S.P. Fitzgerald, Y. Wang, From seconds to milliseconds to microseconds through tailored microchannel reactor design of a steam methane reformer, *Catalysis Today* 120 (1) 21-29, 2007.
- [5] W. Shuyan, Y. Lijie, L. Huilin, H. Yurong, J. Ding, L. Guodong, L. Xiang, Simulation of effect of catalytic particle clustering on methane steam reforming in a circulating fluidized bed reformer, *Chemical Engineering Journal* 139 (1) 136-146, 2008.