Alumina based catalytically active components carriers with improved properties

V. Nikolić [1], Ž. Kamberović [2] corresponding author: kamber@tmf.bg.ac.rs, Z.Anđić [3], M. Korać [1], A. Vujović [3], M. Sokić [4]
[1]Innovation Center of the Faculty of Technology and Metallurgy, University of Belgrade
[2]Faculty of Technology and Metallurgy, University of Belgrade
[3]Innovation Center of the Faculty of Chemistry, University of Belgrade
[4]Institute for Technology of Nuclear and other Raw Materials, University of Belgrade

Abstract

Present paper shows the alumina based catalyst supports synthesis process investigation, with improved properties than existing. Process was optimized to determine suiting polymer foam porosity, suspension contents, clay addition and sintering temperature. Polymer foams of 10 and 20 PPI (pores per inch) were soaked into suspension that consisted of α-alumina with 30 mas.% of clay ('VN-25'), with lower sintering temperature for the process economic enhancement. Sintering temperature was optimized for suitable mechanical properties. Green bodies were sintered at five temperatures, from 1573 to 1773 K for 60 minutes. The best mechanical properties were obtained with VN-25 suspension, 10 PPI polyester foam, sintered at 1673 K for 60 minutes. The compressive strength of this system, achieved in the above temperature-time mode, was 6.2 MPa.

Key words: *alumina; reticulated foam; catalyst; carrier*

1. Introduction

Open porosity ceramic foams, as catalytically active components carriers, are mostly produced by polymer replication method – polymer foam immersing into ceramic suspension, drying and sintering at 1273 K to 1973 K. Faure et al. [1] prepared Al_2O_3 foam, sintered at 1873 K for 1 h, with compressive strengths 1.4 and 3 MPa for 5 and 10 PPI, respectively. Apparent porosity was between 82 and 94% for 5 and 10 PPI. Alumina foams preparation requires high sintering temperatures, that need to be lower. Buciuman and Kraushaar-Czarnetzki [2] prepared alumina-mullite and China porcelain foam monoliths. Samples were dried 24 h at room temperature and calcined at 1873 K, same as [1], except for 5 h instead of 1 h. China porcelain was calcined at 1423 K. Ceramic foams properties mainly depended on suspension viscosity and polymer pore density. Alumina-mullite foams had porosities from 83.4 to 87.8% for polyester foams with 10 to 60 PPI, less than in research [1]. Porcelain foams had porosities from 77.4 to 88.4% for 60 to 10 PPI. M. Al Amin Muhamed Nor et al. [3] also produced China porcelain foams. Differently from [1] and [2], samples were dried at 333-343 K for 72 h and additionally at 373 K for 1 h. Sintering was performed at 1473 K for 2 h. Suspension density increase improved the foams compressive and flexural strengths, with the highest values achieved with density of 1.3653 g/cm^3. Y. Han et al. [4] prepared alumina foams sintered at 1673 to 1873 K, obtaining porosities of 89.5 and 86.75 % at 1673 and 1773 K, respectively, and strengths from 0.27 to 0.627 MPa. Akpinar et al. [5] obtained alumina-clay monolith foams with 20 PPI polyurethane sponges, drying at room temperature for 24 h and sintering at 1773 and 1873 K for 2 and 4 h, respectively, in different furnaces. Specimens shrinkage reached values of 14.21 and 10.44% for conventional sintering, respectively, and 10.86% for microwave assisted sintering. Samples conventionally sintered at 1873 K had highest compression strength of 0.26 MPa.

2. Experiment

Optimal process parameters, such as polymer foam pore density (PPI), clay addition and sintering temperature, were investigated and compressive strengths of sintered foams were determined. Polyester with 10 and 20 PPI were soaked into suspension for at least 3 minutes with constant suspension stirring. Suspension consisted of commercial α-alumina and 30% clay with water content 25% (further denoted as VN-25). Excess suspension was removed by gravity and shaking. Green bodies were dried for 24 h at room temperature and sintered at 1573 to 1773 K during 1h in air atmosphere. Process block scheme is presented in Fig. 1.

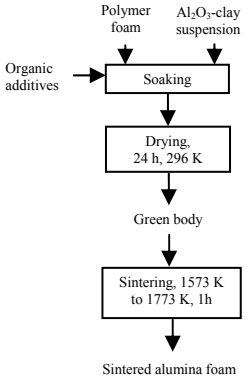


Fig.1. Block scheme of sintered alumina foam production

Starting powder microstructure of α-Al_2O_3 and clay, obtained by VN-25 suspension drying at 378 K for 24 h, was analysed by JEOL SEM JSM 5800 scanning electron microscope. Suspension was dried only for powder obtaining, in order to conduct microstructural analysis. Suspension density was determined and viscosity measured by Ostwald's viscometer. Chemical composition was known prior to measurings. Polymer foams and green bodies were analyzed by KVI software for quantification of visual information to determine volume porosity, pores diameter and struts thickness. Green samples dimensions were measured in order to determine shrinkage degree after sintering. Quantity of material applied to polymer templates was determined from the mass difference and it was converted to grams per cubic centimeter of sample for better comparison.

Volume porosities of sintered foams are calculated using the following equation:

$$P=(\rho_r-\rho_b)/\rho_r \cdot 100\%, \quad (1)$$

where ρ_r and ρ_b are the real and bulk densities, respectively.

Linear shrinkage due to sintering was calculated using the following equation:

$$S=(L_g-L_s)/L_g \cdot 100\%, \quad (2)$$

where L_g is height of green foam and L_s is height of sintered foam.

Pressure strength was determined using INSTRON 1332-retrofitted Fast track 8800 and the force of 1N/mm was applied. Samples were photographed on JEOL SEM JSM 5800 scanning electron microscope in order to investigate microstructure development, as parameter which is relationship between technology and properties.

3. Results

The microstructure of powder obtained by VN-25 suspension drying is shown in Figure 2.

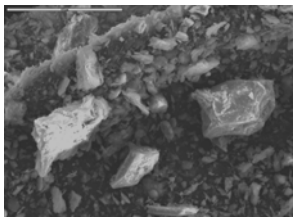


Fig.2. SEM microphotographs of starting powder for suspension preparation

Suspension properties are presented in Table 1.

Table 1. Properties of VN-25 suspensions

Water content (mas.%)	25
Suspension type	VN-25
Density (kg/m^3)	2096
Viscosity (Pa·s)	$2.91 \cdot 10^{-2}$

Polymer foams and green samples characterization are shown in Table 2. and 3., respectively. D and d are pore size and strut thickness.

Table 2. Polymer foams characterization

Material,PPI	**D_{mean} (mm)**	**D_{max} (mm)**	**D_{min} (mm)**	**Std. Err.**	**Std. Dev.**	**d_{mean} (mm)**	**d_{max} (mm)**	**d_{min} (mm)**	**Std. Err.**	**Std. Dev.**
Polyester, 10	2.48	4.50	0.65	1.32	0.20	0.28	0.46	0.12	2.01	0.38
Polyester, 20	1.87	2.98	0.43	1.30	0.15	0.35	0.58	0.19	1.98	0.32

Table 3. Characterization of green samples based on VN-25 suspension

Porosity	**Vis. por.(%)**	***Mat. quant. (g/cm^3)**	**D_{mean} (mm)**	**D_{max} (mm)**	**D_{min} (mm)**	**Std. dev.**	**Std. err.**	**d_{mean} (mm)**	**d_{max} (mm)**	**d_{min} (mm)**	**Std. dev.**	**Std. err.**
10 PPI	78.42	0.56	2.30	3.89	0.75	0.79	0.11	0.61	1.30	0.30	0.21	0.03
20 PPI	78.31	0.68	1.74	3.37	0.65	0.63	0.08	0.64	1.31	0.25	0.20	0.03

*Material quantity applied to polymer foam

Bulk densities were calculated from dimensions and volume of the disk, and using Eq. (1). Real densities are considered to be material densities. Volume porosity, linear shrinkage and compressive strength dependence on sintering temperature is shown in Fig.3.

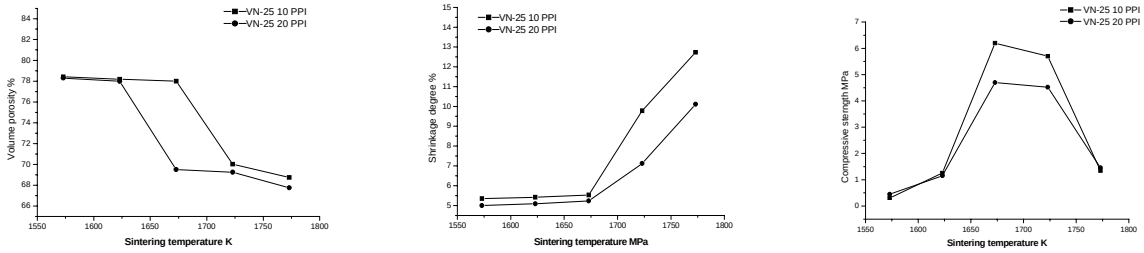
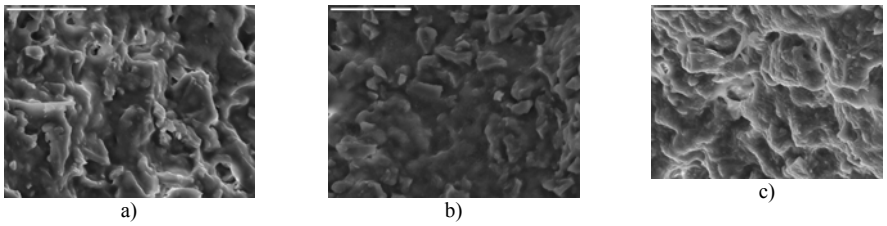


Fig.3. Volume porosity, linear shrinkage and compressive strength dependence on sintering temperature

SEM images of sintered foams strut surface is presented in Figure 5.



a) b) c)

Fig. 4. SEM of strut surface, VN-25 suspension based foam, sintered at: a) 1573 K, b) 1673 K and c) 1773 K, for 60 minutes

4. Discussion

The main goal of present research was the catalytically active components carrier synthesis, with improved mechanical properties compared to existing. Investigations of the polymer pore density, quantity of applied material, sintering temperature, volume porosity, compressive strength and shrinkage intensity of synthesized monolithic foam, were made. SEM of powder obtained by VN-25 suspension drying (Fig. 2.) clearly indicate the irregularity of particle morphology, surface roughness and the prevailing presence of agglomerates, due to fine particles, their large surface area, surface energy and the attractive forces between them, as well as the presence of clay as a binder. Individual particles of less than 25 μm in size were present.

VN-25 suspension had high density in combination with relatively low viscosity (Table 1.), due to clay addition as a binder and the fine particles presence. Results of KVI analysis shown that pore size decreases and strut thickness increases with the material application (Tables 2. and 3.). Green sample had volume porosity of 78.42 % with 10 PPI polyester. After drying at room temperature for 24 h, samples were sintered at 1573 to 1773 K for 60 minutes, then subjected to compressive strength investigation and microstructure analysis. With increasing sintering temperature, to a certain value, compressive strength and linear shrinkage increase and the volume porosity decreases (Fig. 3.). The compressive strength is a function of the volume porosity and linear shrinkage change. Until 1723 K, compressive strength increases, and then it declines. In Fig. 4., the SEM of strut surface is presented. During sintering, there has been intensive contact between the individual particles at 1573 K (Fig. 4.a.) and increase in surface contact (due to clay addition), with a significant reduction in porosity (4.b and 4.c) at 1673 and 1773 K and the linear shrinkage and compressive strength increase (Fig. 3.), until temperature of 1673 K. At 1723 K approximately the same value of compressive strength was achieved, followed by its significant drop in the temperature of 1773 K, as a result of intensive microstructure coarsening due to the abnormal growth of individual particles (Fig. 4.c). The best mechanical properties were obtained using 10 PPI polyester foam, VN-25 suspension and sintering at 1673 K for 60 minutes, with the compressive strength of 6.2 MPa. This indicates that the catalyst support with improved mechanical properties compared to existing has been synthesized, with higher compressive strength achieved at low temperatures [1, 8, 9], and significantly simplified by means of the technological process applying [1].

3. Conclusions

The main objective of this research was the catalytically active components carrier synthesis study, with improved mechanical properties compared to existing. Examinations of the relevant process parameters, such as polymer pore density, suspension contents, clay addition, sintering temperature and their influence on the volume porosity, shrinkage, and the compressive strength values were made. Technological processes was optimized and best mechanical properties were achieved with VN-25 suspension, 10 PPI polyester foam, drying 24 h at room temperature and sintering at 1673 K for 60 minutes. Green foam had volume porosity of 78.42 %. The optimal sample compressive strength was 6.2 MPa. With increasing sintering temperature, the volume porosity decreases and the linear shrinkage intensity and compressive strength increases, as a result of increasing the contact area between particles and their movement towards the interior. Higher compressive strength values at lower temperatures were achieved, and the technological process was significantly simplified.

Acknowledgements

This paper was done in the frame projects N^{o}34033 and N^{o}34023 by Ministry of Education and Science of Republic of Serbia.

References

[1] R. Faure, F. Rossignol, T. Chartier, C. Bonhomme, A. Maître, G. Etchegoyen, P. Del Gallo, D. Gary, Alumina foam catalyst supports for industrial steam reforming processes, Journal of the European Ceramic Society 31 (2011) 303-312.

[2] F. C. Buciuman, B. Kraushaar-Czarnetzki, Ceramic Foam Monoliths as Catalyst Carriers, 1. Adjustment and Description of the Morphology, Ind. Eng. Chem. Res. 42 (2003) 1863-1869.

[3] M. Al Amin Muhamad Nor, L. C. Hong, Z. Arfin Ahmad, H. Md Akil, Preparation and characterization of ceramic foam produced via polymeric foam replication method, J. Mater. Process. Technol. 207 (2008) 235-239.

[4] Y. Han, J. Li, Q. Wei, K. Tang, The effect of sintering temperatures on alumina foam strength, Ceram. Int.28 (2002) 755–759.

[5] S. Akpinar, I.M. Kusoglu, O. Ertugrul, K. Onel, In situ mullite foam fabrication using microwave energy, Journal of the European Ceramic Society 32 (2012) 843-848.