CHEMICAL ENGINEERING TRANSACTIONS
VOL. 76, 2019

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar S. Varbanov, Timothy G. Walmsley, Jiří J. Klemeš, Panos Seferlis

ISBN 978-88-95608-73-0; **ISSN** 2283-9216
DOI: 10.3303/CET1976026

Synthesis of Block Ceramic Catalyst Carriers Based on Natural Raw Materials and Metallurgical Slags

Meruyert Erkinovna Utegenova[a], Marzhan Anuarbekovna Sadenova[a,*], Jiří Jaromír Klemeš[b]

[a]Priority Department Centre «Veritas», D. Serikbayev East Kazakhstan State Technical University, 19, Serikbayev str. 070000, Ust-Kamenogorsk, Kazakhstan
[b]Sustainable Process Integration Laboratory – SPIL, NETME Centre, Faculty of Mechanical Engineering, Brno, University of Technology - VUT Brno, Technická 2896/2, 616 00 Brno, Czech Republic
MSadenova@ektu.kz

For ecological catalysis, including the purification of exhaust gases, the most promising are block catalysts. The synthesis of ceramic block catalyst carrier was carried out based on classical methods of powder metallurgy, in which moulding compounds were prepared from the starting materials in the form of powders, which were then extruded with thermal training at each stage. It is proposed to use ceramic block carriers synthesized from a mixture of natural Kazakhstan aluminosilicates and metallurgical slag of lead and copper production for environmental catalysis. The obtained results prove the possibility of extruding new materials for use as ceramic carriers for catalysts from a mixture of natural Kazakhstan's aluminosilicates and metallurgical slag of lead and copper production without additional preliminary chemical treatments. In works of other authors haven't found such combinations of components for the manufacture of catalysts

1. Introduction

The development of the advanced level of industrial catalytic chemistry requires fundamentally new solutions for the development of catalyst technology of effective geometric shapes, in particular, block type, with high-performance characteristics. Ceramic block materials with a combination of properties such as high structural strength, low hydraulic resistance, developed specific surface area are predetermined for use as carriers for catalytic systems.

The use of secondary sources remains a serious concern for the metallurgical industry and environmental agencies. Recycling of metallurgical slag will make it possible to free land intended for dumps and slag storages and reduce the environmental effect on the environment (Yang et al., 2013). The main components of metallurgical slag, as well as aluminosilicate natural raw materials, are oxides of silicon, aluminium and iron, which allows them to be used in the preparation of ceramics as an additional component of the charge.

For ecological catalysis, including the purification of exhaust gases, the most promising are block catalysts. To solve the problem under study, special attention should be paid to powder metallurgy methods. Powder metallurgy, used for the production of ceramics or composite materials, is a process consisting of mixing powdered materials, compacting them into the desired shape, heating and sintering the synthesized material in a controlled atmosphere, followed by cooling to room temperature. According to Omole et al. (2015) great progress in sintering technology and powder metallurgy technology allows us to constantly develop modern materials, such as composites - materials formed from two (or more) components (for example, metal, intermetallic or ceramic) with different physical and chemical properties, which together allow one to get various and usually improved characteristics in relation to the individual components. The authors (Nosewicz et al., 2016) note that the use of modelling and simulation can help to better understand the influence of powder characteristics and process parameters on the production process and the final properties of sintered material. It is known that currently modelling the process of powder metallurgy of composites is a new and complex research task. The need to build an effective model of powder metallurgy and sintering processes is due to the

Paper Received: 22/08/2019; Revised: 12/09/2019; Accepted: 12/09/2019
Please cite this article as: Utegenova M.E., Sadenova M.A., Klemes J.J., 2019, Synthesis of Block Ceramic Catalyst Carriers Based on Natural Raw Materials and Metallurgical Slags, Chemical Engineering Transactions, 76, 151-156 DOI:10.3303/CET1976026

need to accurately analyze the production process. The properties of the sintered material, such as its density, porosity, as well as its mechanical properties, should be predicted. The microstructure of the material during sintering undergoes changes as a result of compaction and rearrangement of particles, the formation and growth of bonding bonds, leading to a decrease and elimination of porosity. Microscopic processes cause changes in macroscopic physical properties.

The role of the carrier is to improve the structure of the catalyst. The carrier must have sufficient mechanical strength and a specific surface with a pore structure, together with a shape suitable for the reaction. So block carrier is increasingly being developed in the catalysis (Tsai et al., 2018). One of the main reasons for using the block form in environmental catalysis is better mass transfer, low-pressure drop, thermal stability and good mechanical strength compared to other catalytic structures such as granules, tablets or powders. Boger et al. (2004) emphasize that it is necessary to distinguish between catalysts in which the active phase is applied in the form of a coating (for example, a primer coating) on an inert support, and catalysts in which the entire monolithic structure is made of active material, for example, bulk catalysts. Coated monoliths are usually considered when the intrinsic reaction rates are high compared to diffusion and mass transfer in the catalyst structure, and the performance depends on the geometric surface area, and not on the weight of the catalyst.

Combinations of ceramics obtained from mixtures of clay materials are generally referred to in the literature as refractory materials because of their ability to withstand abrasive and corrosive solids, liquids, or gases at high temperatures. Govender et al. (2017) suggest that one of the main factors in choosing a combination of materials for the production of composites should be a lower cost of production compared to other composites. They investigated the properties of ceramics synthesized from a clay mixture in combination with iron filings in order to study the usefulness of the products obtained and substantiated that the resulting composite will find application in areas where high wear resistance and abrasion resistance are required. They obtained block systems representing homogeneous blocks consisting of parallel channels, which are obtained by extrusion.

For widespread use of catalysts in practice, it is necessary that they satisfy certain requirements. Essential characteristics of the catalyst: the constancy of the chemical composition, the constancy of the phase composition, the absence of harmful impurities, the required particle size, the required humidity. Commercial catalysts, according to (Keane, 2003) must have sufficient mechanical strength to withstand loss due to crushing (when operating in a packed bed) or attrition (in intensive mixing reactors). High surface areas can be achieved either by manufacturing small particles or clusters where the surface to volume ratio of each particle is high or by creating materials whose void surface (pore) area is high compared to the amount of bulk substrate of the material. The most common methods for forming catalysts and carriers are droplet coagulation, extrusion, tabletting, plate granulation, spray drying, and grinding of the material. The preparation method determines the degree of dispersion of the catalytic component, the shape, porous structure and activity of the contact mass. Govender et al. (2017) believe that preference when choosing the form of catalysts should be given to monolithic structures. They claim that monolithic structures are an attractive alternative to traditionally prepared catalytic granules or powders due to a number of properties. Monoliths provide better mass transfer, low-pressure drop, thermal stability and good mechanical strength compared to conventional catalytic tablets or powders. Monoliths are essentially homogeneous blocks consisting of parallel channels that can be extruded into various shapes and sizes and can be extruded from zeolites. The primary producers of ceramic and metal monoliths are Corning and Johnson Matthey.

A review of the literature showed that researchers are actively using aluminosilicates and various metallurgical wastes to develop new ceramic materials. It is of interest to study the possibility of synthesizing new ceramic materials with desired properties from a mixture of aluminosilicates and metallurgical slags. The authors suggest that the most promising approach is the use of specific techniques of powder metallurgy for the synthesis of ceramics. The aim of the work is to create a catalytic composite system from a mixture of natural aluminosilicates of Kazakhstan and metallurgical slag of lead or copper production.

2. Methodology

Natural aluminosilicates in the form of zeolite, bentonite and metallurgical slags of lead and copper production were used as objects of study. The possibility of using natural aluminosilicates represented by natural zeolite of the clinoptilolite type and bentonite clay represented by montmorillonite as a part of complex gas purification catalysts was studied in (Sadenova et al. 2016). In (Tahir et al., 2016), a system based on a clay material, montmorillonite, was also successfully used as a basic component of a catalyst for selective reduction of CO_2.

The synthesis of ceramic block catalyst carrier was carried out on the basis of classical methods of powder metallurgy, in which moulding compounds were prepared from the starting materials in the form of powders, which were then extruded with thermal training at each stage. It is known that a characteristic feature of extrusion as an industrial method of manufacturing various kinds of materials is the use of raw materials in the form of

powders, which are then pressed through special technological equipment (matrix) and molded into products of specified sizes (Fan et al., 2016).
For the manufacture of ceramic block catalyst carrier, natural aluminosilicates were used - zeolite from the Taizhuzgen deposit, bentonite from the Tagansky deposit and representative technological samples of slag from copper and lead production. The components of the mixture were previously subjected to fine grinding to a fraction of 0.01 mm on a vibratory grinder IV-4 to ensure a homogeneous mixture. The initial charge components - natural zeolite and bentonite - were mixed with metallurgical slags. An important characteristic is the moisture capacity of the starting components and the resulting mixture. The moisture content was varied in the range of 15 ÷ 20 % to ensure the required moulding moisture. To obtain a mass of a given composition, the zeolite, bentonite and slag powders were mixed until a homogeneous mass was obtained in the mixer.
The difficulty in complying with the requirements of quality standards for block catalysts is due to the dependence on many technological parameters. Therefore, the modelling method was used in work, which allowed the data obtained during the study of the model to be applied in real conditions for the synthesis of block ceramic carriers for catalysts. The visualization of the extrusion process of a block ceramic carrier was modelled in SolidWorks using the Flow Simulation module. For calculations, a model of the non-Newtonian fluid flow was chosen. When using this method, slippage conditions are applied that apply to all walls of the model, as well as the yield strength. Modeling was carried out with the following parameters: yield strength: 5.8 Pa; roughness: 10 µm; punch feed rate: 0.5 mm/s (30 mm/min); outlet pressure: 101,325 Pa.
After mixing, the prepared mixture was sent to moulding. The moulding (extrusion) of block ceramic carriers was carried out on a Shimadzu Autograph AG-Xplus universal machine. The software tool TRAPEZIUM X was used, allowing full control of the test process.
To obtain blocks of the honeycomb structure, the moulding material was pressed through special dies. The use of a catalyst based on a carrier of this form can significantly increase the surface area and reduce the gas-dynamic resistance of the reactor. For forming blocks, steel moulds are used, including a matrix with a forming punch.
The resulting materials were kept in the air and then subjected to heat treatment in a muffle electric furnace in the temperature range 100 – 1,000 °C. During calcination, evaporation of moisture occurs and the physical structure of the carrier is formed due to sintering processes. The compression strength of the catalyst carrier was determined using a hydraulic press. The compressive strength (R_{str}, MPa) was calculated by the formula:

$$R_{str} = P/S, \quad (1)$$

where P is the breaking load, N (kgf); S is the cross-sectional area of the sample, mm^2. The pressing was carried out under double-sided loading, and the pressing pressure was the same order that occurs during extrusion of the press mass.

3. Results and discussion

3.1 Technological tooling

The complexity of managing and investigating the properties of various types of catalytic materials is determined by the choice of the manufacturing method and sensitivity when choosing control actions at the manufacturing stage. The development of computer simulation of the synthesis process has increased the information content and efficiency of the process of obtaining new ceramic materials. The created virtual prototype of the product (Figure 1), contains all the information about its geometry, manufacturing and control requirements.

Figure 1: Modeling an extrusion process for the production of block ceramics (a) a matrix, (b) an extrusion process, (c) catalyst block carrier

The developed model of the synthesis process made it possible to fabricate technical toolings for producing block ceramic materials by extrusion based on the forcing of the plastic mass through a forming head with channels (Figure 2).
Technical accessories are made of structural alloyed steel with high strength, a viscous core and high surface hardness, designed for the manufacture of products operating at high speeds and high specific pressures under

the action of shock loads, including a matrix with a forming punch. Technical accessories are made from simple to more complex geometric shapes.

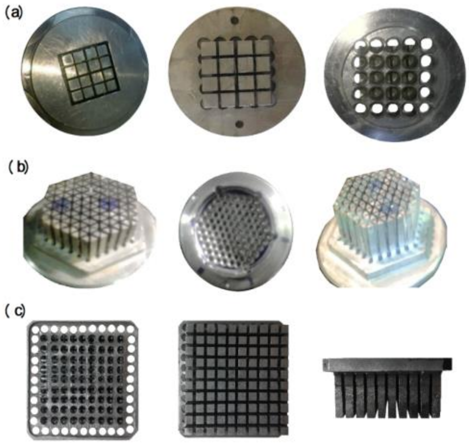

Figure 2: General view of the manufactured technical tooling for extrusion (matrix)

At the next stage of the study, using the manufactured equipment, synthesized samples of block ceramic materials for use as a catalyst carrier for various processes.

3.2 Synthesis of block ceramic catalyst carriers

For the first time, it was proposed to use ceramic block carriers synthesized from a mixture of natural Kazakhstan aluminosilicates and metallurgical slag from lead and copper production for ecological catalysis. To ensure the required thermal stability of the ceramic carrier for the catalyst, a composite system of a mixture of natural aluminosilicates and metallurgical slags is considered. These materials are promising because each of them individually is sufficiently thermally stable up to 800 - 1,000 °C. Metallurgical slags are smelting products in the range up to 1,500 °C, and therefore it can be assumed that they should no longer undergo significant structural changes upon repeated thermal exposure in the same temperature ranges.

The use of metallurgical slag in the production of ceramic materials requires determining the composition of the material, structure and properties. According to the developed technology (Figure 3) before the synthesis of block ceramic materials, the initial components were studied using X-ray diffraction (XRD), simultaneous thermal analysis (thermogravimetry / differential thermal analysis) (TGA / DTA), optical microscopy (OM) and scanning electron microscopy. According to the data obtained, it was determined that the main components of metallurgical slags, as well as aluminosilicate natural raw materials, are oxides of silicon, aluminum and iron, which allows them to be used in the manufacture of ceramics as an additional component of the charge.

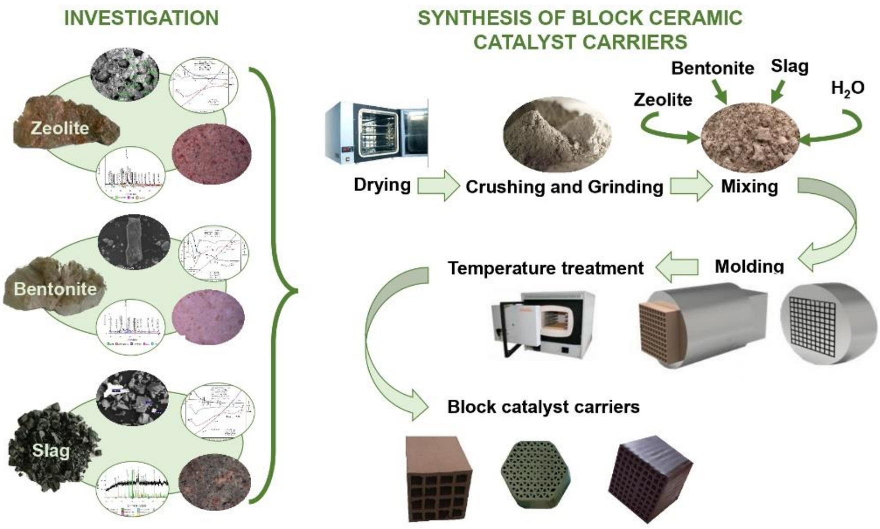

Figure 3: The synthesis scheme of block ceramic catalyst carriers

For the synthesis of block ceramic materials, a series of compositions based on natural aluminosilicates and metallurgical slags have been prepared. To obtain a moulding material with the required characteristics, the ratio of zeolite:bentonite:slag components was varied over a wide range. In powder metallurgy, when choosing a composition for moulding a ceramic material, mass moisture, pressing pressure, calcination temperature, and other characteristics are usually selected taking into account the design of technological tooling. Optimization of the composition and sintering temperature leads to various microstructures and phases, giving strength characteristics to the product (Rawlings et al., 2006). In this investigation, compositions were prepared to contain 50 to 80 wt.% zeolite, 20 - 40 wt.% bentonite and 10 - 30 wt.% slag. According to the results of the selection of the composition to ensure the maximum possible porosity and specific surface area, it was found that the highest content in the charge should be zeolite. To develop the specific surface of block carriers, to give the charge plastic properties to the zeolite, bentonite clay additives were introduced.

By extruding the mouldable mixture through a die (Figure 3), an article was obtained in the form of a block with a wall thickness of 1 mm and a length of 30 - 100 mm, which has a strength sufficient for manual movement and transportation. Some samples of the synthesized batch of block catalyst carrier are shown in Figure 3. It was experimentally established that the optimal composition of the mixture is based on (wt.%) zeolite 60, bentonite 20, metallurgical slag 20 (copper and lead slags were used in this investigation).

The prepared mixture for forming blocks of a honeycomb structure has structural homogeneity, which is ensured by efficient mixing of the dispersed medium and the completeness of spontaneous dispersion of particles in contact with water. During the extrusion process, the flow of the press mass is organized in such a way that the stress-strain state makes it possible to separate the mass into separate streams and then form them into a honeycomb structure with the thixotropic restoration of strength along the lines connecting the streams.

The use of powder metallurgy methods in the technology of manufacturing catalyst carriers allows one to obtain ceramic materials capable of becoming less viscous and extrudable under the influence of mechanical forces. After stress relieving, they acquire thixotropic properties that restore plasticity and strength, as a result of which the moulded product becomes suitable for further transportation.

2.1 Strength characteristics

It is not possible to assess the prospects of using natural aluminosilicates and metallurgical slags for the manufacture of carriers for gas purification catalysts without a preliminary study of the structural and mechanical properties. Figure 4 shows the research data on the strength of ceramic catalyst carriers depending on the composition of the charge and the calcination temperature. To determine the mechanical strength, a batch of samples was prepared from a zeolite: bentonite (Z: B) mixture in a ratio of 60:40 and a zeolite: bentonite: slag mixture in a ratio of 60:20:20 (Z: B: S (Cu) and Z: B : S (Pb)). The results of the strength characteristics are presented in Figure 4.

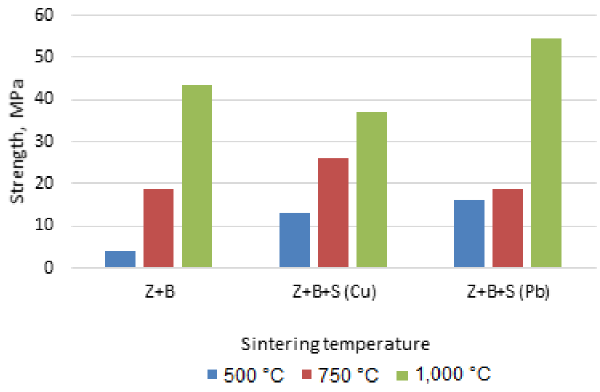

Figure 4: Strength of ceramic catalyst carriers

Figure 4 shows that the lowest strength value at an annealing temperature of 500 °C for a zeolite-bentonite sample is 4 MPa. With the introduction of copper and lead slag into the zeolite-bentonite mixture, the values increased and amounted to 13 MPa for Z + B + S (Cu) and 16 MPa for Z + B + S (Pb). At an annealing temperature of 750 °C, the indicator for all three samples increased. After increasing the calcination temperature from 750 °C to 1,000 °C, the strength values also increased and fluctuated within 37 - 54 MPa. For all three samples, the strength values at 1,000 °C are more than 30 MPa, which corresponds to the requirements for catalyst carriers.

3. Conclusion

In the present study, the synthesis of a block catalyst carrier based on natural aluminosilicates and metallurgical slags was carried out by powder metallurgy. Powder metallurgy technology opens up extensive opportunities for the development of ceramic products of new geometric shapes for various purposes, including catalysis.

The optimal compositions based on a zeolite-bentonite-slag mixture to obtain block ceramic catalyst carriers (wt.%) with a component ratio of 60:20:20 were determined. It was found that in order to ensure the maximum possible porosity and specific surface area, the zeolite should have the highest content in the composition. The use of metallurgical slag as an additional component in the composition of the charge not only provides a reduction in the environmental impact associated with its disposal but also provides a productive role by increasing the strength characteristics of the catalyst carriers. At the next stage, using developed ceramic carriers of a honeycomb structure, catalysts will be manufactured for purification of exhaust gases from nitrogen and carbon oxides and an assessment of their catalytic activity will be carried out.

In the work on the basis of classical methods of powder metallurgy, the experimental batch of ceramic block catalyst carriers was synthesized from a mixture of natural aluminum silicates of Kazakhstan and metallurgical slag of lead or copper production. The obtained results prove the possibility of extruding new materials for use as ceramic carriers for catalysts from a mixture of natural aluminosilicates of Kazakhstan and metallurgical slag of lead or copper production without additional preliminary chemical treatments. In works of other authors haven't found such combinations of components for the manufacture of catalysts for environmental catalysis.

Acknowledgements

This research has been supported by the Project IRN AP05134733 “Development of technology for obtaining new ceramic materials based on domestic raw materials and technogenic wastes of metallurgical companies of Kazakhstan”, funded by the Science Committee of The Ministry of Education and Science of the Republic of Kazakhstan and by EU project “Sustainable Process Integration Laboratory – SPIL”, project No. CZ.02.1.01/0.0/0.0/15_003/0000456 funded by EU “CZ Operational Programme Research, Development and Education”, Priority 1: Strengthening capacity for quality research.

References

Boger T., 2004, Monolithic Catalysts for the Chemical Industry, Industrial & Engineering Chemistry Research, 43, 4602-4611.

Fan P.M., Zhen K.F., Zan Z.Y., Chao Z., Jian Z., Yun J.Z., 2016, Preparation and development of porous ceramic membrane supports fabricated by extrusion technique, Chemical Engineering Transactions, 55, 277-282

Govender S., Friedrich H.B., 2017, Monoliths: A Review of the Basics, Preparation Methods and Their Relevance to Oxidation, Catalysts, 7(2), 1-29

Keane M. A., 2003, Ceramics for catalysis, Journal of Materials Science, 38, 4661 – 4675.

Nosewicz S., Rojek J., Chmielewski M., Pietrzak K., 2019, Discrete Element Modeling of Intermetallic Matrix Composite Manufacturing by Powder Metallurgy, Materials, 28, 1-18.

Omole S.O., Barnabas A.A., Akinfolarin J.F., 2015, Production and evaluation of ceramic and metal matrix composite by powder metallurgy, Research on Engineering Structures & Materials, 2, 73-79.

Rawlings R. D., Wu J. P., Boccaccini A. R.,2006. Glass-Ceramics: Their Production from Wastes, Journal of Materials Science, 41, 733-761.

Sadenova M.A., Abdulina S.A., Tungatarova S.A., 2016, The use of natural Kazakhstan zeolites for the development of gas purification catalysts, Clean Technologies and Environmental Policy, 18, 449-459.

Tahir B., Tahir M., Amin N.A.S., 2018, Photocatalytic CO_2-Hydrogen Conversion via RWGSR over Ni/TiO_2 Nanocatalyst Dispersed in Layered MMT Nanoclay, Chemical Engineering Journal, 63, 115-120.

Tsai S.B., Ma H., 2018, A Research on Preparation and Application of the Monolithic Catalyst with Interconnecting Pore Structure, Scientific Reports, 8, 1-9

Yang, Y.G., Xu J.H., Cai B., Wang Q.C., Xiu D.P., Zhao Z.B., 2013, Synthesis and applications of black ceramic from recycled industrial wastes, Advances in Applied Ceramics, 112, 146-148.