CHEMICAL ENGINEERING TRANSACTIONS

VOL. 45, 2015

A publication of

AIDIC

The Italian Association
of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Sharifah Rafidah Wan Alwi, Jun Yow Yong, Xia Liu

ISBN 978-88-95608-36-5; **ISSN** 2283-9216

DOI: 10.3303/CET1545105

Using of Natural Kazakhstan's Sorbents for Catalytic Purification of Gas Emissions

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The study of mineral resources of the Republic of Kazakhstan to build on its base catalysts in order to increase the effectiveness of waste gas cleaning of industrial enterprises and thermal power plants has important theoretical and practical significance. Mineralogical characteristics of montmorillonite-containing clays and zeolites of clinoptilolite-type have been refined, molded mass from the mixture of clinoptilolite and montmorillonite with the desired mechanical properties (high strength and ductility) were prepared. Catalytic properties of the synthesized granular Cu-Ni- and Cu-Ni-Cr-catalysts in the reduction of nitrogen oxides by carbon monoxide and/or hydrocarbons were analyzed. Data on the effect of nature the catalyst carrier on metal particles dispersion - the active components over the catalyst surface was obtained.

1. Introduction

The amount of harmful substances emitted into the atmosphere is increased from year to year. Energy industry is the largest source of emissions of nitrogen oxides, carbon monoxide and sulphur into the atmosphere (Gartman et al., 2014). Pollution degree of megacities significantly exceeds the allowable regulatory limits due to harmful substances released into the air with the exhaust gases of vehicles. Currently, the search for optimal catalytic systems remains relevant and important area as the main way to reduce the toxicity of emissions. In this paper the data on development of effective competitive catalytic systems for the neutralization of gas emissions from combustion products associated with the problem of air protection with the use of modern achievements in environmental catalysis are presented. Limited use of catalytic gas-cleaning methods connected with the high cost and short life of known catalysts (Moioli et al., 2013). Therefore, the problem of finding new approaches to the development of effective catalysts with long operational life remains relevant. The catalytic activity and specificity of the catalysts are mainly determined by their chemical composition (Noskov, 2005). The interaction between the metal and carrier depending on their nature leads to the formation of the catalyst system having novel physical and chemical properties. Information on nature of the metal-carrier bond and surface characteristics of such systems is necessary for the directed synthesis of highly active and selective catalysts (Palma et al., 2014).

2. Methodology of carrying out experimental researches

Polycomponent Cu-Ni- and Cu-Ni-Cr-catalysts were prepared by sorptive impregnation with aqueous solutions of salts (copper, nickel and chromium). The molded and calcined zeolite - bentonite was used as the carrier, followed by drying and calcination at a temperature of 600 - 1,000 °C for 1 h. The total content of active ingredients in Cu-Ni catalyst was varied from 10 to 15 %, and in Cu-Ni-Cr catalyst - from 10 to 20 %. Samples of catalysts were prepared by sequential or joint supporting of active components on carrier. The carrier is made by powder metallurgy method. Initially, the starting components for preparing the carrier (zeolite and bentonite) are dried and milled in vibration attritor to 0.01 mm fraction. Use of zeolite (Isakov, 1998) is caused by the fact that it has the catalytic activity (Ione, 1982). Bentonite is used as a

Please cite this article as: Sadenova M.A., Abdulina S.A., Tungatarova S.A., 2015, Using of natural kazakhstan's sorbents for catalytic purification of gas emissions, Chemical Engineering Transactions, 45, 625-630 DOI:10.3303/CET1545105

plasticizer, which forms with water stable viscous slurry having pronounced thixotropic properties. This is important in making the compositions suitable for extrusion. In addition, montmorillonite has a high adsorption and cation-exchange properties (Kaunova et al., 2010). Ground powders were mixed to a homogeneous mass after drying. The resulting mixture is moistened to form a mass with the required molding moisture in the range of 15 - 20 wt. %. The prepared mass is directed on molding and extrusion in the form of cylinders or extrusion to form of granules and blocks after mixing. Molding of carriers in the form of cylinders with a diameter of 12.6 mm was performed in a hydraulic press under a load duplex; compaction pressure was 40 -120 MPa. The mass was forced through a shaping orifice of laboratory extruder to produce extrudates with a diameter of 3 mm. Then the granules were prepared with a size of 3 × 3 mm by cutting of extrudates.

The resulting carriers were kept in air for three days and then subjected to heat treatment in a muffle electric furnace at temperatures of 500 – 1,000 °C for 1 h. Evaporation, decomposition of aluminium hydroxide and formation of physical structure of the carrier by the sintering process takes place during calcination. The total residence time of carrier in the furnace was approximately 8 h. Preparation of catalysts by supporting the active component onto the carrier has several advantages over other methods: relative simplicity, less waste and more efficient use of the active ingredient. Preparation of catalysts by impregnation method consists of the following steps: 1) preparing the solutions of desired concentration; 2) impregnating the carrier in these solutions by incipient wetness; 3) drying; 4) calcination. A series of granular zeolite - bentonite contacts containing copper, nickel and chromium in various combinations and amounts, intended for the reduction of NO with CO and/or hydrocarbons (Mikulcic et al., 2013) was synthesized during the preparation of catalytic samples.

Thermal studies of samples were performed on derivatograph Q -1000 / D of the F. Paulik, J. Paulik and L. Erdey system. Investigations carried out in air in the temperature range 20 – 1,000 °C, the heating mode - dynamic (dT / dt = 10 °C / min), reference substance - calcined Al_2O_3, weighed sample - 100 mg with a scale interval of the change of sample weight - 500 μV. Sensitivity of the measurement system of device for all samples was set equal: DTA = 250 μV, DTG = 500 μV, T = 500 μV. Identifying of the components of powder sample was carried out on the morphology of thermal curves and numerical values of intensities of endothermic and exothermic effects using thermo gravimetrical TG-lines values associated with them. Results of analysis were compared with the data contained in atlases of thermal curves of minerals and rocks and compared with the descriptions of thermal behaviour of mono-mineral samples contained in other reference sources.

Studying the structure of initial sorbents and synthesized samples of catalysts was carried out using optical metallographic microscope Olympus BX 51, using the method of light field in the reflected light. Preparation of the surface of samples consists in grinding and polishing. Microsection was washed with water after polishing, then washed with ethanol and dried with filter paper in the case of the oxidation of the alloy.

Electron microscopic examination of the samples was done by a scanning electron microscope JSM-6390LV (Jeol, Japan) with system of energy dispersive microanalysis INCA Energy at an accelerating voltage from 5 to 20 kV, equipped with detectors of backscattered and secondary electrons. Samples of raw materials in powder form were supported on bilateral electrically conductive adhesive tape for electron microscopy studies. Samples of granulated catalysts were observed in the initial state without mechanical processing.

3. Results

The results of studies on the preparation of Cu-, Ni-, Cr-catalysts of different composition supported on the synthesized zeolite - bentonite carrier by powder metallurgy method when using sorption impregnation (Tagawa et al., 2013) are presented. The method of preparation of catalysts consists of several stages, providing consistent creation of developed catalyst surface and formation of the active surface sites (Sannino et al., 2013). Zeolite - bentonite in a ratio of 1: 1, 2: 1, 1: 2 is used as a carrier, which is produced by molding of powder. The ability to absorb and hold firmly the particles of different substances in its structure, as well as well-developed surface carcass is distinctive properties of these sorbents (Muenpol et al., 2014). Besides the natural zeolite is regenerated easily and can be reused in other industries (Guenther et al., 2013).

The analysis of derivatograms of zeolite-bentonite mixture (Figure 1) showed conformity of composition of the sample with a real mixture and confirmed the concentration of zeolite and bentonite. The study of thermal characteristics of sample, which included two hydrosilicates, is connected with difficulties of differentiating of their weight loss in the temperature zones of simultaneous dehydration.

Siliceous powder mixture of two samples gives series of thermal effects associated with the destruction of its water-containing mineral impurities under conditions of dynamic heating from 20 to 1,000 °C. DTA curves of samples give such curvature in each interval of temperatures, which are marked on the lines separately heated samples of bentonite and zeolite. Heating the powder mixture (zeolite + bentonite) leads to gradual decomposition of its components. The analyzed sample loses 7.45 % of their weight in the range of 60 – 220 °C. Then the loss is 3.95 % with increasing the heating temperature up to 1,000 °C. As bentonite and zeolite undergo low temperature dehydration, in which the latter loses 1.74 % of its weight. The weight ratio is determined by analysis of separate zeolite taking into account its amount in mixture. Weight of bentonite is decreased by 5.71 %. Both weight losses occur within a single range of temperatures, although the nature of their bond in the crystal structures is different. The zeolite in this case gives adsorbed water, whereas the clay sample loses H_2O molecules of other affiliation – from interlayer space of the silicon-oxygen frame. Further joint dehydration occurs in the range of 220 - 370 °C. It is noted by m_2 and m_3 steps with the appropriate values 0.35 % (OH) and 1.15 % (OH) on the thermo gravimetric curve. Above 370 °C, way out of OH into the atmosphere is performed mainly due to the dissociation of bentonite. Number of allocated here hydroxyl water reaches m4 = 2.45 % by weight of the sample. Pronounced endothermic effect at 490 °C can be seen after reaction on the DTA curve. Changes in the high-temperature region are caused by the clay component of the sample. Representatives of the montmorillonite series, as well as layered silicates, representative of which is bentonite usually are marked on the DTA curves as S-shaped bend, associated with the transition the system to a new phase in the range of 700-800 °C. Fulfilled thermal analysis showed good conformity the content of bonded water in mixture with the real quantitative composition of zeolite and bentonite therein.

Biphasic structural component, which is a mixture of zeolite and bentonite clay calcined in the temperature range of 500 – 1,000 °C is shown in the optical micrographs of granular zeolite - bentonite catalyst carrier shown in Figure 2.

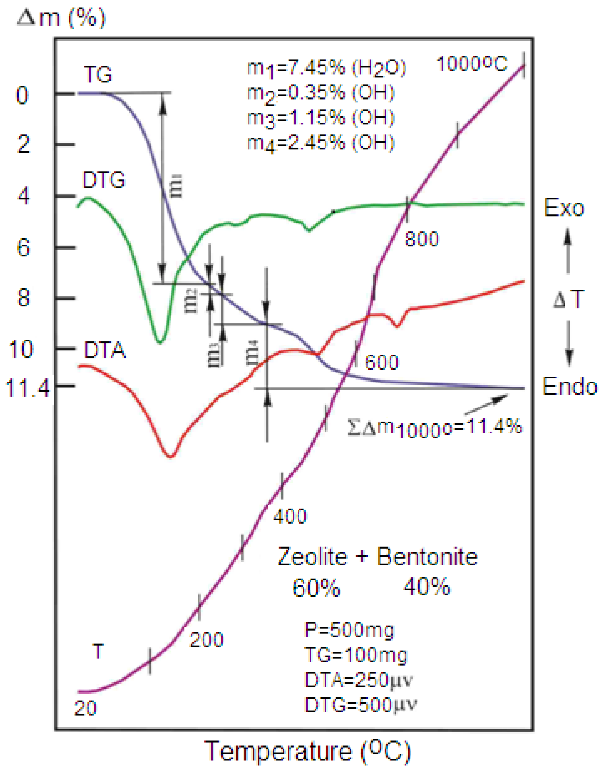

Figure 1: Data of DTA analysis of the bentonite and zeolite mechanical mixture

It is seen that the basic mixture changes colour acquiring bricks hue with increasing the calcination temperature. Three main phases of brick, black and white can be seen visually. Since the clay minerals are converted into other minerals (mullite, kristobalit), acquiring hardness of the stone after calcination, black mullite grains are visible on all three samples.

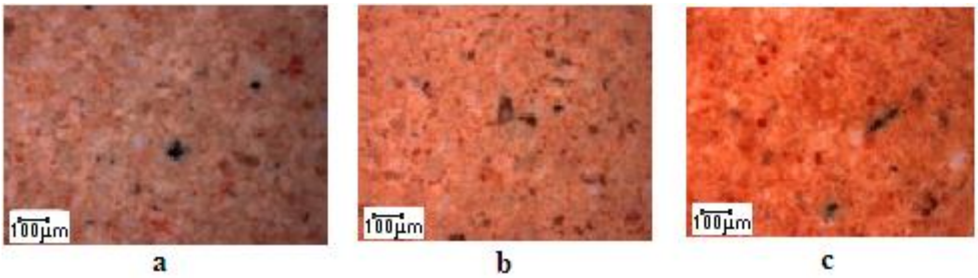

Figure 2: Optical micrographs of granular zeolite-bentonite catalyst carrier at different temperatures: a – 500 °C, b – 750 °C, c – 1,000 °C

Apparently, the clay components are diffused into the quartz, sodium migrated into albite and other components penetrated into mullite on melting of sample under the influence of temperature. It has been shown that the grains are uniformly distributed across the sample surface at a calcination temperature of 500 °C. Highly-dispersed particles with a grain size of about 0.01 - 0.04 µ predominate, but there are some larger grains. The particles are in the form of isometric plates with precise smooth contours. Main mass changes slightly acquiring light brick colour at a temperature of 750 °C. The sample calcined up to 1,000°C is more homogeneous. It is non-uniform fine-grained rocks, judging by the sizes. Crystal faces are visible. The specific surface area of the initial granular carrier is 40.56 m^2/g and tableted carrier - 29.64 m^2/g (Figure 3). The specific surface area does not change after impregnation with a solution of metal salt and reductive calcination, which means the formation of small thickness of the supported active layer.

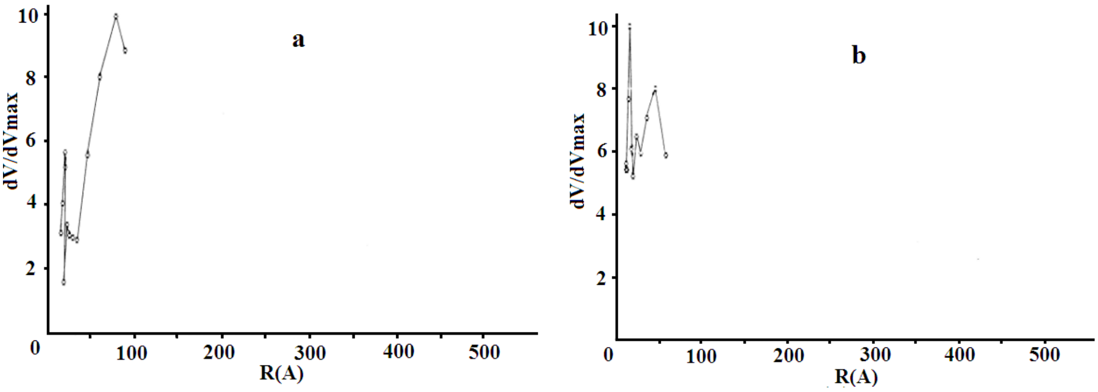

Figure 3: Pore distribution and specific surface area of the catalyst carrier: a - in the form of granules, S_w – 40.5634 m^2/g, V – 93.3019 mL/g; b - in the form of tablets, S_w – 29.6301 m^2/g, V – 22.3602 mL/g

Electron microscopic studies of dispersion, structure and condition of the active sites of catalysts (Figure 4) revealed significant heterogeneity of the surface, which is associated with the formation of heteronuclear surface nano-sized particles of different structures. Particle size on the surface varies widely from 2.0 to 50.0-100.0 nm.

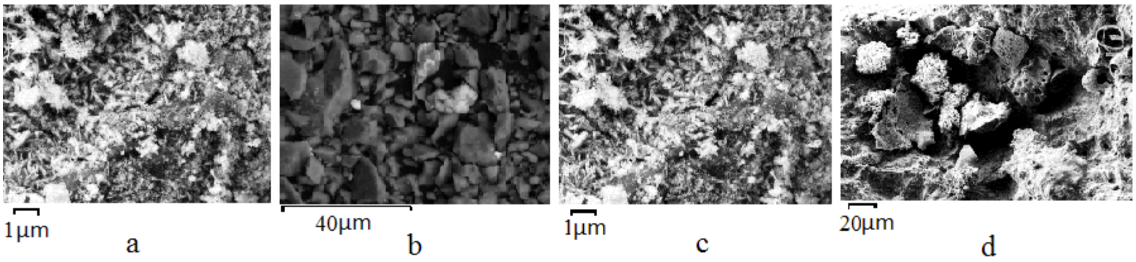

Figure 4: Electron micrograph of the initial and spent catalysts: a - Cu - Ni / zeolite – bentonite, initial, b - Cu - Ni / zeolite – bentonite, spent, c - Cu - Ni - Cr / zeolite – bentonite, initial, d - Cu - Ni - Cr / zeolite – bentonite, spent

It should be noted that large fragments having d ~ 50.0 - 100.0 nm are formed by more dispersed particles with $d \leqslant 0.5$ nm. The surface of the Cu - Ni / zeolite - bentonite catalyst is fairly uniform in their composition and represents the irregular-shaped polycrystals consisting of accreted monocrystals in the form of prisms. Particles of the Cu - Ni - Cr / zeolite - bentonite catalyst of irregular shape without the expressed planes have a size of 10-60 μ. These particles are aggregates of smaller isometric particles and layered irregular shape intergrowths. Metal particles are located on the surface of polycrystals (Sadenova et al., 2014).

The conversion of nitrogen oxides to elemental nitrogen using reduction reactions by carbon monoxide (II) and / or hydrocarbons is proposed to carry out in present work. A feature of this method is that the carbon compounds are contained in the initial gas phase, along with the nitrogen oxides (Ramli et al., 2014) and in the presence of catalyst can act as a reducing agent (Ved et al., 2013).

Determination of the optimal composition is performed experimentally for supported catalysts since, on the one hand, there is a direct relationship between the catalytic activity per unit volume and its specific surface and, on the other hand, the accessibility of surface decreases as the saturation of carrier by active compound as a result of pore filling (Raimondi, 2014). Similar picture is clearly illustrated by the curves shown in Figure 5.

Experiments on the reduction of nitrogen oxides by carbon monoxide in the presence of Cu-Ni / zeolite - bentonite catalyst obtained by impregnating the carrier showed that the degree of conversion of nitrogen oxides and carbon monoxide increases with temperature and reaches ≈ 90 % for NO_x even at 350 °C, while CO conversion even at achievement 500 °C does not exceed 65 %. It can be seen that the conversion of the toxic components such as CO and NO_x on the Cu - Ni - Cr / zeolite - bentonite catalyst begins at the minimum contact time at temperature of 50 °C, while 20 % conversion or more is achieved only at 180 °C on the Cu-Ni / zeolite – bentonite catalyst. Possibly, additional incorporation of chromium into the catalyst composition together with copper and nickel promotes more uniform distribution of active sites on the surface of catalyst and raises its efficiency.

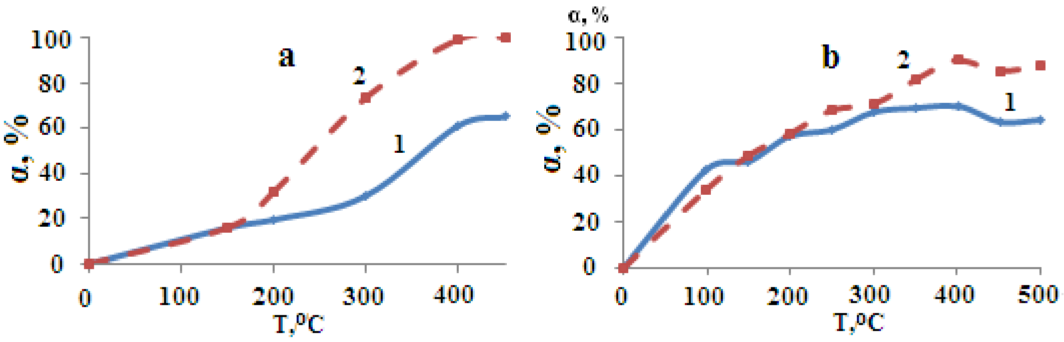

Figure 5: Efficiency of the reduction of NO_x and CO on granular catalyst: a - Cu - Ni / zeolite – bentonite, 1 – CO, 2 – NO_x; b - Cu - Ni - Cr / zeolite – bentonite, 1 – CO, 2 – NO_x

4. Conclusions

Chemical and mineralogical composition was determined, surface morphology, crystal structure and thermal stability of the catalyst carriers based on natural sorbents in the temperature range of 100 - 1,000 °C were studied by complex of physical and chemical methods. The crystal structure of carriers is modified by the introduction of transition metals, especially after high temperature calcination. Effect of the method and conditions of preparation of granular catalyst systems was installed as a result of simultaneous mixing of all components of the catalyst mass and subsequent manufacture of the granules and by means of extrusion blocks and by successive manufacturing of the carrier, followed by supporting an active ingredient by incipient wetness. Effect of the method and conditions of preparation of granular catalyst systems was installed as a result of simultaneous mixing of all components of catalyst mass and subsequent manufacture of the granules and blocks by means of extrusion and by successive manufacturing of the carrier, followed by supporting an active ingredient by incipient wetness method. Effect of natural components on the catalytic activity in conversion of nitrogen oxides and carbon monoxide were established. The efficiency of catalyst depends not only on the physical and chemical properties, but is largely determined by their geometrical form. This phenomenon becomes obvious when one considers that the geometric shape of catalysts and sorbents significantly affects the nature of processes for mass and heat transfer in the bed and on the flow resistance. Catalysts and sorbents with complex geometric shapes have proven themselves with the best hand. Extrusion molding method differs by relative simplicity and does not require using of expensive equipment, providing preparation of catalysts with a relatively high mechanical strength. Selection of the mass for molding of granules of catalysts is usually carried out empirically, that is a disadvantage of extrusive techniques. This fact complicates the selection of optimal method and process for preparation of the molding composition. Development of new and improvement of existing methods for preparing the catalyst mass is impossible without profound study of the processes of structure formation. Therefore, uniform development of all kinds of deformations provides the ability of extrusion molding of catalyst mass into granules.

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