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# Influence of Mechanical Activation Conditions upon the Physicochemical Properties of Manganese-Substituted Cordierite Ceramics

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## Abstract

An effect of different mechanical activation conditions (different activator types) on the phase composition, texture characteristics of catalysts based on manganese-substituted cordierite ceramics, as well as the activity thereof in the reaction of ammonia oxidation was studied. It is demonstrated that it is preferable to use an energy-intensive planetary ball mill with a high power density, since it provides the preparation of smaller particles. The finely crystallized manganese cordierite with a minor impurities content, low specific surface, low pore volume and a high activity in the reaction of ammonia oxidation is obtained at their subsequent sintering.

**Key words:** substituted cordierite, mechanical activation, ammonia oxidation

## INTRODUCTION

The mechanical activation is has been used successfully for a long time for the preparation of cordierite from naturally occurring materials, since this technique allows to reduce significantly the temperature and duration of the synthesis [1]. Varying the conditions of the preliminary mechanical activation of the initial components, one could adjust the parameters of the thermal synthesis of cordierite ceramics, the properties of the target product, as well as the structural, mechanical and rheological properties of moulding compounds for the further preparation of block catalysts with a honeycombed structure for high temperature processes [2]. Furthermore, *via* modifying cordierite by transition metals oxides one can significantly change and extend the properties thereof [3], which is promising from the standpoint of the development of catalysts based on modified cordierites.

Earlier, we demonstrated [4] that the modification of cordierite by manganese dioxide $MnO_2$ accelerates the crystallization of cordierite, reduces the content of impurity phases in the samples, and increases the activity of cordierite with respect to sintering, thereby reducing the specific surface area decreases with changing the porous structure of the catalyst. The resulting Mn-substituted cordierite exhibit a high activity in the high temperature reaction of ammonia oxidation.

The purpose of this work consisted in studying the influence of various conditions of the mechanical activation of the mixture of initial reactants with the use of various type activators upon changing physicochemical properties of catalysts based on manganese-substituted cordierite ceramics and the activity thereof in the reaction of ammonia oxidation.

## EXPERIMENTAL

As the starting materials for the synthesis, clay was used (the Ob deposit; the clay is characterized by a high content of kaolinite), $Al_2O_3$-containing compounds, $MnO_2$. The amount input of manganese dioxide was calculated from taking into account a complete

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replacement of magnesium oxide in the cordierite structure. The activation of starting components was performed with the use a disintegrator (DI), a planetary ball mill (PBM) and a vibration ball grinder (VBG).

The DESI-15 disintegrator brand is characterized by power value amounting to 4.1 kW/h, the productivity being equal to 100 kg/h, the rotational speed of 3000 $\text{min}^{-1}$. The power of the Fritsch Pulverisette PBM is equal to 0.37 kW at the rotational speed of the planetary disk amounting to 1400 $\text{min}^{-1}$ and the acceleration of 20*g*. The ratio between the grinding balls and the load under activation load is equal to 5 : 1, the mass of the load amounting to 100 g, the grinding time being equal to 90 s. The VTsM-25 vibration ball grinder is characterized by the capacity of drums equal to 2 L, the ratio between grinding balls and the load amounting to 10 : 1, the acceleration up to 10*g*. The particle size of activated powders was determined by means of laser diffraction using a Microsizer 201 analyzer (Russia).

A portion of 0.5 % of methylcellulose solution was added to the obtained powder, blocks shaped as hexagonal prisms with the side of base of 15 mm and height equal to 50 mm with triangular channels of 2.5×2.5×2.5 mm in size and wall thickness of 0.4 mm were extruded from the resulting homogeneous plastic mass. The blocks prepared were dry-cured at a room temperature for 1 day, and then dried at 350 °C for 4 h, followed by the further calcination at 1150 °C for 4 h. The density of the channels in the blocks obtained was no less than 120 cells per 1 square inch.

The resulting catalysts were examined by means of X-ray diffraction (XRF) phase analysis, mercury porosimetry, thermo-programmed recovery (TPR).

The XRD phase analysis was carried out using a Siemens diffractometer (Germany), $\text{Cu}K_\alpha$ radiation with a graphite monochromator in a reflected beam. The registration was carried out *via* scanning the points with a scanning pitch $S = 0.05$ deg of $2\theta$ with the signal accumulation during 3 s at a point, the range of angles $2\theta = 5-60$ deg. The phase composition was identified using a JCPDS database (version PC PDF Win 2000).

The porous structure of the catalysts was determined by means of mercury porosimetry using the Porosizer-9300 unit. The specific surface of the samples ($S_{\text{sp}}$) was determined by means of the thermal desorption of argon.

The examination of samples by means of TPR was performed using a flow-through unit with a thermal conductivity detector for the sample fraction of 0.25–0.5 mm. The preliminary training of the samples was conducted in oxygen at 500 °C during 30 min. The sample mass was equal to 100 mg, the reducing mixture feed rate (10 % $H_2$ in argon) amounted to 40 mL/min. The samples were heated at a heating rate equal to 10 °C/min up to 900 °C.

The catalytic activity in the reaction of ammonia oxidation was determined using a flow-through unit at an atmospheric pressure and at a temperature amounting to 700–900 °C. The samples were tested in the form of the fragments of blocks 22 mm in diameter and 45 mm high. The feed rate of the ammonia-air mixture (AAM) amounted to 8.4 L/min; the initial concentration of ammonia in the AAM was of about 5 %. In order to determine the concentration of ammonia and nitrogen oxides (NO, $NO_2$) we used a spectrophotometric analysis technique in an on-line mode [5].

TABLE 1

Parameters of activators

| Type of activator | Power density, W/kg | Mechanism of activation | Activation time*, s | $D_{\text{av}}$**, μm |
|---|---|---|---|---|
| VBG | 42.8 | Friction | 150 | 18 |
| DI | 18.5 | Impact | 6 | 12 |
| PBM | 95.2 | Impact, friction | 90 | 4 |

* As calculated for 100 g of substance.

** Average particle diameter.

## RESULTS AND DISCUSSION

It is known that properties of products obtained with the use of different grinding machines, depend both on the dispersity level of the components used, and on the nature of the mechanical action. Table 1 presents data concerning the nature and the action intensity on the starting materials for the activators used, as we; as the mean size of the particles obtained.

The mechanical treatment in the PBM is usually described as a combination of impact and shear deformation effects exerted on the particles of the powder under treatment occurring in the contacting areas between the balls. In case of PBM, the material is grinded mainly due to high energy impact by grinding balls in the rotating grinding jars. Using the PM that exhibits the most high power density provides the smallest particle size.

Grinding the material in VBG occurs mainly *via* abrasion [6]. The impact action on the material processed, caused by the collisions of the milling bodies, is extremely weak and ineffective. Among all the activators used, just the use of VBG causes obtaining the particles with a maximum size.

A disintegrator predominantly exerts an effect of the impact destruction mechanism. The powders mechanically activated in a disintegrator are usually characterized by minor violations of the structure and by a lower heating of the material [7]. In the case of this grinding method, the material is destructed within the sites of structural defects, whereas the resulting particles have mainly a splint-like shape.

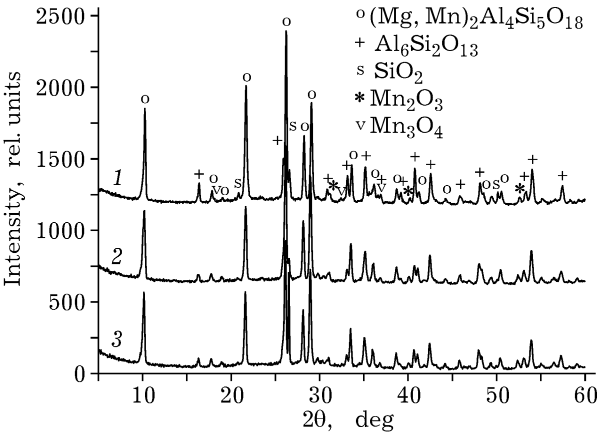

Fig. 1. XRD patterns of catalysts based on Mn-substituted cordierite obtained using a vibration ball grinder (*1*), disintegrator (*2*) and planetary ball mill (*3*).

### *XRF*

Figure 1 demonstrates the XRF patterns of Mn-cordierites cordierite obtained with the use of different activators. All the samples represent well-crystallized cordierite $(Mg,Mn)_2Al_2Si_5O_{18}$, that contains different amount of impurities such as mullite ($Al_6Si_2O_{13}$), quartz ($SiO_2$) and the traces of manganese oxides ($Mn_2O_3$ and $Mn_3O_4$).

It has been found that the amount of impurity phases depends on the level of particle grinding at the stage of activation. The largest number of the impurity phases of mullite and quartz was revealed in the samples prepared using the VBG. There were also $Mn_3O_4$ traces revealed, whose formation could be, to all appearance, caused by weak interaction between the starting components at the activation stage.

TABLE 2

Physicochemical characteristics of the catalysts obtained: specific surface ($S_{sp}$), total pore volume ($V_{por}$), average pore diameter ($D_{por}$), ratio between the amount of hydrogen absorbed and the total content of Mn ($\Sigma H_2/Mn$), the content of $Mn^{3+}$ in the catalysts according to the TPR, the yield of nitrogen oxides ($Y_{NO}$) at 900 °C

| Type of activator | $S_{sp}$, m$^2$/g | $V_{por}$, cm$^3$/g | $D_{por}$, μm | $\Sigma H_2/Mn$ | $Mn^{3+}$ content in $Mn_2O_3$, $10^{-6}$ mol/g | $Y_{NO}$, % |
|---|---|---|---|---|---|---|
| VBG | 0.12 | 0.104 | 3.5 | 0.050 | 8.4 | 41.8 |
| DI | 0.02 | 0.082 | 16.4 | 0.027 | 15.1 | 65.4 |
| PBM | 0.002 | 0.034 | 67.2 | 0.042 | 32.7 | 77.4 |

When a disintegrator and PBM are used, smaller particles are formed in the course of mechanical activation, whereby the amount of impurity phases decreases, whereas the initial components interact between each other in a better manner.

### *Textural characteristics*

The catalysts obtained have a low surface area and low pore volume (Table 2). Owing to the formation of smaller particles in the course of activation in the PBM, the cordierite is sintered to a great extent, so the surface area value is decreased to a considerable extent with the formation of sufficiently large pores. It can be assumed that the use of a more energy-intensive PBM would allow reducing the temperature of the cordierite synthesis.

The formation of Mn-substituted cordierite with a higher surface area and large and a greater pore volume in the case of using the DI and VBG is, to all appearance, caused by a large size of the particles formed in the course of activation.

### *TPR*

The samples obtained are slightly reduced in hydrogen (see Table 2), which could indicate the prevailing presence of reduced $Mn^{2+}$ ions in the catalysts because the occurrence thereof in the structure of cordierite. The manganese ions can be reduced both at the stage of $MnO_2$ mechanical activation [10], and in the course of the calcination of the samples, since the manganese dioxide $MnO_2$ under heating can be sequentially reduced to give $Mn_2O_3$ and MnO.

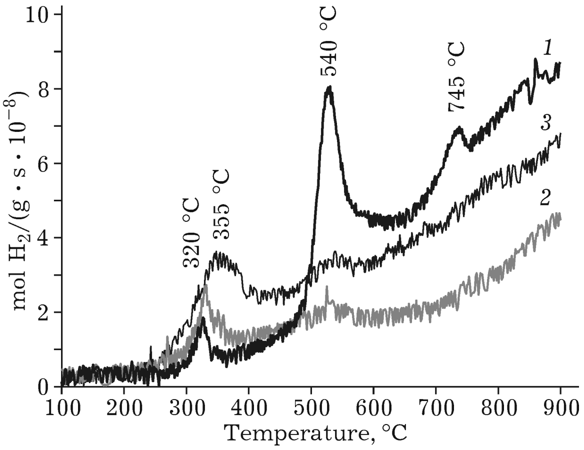

Fig. 2. TPR curves for the catalysts based on Mn-substituted cordierite obtained using vibration ball grinder (*1*), disintegrator (*2*), planetary ball mill (*3*).

The analysis of TPR curves for catalysts prepared using the PBM and DI (Fig. 2) demonstrated that their reduction thereof occurs in two stages. The first peak could correspond to the process of oxidation of $Mn_2O_3$ into MnO at about 320–350 °C. The second peak at about 530 °C, to all appearance, corresponds to the reduction of $Mn_3O_4$ into MnO. This is in a good agreement with the data concerning reduction of $Mn_2O_3$ reported by the authors of [8, 9] and indicates that the samples contain a minor amount of impurities of manganese (+3) or (+2, +3) oxide. It has been found that the catalyst prepared using DI, has the lowest total level of hydrogen absorption and therefore it exhibits a minimal content of manganese oxide impurities.

The total level of hydrogen absorption by the catalyst made with the use of VBG is much greater, mainly due to increasing absorption of hydrogen at 540 °C (*i. e.* due to a greater amount of $Mn_3O_4$ impurity, which is consistent with XRF data). In addition, the TPR curve exhibits a third peak to appear at about 745 °C. To all appearance, the peak corresponds to the reduction of $Mn^{3+}$ ions those are located in a six-coordinated environment, which is inherent, for example, in perovskite or in spinel [11].

According to the area of a low-temperature peak (400 °C) we calculated the amount of manganese ions $Mn^{3+}$, those are present in the catalysts supposedly in the form of $Mn_2O_3$. It is revealed that the content thereof is maximum for the catalyst obtained using a planetary ball mill (see Table 2).

### *Catalytic activity*

Figure 3 presents data concerning the activity of the catalysts obtained in the reaction of ammonia oxidation: the ammonia conversion level ($X_{NH3}$) and the selectivity level with respect to nitrogen oxides ($S_{NO}$). The reaction of ammonia oxidation at high temperature values, as a rule, takes place in the external diffusion mode, so the conversion level depends

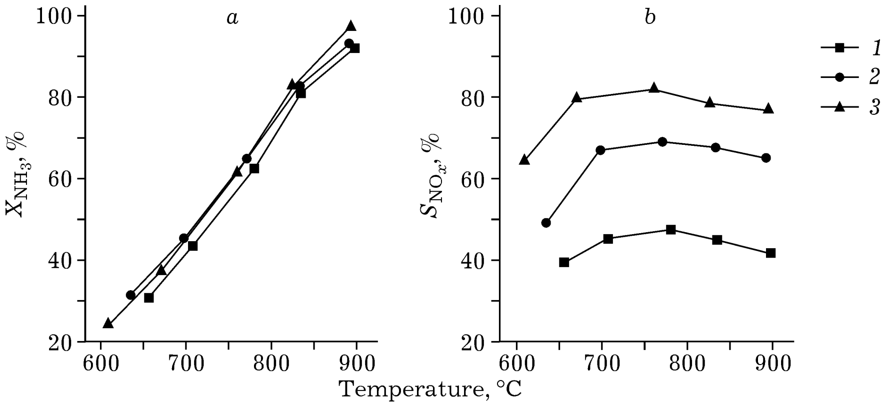

Fig. 3. Conversion level of ammonia (*a*) and the selectivity level with respect to nitrogen oxides (*b*) for the catalysts obtained *via* using: *1* – vibration ball grinder, *2* – disintegrator, *3* – planetary ball mill.

mainly on the ammonia diffusion rate to the walls of the block and on the geometric parameters of the block. Thus, the blocks with the same geometry should have similar values of the ammonia conversion level.

The selectivity level with respect to nitrogen oxides depends to a considerable extent on the physicochemical properties of the catalyst. It has been found that the highest selectivity level with respect to nitrogen oxides is exhibited by a catalyst prepared using the PBM. It is composed of a minimum content of impurity phases (mullite and quartz), those could reduce the selectivity level and a maximum amount of $Mn^{3+}$ ions in the form of $Mn_2O_3$. Furthermore, it has large pores, which, as it was demonstrated earlier [12], causes decreasing the contribution of side reactions between unreacted ammonia and nitrogen oxides within narrow pores of the catalyst.

The lowest selectivity level with respect to nitrogen oxides is exhibited by a catalyst prepared using VBG. This catalyst contains large amounts of impurity phases and, even though the total content of the manganese (+3) ions therein is higher, the amount of $Mn^{3+}$ ions in the form of $Mn_2O_3$ is minimal. Moreover, the catalyst has the most developed porous structure with a predominance of small pores. The catalyst prepared using a disintegrator exhibits moderate characteristics

Thus, the higher the level of the interaction and sintering in the catalysts and the smaller the specific surface area and the larger average pore diameter, the higher is the observed yield of NO resulting from ammonia oxidation, which could be caused, to all appearance, by lowering the contribution of secondary reactions within narrow pores. It should be noted that the level of the interaction depends not only on the power supplied. Thus, at a lower supplied power, the level of the interaction in the course of disintegration appeared to be higher than that in the course of processing the powder using the mill VTsM-25, although for mills with a similar action character (VTsM and Fritsch Pulverisette) such a correlation was established. The correlation between the content of $Mn_2O_3$ in samples and the yield of NO needs to be further investigated under the conditions wherein the influence of the porous structure is not observed.

## CONCLUSION

In this work, with the use of various type activators (disintegrators, vibration ball grinders and planetary ball mills) we prepared catalysts based on manganese-substituted cordierite ceramics. The activators used differ both in the power density and type of the impact on the precursor particles.

It has been found that the way of the mechanical treatment of the cordierite blend influences upon the size of particles obtained and, consequently, upon the level of the interaction between the initial components and upon the textural characteristics of the catalysts. In the course of sintering the finer particles, Mn-substituted cordierite having a lower specific surface area and a low pore volume with the predominance of large pores is formed. In the course of the impact force (disintegration) the level of interaction at the same power value, to all appearance, is higher than that in the course of shearing (the processing in planetary ball mills).

The catalysts obtained are active with respect to the high-temperature reaction of ammonia oxidation. A greater yield of nitric oxide is observed for catalysts with the lowest specific surface area and porosity. The presence of the correlation between the yield of NO and the number of $Mn^{3+}$ions, that are present in a small amount, probably in the form of $Mn_2O_3$, requires clarification, because the role of $Mn^{3+}$ in the selectivity of the process could not be excluded.

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