

The selection of oxide support of the catalyst for N₂O emission abatement

Marek INGER*, Katarzyna ANTONIAK-JURAK, Monika RUSZAK, Paweł KOWALIK, Marcin WILK – New Chemical Syntheses Institute, Puławy, Poland

Please cite as: CHEMIK 2016, 70, 5, 255–260

1. Introduction

Nitric acid plants are one of the largest industrial sources of nitrous oxide (N₂O) emission, which is an undesirable by-product, formed during catalytic oxidation of ammonia. Its concentration in exhaust gases (so-called *tail gases*) depends on the operating parameters of the installation and can achieve the level of 2000 ppm [1]. *Industrial Emissions Directive 2010/75/EU* imposes on EU countries an obligation to limit N₂O emission to the level below 300 ppm for existing installations and below 100 ppm for the new nitric acid plants [2]. To comply with N₂O emission standards, especially in existing installations, the use of catalytic processes is required. The analysis of the operating parameters of nitric acid plants indicates, that the catalytic process can be realized in the nitrous gases stream (T = 750 - 940°C) and/or in the tail gas stream (T = 200 - 450°C).

Our previous studies on N₂O decomposition in the tail gas stream, with using multicomponent cobalt spinel catalyst, obtained by the precipitation method and formed by a compression into tablets, showed that the overall rate of deN₂O reaction is limited by the internal diffusion resistance [3]. It means, that significant part of the catalyst grain interior does not take part in the catalytic reaction. In the case of catalysts, based on the relatively expensive components, it seems to be more beneficial to use the catalytic systems obtained by impregnation. In these systems the active phase is located mainly on the outer (superficial) layer of the catalyst grain and its accessibility for the reactants depends on the degree of pore structure development.

The issue of the support influence on the catalyst properties is a constant topic of the scientific researches and the subject of industry interest. The properties of the active phase support are one of the key factors, determining the catalyst efficiency and its durability. The basic role of the support is to develop the specific surface area of the catalyst and ensuring the active phase availability, as well as providing the adequate mechanical strength and thermal resistance. Its role is particularly important for the processes, occurring in the presence of multicomponent catalysts, which are synthesized by a multi-stage impregnation, combined with a thermal treatment and activation.

Taking into account the above, it is necessary to define well the support properties, i.e.: texture, structure and chemical nature of its surface, in terms of further correlation of these properties with the activity of supported catalysts. It allows to understand better the role of the support in the catalysts preparation and enables to obtain the catalysts of desired properties for a given process.

The paper presents the selection path of the composition and preparation method for the support of multicomponent cobalt spinel catalyst for a low temperature N₂O decomposition in the tail gas stream in nitric acid plants. The catalyst support for such application should have a good formability on the industrial scale, while the shaped catalyst should be characterized by a high mechanical strength, resistance to aqueous solutions and low abrasion. The shaped support after calcination should have the highest possible total pore volume with a maximum contribution of meso- and macropores. At the stage of the

support selection, its passivity to an active phase and its possible positive influence on the catalyst activity, should be taken into account. The phenomenon of the support-active phase synergistic interaction may occur in the case of mixed oxide systems, consisted of CaO and ZnO. Such interaction appears for example in the process of NO_x reduction with methane on La₂O₃/CaO catalyst [4].

Among the conventional support materials, alumina and zinc oxides or their mixture, optionally with the addition of aluminous cement as a binder, were chosen as the most promising for an objective application. These materials were examined in terms of their formability by an extrusion method and were evaluated for their physicochemical properties in respect to the quality of an active phase deposition.

2. Experimental

2.1 Materials and methodology

The catalyst supports were synthesized from the following raw materials: technical pseudo-boehmite type aluminium hydroxide, alumina cement (*Górkal-70*) and technical zinc oxide. Selected substrates were mixed with the demineralized water and plasticizer in the following weight proportions:

- Ca-Al support: 47.3% wt. of aluminium hydroxide, 8.3% wt. of aluminous cement, 43.7% wt. of demineralized water, 0.7% wt. of plasticizer,
- Zn-Al support: 31.0% wt. of aluminium hydroxide, 20.2% wt. of zinc oxide, 48.3% wt. of demineralized water, 0.5% wt. of plasticizer,
- Zn-Ca-Al support: 45.0% wt. of zinc oxide, 6.0% wt. of aluminous cement, 48.2% wt. of demineralized water, 0.8% wt. of plasticizer,
- Al₂O₃ support: 57.9% wt. of aluminium hydroxide, 41.6% wt. of demineralized water, 0.5% wt. of plasticizer.
- The differences in the chemical composition of the investigated supports illustrate the Gibbs triangle (Fig. 1).

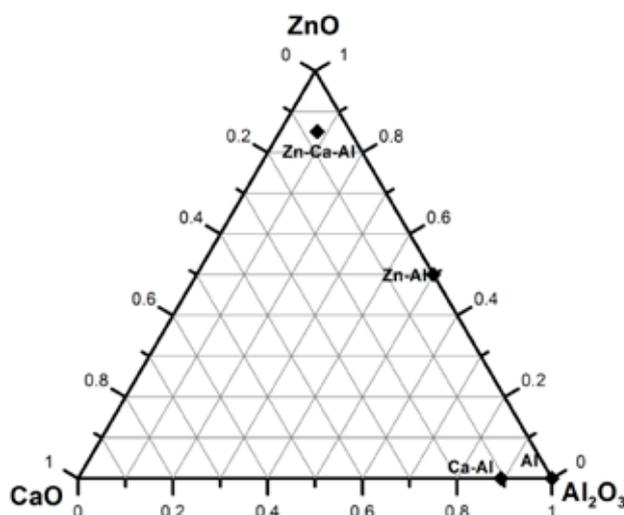


Fig. 1. The Gibbs triangle with marked formulas of investigated supports

Corresponding author:

Marek INGER - Ph.D., (Eng.), e-mail: marek.inger@ins.pulawy.pl

All the supports were prepared according to the same procedure. The dry powders of ingredients were mixed, then a suitable amount of water was added and the mixture was homogenized for 1 hour with using low-speed moulder. The resulting uniform plastic mass was formed by an extrusion method into cylindrical extrudates with the diameters of 2.2, 4.2 and 9 mm. Obtained extrudates were conditioned at a room temperature, dried at 105°C and then calcined at a temperature from the range 550 – 1400°C for 4 hours.

The phase composition of the supports was studied by the Panalytical-Empeyan X-ray diffractometer, equipped with a Cu lamp ($\lambda = 1.54 \text{ \AA}$) and PIXcel^{3D} detector. The phase analysis was performed on the basis of ICDD PDF4+2012 database.

The porosity of the supports was determined by a mercury porosimetry method with using Micromeritics AutoPore IV 9510 porosimeter, in the pressure range of 0.1 - 400 MPa.

The BET specific surface area was measured by a Micromeritics ASAP 2050 sorption analyzer, in the partial pressure range of $p/p_0 = 0.05 - 0.3$.

The mechanical strength to crushing of the extrudates after calcination was investigated by a Tinius Olsen H10K-S testing machine, on the basis of the destructive force measurement in a direction perpendicular to the extrudates axis. The mechanical strength was calculated as an average value of the ratio of breaking force to extrudates length for 50 randomly chosen extrudates.

2.2 Results and discussion

Table I shows the textural and strength properties of the supports, differing in chemical composition and the temperature of calcination (t_{calc}). The following parameters of the supports were determined: absorbability (A), porosity (P), pores volume (V_{pores}), BET specific surface area (SBET) and the diameters of the extrudates after calcination (dextrudate). The crushing strength in a radial direction (W) was measured for the extrudates of three different diameters.

Table I

The comparison of textural parameters of oxide supports with the extrudates diameters of ϕ 2.2 mm, ϕ 4.2 mm and ϕ 9.0 mm (diameters of the extrudates before calcination)

support	T_{calc} , °C	d _{extrudate} , mm	A, %	P, %	V_{pores} , ml/g	S_{BET} , m ² /g	CS, daN/mm
Ca-Al	900	1,9	142	83	nm	127	0,05
		3,7					0,10
		8,5					0,28
Ca-Al	1100	1,8	105	79	1,03	41	0,09
		3,6					0,07
		8,4					0,24
Zn-Al	1100	1,4	40	64	0,47	3,5	0,08
		2,7					0,16
		6,4					0,17
Zn-Al	1400	1,2	13	37	0,15	0,5	nz.
		2,4					1,35
		5,6					1,56
Zn-Ca-Al	900	2,0	32	62	nm	5,1	0,74
		3,8					0,64
		8,8					0,50
Zn-Ca-Al	1400	1,9	nm	nm	nm	< 1	< 0,05
		3,8					
		8,7					
Al ₂ O ₃	550	1,7	88	71	0,87	226	0,67
		3,5					0,79
		8,0					1,49
Al ₂ O ₃	1000	1,6	88	69	0,75	100	0,61
		3,3					0,72
		7,6					1,20
Al ₂ O ₃	1400	1,3	41	53	0,35	3,1	1,42
		2,7					1,18
		6,4					2,01

* nm – not measured

The results, shown in Table I, indicate that the differences in the properties of investigated supports are significant, depending on the chemical composition and calcination temperature.

The advantage of Ca-Al oxide support is high porosity and specific surface area. Simultaneously, support extrudates after calcination are characterized by a relatively low crushing strength. It was further observed that, in contact with water, this material has a tendency to hydrate, which leads to unfavourable structure changes and to increase in water absorbability.

In the case of Zn-Al support, the calcination temperature of 1100°C is too low to obtain the extrudates with a suitable crushing strength. Increasing the temperature to 1400°C allows to obtain the extrudates of a high crushing strength, but it is accompanied by an intensive sintering of the material. This significantly reduces the specific surface area and porosity of the support and leads to drastic decrease in water absorbability.

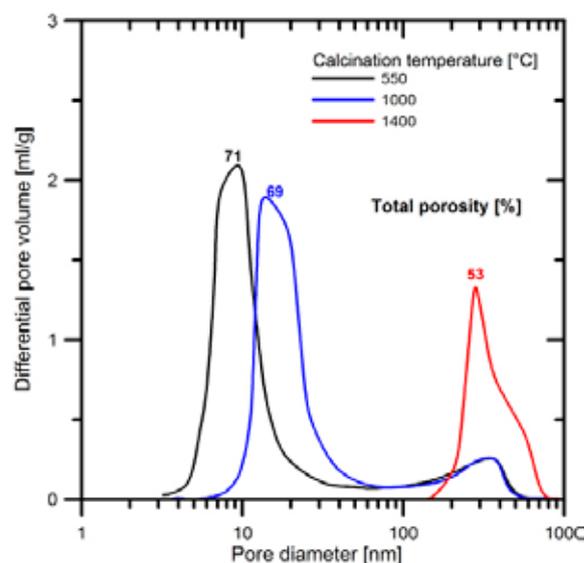


Fig. 2. Pore size distribution in Al₂O₃ support, calcined at different temperatures

Taking into account, that each of these materials has one beneficial property for the potential catalyst support, that is high porosity, developed surface area (Ca-Al support) and high crushing strength (Zn-Al support), the synthesis of tertiary oxide system ZnO-CaO-Al₂O₃ was carried out. The material, calcined at the temperature of 900°C, had a relatively high water absorbability and high porosity. The presence of calcium in the support resulted in reduction of crushing strength. While, the calcination of ZnO-CaO-Al₂O₃ extrudates at 1400°C led to practically complete destruction of the support extrudates.

Next to the mixed oxide systems, the alumina extrudates were also prepared. In comparison to other investigated materials, they had the best textural and crushing strength parameters. Therefore, in further part of the paper, the influence of calcination temperature on alumina support properties was analyzed. The alumina support, obtained by calcination at the temperatures of 550 and 1000°C had similar water absorbability, porosity and crushing strength. The increase of the calcination temperature to 1400°C had positive influence on crushing strength, but resulted in a reduction of absorbability and porosity. As the calcination temperature raised, the lowering of the BET surface area and a significant increase in the dominant pore diameter were observed, due to the progressive process of sintering and growing transversal shrinkage (Fig. 2).

X-ray diffraction patterns of alumina support, calcined at different temperatures, are shown in Figure 3.

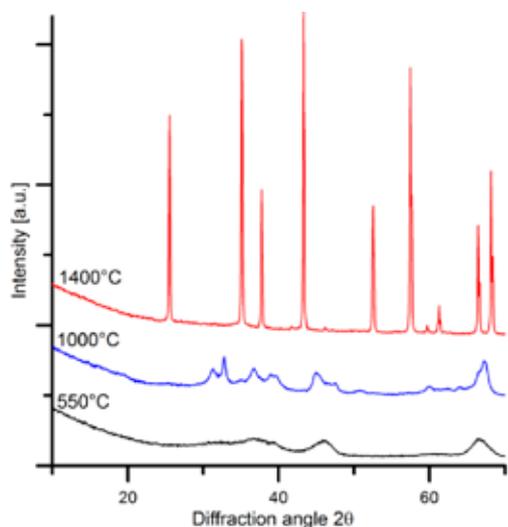


Fig. 3. X-ray diffraction patterns of Al_2O_3 support at different calcination temperatures

After the calcination at the temperature of 550°C , the support with a predominant content of amorphous Al_2O_3 phase was obtained. The broad diffraction bands (at an angle 2θ : 39.48° , 46.12° , 66.63°) of a low intensity suggest the presence of small amounts of $\gamma\text{-Al}_2\text{O}_3$ and $\eta\text{-Al}_2\text{O}_3$ phases with a low degree of crystallinity. The diffraction pattern of alumina support, calcined at 1000°C is characterized by well-developed diffraction bands (at an angle 2θ : 32.76° , 36.62° , 44.86° , 67.26°), which are distinctly narrower than the bands observed for the support heat treated at 550°C . Phase analysis of this sample indicates the presence of alumina crystallites in the form of $\theta\text{-Al}_2\text{O}_3$ phase. The diffraction pattern of the sample, obtained at the temperature of 1400°C is radically different from the others. It consists of intensive, very sharp diffraction bands. This indicates the presence of the alumina structure with a high degree of crystallinity, corresponding to $\alpha\text{-Al}_2\text{O}_3$ phase.

Extrudates of $\alpha\text{-Al}_2\text{O}_3$ support (photograph 1) constitute the core of the multicomponent cobalt spinel catalyst for the low temperature N_2O decomposition. The optimization of an active phase deposition method is the subject of current investigations.



Photograph 1. Extrudates of $\alpha\text{-Al}_2\text{O}_3$ support

3. Conclusions

The article presents a path selection of the catalyst support for modified cobalt spinel catalyst. From the technological side, the best support among investigated systems, was the system obtained on the base of pseudo-boehmite, which was converted after calcination at 1400°C to a porous $\alpha\text{-Al}_2\text{O}_3$. About the usefulness of $\alpha\text{-Al}_2\text{O}_3$, as a support of the catalyst for the low temperature N_2O decomposition, decided the following features: good formability, high crushing strength of the support after calcination, beneficial pore size distribution and relatively high total pore volume. These parameters

indicate the possibility for introducing an adequate amount of the active phase on the support surface and the opportunity to obtain the catalyst of good utilitarian features.

4. Acknowledgement

The authors would like to thank the National Research and Development Centre for funding the presented investigations, in the framework of the Applied Research Program, project No. PBS2/A5/38/2013, "Development of the innovative catalyst for the low temperature nitrous oxide decomposition".

Literature

- Perez Ramirez J., Kapteijn F., Schöffel K., Moulijn J. A.: "Formation and control of N_2O in nitric acid production. Where do we stand today?", *Appl. Catal. B: Environ.* 2003, **44**, 117–151.
- Kamphus M.: "Emission monitoring in nitric acid plants", *Nitrogen+Syngas* 2014, **328**, 48–53.
- Inger M., Saramok M., Migdal G., Wilk M.: "Niskotemperaturowa redukcja emisji N_2O z gazów resztkowych w instalacjach kwasu azotowego", *Przemysł Chemiczny* 2013, **12**, 2237–2240.
- Costa C. N., Anastasiadou T., Efstathiou A. M.: "The Selective Catalytic Reduction of Nitric Oxide with Methane over $\text{La}_2\text{O}_3\text{-CaO}$ Systems: Synergistic Effects and Surface Reactivity Studies of NO , CH_4 , O_2 , and CO_2 by Transient Techniques", *Journal of Catalysis*, 2000, **194** (2), 250-265.

*Marek INGER - Ph.D., (Eng.), graduated from Faculty of Chemistry at the Rzeszów University of Technology (1999) and postgraduate studies from Faculty of Chemical and Process Engineering at the Warsaw University of Technology (2009). He received his doctoral degree at the Faculty of Chemistry of Jagiellonian University (2013). He currently works in New Chemical Syntheses Institute in Nitric Acid Technology Department. Research interests: nitric acid technology, applied catalysis, modeling and simulation of chemical processes.
e-mail: marek.inger@ins.pulawy.pl, phone: +48 81 473 14 15

Katarzyna ANTONIAK-JURAK - Ph.D., graduated from Faculty of Chemistry at the Marie Curie Skłodowska University, Lublin (2007) and postgraduate studies from Faculty of Chemical and Process Engineering at the Warsaw University of Technology (2009). She was a scholarship holder of Erasmus-Sokrates program in Faculdade de Engenharia da Universidade do Porto, Portugal (2006-2007). She received her doctoral degree at the Faculty of Chemistry of Marie Curie Skłodowska University, Lublin (2014). She currently works in New Chemical Syntheses Institute in Catalyst Department. Research interests: preparation and investigation of catalysts and sorbents for ammonia production process.
e-mail: katarzyna.antonik@ins.pulawy.pl, phone: +48 81 473 17 54

Monika RUSZAK – Ph.D., graduated from Faculty of Chemistry, Jagiellonian University In Krakow (2003). She received her doctoral degree at the Faculty of Chemistry at Jagiellonian University (2013). She was a scholarship holder of Ventures program, awarded by Foundation for the Polish Science (2009-2010). She currently works in New Chemical Syntheses Institute in Nitric Acid Technology Department. Research interests: nitric acid technology, applied catalysis, process of NO_x reduction from exhaust gases in power plants.
e-mail: monika.ruszek@ins.pulawy.pl, phone: +48 81 473 17 15

Paweł KOWALIK - Ph.D., graduated from the Faculty of Chemistry at the Marie Curie Skłodowska University, Lublin (1998) and postgraduate studies at Faculty of Chemical and Process Engineering at Warsaw University of Technology (2009). He received his doctoral degree at the Faculty of Chemistry of Marie Curie Skłodowska University, Lublin (2006). He currently works in New Chemical Syntheses Institute as a Head of Catalyst Department. Research interests: applied catalysis.
e-mail: pawel.kowalik@ins.pulawy.pl, phone: +48 81 473 14 41

Marcin WILK - Ph.D., D.Sc., (Eng.), Assoc. Prof., at the New Chemical Syntheses Institute, graduated from Faculty of Chemical Engineering at the Lodz University of Technology (1974). He received his doctoral degree and habilitation at the Faculty of Chemistry at Wrocław University of Technology (2000 and 2012, respectively). He currently works in New Chemical Syntheses Institute as a Head of Nitric Acid Technology Department. Research interests: nitric acid technology, chemical engineering, inorganic technology, modeling and simulation of chemical technology processes.
e-mail: marcin.wilk@ins.pulawy.pl, phone: +48 81 473 14 62