

Ammonia synthesis catalysts produced in Azoty Tarnów

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Introduction

A dynamic technological development resulting in enhancing radically the efficiency in producing basic goods, e.g. food, energy carriers, medicines, and satisfying human needs in that field would be impossible without the progress in the field of chemical technology and also industrial catalysis. The production processes of synthesis gases for ammonia, methanol and synthetic fuels exemplify a considerable significance of applied catalysis. It particularly refers to ammonia synthesis because this is a very energy-consuming process and its realisation would be impossible without a catalyst. Ammonia synthesis also requires obtaining the synthesis gas of high purity, which is also done by processing raw materials (natural gas, coal, tail gases from crude oil processing) in many catalytic processes.

Taking into account geographical conditions and the access to raw materials in Europe, ammonia is mainly obtained from natural gas, and the technology of obtaining ammonia includes the following catalytic processes:

- raw material deep cleaning of undesirable substances (particularly sulphur and chloride compounds) by catalytic hydrogenation and sorption on selective sorbents
- obtaining crude process gas with a high content of hydrogen and carbon oxides in the process of steam reforming
- adjustment of process gas composition based on hydrogen enrichment and achievement of stoichiometric mole ratio N/H=3
- final adjustment of process gas composition – catalytic methanation of CO_x – obtaining synthesis gas
- ammonia synthesis.

The engineering solutions, at particular stages, applied in older and modern ammonia production plants (with very high production capacities), differ considerably. Substantial progress in many key areas, e.g. the technology of steam reforming processes, ammonia synthesis reactor engineering and applied catalysts has been made in recent decades [1]. Consequently, the capacity of ammonia production plant was radically improved and simultaneously energy consumption during its production was reduced (Fig. 1). Nowadays, the largest global ammonia production plant produces 3300 t/day at energy consumption below 29 GJ/Mt NH₃ [2] while the theoretical minimum is 20 GJ/Mt NH₃.

Radically reduced energy consumption during ammonia production was achieved, inter alia, by introducing new catalytic processes into the technological sequence and continuous improvement of catalysts used in such processes. In Poland, Fertilizer Research Institute in Puławy (INS) and Nitrogen Plant, Zakłady Azotowe in Tarnów-Mościce are the leading units in developing ammonia sequence technologies and producing catalysts. A long-term cooperation between Azoty Tarnów, universities (Szczecin University of Technology and Warsaw University of Technology) and research institutions (mainly INS) has yielded the development of unique technologies for obtaining industrial catalysts for water-gas shift reaction, as well as ammonia and methanol synthesis. The

listed catalysts have been used in all ammonia production plants in Poland for many years. They also have a high reputation among foreign buyers.

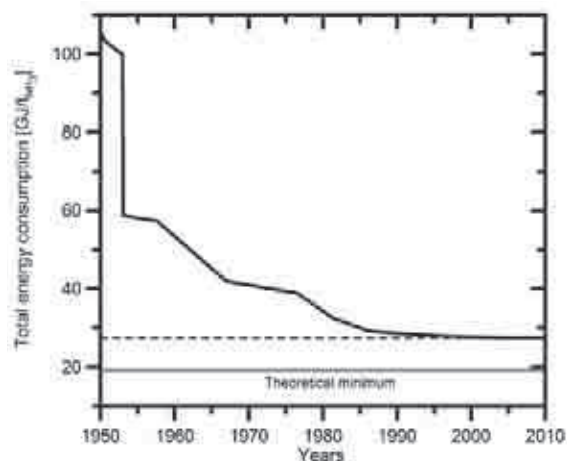


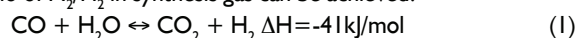
Fig. 1. Advancement of energy efficiency in ammonia production plants [2]

Catalysts used in ammonia sequence

Suitable high purification of raw material (up to not more than 0.01 ppmv S and 20 ppbv Cl [3]) is a required condition to provide the effective operation of ammonia production plant. Removal of H₂S by the sorption on zinc sorbent (active ZnO) preceded by hydrogenation of organic sulphur compounds on hydrodesulphurisation (HDS) catalysts of Ni-Mo or Co-Mo types is the most commonly used solution [4,5]. The adequate catalysts and sorbents for natural gas purification node were developed in INS which also manufactures them [6].

Ammonia production plants usually produce crude process gas from natural gas in the processes of steam reforming. There are a few types of this gas [7,8], and for all of them nickel catalysts having the parameters adjusted to specified operational conditions are applied. For many years, technologies and catalysts for steam reforming have been developed in INS, which offers four types of catalysts that differ in form, shape size and chemical composition [6, 9].

Subsequent processing of process gas is based on water-gas shift reaction according to the reaction (1). Thus, hydrogen content can be increased by partial or nearly complete (depending on the process parameters) removal of carbon oxide from process gas and a proper ratio of N₂/H₂ in synthesis gas can be achieved.



Water-gas shift reaction is reversible, poorly exothermic and occurs without any changes in volume [10]. Low temperature and excess of steam are favourable for a high degree of conversion. Because of equilibrium restrictions (Fig. 2), the process in the ammonia production plants is conducted in two temperature ranges in single or multi-bed adiabatic reactors connected in series under the pressure up to 7 MPa:

- (320-450°C) high-temperature phase where fundamental reduction of CO content takes place (usually up to 2-3%) (HTS)
- (180-240°C) low-temperature phase where carbon oxide content is reduced to the level of 0.1-0.3% (LTS).

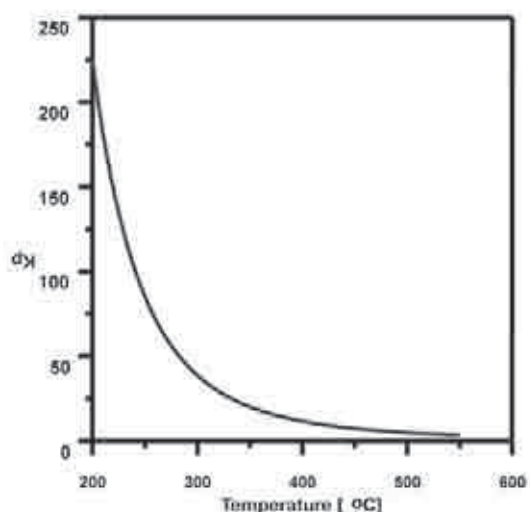


Fig. 2. Dependence of equilibrium constant for CO shift on temperature

Considering the above issues, CO shift in the ammonia production plant requires two types of catalysts with optimised properties to be applied. The industrial HTS catalysts are usually in the form of pellets with equivalent diameter up to 10 mm and the height up to 6 mm. A typical HTS catalyst consists of:

- Fe₂O₃ (80–95% wt.) - which is partially reduced to Fe₃O₄, functioning as an active catalyst component, in the industrial reactor
- Cr₂O₃ (5–15% wt.) - which serves as a structural promoter and activator
- CuO (1–5% wt.) – which serves as an activator and inhibitor of side reactions after being reduced to Cu.

A catalyst may contain a certain amount of sulphur and thus, it may be its source and contaminate process gas. Therefore, desulphurisation of catalyst is necessary prior to the right operation. HTS catalysts are little susceptible to poisons and the temperature factor is the main reason for their gradual deactivation, inducing unfavourable changes in the structure (sintering).

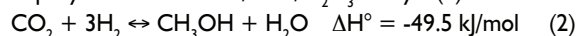
A traditional LTS catalyst consists of 3 fundamental components:

- CuO (20–60% wt.) – precursor of the copper active phase
- ZnO (15–60% wt.) – influences copper activity and performs a protective function
- Al₂O₃ (10-40% wt.) – provides an adequate porous structure and enhances thermal stability of a catalyst.

Copper reveals high activity in CO shift within the area of low temperatures. For this reason, it is also a fundamental component of LTS catalyst. Copper combinations with hard-reducible oxides, e.g. ZnO and Al₂O₃, are more active in comparison with pure copper. The nature of the active component in LTS process is complex [11,12]. A thesis about the course of CO shift taking place on completely reduced Cu prevails as a heavy dependence between the development of copper active surface and catalyst activity is observed [13,14]. The high dispersion state of copper is attempted to be obtained in the course of preparation, whose conditions and a method of performance considerably affect the quality of catalyst. This process involves 3 stages:

- obtaining the precursor of catalytic material using co-precipitation method.
- forming the precursor and its thermal decomposition to catalyst oxides.
- reducing catalyst oxides in the industrial reactor.

LTS catalysts are prone to thermal recrystallisation and contamination with substances that may be present in process gas, e.g. HCl, H₂S. Metallic copper in a high state of dispersion demonstrates strong catalytic properties in methanol synthesis. Regarding the above, a side reaction and a generation of a certain amount of methanol accompany CO shift on Cu/ZnO/Al₂O₃ catalyst (2).



This process is undesirable because it occurs along with hydrogen consumption. Methanol problem at the stage of LTS can be eliminated by introducing technological changes, which is usually difficult to be done. The application of a proper high-selective LTS catalyst is a better solution.

Considering the above, a high-quality HTS or LTS catalyst should have the following parameters: demonstrate high activity in the area of low temperatures, have high and stable mechanical strength, optimised form of shapes and consequently, low flow resistances of bed. Additionally:

- HTS catalyst should have low content of sulphur and chromium (VI) and should demonstrate high selectivity at the lowest possible content of steam in process gas
- LTS catalyst should be optimised regarding the reduction in an amount of generated methanol.

Catalytic methanation of carbon oxides is the last stage of preparing synthesis gas in the ammonia production plant. The process is conducted within a temperature range of 200-450°C on Ni-Al catalyst. Metallic nickel [15] is its active agent, aluminium oxide serves as a structural promoter and provides high thermal stability and mechanical strength. INS is the creator of this technology and has been producing Ni/Al₂O₃ catalyst under trade name RANG-19 for more than 30 years [6].

TZC-3/I high-temperature shift catalyst

Azoty Tarnów is the sole Polish manufacturer of HTS catalysts. Initially, HTS catalyst (TZC-3) based on Fe-Cr was offered. In the 1990s, the works on modifying the catalyst focusing on an aspect of improving its activity and selectivity along with reducing sulphur content were undertaken in cooperation with INS. These works have led to a new type of Fe-Cr-Cu catalyst promoted with copper (TZC-3/I).

Hematite (Fe₂O₃) with copper promoter and stabilised with chromium oxide is a basic component of TZC-3/I catalyst and it is partially reduced to mixed iron oxides under the process conditions. The catalyst is characterised by high development of active surface (>50 m²/g) and favourable porous structure with a dominating content of mesopores. Thus, internal surface can be applied to a high extent.

The discussed modifications to the catalyst formula resulted in a radical improvement of its quality and thus provided a number of operational advantages:

- enhanced activity, particularly within a range of low temperatures (favourable regarding thermodynamic issues)
- operational potential at a lower steam/gas ratio.

The additional advantages of TZC-3/I catalyst include a very low content of sulphur which eliminates the necessity of conducting a separate desulphurisation process in an industrial reactor, high mechanical strength, low and stable flow resistance and a long-term operation of even over 10 years depending on the conditions. TZC-3/I catalyst is very resistant to contamination, undergoes gradual deactivation induced, in principle, only by a temperature factor that brings unfavourable changes in the catalyst structure as a consequence of sintering crystallites of the active phase. To meet expectations of catalyst users and the need of fulfilling new standards on the content of carcinogenic Cr⁺⁶ coming into life, modifications in technologies for producing the catalyst were introduced. Consequently, Cr⁺⁶ content in the product was reduced by over 50%.

TZC-3/I is characterised by a unique form (Fig. 3). A standard type is offered in a form of tablets with convex ends having dimensions of 6mm x 6mm. Other dimensions are available at a customer request.



Fig. 3. Catalyst TZC-3/I

TZC-3/I catalyst has the following operational advantages due to such a form:

- relatively high development of geometric surface
- better accessibility of the catalyst shapes and thus better activity from a bed volume unit
- higher homogeneity of gas flows and lower resistance of flows
- reduced susceptibility to abrasion and lower powdering from the bed.

The parameters of TZC-3/I catalyst are listed in Table 1.

Table 1

List of TZC-3/I catalyst properties

	TZC-3/I
Chemical composition, % wt.	Fe ₂ O ₃ - min. 71.5 Cr ₂ O ₃ - min. 8.8 CuO - min. 1.9
Shape and dimensions (D x H), mm	tablets of convex ends 6 x (6 ± 1)*
Sulphur content, % wt.	not more than 0.02
Abrasion resistance, wt. %	< 4
Bulk density, kg/dm ³	1.25 ± 0.15
Average mechanical strength (radial, daN/pellet)	11

* also available the tablets of flat ends and other dimensions

Compared activities of fresh catalysts at 370°C and 330°C and catalysts of other manufacturers overheated at 500°C and 600°C are illustrated in Figure 4. It can be observed that TZC-3/I is characterised by higher thermal stability than its equivalents.

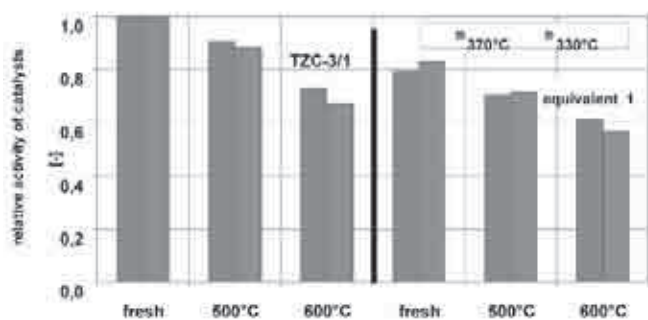


Fig. 4. Compared activities of selected HTS catalysts and TZC-3/I catalyst at 370°C

The comparison of changes in activities of selected HTS catalysts in the course of a long-term test at 370°C is presented in Figure 5 which shows that the lowest drop in activity is observed for TZC-3/I catalyst.

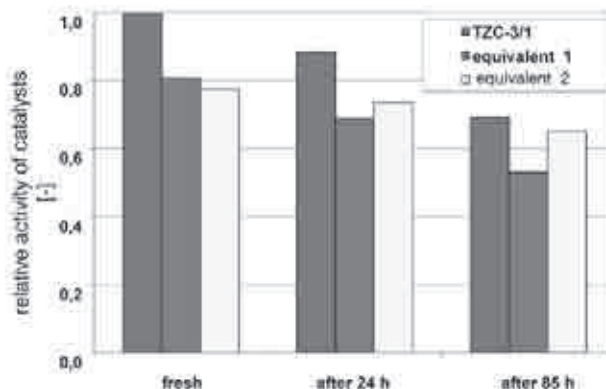


Fig. 5. Compared activities of selected HTS catalysts and TZC-3/I catalyst at 370°C

The comparison of TZC-3/I catalyst with HTS catalysts offered by leading global companies shows that it is highly competitive compared to its equivalents [16]. Sale volume and a deep interest from catalyst users from Poland, Europe as well as the Far East prove its quality.

TMC-3/I low-temperature shift catalyst

LTS catalysts are estimated to make the greatest contribution to the purchase costs of all catalysts of ammonia sequence. Hydrogen efficiency and economics of the whole ammonia production plant are predominantly affected by applied high-quality LTS catalysts and their proper operation [17].

Besides the tendency towards maximising the efficiency at minimum costs of a production plant, there is also a necessity of improving LTS catalyst to guarantee its longer operational life. A technology for a new TMC-3/I catalyst has been developed within cooperation between INS and Azoty Tarnów (Tab. 2 and Fig. 6).

Table 2

Properties of TMC-3/I catalysts

	TMC-3/I	TMC-3/I-K TMC-3/I-Cs
Chemical composition, % wt. CuO	min. 50	
ZnO	min. 25	
Al ₂ O ₃	min. 10	
promoter	-	alkalies
Dimensions (DxH), mm	4.5x3.5	
Bulk density, kg/dm ³	1.3±0.1	
Mechanical strength, daN/cm ²	min. 400	

* also available the tablets of other dimensions



Fig. 6. Catalyst TMC-3/I

The latest types of TMC-3/I-Cs and TMC-3/I-K catalysts have additional caesium and potassium promoters. Adding alkalis to a catalyst radically improves its selectivity and simultaneously reduces methanol formation on the catalyst [18]. For TMC-3/I-K catalyst, potassium additive, which has close affinity with poisons, e.g. chloride and sulphur compounds, is to increase its protective properties. Considering the above, TMC-3/I-K catalysts are recommended to be mainly installed in the inlet part of a catalytic bed, while TMC-3/I or TMC-3/I-Cs catalysts are recommended for the remaining part of the bed (Fig. 7).



Fig. 7. TMC-3/I catalyst bed in an industrial reactor

Nowadays, 3 types of TMC-3/I catalysts that differ in types and an amount of alkaline promoters are applied in industrial installations. These catalysts are successfully used in all national ammonia production plants as well as in Europe and Asia.

PS3-INS ammonia synthesis catalyst

Azoty Tarnów has been producing ammonia synthesis catalysts for more than 40 years. In the 1990s, a new type of catalyst with parameters corresponding to global products was launched. This was an effect of a close cooperation with Szczecin University of Technology, Warsaw University of Technology and INS Puławy which resulted in introducing PS3-INS catalyst into production in Tarnów. It is an alloy catalyst obtained by melting black iron ore and controlled cooling of the formed lava. The obtained catalytic material is reduced in size and fractionated. The end catalyst has an irregular shape. The offered fractions have diversified grain size that is optimal for a given type of synthesis reactor (Fig. 8).

Metallic iron with adequate structural and electron promoters is an active component of the catalyst [19]. The appropriate form of a catalyst is obtained as a result of reduction after placing the catalyst in the industrial reactor. To meet expectations of catalyst users, a new pre-reduced type of catalyst denoted as PS3-INS-R has been developed which is characterised by shorter time and lower temperature of activation in comparison to a standard PS3-INS catalyst. Table 4 presents a list of the most important parameters of PS3-INS catalysts.



Fig. 8. Catalyst PS3-INS

Table 3

A list of parameters of PS3-INS and PS3-INS-R catalysts

	PS3-INS	PS3-INS-R
Chemical composition, % wt.	Fe ₂ O ₃ - min. 56 FeO - min. 29 Promoters - ca. 10	Fe - ca. 80 Fe ₂ O ₃ + FeO - ca. 10 Promoters - ca. 10
Grain shape	irregular	
Grain size, mm	1.5 ÷ 3.3 ÷ 5.5 ÷ 8.6 ÷ 10.8 ÷ 12	
Bulk density, kg/dm ³	2.5 ÷ 2.8	1.9 ÷ 2.2

The quality of PS3-INS catalysts corresponds to other catalysts offered by global companies, and PS3-INS catalyst charges are successfully used in many plants. High activity, high thermal stability and strength of PS3-INS catalysts ensuring their long operational life confirm their very good quality. In the production plants using synthesis gas of high purity, a drop in PS3-INS catalyst activity is very small over time. The operational life of PS3-INS catalyst typically exceeds 10 years. One of ammonia production plants in Poland used the charge of this catalyst for 16 years and produced more than one million tons of ammonia during that time [20].

Technical support

An offer of very good quality products is not sufficient to compete successfully as a catalyst supplier on the present market. Therefore, Azoty Tarnów offers not only the products, but also technical support including professional supervision over loading and unloading of catalysts, the process of their reduction and activation of a production plant. The company also provides support service for forecasting operational life of a catalyst before its delivery, optimising catalyst operation, evaluating its work within the whole operational life and assistance in eliminating the effects of catalyst operational incidents. The experts from Azoty Tarnów in cooperation with verified partners may assist in organising the replacement of catalytic bed along with reactor cleaning, the taking-back of used catalysts and their recycling at request.

Summary

The catalysts offered by Azoty Tarnów are successfully used both in Polish and foreign production plants of ammonia and hydrogen. Azoty Tarnów has many references about high grade and quality of our products. Despite strong competition on the market, we have maintained an important position as the manufacturer of HTS, LTS and ammonia synthesis catalysts for many years. To satisfy increasing requirements of the international market and maintain the competitiveness with the products of dominant catalyst manufacturers, our catalysts have been continuously and effectively improved.

An important role of the cooperation between Azoty Tarnów and Fertilizer Research Institute in the field of applied tests should be emphasized. Tests on evaluating catalyst properties, their further improvement and implementation of new types are a part of this collaboration. The cooperation between Azoty Tarnów and INS Puławy started in the 1970s and has brought positive results coming up with common patents on the catalysts produced in Tarnów.

Due to considerable industrial demand on these catalysts, the production line equipment is constantly modernised and production capacities are expanded. A few thousand tons of catalysts delivered to national and foreign users were produced in the last decade. Azoty Tarnów, due to its excellent recognition of demands and problems of the national fertilizer industry, is an unquestionable leader on the Polish

market. The catalysts produced in Azoty Tarnów are also bought in many European countries such as Germany, Austria, Hungary, Ukraine, Italy, Russia and Belarus, as well as in more distant ones, e.g. Bangladesh or Indonesia. Repeatability of orders, even from non-European users, confirms the acknowledgment of high quality of these products.

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