



Ivanenko O.,
Radovenchyk V.,
Radovenchyk I.

NEUTRALIZATION OF CARBON MONOXIDE BY MAGNETITE-BASED CATALYSTS

The object of research is the processes of obtaining magnetite particles by the method of chemical condensation with the aim of subsequent use in the conversion of carbon monoxide, which is formed during the combustion of carbon-containing materials in conditions of lack of oxygen or air. One of the most problematic areas for CO neutralization is significant volumes of gas emissions and the complexity of the process of its conversion. Therefore, among the methods existing today – thermal, adsorption, absorption, catalytic – the latter is most often used, as the most acceptable for such conditions. The introduction of catalytic methods is significantly hampered by the need to use noble metals in catalysts, which makes their application on an industrial scale too expensive. The development of cheap and efficient catalysts for the conversion of CO is today a priority line of research in this area.

In the course of research, catalysts based on Fe_3O_4 magnetite particles obtained by chemical condensation are used. The growth method, the freezing-thawing process, and changing the ratio of components in the initial solutions are used to regulate the properties of particles. The ability to control the properties of synthesized particles in a wide range makes magnetite promising for use as a catalyst.

A cheap, effective catalyst for detoxifying carbon monoxide is obtained. A feature of this material is its significant reserves in the earth's crust and the possibility of obtaining it from production waste. The use of waste iron-containing electrolytes and pickling solutions as raw materials will simultaneously solve the complex environmental problem of their neutralization. The ability to easily control the content of iron ions of different valences allows to obtain a catalyst with a predetermined efficiency. The inertness and stability of magnetite in the environment does not create problems with its disposal after use.

This ensures the production of a cheap, affordable and efficient catalyst for the conversion of CO to CO_2 from production waste or natural material.

Keywords: flue gases, carbon monoxide, iron-containing solutions, growth method, chemical condensation, catalytic method.

Received date: 13.05.2020

Accepted date: 22.06.2020

Published date: 31.10.2020

Copyright © 2020, Ivanenko O., Radovenchyk V., Radovenchyk I.

This is an open access article under the CC BY license

(<http://creativecommons.org/licenses/by/4.0>)

1. Introduction

The current state of the atmosphere is formed, among other things, by human anthropogenic activity. At the same time, a large number of pollutants are released into the environment, which can negatively affect the living conditions of humans and living organisms. Some pollutants are highly toxic and even at low concentrations threaten with rather negative consequences. These pollutants include carbon monoxide (CO), 350–600 million tons of which is annually emitted into the atmosphere as a result of anthropogenic human activities [1]. Of this huge number, 56–62 % is emissions from vehicles, which can contain up to 12 % carbon monoxide. And if special devices in the form of catalysts, heaters, etc. are being developed to neutralize and detoxify carbon monoxide emitted by road transport [2], this issue does not find adequate attention in industry. Despite the high toxicity and significant amounts of CO, even today, methods for neutralizing carbon monoxide in the waste gases of industrial enterprises are being developed rather slowly, and progressive technologies are being introduced only in units. As a result, thanks to the activities of the industrial sector, a rather threatening situation has

developed in the world with respect to atmospheric pollution with carbon monoxide. For example, in Ukraine in 2018 1,7611 million tons CO were emitted into the atmosphere, which is 45.81 % of all emissions, excluding carbon dioxide [3]. In this case, both stationary source emissions and road transport emissions are taken into account. The most acute problem of carbon monoxide is in many industrially developed regions, especially in the South and East of Ukraine. For example, only in the Zaporizhzhia region 60–70 % of pollutant emissions are generated by metallurgical enterprises [4]. In the case of the impact of a separate enterprise, then with the current MPC on CO emissions at the level of 250 mg/m^3 , the emissions of JSC «Ukrainian Graphite» (Kyiv, Ukraine) contain carbon monoxide in the amount of $998.3\text{--}1750 \text{ mg/m}^3$ [4]. The problem of neutralizing carbon monoxide at the level of industrial enterprises is complicated by the fact that the most effective method of CO neutralization known today is catalytic methods [2]. And if this problem is successfully solved for road transport with small volumes of emissions, then for industrial enterprises the use of similar equipment with a significant consumption of precious metals and low productivity requires further detailed research.

To date, many different methods have been developed for neutralizing carbon monoxide in gas emissions. The most widely used are absorption, thermal, adsorption and catalytic methods. Absorption methods are bulky equipment, so they are practically not used on an industrial scale. The significant cost of sorbents and the need for their regeneration significantly slows down the introduction of adsorption methods. Thermal methods are effective at concentrations of carbon monoxide in waste gases of more than 3 %. Therefore, today the main attention of researchers and industrialists is focused on catalytic methods. The catalytic method by reducing the process temperature to 200–400 °C is 2–2.5 times cheaper than thermal afterburning through a corresponding reduction in energy consumption for heating gases and provides a more complete removal of impurities up to 97–99.9 %. Among other methods, this group is distinguished by high efficiency of the neutralization process, low operating temperatures, high speed of the catalytic process, and simplicity of the technological process [5].

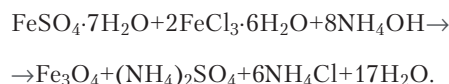
The essence of the process of catalytic detoxification of carbon monoxide consists in passing waste gases through a container filled with granules or equipped with honeycombs, the surface of which is covered with precious metals [6]. Platinum coating provides the greatest efficiency in this case. In some cases, it can reach 96–98 %. At the same time, such a catalyst is distinguished by the highest price, and its use for industry requires significant costs. The modern list of catalysts for neutralizing carbon monoxide is extremely wide – from noble and transition metals and their oxides to natural minerals and wastes from various technological processes. Cheaper in comparison with platinum catalysts with nickel-aluminum intermetallic compounds, however, they also require significant costs in obtaining alloys of these metals [7, 8]. Therefore, in recent years, the attention of some researchers has been focused on the use in the production of catalysts for the neutralization of carbon monoxide sludge formed as a result of wastewater treatment by the ferrite method [9, 10]. It is the use of such sludge that makes it possible to solve both the problem of its utilization and the problem of providing the production of catalysts with cheap raw materials. If to take into account that the efficiency of the investigated catalysts of this type is rather high, then they become the most promising for further implementation. At the same time, research in this direction can't be considered sufficient. Thus, the use of a copper-ferrite catalyst shows that at 140 °C the catalyst provides complete transformation of CO into CO₂ even at an oxygen concentration of about 1 % [10]. More detailed studies in this group of catalysts are currently lacking. At the same time, these catalysts are distinguished by a long service life, low sensitivity to the action of catalytic poisons, have magnetic properties and can be removed from the process stream using a magnetic field for regeneration and reuse [11]. An important aspect is also the fact that ferrites are non-toxic substances and can be easily utilized as alloying additives in metallurgy.

Despite a detailed study of catalytic processes for most types of catalysts, magnetite and ferrites based on it remain out of sight of most researchers in this field. Not only the efficiency of catalysts in the transformation of CO into CO₂ has not been investigated, but also the optimal methods of their synthesis, the possibility of reuse and the intensity

of poisoning during the processing of gas emissions. There are practically no data on the intensity of transformation of carbon monoxide, acceptable operating temperatures, and acceptable parameters of the technological process. This prevents the use of simple and effective catalysts in industrial facilities for various purposes. Therefore, it is urgent to develop cheap and affordable catalysts that can be obtained on an industrial scale by simple methods and safely disposed of after use. Thus, *the object of research* is the processes of obtaining magnetite particles by the method of chemical condensation with the aim of subsequent use in the conversion of carbon monoxide, which is formed during the combustion of carbon-containing materials in conditions of lack of oxygen or air. *The aim of this research* is to study the possibility of using magnetite and ferrites based on it in the processes of CO transformation into CO₂ under different conditions and with different characteristics.

2. Methods of research

Magnetite was obtained by chemical condensation. To synthesize magnetite particles, 2.78 g of FeSO₄·7H₂O and 5.06 g of FeCl₃·6H₂O were dissolved in distilled water and the resulting mixture was treated with an ammonia solution at a temperature of 30–35 °C until a pH value of 9.5–10 was established. As a result of such treatment, fractions of magnetite were formed in the solution in accordance with the reaction:



The resulting suspension of magnetite particles for «maturation» was left in the mother liquor for 30 min, after which the solid phase was separated by decantation, washed with distilled water until neutral, and dried at room temperature with access to atmospheric air. The granulometric composition of the solid phase was determined by the photoelectric method (Fig. 1).

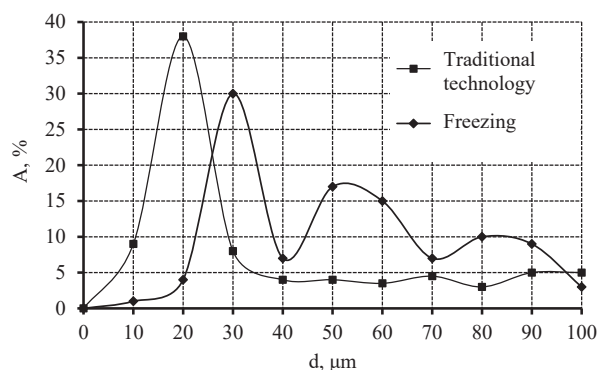


Fig. 1. Granulometric composition of magnetite obtained by the traditional method of chemical condensation and subsequent freezing

To study the transformation of CO into CO₂ using catalysts based on magnetite, let's use the laboratory unit shown in Fig. 2. The unit consists of a heat chamber 4, made of a stainless steel pipe 6 and a ceramic pipe 7, inside which a heating element is located 3. A system for maintaining the set temperature during the experiment,

including thermocouples 5 and a temperature controller 8. By adjusting the duration of the heating element 3, the system maintains the set temperature. A sample of the catalyst under study was poured into a cylindrical container 2 and fixed in a metal tube 6 in such a way as to exclude the passage of a model gas mixture past the catalyst. The volumetric velocity of the model gas flow was changed in the range of 1–5 dm³/min and was measured using gas flow meters 9. During the experiment, using the gas analyzer 1, the content of the components of the gas mixture at the inlet and outlet of the heat chamber was determined. In some cases, molecular nitrogen was additionally used as an inert gas. The concentration of the components of the gas mixture before and after the reaction was analyzed with an accuracy of ±20 ppm or ±5 % of the measured values. To stabilize the conditions of the experiment, before carrying out it, the proportion of the catalyst was calcined for 2 hours at a temperature of 450 °C, determining the loss of the catalyst mass. The studies were carried out in the temperature range 200–400 °C. The molar fraction of carbon monoxide in the model gas mixture at the reactor inlet was maintained at 1.1.

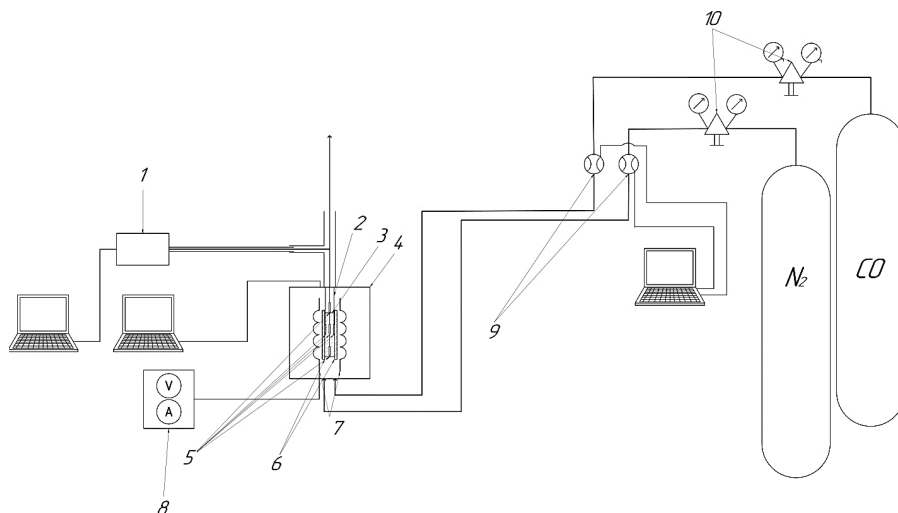


Fig. 2. Diagram of a laboratory unit for studying the processes of catalytic oxidation of carbon monoxide: 1 – gas analyzer VARIO PLUS industrial analyzer MRU air (Germany); 2 – catalyst container made of stainless steel mesh; 3 – heating element; 4 – heat chamber; 5 – thermocouples; 6 – stainless steel tube; 7 – ceramic tube; 8 – temperature regulator; 9 – gas flow meters; 10 – reducers

Carbon monoxide conversion was calculated in accordance with the formula:

$$X_{\text{CO}} = \frac{C_{\text{CO}}^{\text{in}} - C_{\text{CO}}^{\text{out}}}{C_{\text{CO}}^{\text{in}}} \cdot 100\%, \quad (1)$$

where $C_{\text{CO}}^{\text{in}}$ – the mole fraction of CO at the reactor inlet; $C_{\text{CO}}^{\text{out}}$ – the mole fraction of CO at the reactor outlet.

3. Research results and discussion

During the experiment under these conditions, it was found that the magnetite-based catalyst provides fairly good results (Fig. 3). Compared with iron-copper ferrite, the conversion efficiency is 5–12 %. A significant dependence of the conversion efficiency on the rate of flow of the gas mixture through the catalyst bed was noted. Moreover, with an increase in temperature, this dependence becomes

more noticeable and at 400 °C it is about 10 %. The maximum conversion of carbon monoxide is achieved at 400 °C and is 49 %.

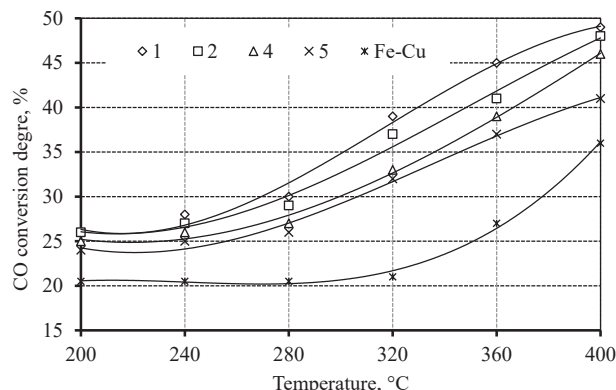


Fig. 3. Temperature dependences of the conversion degree of carbon monoxide when using catalysts based on magnetite at different space velocities of the mixture (dm³/min)

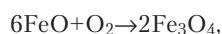
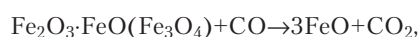
The use of such highly dispersed materials as a catalyst causes some difficulties from the technological point of view. First of all, these are significant energy costs to create the required excess pressure of the gas mixture. Therefore, the possibilities of increasing the size of magnetite particles in various ways were investigated. One of such methods was described earlier under the name of increasing the size of magnetite particles [10]. Its essence lies in the fact that the magnetite obtained by the technology described above was re-processed in a solution of the same composition and precipitated with alkali. In this case, the growth of existing particles and an increase in their size were observed. As a result of the studies carried out, it was found that the most intensive increase in particle size is observed during three cycles of processing magnetite particles.

Further processing was not accompanied by a significant effect. However, the overall effect was quite insignificant. For example, the content of 20 μm particles decreased by 7 %, while the content of 40 μm particles increased by 5 %. The build-up effect for larger particles was even smaller. The properties of the powders obtained under such conditions have been investigated and have shown that the increase in the velocity of the gas mixture with the same experimental parameters is less than 1 %. Under such conditions, given the complexity of the growth process, the additional consumption of reagents and significant environmental problems with additional wastewater, the use of the growth method in the processes of obtaining a catalyst for the conversion of carbon monoxide turns out to be inappropriate.

Another method, investigated with the aim of increasing the size of magnetite particles obtained by the method of chemical condensation, is the freezing method. The essence of the method consisted in freezing and thawing, under

certain conditions, of a magnetite suspension obtained by the traditional method of chemical condensation. It was found that the conditions of synthesis, freezing and thawing of the suspension significantly affect the granulometric composition of the resulting mixture [12]. It was also determined that the optimal in terms of increasing the size of magnetite particles is the synthesis temperature in the range of 30–35 °C, freezing the resulting suspension at –6 °C and thawing in air at 40 °C. The experiments showed that under these conditions it is possible to obtain a mixture of magnetite particles, in which the content of particles with a size of 20 μm decreases by 34 %, the content of particles with a size of 30 μm increases by 22 % (Fig. 1). An increase of 2–10 % in the content of particles with a size of more than 30 microns was also noted. The effect of using such a mixture as a catalyst: it allows to increase the speed of the gas mixture by 5–7 % with the same other parameters of the experiment, more significantly than in the previous case. At the same time, in this case, the changes are rather scarce and can't radically affect the technological process. Obviously, for real units, it will be more acceptable to apply magnetite on support granules with appropriate physical properties.

The traditional technology for obtaining magnetite particles involves the use of a mixture of reagents with a concentration ratio of ions $K = [\text{Fe}^{2+}]/[\text{Fe}^{3+}] = 0.5$. Under such conditions, the shares of magnetite have the most perfect structure and can be stored for a long time without losing their properties. At the same time, the magnetic properties of the suspension deposited from such a mixture are stored in the range of the parameter $K = 0.1–3.0$. It is obvious that the presence on the surface of magnetite particles of different amounts of iron ions capable of oxidation and reduction, significantly affect the catalytic properties of the mixture. Based on the possible oxidation reaction of carbon monoxide using magnetite particles:



It is possible to assume that an increase in the amount of iron (III) oxide in the surface layer of particles will increase the intensity of the CO conversion process. The studies carried out under the conditions described above with the use of magnetite particles obtained for different ratios of the parameter K showed that this assumption has experimental confirmation (Fig. 4).

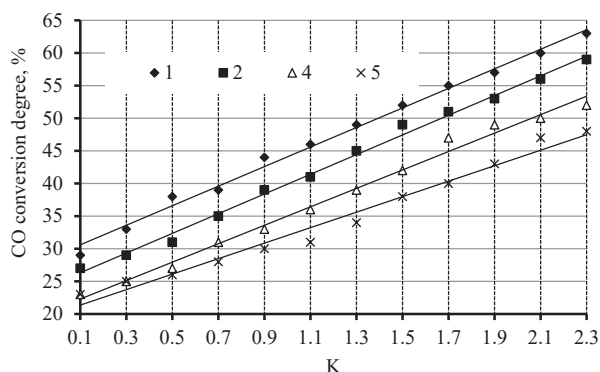


Fig. 4. Temperature dependences of the conversion degree of carbon monoxide when using catalysts based on magnetite at different values of the parameter K and volumetric flow rates of the mixture (dm^3/min)

Experiments carried out at a temperature of 320 °C showed that by adjusting the parameter K it is possible to significantly increase the degree of CO conversion. In this case, it is only worth considering the fact that with an increase in K , the magnetic properties of magnetite particles also decrease almost proportionally and their dispersion increases. Therefore, in practical use, it is necessary to select K depending on the required value of the magnetic permeability of the particles and the desired gas flow rate.

4. Conclusions

The studies confirm the possibility of using magnetite in the processes of neutralizing carbon monoxide in gas emissions of industrial enterprises. By selecting the conditions for the synthesis of magnetite particles, it is possible to obtain a mixture with specified catalytic, magnetic and physical properties. The possibility of obtaining the described mixtures of magnetite particles from production wastes and as a by-product in the purification of certain types of wastewater makes this technology very attractive from both environmental and economic points of view. And also serves as an essential factor for the introduction of technology at industrial facilities.

References

1. Kursov, S. V. (2015). Monooksid ugleroda: fiziologicheskoe znachenie i toksikologiya. *Meditsina neotlozhnykh sostoianii*, 6 (69), 9–16.
2. Patel, D. M., Kodgire, P., Dwivedi, A. H. (2019). Low temperature oxidation of carbon monoxide for heat recuperation: A green approach for energy production and a catalytic review. *Journal of Cleaner Production*, 245, 118838. doi: <http://doi.org/10.1016/j.jclepro.2019.118838>
3. *Statistical Yearbook «Environment Of Ukraine 2018»* (2019). Kyiv: State Statistics Service of Ukraine, 214. Available at: http://ukrstat.gov.ua/druk/publicat/kat_u/2019/zb/11/Zb_dovk_2018.pdf
4. *Ekolohichniy pasport Zaporizkoi oblasti za 2018* (2019). Ofitsiyniy portal Ministerstva enerhetyky ta zakhystu dovkillya Ukrainy, 173. Available at: <https://menr.gov.ua/news/33529.html>
5. Pavlovich, L. B., Titova, O. O. (2015). *Ekologicheskyye problemy metallurgicheskogo proizvodstva*. Novokuznetsk: Izd. tsentr SibGIU, 2111.
6. Kašpar, J., Fornasiero, P., Hickey, N. (2003). Automotive catalytic converters: current status and some perspectives. *Catalysis Today*, 77 (4), 419–449. doi: [http://doi.org/10.1016/s0920-5861\(02\)00384-x](http://doi.org/10.1016/s0920-5861(02)00384-x)
7. Sanin, V. N., Andreev, D. E., Pugacheva, E. V., Zhuk, S. Ia., Sanin, V. N., Iukhvid, V. I. (2009). Poluchenie intermetallicheskikh katalizatorov glubokogo okisleniya CO i uglevodorodov. *Neorganicheskie materialy*, 45 (7), 839–846.
8. Borsch, V. N., Pugacheva, E. V., Zhuk, S. IA., Andreev, D. E., Sanin, V. N., Iukhvid, V. I. (2008). Mnogokomponentnye metallicheskie katalizatory glubokogo okisleniya SO i uglevodorodov. *Doklady Akademii Nauk*, 419 (6), 775–777.
9. Radovenchyk, V. M., Ivanenko, O. I., Radovenchyk, Ya. V., Krysenko, T. V. (2020). *Zastosovannia ferytnykh materialiv v protsesakh ochyshchennia vody*. Bila Tserkva: Vydavnytstvo O. V. Pshonkivskyyi, 215.
10. Lou, J.-C., Chang, C.-K. (2006). Catalytic Oxidation of CO Over a Catalyst Produced in the Ferrite Process. *Environmental Engineering Science*, 23 (6), 1024–1032. doi: <http://doi.org/10.1089/ees.2006.23.1024>
11. Kharisov, B. I., Dias, H. V. R., Kharissova, O. V. (2019). Mini-review: Ferrite nanoparticles in the catalysis. *Arabian Journal of Chemistry*, 12 (7), 1234–1246. doi: <http://doi.org/10.1016/j.arabjc.2014.10.049>
12. Radovenchyk, Ya. V., Romanenko, M. I., Radovenchyk, V. M. (2017). Zalozmistki sorbenty dlia ochyshchennia vody vid naftoproduktiv. *Ekolohiya y promishlennost*, 1, 74–80.

Ivanenko Olena, PhD, Associate Professor, Department of Ecology and Technology of Plant Polymers, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine, e-mail: olenka.vasaynovich@gmail.com, ORCID: <http://orcid.org/0000-0001-6838-5400>

Radovenchyk Vyacheslav, Doctor of Technical Sciences, Professor, Department of Ecology and Plant Polymers Technology, National

Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine, e-mail: dokeco@ukr.net, ORCID: <http://orcid.org/0000-0001-5361-5808>

Radovenchyk Iaroslav, PhD, Associate Professor, Department of Ecology and Plant Polymers Technology, National Technical University of Ukraine «Igor Sikorsky Kyiv Polytechnic Institute», Ukraine, e-mail: r.yar@ukr.net, ORCID: <http://orcid.org/0000-0002-0101-0273>