A modified MnO_2 clinoptillolite was obtained by using the available zeolite rock from the Sokyrnytsia deposit (Khust district of the Zakarpattia region, Ukraine) using a simple technique of mixing solutions containing separately Mn^{2+} and MnO_4^-. It was determined that the total manganese content in the air-dry modified thermally untreated clinoptyllolite was 11.42 mg/g, which is 1.8 % in terms of MnO_2.

Structural characteristics, namely, the pore size distribution and specific surface area as the main basic characteristics of the catalyst, were studied, which were obtained from the isotherms of low-temperature nitrogen adsorption-desorption. These studies are necessary to determine the limiting stage of CO oxidation.

It has been determined that the kinetics of the oxidation process is described by a first-order equation. Based on the obtained characteristics of the catalyst, the kinetic parameters of the process were calculated, namely, the effective and true rate constants and the activation energy, which is 31 kJ/mol. It has been proved that the oxidation reaction of carbon monoxide on an oxide-manganese catalyst proceeds in the intra-diffusion mode. This makes it possible, using the criterion dependences, namely, the Carberry criterion, which is less than 0.05, to assert that the reaction is not limited by the diffusion of CO from the gas stream to the outer surface of the catalyst. It is shown that the transport of carbon monoxide molecules inside the catalyst granules proceeds in the Knudsen regime.

The obtained scientific result in the form of a kinetic description of the catalytic oxidation of carbon monoxide with atmospheric oxygen on a manganese oxide catalyst based on zeolite is interesting from a theoretical point of view. From a practical point of view, the calculated kinetic parameters of this process make it possible to calculate a catalytic CO oxidation reactor

Keywords: carbon monoxide, oxidation kinetics, structural parameters, manganese dioxide, zeolite, clinoptilolite

THE KINETIC PARAMETERS OF THE SMOKE GASES PURIFICATION PROCESS FROM CARBON MONOXIDE ON A ZEOLITE-BASED MANGANESE OXIDE CATALYST

O. Ivanenko
PhD, Associate Professor*
E-mail: olenka.vasaynovich@gmail.com
A. Trypolskyi
Doctor of Chemical Sciences, Senior Researcher**
E-mail: atripolski@gmail.com
O. Khokhotva
Doctor of Technical Sciences, Associate Professor*
E-mail: khokhotva@bigmir.net
P. Strizhak
Doctor of Chemical Sciences, Professor**
E-mail: pstrizhak@hotmail.com
S. Leleka
PhD, Senior Researcher***
E-mail: sleleka@rst.kpi.ua
I. Mikulionok
Doctor of Technical Sciences, Professor, Senior Researcher***
E-mail: i.mikulionok@kpi.ua
*Department of Ecology and Technology of Plant Polymers
National Technical University of Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute"
Peremohy ave., 37, Kyiv, Ukraine, 03056
**Department of Catalytic Synthesis of
Single-Carbon-Based Molecules
L. V. Pisarzhevskii Institute of Physical Chemistry of
the National Academy of Sciences of Ukraine
Nauky ave., 31, Kyiv, Ukraine, 03028
***Department of Chemical, Polymeric and
Silicate Mechanical Engineering
National Technical University of Ukraine
"Igor Sikorsky Kyiv Polytechnic Institute"
Peremohy ave., 37, Kyiv, Ukraine, 03056

1. Introduction

Carbon monoxide is one of the priority environmental pollutants. On average, gas emissions from petrochemical [1], metallurgical and electrothermal industries in kilns [2] and graphitization furnaces for electrode products [3] can contain up to 20 % CO.

From an environmental point of view, CO is a highly toxic and life-threatening gas that leads to hypoxia, asphyxiation and sudden death [4]. CO poisoning accounts for the

largest share of reported toxic gas intoxication in the world in cases not related to fire. However, CO is also a raw material for the production of methanol, which in turn is used to produce many chemicals that are valuable to human life, such as plastics, automotive fuels, etc. [5].

One of the most effective methods of air protection is catalytic processes. Therefore, the development and creation of an oxide-metal catalytic system based on zeolite, intended for the oxidation of carbon monoxide flue gases, is relevant. Experimentally determined kinetic parameters of the process can be used for further calculation of a catalytic reactor for cleaning flue gases from CO.

2. Literature review and problem statement

It is known that in the world carbon monoxide is annually emitted into the atmosphere as a result of anthropogenic human activity in the amount of 350−600 million tons [4], however, at the level of industrial production, methods of sanitary cleaning of industrial waste gases from this component have not been practically introduced.

According to the State Statistical Service [6], for example, in Ukraine in 2019 748.4 thousand tons of carbon monoxide were released into the air by stationary sources. The largest amount of carbon monoxide is observed in industrially developed areas with a high concentration of mining and processing enterprises. For example, in the Zaporizhzhia region, an increased technogenic load on the air is formed not only for a large number of environmentally hazardous objects of critical infrastructure in Ukraine, but in connection with the ineffective operation of gas cleaning facilities [7]. In particular, the accumulation of industrial enterprises in the city of Zaporizhzia, such as JSC "Zaporizhstal", JSC "Zaporizhzhia Ferroalloy Plant", JSC "Ukrainian Graphite", JSC "Zaporizhkoks" and others led to the formation of a territory of significant technogenic impact. In the composition of emissions from these enterprises, the share of carbon monoxide reaches 40−80 % [8]. In order to improve the environmental safety of enterprises related to critical infrastructure facilities, it is necessary to develop measures to reduce carbon monoxide emissions.

It has been shown that, in addition to reducing CO emissions into the air, only automobile exhaust gases are purified by the method of CO catalytic oxidation [9]. This is the most effective and most expensive method of combating carbon monoxide. The issues related to the cost and throughput of catalysts remained unresolved in the field of neutralization of flue gases of industrial enterprises. For example, a catalyst used to remove CO from automobile exhaust gases, which contains precious metals such as palladium, platinum, and rhodium [10, 11]. However, equipment with a catalyst based on noble metals has a high cost, low throughput, therefore, for these reasons, it can't meet the needs of large enterprises.

A variant of overcoming these obstacles is the use of metal oxide catalysts. Metal oxides can be used both in pure form in the form of a powder [12, 13], and deposited on a granular mineral carrier, for example, zeolite. It is this approach that is used in [14, 15]. In addition to noble metals, in the series of transition metal oxides, cobalt [16] and manganese [17, 18] oxides exhibit high catalytic activity in CO oxidation. Manganese oxides in the composition of hopcalite 60 % MnO_2, 40 % CuO or 70 % MnO_2, 30 % CuO are widely used for the oxidation of CO [17]. According to

the authors of [18], the highest conversion of carbon monoxide is provided when using a copper-manganese oxide catalyst 30:70. However, most of the advantages for use have an oxide-manganese catalyst based on clinoptilolite, since it can be obtained from waste sorbents for purification of manganese-containing natural water [18]. In the case of cobalt, the most active oxide is the Co_3O_4 spinel, in which cobalt is present in two valence states (2 and 3). Similarly, manganese oxides exist in the form of a number of stoichiometric and non-stoichiometric phases (MnO, Mn_2O_3, Mn_3O_4 Mn_5O_8 and MnO_2), in which the manganese valence changes from +2 to +4 [19−21]. According to publications [22, 23], in the series of manganese oxides, the catalytically oxidative activity increases with an increase in the valence of manganese. Manganese oxides are structurally flexible and can change from one form to another upon heating [24]. Since the development of catalytic systems is intended for use at enterprises in Ukraine, the most efficient catalysts should be based on available raw materials. Therefore, manganese oxides are chosen as the active component, and natural zeolite are chosen as the carrier. According to the authors of [25], it is advisable to use clinoptilolite from the zeolite rock of the Sokyrnytsia deposit as a natural zeolite. This natural material has, in comparison with other carriers, such advantages as low cost, availability, high performance and availability in sufficient quantities in Ukraine.

3. The aim and objective of research

The aim of this research is to study the effect of the structural properties of an oxide-manganese catalyst based on natural zeolite on the kinetic parameters of the catalytic oxidation of carbon monoxide by atmospheric oxygen. This will make it possible to calculate a catalytic CO oxidation reactor.

To achieve the aim, the following objectives should be set:
– to obtain a modified MnO_2 clinoptilolite using zeolites from the Sokyrnytsia deposit;
– to study the kinetic features of the oxidation of carbon monoxide by atmospheric oxygen in the presence of a manganese oxide catalyst based on zeolite.

4. Technique for studying the properties of an oxide-manganese catalyst and the kinetics of the catalytic oxidation of carbon monoxide

To obtain the clinoptilolite modified with MnO_2, let's use zeolites from the Sokyrnytsia deposit with a fraction of 3−5−8 mm and a chemical composition declared by the manufacturer (wt. %): %: SiO_2 – 71.5; Al_2O_3 – 13.1; Fe_2O_3 – 0.9; TiO_2 – 0.5; CaO – 3.44; MgO – 0.68; K_2O+Na_2O – 3.03.

Obtaining a manganese oxide catalyst based on zeolite proceeded according to the following procedure. First, a sample of natural zeolite weighing 150 g for 1 hour was brought into contact with 150 cm^3 of a 0.475M $MnCl_2$ solution. Then the solution of $MnCl_2$ decanters and zeolite were treated with 0.316M $KMnO_4$ solution for 24 hours.

After modification, the zeolite sample was washed from weakly caked on the surface of the modification products with distilled water and kept under normal conditions in a wet-dry state. Part of the resulting dry preparation was placed in a muffle furnace and kept at 450 °C for 2 hours to

study the effect of moderately elevated temperatures on the structural characteristics of the catalyst support.

The MnO_2 content in the modified clinoptilolite was determined as follows. An accurately weighed sample was treated with 1M H_2SO_4 solution with addition of Na_2SO_3 on heating to reduce Mn(IV) to the water-soluble state of Mn(II). The concentration of Mn^{2+}, which passed into the solution phase, was measured by the atomic absorption method using an AAS-1N spectrophotometer (Germany) [26].

The structural parameters of the samples of clinoptilolite modified with MnO_2 (without heat treatment and after heat treatment at 450 °C for 2 h) were determined by low-temw perature nitrogen adsorption/desorption methods. To do this, the samples were ground to obtain grains with a diameter of 0.5–1 mm, washed with distilled water, and dried at room temperature in air (25 °C, relative air humidity 45 %). The samples were prepared by degassing them with nitrogen at a temperature of 150 °C for 6 hours. The specific surface area and pore size distribution were calculated using adsorption data obtained using Sorbtometers Nova Quntachrome 4200e (USA) at a temperature (−196 °C) [18].

The study of the CO oxidation process was carried out using device (Fig. 1), which includes a heat chamber 8, consists of a metal tube made of stainless steel 9 and a ceramic tube 10 with a heating element 11. In the heat chamber 8, thermocouples 12 and thermo relay 14 were supported by means of element 11 set temperature. A sample of catalyst with a grain size of 3–5–8 mm in a cylindrical container 13 was placed in a metal tube 9. The dimensions of the container were: height 160 mm, diameter 56 mm. A container with a catalyst 55 mm high was inserted into tube 9 in such a way as to prevent the passage of the gas mixture past the catalyst.
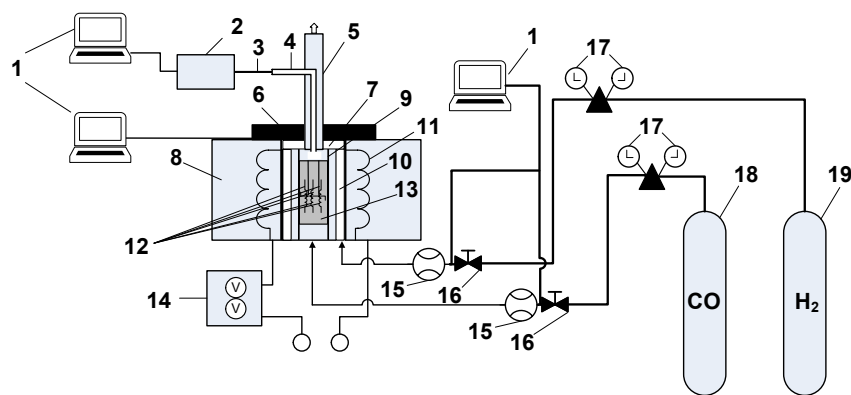

Fig. 1. Diagram of a laboratory device for studying the processes of catalytic oxidation of carbon monoxide: 1 — digital measurement interface; 2 — gas analyzer VARIO PLUS industrial analyzer MRU air fair; 3 — gas sampler of the gas analyzer; 4 — tube for sampling the gas mixture from the chamber to the gas analyzer; 5 — outlet of the gas mixture; 6 — metal gasket; 7 — asbestos gasket; 8 — heat chamber; 9 — stainless steel tube; 10 — ceramic tube; 11 — heating element; 12 — thermocouples; 13 — container for catalyst made of stainless steel mesh; 14 — temperature controller; 15 — gas flow meters; 16 — control valves; 17 — reducers; 18 — carbon monoxide cylinder; 19 — nitrogen cylinder

An experimental study of the oxidation reaction of carbon monoxide with molecular oxygen was carried out in a flow-through unit at atmospheric pressure. During heating, the composition of the gas mixture at the inlet and outlet of the heat chamber was constantly monitored. The concentration

of the reaction products was analyzed using a VARIO PLUS industrial analyzer MRU air fair. The range of measurements of molar fractions of gases in the mixture in the used gas analyzer is CO – from 0 to 10 % with the limit of the permissible absolute error of ±0.02 %, O_2 – from 0 to 21.0 % with the limit of the permissible absolute error of ±0.2 %. The process was carried out at various volumetric gas flow rates, with a constant concentration of CO and O_2 reagents equal to 2 and 20 vol. % respectively. The reaction rate was related to the bulk volume of the catalyst. The catalyst was examined under the same conditions in the temperature range 200–500 °C.

The catalytic activity of the samples in the oxidation of carbon monoxide was characterized by the conversion of CO to CO_2 and the specific rate of the reaction.

Carbon monoxide conversion was calculated using the formula:

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

where C_{CO}^{in} – molar fraction of CO at the inlet to the reactor, C_{CO}^{out} – molar fraction of CO at the exit from the reactor.

The activation energy (E_a) of the CO oxidation reaction was calculated using the Arrhenius equation.

5. Obtaining clinoptilolite modified with MnO_2 using the zeolite rock of the Sokyrnytsia deposit

To calculate Knudsen diffusion, it is necessary to take into account the pore size distribution for the heat-treated catalyst obtained from adsorption-desorption isotherms, and the specific power as the main basic characteristic of the catalyst.

The total manganese content in the air-dry modified thermally unrefined sample of clinoptilolite was 11.42 mg/g, which is 1.8 % in terms of MnO_2. Thus, the formation of a manganese oxide layer on the surface of zeolite-clinoptilolite could significantly affect its structural characteristics.

As seen from Fig. 2, the adsorption isotherms obtained for the samples of MnO_2-modified zeolites (heat-treated and thermally non-crushed) do not belong to any type, although such isotherms can be attributed to type V, which are characteristic of typical microporous materials. The difference is that at a pressure close to the saturated vapor pressure, the isotherm inflection is not observed, which is attributed to adsorption in large mesopores and macropores [27]. It should also be noted that the obtained nitrogen adsorption and desorption isotherms for each individual sample practically coincide with each other, confirming the conclusions of the authors [28–30].

As it is shown [25], the specific surface area of the heat-treated MnO_2-zeolite significantly decreases in comparison with the specific surface area of the thermally uncured modified sample from 210.345 m^2/g to 71.823 m^2/h. This effect can be explained by the loss of the hydrated mass of manganese dioxide in the

dry state of surface water molecules under the influence of elevated temperatures. In this case, due to the released bonds, a denser aggregation of MnO_2 microcrystals occurs both with each other and with the outer surface of clinoptilolite. Clogging of the mouths of the zeolite channels leads to the inaccessibility of nitrogen molecules in a more porous space.
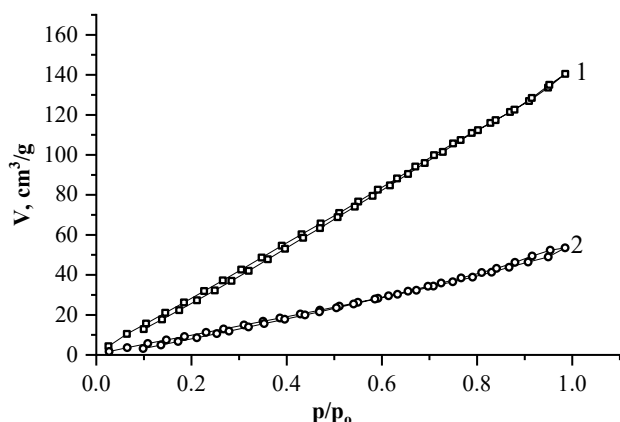

Fig. 2. Isotherms of nitrogen adsorption and desorption on samples of: 1 — MnO_2-modified zeolite without heat treatment; 2 — MnO_2-modified zeolite after heat treatment (450 °C for 2 hours)

The certain average pore radius of the zeolite modified with MnO_2 without and with heat treatment is 1.524 and 1.530 nm, respectively [25], which, according to [31], is 4–8 times overestimated. In other similar studies using natural zeolites, a similar picture is observed [32–34], which indicates that the geometry of the two-dimensional system of zeolite channels to clinoptilolite and the specifics of interaction of nitrogen molecules with it are not fully taken into account.

The kinetics of carbon monoxide oxidation in the presence of a manganese oxide catalyst based on zeolite was studied by investigating the dependence of the CO oxidation state on the volumetric gas flow rate at a constant concentration of reagents. The obtained experimental dependences of the CO conversion degree on the contact time τ are shown in Fig. 3.
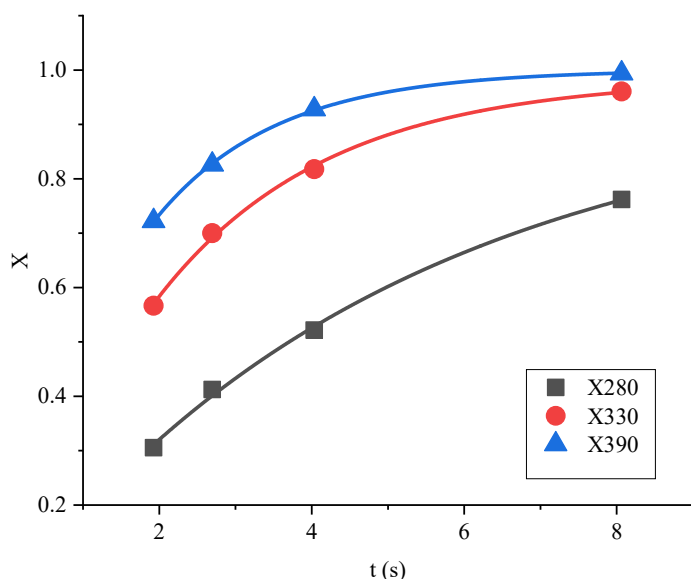

Fig. 3. The oxidation state of CO on an oxide-manganese catalyst depending on the contact time at temperatures of 280, 330 and 390 °C

Oxidation of carbon monoxide proceeds by the reaction:

$$CO + 1/2\ O_2 = CO_2. \tag{2}$$

It is known that this reaction is exothermic ($\Delta H\,°298 = -282.6$ kJ/mol) and practically irreversible up to 1500 K ($\Delta G\,°298 = -256.7$ kJ/mol; $\Delta S\,°298 = -86.5$ J/(mol·K). In spite of a significant decrease in free energy for CO oxidation, the reaction occurs due to weakening of bonds in O_2 and CO molecules, caused by the activation of the reacting components during their adsorption on the catalyst surface.

6. Study of the kinetic features of the oxidation of carbon monoxide by atmospheric oxygen in the presence of an oxide-manganese catalyst based on zeolite

According to the literature data [17, 35, 36], the oxidation of carbon monoxide on oxide catalysts at elevated temperatures proceeds according to a stepwise mechanism:

$$O_2 + 2[\ ] \rightarrow 2[O], \tag{3}$$

$$CO + [O] \rightarrow CO_2 + [\ ], \tag{4}$$

where [ ] – oxygen vacancy on the oxide surface [O] are surface oxygen atoms.

According to this mechanism, at the first stage, oxygen from the gas phase is absorbed at the oxygen vacancy of the oxide. At the second stage, the interaction of carbon monoxide molecules from the gas phase with surface oxygen atoms occurs to form carbon dioxide. The limiting stage of the process is the second stage of oxygen separation from the oxide, and the oxidation stage on the oxide surface proceeds much faster.

The following expression for the reaction rate corresponds to this mechanism:

$$r = \frac{k_1 \cdot k_2 \cdot C_{O_2} \cdot C_{CO}}{k_1 \cdot C_{O_2} + \sqrt{k_2 \cdot C_{CO}}}, \tag{5}$$

where r – reaction rate, k_1 and k_2 – the rate constants of the first and second stages, C_{O_2} and C_{CO} are the molar fractions of oxygen and carbon monoxide, respectively.

Taking into account that the oxidation process of carbon monoxide is carried out with a significant excess of oxygen, it is possible to write:

$$k_1 \cdot C_{O_2} \gg \sqrt{k_2 \cdot C_{CO}}. \tag{6}$$

Then the reaction rate equation for this case will be as follows:

$$r = k_2 \cdot C_{CO}. \tag{7}$$

In the given kinetic reaction scheme, the stage of oxygen adsorption on the oxide oxygen vacancy is considered irreversible. There may also be another case, when equilibrium is established during oxygen adsorption, and the second stage, as for the first mechanism, is limiting. In this case, the kinetic equation will be:

$$r = k_2 \cdot C_{CO} \cdot \frac{\sqrt{b_{O_2} \cdot C_{O_2}}}{1 + \sqrt{b_{O_2} \cdot C_{O_2}}}, \tag{8}$$

where $b_{O_2} \cdot C_{O_2}$ – product of the adsorption coefficient of oxygen by its mole fraction.

According to this equation, the rate of CO oxidation is of the first order in CO and fractional in oxygen. Considering that the process of oxidation of carbon monoxide was carried out with a significant excess of oxygen $1 \ll \sqrt{b_{O_2} \cdot C_{O_2}}$, the reaction rate equation can be written in a simplified form:

$$r = k_2 \cdot C_{CO}. \qquad (9)$$

Thus, in spite of the mechanism by which the oxidation reaction of carbon monoxide occurs, with a significant excess of oxygen, the reaction rate equations coincide. That is, the rate of the CO oxidation reaction can be described by a first-order equation. Considering that the CO oxidation reaction was carried out at a constant initial CO concentration, the reaction rate is determined by the rate constant of the second stage k_2 in accordance with eq. (7).

In a flow reactor, the reaction rate varies along the catalyst bed. For the first-order reaction [22, 37], let's obtain the equation for the rate constant of the reaction in the flow (in the ideal displacement mode) for the condition when the reaction in the flow occurs while maintaining a constant volume by the responsive system, is observed while maintaining the number of moles in the gas phase:

$$k = \frac{1}{\tau} \cdot \ln \frac{C_0}{C} = \frac{1}{\tau} \cdot \ln \frac{1}{1-x}. \qquad (10)$$

To find the rate constant of the CO oxidation reaction in a flow-through reactor in the case when the kinetics of the process is described by a first-order equation, the dependences $\ln \frac{C_0}{C}$ or $\ln \frac{1}{1-x}$ on the contact time τ were plotted (Fig. 4).

Form Fig. 3 it is obvious that equation (10) describes well the experimental data. The calculated values of the rate constant are given in Table 1.
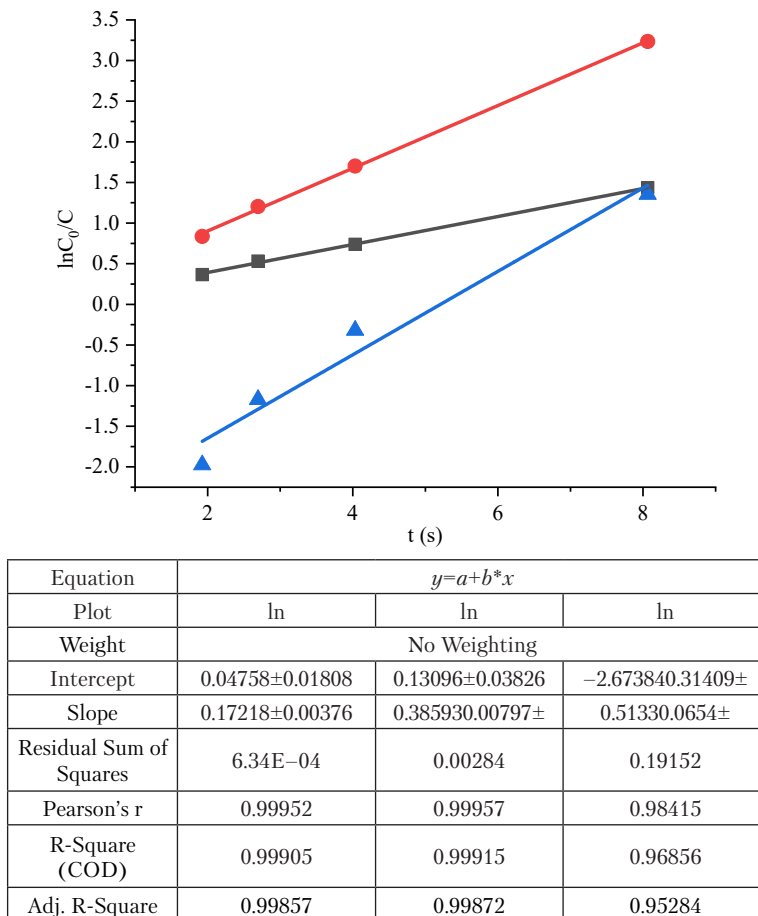

Equation	$y=a+b*x$		
Plot	ln	ln	ln
Weight	No Weighting		
Intercept	0.04758±0.01808	0.13096±0.03826	−2.67384 0.31409±
Slope	0.17218±0.00376	0.38593 0.00797±	0.5133 0.0654±
Residual Sum of Squares	6.34E−04	0.00284	0.19152
Pearson's r	0.99952	0.99957	0.98415
R-Square (COD)	0.99905	0.99915	0.96856
Adj. R-Square	0.99857	0.99872	0.95284

Fig. 4. Linearization of a first-order equation in a flow

Table 1

CO oxidation reaction rate constant

Effective rate constant, k, s^{-1}	Standard deviation	T, °C	True rate constant, k_2, (m^{2}s)$^{-1}$	Overexponential factor, k_2^0, (m^{2}s)$^{-1}$
0.17218	0.00376	280	$8.00 \cdot 10^6$	
0.38593	0.00797	330	$4.02 \cdot 10^7$	$5.0 \cdot 10^{12}$
0.5133	0.0654	390	$7.12 \cdot 10^7$	

With the Arrhenius dependence (Fig. 5) of the rate constant on temperature, the value of the activation energy $E = 31$ kJ/mol, $k_0 = 160$ was found.

Thus, the kinetics of CO oxidation is described by a first-order equation. It should be noted that, formally, the first-order equation can also describe the course of the process in the internal and external diffusion regions.

Equation	$y=a+b*x$
Plot	$\ln k_1$
Weight	No Weighting
Intercept	5.0737 1.85264±
Slope	−3742.397851 115.44556±
Residual Sum of Squares	0.05234
Pearson's r	−0.95834
R-Square (COD)	0.91841
Adj. R-Square	0.83682

Fig. 5. Dependence of the effective rate constant k on temperature

Comparison with the literature data [17] shows that the activation energy for CO oxidation on manganese catalysts is usually about 60 kJ/mol. The activation energy obtained in this work indicates the occurrence of the CO oxidation reaction in the intradiffusion mode. In this case, the calculated reaction rate constant is effective and for the reaction, which is described by the first-order kinetic equation (9), has the expression:

$$k = \sqrt{k_2 \cdot D^*}, \tag{11}$$

where k_2 – reaction rate constant determined in the kinetic region, D^* – effective diffusion coefficient.

As follows from the above expression, the effective activation energy found under the conditions of the reaction in the intradiffusion mode should be approximately half the activation energy of the process in the kinetic region.

Estimating the constants in equation (11), it can be argued that the diffusion coefficient D in the pores of the catalyst will be close to the coefficient of molecular interdiffusion of CO in the pore. In this case, the mean free path of the CO molecule will be greater than the pore diameter of the catalyst. Taking into account that the average free path of a CO molecule under experimental conditions calculated according to [38] is approximately $1.1 \cdot 10^{-7}$ m, which significantly exceeds the average pore size of the catalyst, diffusion of carbon monoxide occurs in the Knudsen region, and the diffusion coefficient can be calculated according to the formula:

$$D^* = \frac{d}{3} \cdot \sqrt{\frac{8 \cdot R \cdot T}{\pi \cdot M}}, \tag{12}$$

where RT – product of the universal gas constant and absolute temperature, – molecular weight of CO, d – average pore diameter, m. According to equation (12), for $T=560$ K the diffusion coefficient $D^*=3.7 \cdot 10^{-9}$ m^2/s. The exact value of D^* can be found experimentally by the diaphragm method.

Using the Knudsen diffusion coefficient D^*, according to equation (11), it is possible to calculate the true rate constant of the oxidation reaction k_2, which is given in Table 2. By the dependence of the true rate constant of the oxidation reaction on temperature (Fig. 6), the true activation energy of the CO oxidation reaction on a manganese oxide catalyst was calculated, which was 61 kJ/mol. The same table shows the values of the overexposure factor of the rate constant of the CO oxidation reaction.

In the case of the process proceeding in the external diffusion region, the dependence of the reaction rate on the concentration of the initial substances will also correspond to the first order, regardless of the form of the kinetic equation of the chemical transformation proper. With this process mode, the dependence of the reaction rate on temperature will be determined only by the mass transfer coefficient, which usually corresponds to an activation energy of the order of 3–10 kJ/mol. In this case, the reaction rate is independent of the true activation energy, which is much less than the effective activation energy indicated in this work. In addition, the Carberry number (Ca) is the criterion for the reaction in the external diffusion region. If the process is controlled by external mass transfer, the following condition must be met:

$$Ca = \frac{r_{abs}}{k_f \cdot \left(\dfrac{6W}{d_p \cdot \rho_p} \right) \cdot C} > 0.05, \tag{13}$$

where r_{abs} – reaction rate, which is observed under the given conditions, mol/s; W – mass of the catalyst, g, ρ_p – bulk density of the catalyst, 2.37 g/cm^3; C – CO concentration, mol/m^3; k_f – mass transfer coefficient, m/s.
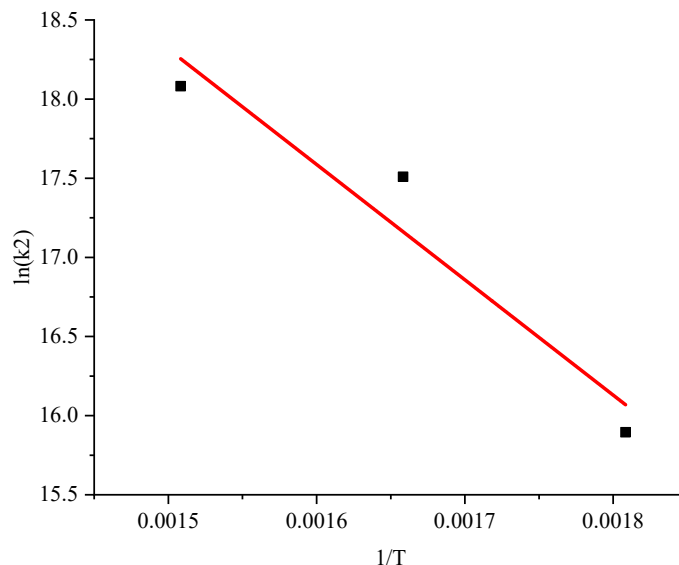
Equation	$y=a+b*x$
Plot	ln(k2)
Weight	No Weighting
Intercept	29.243973.34003±
Slope	−7285.763262008.6199±
Residual Sum of Squares	0.18158
Pearson's r	−0.96403
R-Square (COD)	0.92936
Adj. R-Square	0.85873

Fig. 6. Dependence of the rate constant k_2 on temperature

As shown above, the reaction rate observed under these conditions obeys the following relationship:

$$r_{abs} = k \cdot C. \tag{14}$$

The mass transfer coefficient k_f is found from the Sherwood criterion according to the equation:

$$k_f = \frac{Sh \cdot D}{d_p}, \tag{15}$$

where d_p – average particle diameter, m; in this work $d_p=5$ mm$=5 \cdot 10^{-3}$ m; Sh – Sherwood criterion; D – diffusion coefficient of the reagent, m^2/s.

In turn, the Sherwood criterion (also called the Nusselt criterion) is determined by the following formula:

$$Sh = 2 + 0.55 \cdot Re^{\frac{1}{2}} \cdot Sc^{\frac{1}{3}}, \tag{16}$$

where Sc – Schmidt criterion, Re – Reynolds criterion.

This formula is used in the case of molecular diffusion towards a spherical particle.

The Schmidt criterion is:

$$Sc = \frac{\nu}{D} = \frac{2.8 \cdot 10^{-5}}{0.3 \cdot 10^{-4}} = 0.103.$$

The Reynolds criterion is calculated according to the equation [39]:

$$Re = \frac{w_0 \cdot d_0}{\nu}, \qquad (17)$$

where $d_0 = \frac{4 \cdot (V - V_0)}{F}$ –equivalent diameter of the intergranular channels, m; w_0 – gas velocity in the channels, m/s; F – perimeter of all particles.

Let's find the perimeter of all particles by the formula $F = \frac{6 \cdot V_0}{d} = 0.38.$

To calculate the Reynolds criterion, let's take into account that the equivalent diameter $d_0 = 7.5 \cdot 10^{-4}$ m, the dynamic viscosity of the gas flow is $\mu = 2.8 \cdot 10^{-5}$ Pa·s, the calculated gas density is 0.56 kg/m^3.

Then

$$Re = \frac{w_0 \cdot d_0}{\nu} = \frac{0.025 \cdot 7.5 \cdot 10^{-4}}{\dfrac{2.8 \cdot 10^{-5}}{0.56}} = 0.37.$$

Sherwood criterion is:

$$Sh = 2 + 0.55 \cdot Re^{\frac{1}{2}} \cdot Sc^{\frac{1}{3}} = 2.16.$$

Mass transfer coefficient:

$$k_f = \frac{Sh \cdot D}{d_p} = 0.013 \text{ m/s.}$$

Carberry number is:

$$Ca = \frac{r_{abs}}{k_f \cdot F \cdot C} = \frac{0.39 \cdot 6 \cdot 10^{-5}}{0.015 \cdot 0.38 \cdot 0.45} = 0.011 < 0.05.$$

Since the Carberry number is less than 0.05, it can be argued that the process is not controlled by external mass transfer, that is, it is not limited by CO diffusion from the gas stream to the outer surface of the catalyst. Thus, the CO oxidation reaction when using a manganese oxide catalyst based on natural zeolite proceeds in the intradiffusion region.

7. Discussion of the research results of the catalytic oxidation process of carbon monoxide on a manganese oxide catalyst

Summing up the results of the studies, it can be noted that due to the preparation of the oxide-manganese catalyst based on zeolite, the necessary parameters of purification from carbon monoxide were achieved, supplementing the research results [18]. At the same time, a feature of the proposed solution is the use of the obtained catalyst under conditions of large volumes of flue gases and low concentrations of CO at electrode production enterprises.

The advantages of using the obtained oxide-metal catalytic system are its low cost and availability compared to the use of precious metals [10, 11]. In the case of using an inert material – zeolite, there is no increase in the loss of carbon material, while the deposition of manganese dioxide on the electrode sprinkles accelerates the processes of carbon oxidation, is an undesirable process [40].

A limitation of the use of the obtained catalyst is the impossibility of increasing the rate of the oxidation reaction of carbon monoxide, it is limited by the rate constant and the activation energy. In addition, when using natural zeolite as a carrier, it is impossible to bypass the internally diffuse inhibition of the CO oxidation process due to the influence of the porous system of the zeolite.

The use of the calculated kinetic parameters of this process in further studies will make it possible to calculate the catalytic CO oxidation reactor.

8. Conclusions

1. The modified MnO_2 clinoptilolite is obtained by using the available zeolite rock of the Sokyrnytsia deposit using a simple technique of mixing solutions containing separately Mn^{2+} and. MnO_2 is 1.8 %.

2. It is determined that the kinetics of the oxidation of carbon monoxide by atmospheric oxygen is described by a first-order equation. Based on the obtained characteristics of the catalyst, the kinetic parameters of the process are calculated, namely, the effective and true rate constants and the activation energy, equal to 31 kJ/mol. Using the criterion dependences, namely, the Carberry criterion, it is shown that the reaction is not limited by the diffusion of CO from the gas flow to the outer surface of the catalyst. It is shown that the transport of carbon monoxide molecules inside the catalyst granules proceeds in the Knudsen mode.

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