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OZONE DECOMPOSITION ON THE SURFACE OF METAL OXIDE CATALYST. PART 1

Keywords: ozone, catalyst, decomposition, synthesis, kinetics, mechanism.

The catalytic decomposition of ozone to molecular oxygen over catalytic mixture containing manganese, copper and nickel oxides was investigated in the present work. The catalytic activity was evaluated on the basis of the decomposition coefficient γ which is proportional to ozone decomposition rate and it has been already used in other studies for catalytic activity estimation. The reaction was studied in the presence of thermally modified catalytic samples operating at different temperatures and ozone flow rates. The catalyst changes were followed by kinetic methods and surface measurements. The catalyst mixture has shown high activity in ozone decomposition at wet and dry O₃/O₂ gas mixtures. The mechanism of catalytic ozone degradation was suggested.

Ключевые слова: озон, катализатор, разложение, синтез, кинетика, механизм.

В настоящей работе исследовано каталитическое разложение озона на молекулярный кислород в каталитической смеси, содержащей оксиды марганца, меди и никеля. Каталитическую активность оценивали на основе коэффициента разложения γ, который пропорционален скорости разложения озона и уже был использован в других исследованиях для оценки каталитической активности. Реакцию изучали в присутствии термически модифицированных каталитических образцов, работающих при различных температурах и расходах озона. Изменения катализатора исследованы кинетическими методами и измерениями поверхности. Смесь катализаторов показала высокую активность при разложении озона на влажных и сухих смесях газов O₃/O₂. Был предложен механизм каталитического разложения озона.

Introduction

Ozone finds wide application in such important industrial processes like: purification of drinking water, bleaching of textiles, oxidation of sulfurous gas, complete oxidation of exhaust gases from production of nitric acid and production of many organic compounds [1]. Ozone in the atmosphere protects the Earth's surface against UV- radiation, but on the ground level it is an air contaminant [1-3]. At this level ozone can be removed by adsorption, absorption, thermal and catalytic decomposition. The most effective catalysts for ozone decomposition are based on manganese oxide [4-7]. The main method for purification of waste gases containing residual ozone is the heterogeneous catalytic decomposition. Noble metals like Pt, Ag, Pd and transition metal oxides including Co, Cu, and Ni supported on γ-Al_2O_3, SiO_2 and TiO_2 also are effective catalysts in this reaction [8-14], as it can be mentioned for activated carbon fibers [15].

The decomposition of ozone is a thermodynamically favored process with a heat of reaction of $\Delta H_{0298}=-138$ kJ/mol and free energy of reaction *of* $\Delta G_{0298}=-163$ kJ/mol [16]. The ozone structure is resonance stabilized that is a reason for its relative stability. The coefficient of ozone decomposition γ was used in other studies for investigation of NiO addition influence over cement-containing catalysts activity [17] and for study of thermal treatment influence over oxide catalyst activity [18].

The aim of present study is to apply mixed metal oxide catalyst for ozone decomposition, to investigate its behavior at different conditions and to determine its composition and surface properties using different physical methods for analysis.

Experimental

The basic copper, manganese, nickel carbonates and clay-bearing cement are milled in advance, then carefully mixed, crushed and compressed under pressure 4 t/cm2. The resulting tablets were treated hydrothermally at temperature of 80°C for 6 hours, dried at 120°C for 6 hours and calcinated at 420°C for 6 hours. The metal oxide catalyst based on the mixture of manganese oxide (20 wt%), copper oxide (10 wt%), nickel oxide (30 wt%) and clay-bearing cement (40 wt%) was thermally modified at 500°C for 2 h and finally was applied in our investigation as catalyst for ozone decomposition in dry and water enriched gas flows. The catalyst was granulated and contained cylindrical grains with a diameter of about 5 mm and thickness of 3 mm.

The reactor for kinetic measurements was a glass tube (6×150 mm) filled in with 0.08-0.12 g of catalyst.

The kinetic measurements of ozone degradation were performed at flow rates ranging from 6.0 to 24 l h-1 and ozone concentration - from 1.0 to 1.2 mM. Ozone was generated by passing dry oxygen through a high-voltage silent-discharge ozone generator. At 15-20 kV was achieved ozone concentration about 1 mM. The inlet and outlet ozone concentrations were monitored using an UV absorption-type ozone analyzer at 300 nm.

The specific surface area of the catalyst (72 m2/g) was measured by N_2 adsorption-desorption isotherms at 77 K using BET method in a FlowSorb 2300 instrument (Micromeritics Instrument Corporation).

Results and Discussion

The catalytic activity was evaluated on the basis of the coefficient γ [19] that is proportional to ozone decomposition rate and to catalyst efficiency. It has been already used in other studies [17, 18]:

$$\gamma = \frac{4\omega}{V_t S} \ln \frac{[O_3]_0}{[O_3]}$$

where ω is the flow rate, Vt–specific heat rate of ozone molecules, S–geometrical surface of catalyst sample and $[O_3]_o$ and $[O_3]$ - inlet and outlet ozone concentrations, respectively.

In general, there is not exist precise estimation of γ by solving the diffusion-kinetic equation. This is possible in some special cases, for example to find γ using the approximate method of Frank-Kamenetsky (method of equally accessible surface) [20]. Equally accessible surface is that surface where in each section the molecules fall with equal probability. The rate of the chemical reaction on the surface is expressed by concentration of reacting molecules in the volume near the surface. For reactions of first order:

$$ws = \kappa s c s = \kappa c'$$

The parameters dimension is as follows: ws – (molecules/cm2.s), κs и κ – (s-1) и (cm/s), cs и c' – (molecules/cm2) и (molecules/cm3). It has been suggested that the molecular flow from volume to surface does not depend on the reaction rate, and with approximation it is defined of the equation:

$$j = \beta(c - c')$$

where: β - coefficient of mass transfer, having dimension as the rate constant k, equal to cm s-1, c and c'- concentration in the regions of the volume, where the flow is passing trough.

The distance between the surface and the region with concentration c' the ozone molecules pass without collisions with average specific heat rate vT. The number of hits on unit of surface per unit of time $z = vT \; c'$ and taking into account the definition of coefficient of ozone decomposition it has been found that:

$$\gamma = \frac{kc'}{z} = \frac{4k}{v_T}$$

Thus the coefficient γ is related to the rate constant k. Now we could consider the case when the surface, where the reaction takes place, is located in an unlimited volume of gas. In stationary conditions the molecular flow toward the surface is equal to the chemical reaction rate:

$$w_s = \frac{\beta k c}{k + \beta} = k_{eff} c$$

where c – concentration of actives molecules standing to great distance from the catalytic surface.

Thus the rate of reaction on the surface is expressed by the concentration in the volume and the effective rate constant that depends on the rate constant k and the coefficient of mass transfer β. Obviously:

$$\frac{1}{k_{eff}} = \frac{1}{k} + \frac{1}{\beta}$$

If $\beta \gg k$, then $c' = c$ and $keff = k$: the total reaction rate is limited by the no hits stage with constant k. In this case the reaction proceeds in the kinetic region. If $\beta \ll k$, $c' \ll c$ and $keff = \beta$ the reaction rate is determined by the rate of mass transfer and the reaction occurs in the diffusion region.

On the other hand [19], when operating in stationary conditions the relationship between the rate constant of the reaction of heterogeneous ozone decomposition and the coefficient of ozone decomposition γ is given by the formula:

$$\gamma = \frac{4k_{het}V}{Sv_T}$$

where: V – volume of reactor, S – geometric surface of catalyst, vT – specific heat rate of ozone molecules.

Taking into account the dependence of the gas flow rate from the reactor radius, and considering the concentration of active ozone molecules and the reaction time of ozone decomposition, after complex mathematical transformations the latter formula passes into the expression:

$$\gamma = \frac{4\omega}{Sv_T} \ln \frac{[O_3]_0}{[O_3]}$$

where: ω – gas flow rate, $[O_3]_o$ и $[O_3]$ – inlet and outlet ozone concentrations.

This formula is applicable for tubular type reactor, when the catalyst is supported as thin layer on the walls in the inner side of the tube. The expression is also convenient for calculation of catalytic activity in the case when the reactor is filled with granulated catalytic samples having specific geometric surface. Therefore, this method has been used by us for calculation of the catalysts activity in the process of ozone decomposition.

On Fig. 1 is done how is changing the catalytic activity of the cement containing catalyst when the calcination temperature of the samples is different. All the experiments were made in dry conditions and ozone flow rate of 6 l h-1. The MnOx/CuO/NiO catalyst has catalytic activity in ozone decomposition that does not change dramatically with calcination temperatures increasing.
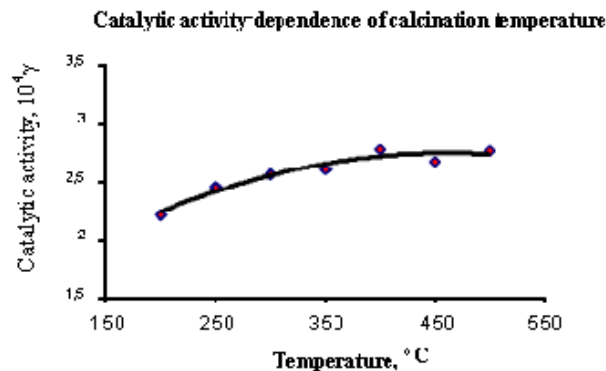

Catalytic activity dependence of calcination temperature

Fig. 1 - Dependence of the catalytic activity in ozone decomposition on calcination temperature

However we can see that the catalyst is more active when the calcination temperature is in the range 400-500°C. On Fig.2 are shown the changes of γ at two different flow rates in temperature range of 258-323 K. The calculated activation energy is 5 kJ/mol. In these experiments the reactor was kept up at constant temperature enough time to get the necessary value. The duration of the decomposition reaction and the reaction time were much smaller than the time of cooling or heating the reactor. That means that the temperature inside the reactor was maintained constant during the measurement of ozone decomposition rate. The

difference between the values of γ at different flow rates is due to the low loading of catalyst. The low values of *Ea* are directly connected with the fact that limited stage of reaction is the adsorption of ozone on catalytic surface.
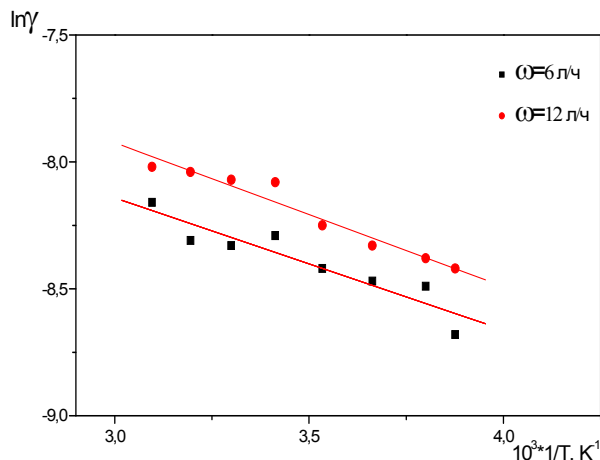

Fig. 2 - Dependence of the catalytic activity in ozone decomposition on reaction temperature at two different flow rates

On Fig. 3 are presented the changes of γ depending on temperature and humidity of the gas flow. The measured activation energy was also 5 kJ/mol. It was found out that the humidity of the gas flow decreases the catalytic activity by 10%, but the catalyst does not disturb its stability in the time of ozonation.
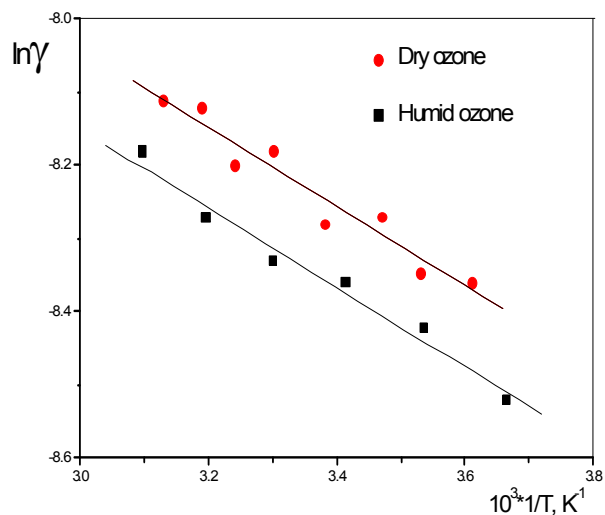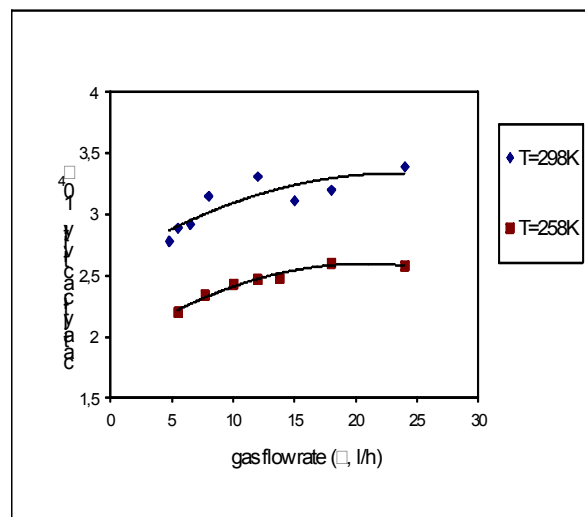

Fig. 3 - Temperature dependence of catalytic activity at dry and humid conditions, temperature range 273-323 K, ozone flow rate 8 l h-1

Figure 4a presents the changes of γ at different flow rates at two temperatures−258 and 298 K. It can be seen that γ is proportional to the flow rate at both temperatures. The coefficient of decomposition depends on temperature, but at 258 K the steady state of the curve is reached faster. The obtained values of γ are close to the coefficients reported in literature [17]. Therefore, it could be concluded that at low values of gas flow rate, a reason for the dependence of the catalytic activity from gas flow rate is the influence of

the external diffusion over the kinetics of the process of heterogeneous catalytic ozone decomposition on catalyst surface, i.e. the process takes place mainly in the outer diffusion region or in the transition diffusion−kinetic region.

On Fig. 4b is shown the dependence of γ on gas flow humidity at 298 K. The values of γ decrease with increasing the humidity, but nevertheless these values remain relatively high. The effect of water vapor may be result of thin film formation on the catalytic surface that makes the diffusion of ozone to catalytic centers more difficult. The humidity of O3/O2 gas flow was measured to be 50%.

a
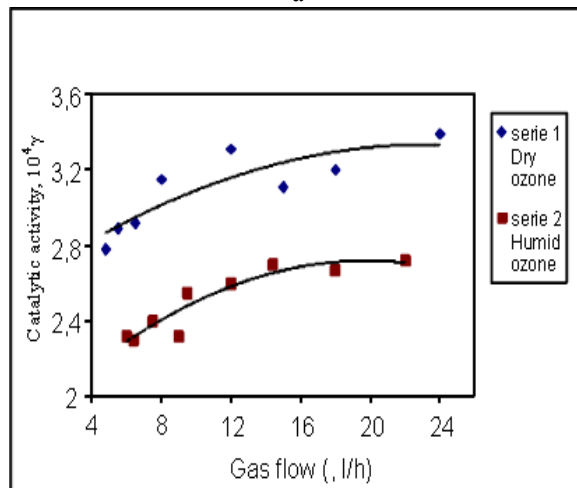
b

**Fig. 4 - Flow rate dependence of catalytic activity at :
a - 258 and 298 K, ozone flow rate range 5-25 l h-1,
b - dry and humid conditions, ozone flow rate range 4-26 l h-1**

Conclusions

1. The catalyst based on MnOx/CuO/NiO has high efficiency in the reaction of ozone decomposition both at dry and wet conditions.
2. The catalyst work is stable and its activity does not change dramatically by varying temperature, O_3/O_2 flow rate and humidity.

References

1. S. Rakovsky, G. Zaikov, "Kinetic and Mechanism of Ozone Reactions with Organic and Polymeric Compounds in Liquid Phase", monograph (second edition), Nova Sci. Publ., Inc. New York, 1-340, (2007).
2. C. Heisig, W. Zhang, S. T. Oyama, Decomposition of Ozone using Carbon Supported Metal Oxide Catalysts, Appl. Catal. B: Environ., 14, 117 (1997).
3. T. L. Rakitskaya, A. Yu. Bandurko, A. A. Ennan, V. Ya Paina., A. S. Rakitskiy, Carbon-fibrous-material-supported Base Catalysts of Ozone Decomposition, Micro. Meso. Mater., 43, 153 (2001).
4. R. Radhakrishnan, S. T. Oyama, Y. Ohminami, K. Asakura: Structure of MnOx/Al2O3 Catalyst: A Study Using EXAFS, In Situ Laser Raman spectroscopy and Ab Initio Calculations, J. Phys. Chem., 105, 9067 (2001).
5. R. Radhakrishnan, S. T. Oyama, J. Chen, A. Asakura, Electron Transfer Effects in Ozone Decomposition on Supported Manganese Oxide, J. Phys. Chem. B, 105 (19), 4245 (2001).
6. W. Li, G. V. Gibbs, S. T. Oyama, Mechanism of Ozone Decomposition on Manganese Oxide: 1. In situ Laser Raman Spectroscopy and ab initio Molecular Orbital Calculations. J. Am. Chem. Soc., 120, 9041 (1998).
7. W. Li, S. T. Oyama, The Mechanism of Ozone Decomposition on Manganese Oxide: 2. Steady-state and Transient Kinetic Studies. J. Am. Chem. Soc., 120, 9047 (1998).
8. B. Dhandapani, S. T. Oyama, Gas Phase Ozone Decomposition Catalysts, J. Appl. Catal. B: Environmental, 11, 129 (1997).
9. S. T. Oyama, Chemical and Catalytic Properties of Ozone, Catal. Rev. Sci. Eng., 42, 279 (2000).
10. H. Einaga, S. Futamura, Comparative Study on the Catalytic Activities of Alumina-supported Metal Oxides for Oxidation of Benzene and Cyclohexane with Ozone, React. Kinet. Catal. Lett., 81, 121 (2004).
11. S. Tong, W. Liu, W. Leng, Q. Zhang, Characteristics of MnO2 Catalytic Ozonation of Sulfosalicylic Acid Propionic Acid in Water. Chemosphere, 50, 1359 (2003).
12. W. Li, S. T. Oyama, Absolute Determination of Reaction Mechanisms by in situ Measurements of Reaction Intermediates, Top. Catal., 8, 75 (1999).
13. P. Konova, M. Stoyanova, A. Naydenov, St. Christoskova, D. Mehandjiev, Catalytic oxidation of VOCs and CO by ozone over alumina supported cobalt oxide, J. Appl. Catal. A: Gen. 298, 109 (2006).
14. Stoyanova M., P. Konova, P. Nikolov, A. Naydenov, ST. Christoskova, D. Mehandjiev, Alumina-supported nickel oxide for ozone decomposition and catalytic ozonation of CO and VOCs, Chem. Eng. Journal, 122, 41 (2006).
15. C. Subrahmanyam, D. A. Bulushev, L. Kiwi-Minsker, Dynamic Behaviour of Activated Carbon Catalysts during Ozone Decomposition at Room Temperature, J. Appl. Catal. B: Environmental, 61, 98 (2005).
16. R. H. Perry, D. Green, Perry's Chemical Engineer's Handbook, McGraw-Hill, New York, 1989, 3-147.
17. I. V. Martinov, S. N. Tkachenko, V. I. Demidyuk, G. V. Egorova, V. V. Lunin, NiO Addition Influence over Cement-containing Catalysts Activity in Ozone Decomposition, J. of Moscow Univ. (in Rus.), Ser. 2, Chemistry, 40, 355 (1999).
18. A. V. Zavadskii, S. G. Kireev, V. M. Muhin, S. N. Tkachenko, V. V. Chebkin, V. N. Klushin, D. E. Teplyakov, Thermal Treatment Influence over Hopcalite Activity in Ozone Decomposition, J. of Phys. Chem. (in Rus.), 76, 2278 (2002).
19. V. V. Lunin, M. P. Popovich, S. N. Tkachenko, Physical Chemistry of Ozone (in Rus.), Moscow University Publ. House, Moscow, 1998, 377-444.
20. Frank-Kamenetskii D. A., Diffusion and heat transfer in chemikal kinetics (in Rus.), M., (1987).

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