



ACTIVITY OF Pd-MnO_x/CORDIERITE (Mg,Fe)₂Al₄Si₅O₁₈) CATALYST FOR CARBON MONOXIDE OXIDATION

V. Bakhtadze,^{*[a]} V. Mosidze,^[a] T. Machaladze,^[a] N. Kharabadze,^[a]
D. Lochoshvili,^[a] M. Pajishvili,^[a] R. Janjgava,^[a] and N. Mdivani^[a]

Keywords: CO oxidation; manganese oxides; aluminosilicate blocks, promoting, active surface.

Physical-chemical characteristics and activity of the Pd-MnO_x-catalyst, deposited on cordierite carrier, was studied in the CO oxidation reaction. The results obtained on the catalyst Pd-MnO_x-Al-Si showed the similar activity in the CO oxidation reaction as in the case of the Pd-MnO_x/CaO.2Al₂O₃ catalyst.

*Corresponding Authors

Fax: +995 32 2301430

E-Mail: vbakhtkat@yahoo.com

[a] Iv. Javakhishvili Tbilisi State University, R. Agladze Institute of Inorganic Chemistry and Electrochemistry, Georgia, 0186, Tbilisi, Mindeli str. 11.

INTRODUCTION

Manganese oxides are well-known as the highly efficient catalysts of deep oxidation. The catalysts, prepared on their basis, are used in the processes of gas purification and other important chemical-technological processes.¹⁻³ Manganese oxides, together with copper and cobalt oxides, are considered as possible replacement of platinum metals in automobile catalysts for purification of exhaust gases from CO, CH_x, NO_x.^{4,5} The catalysts, obtained by their combination with the oxides of some metals of variable valency and with the metals of platinum group (Pt, Pd) or Ag, exhibit the mutual-promoting effect in the oxidation reaction.^{6,7} Simultaneously they retain the high activity after calcination over prolonged period at high temperatures. By the use, in the technology of the catalysts of aluminium oxide, of the carrier, preliminary modified by calcium oxide, the Mn-Pd catalyst was elaborated available for oxidation of CO and hydrocarbons of spent gases of the motor transport.^{8,9} The mixed Mn-Pd catalysts (MPC-1), containing the minimum amount of palladium (up to 0.05 wt. %), was successfully tested in the systems for purification of spent gases of petrol engines and diesel locomotives operating on diesel fuel.¹⁰

Comparison of texture characteristics and activity of the Mn-Pd catalysts on calcium aluminate carrier (CaO.2Al₂O₃, CA₂) of ShN-2M mark in the reaction of CO oxidation, the sample with 4.0÷5.0 wt. % of Mn+0.05 wt. % of Pd content was proved to be the most active.⁹ On the carrier, apart from the phase of β-MnO₂, the formation of the phase β-Mn₂O₃ is observed in nearly equal proportion. The addition of palladium to the oxide-manganese catalyst leads to the formation of new centers on the surface which are active in the reaction of CO oxidation. The particles of palladium are dispersed in the matrix of MnO₂, they don't penetrate into the depth of the pores.^{11,12} In accordance with Ref.¹³ the

addition of palladium and manganese to γ-Al₂O₃, hydrothermally treated even at the stage of impregnation and calcination of the catalyst, leads to the interaction between active components and carrier. As a result the variation of valence state of the part of Mn²⁺ and formation of palladium complexes with γ-Al₂O₃ takes place. Moreover, the active components interact with each other which leads to the shift of the equilibrium Mn³⁺+e⁻↔Mn²⁺ on the surface in the direction of the formation of the ions of divalent manganese and to the growth of palladium dispersity.

For preparation of automobile catalysts, the aluminosilicate blocks with cellular structure¹⁴ are intensively developed. Their specific surfaces, as a rule, don't exceed 1-2 m² g⁻¹. The results of manganese and palladium deposition on the cordierite aluminosilicate blocks (Mg,Fe)₂Al₄Si₅O₁₈) are presented and the results of the study of their activity and physical-chemical properties in the reaction of CO-oxidation are given.

EXPERIMENTAL PART

For laboratory testing, the manganese oxides used were deposited on plates and ground particles (Ø1,5–2.0 mm) of cordierite blocks via impregnation with aqueous solution of manganese(II) nitrate at various concentration of impregnating solution, changing the temperature and duration of impregnation. The Pd-MnO_x/cordierite catalysts were prepared by impregnation of the carriers prepared with aqueous PdCl₂ solution. The samples prepared in this way were dried at 80-100 °C then calcined in an electric furnace at 350-450 °C for 2 h. The formed composites were treated by 4-5 % solution of aqueous NH₄OH, then dried and calcined at 400 °C for 2 h.

Activity of the catalyst samples in the CO oxidation reaction was determined in a flowing plant at laboratory scale. Thermal analysis was performed on a STA-2500 device. ISM 65 LV scanning electron microscope was used to study the morphology of the catalyst surface. Specific surfaces of the samples were determined by application of the automated system ASAP 2020.

RESULTS AND DISCUSSION

SEM pictures of the surface components of catalyst Pd-MnO_x/cordierite at 1 μm of the layer depth could be seen in Fig. 1. The oxides of Mn and Pd are distributed uniformly on the cordierite surface. The dispersity of manganese oxide particles comprises nearly 100 nm. X-Ray phase and thermal analyses of the catalyst showed the presence of β-MnO₂ and β-Mn₂O₃. Specific surface area of the Pd-MnO_x/cordierite comprises 3.0–5.0 m² g⁻¹ while the specific surface of initial cordierite doesn't exceed the value of 0.5–0.7 m² g⁻¹. The activities of the catalyst samples before and after their treatment with aqueous ammonia in the CO oxidation reaction are showed in Fig. 2.

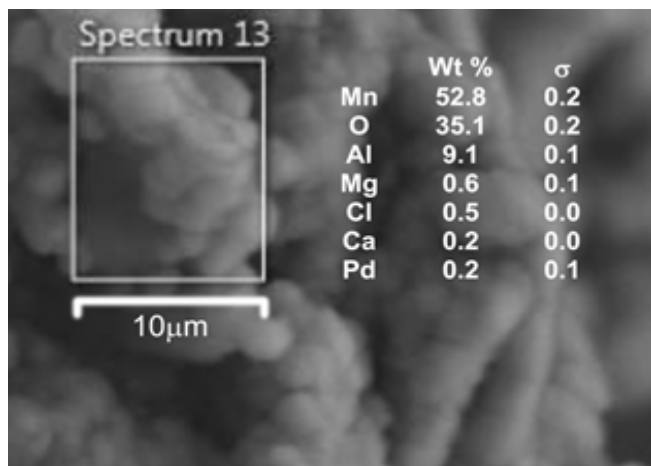


Figure 1. Surface distribution of active components in the catalyst Pd-MnO_x/cordierite.

Before treatment by aqueous ammonia, the CO oxidation reaction on the catalyst comprised 98-100% in the temperature range from 205 °C to 210 °C. After treatment by aqueous ammonia, the same degree of CO-oxidation could be attained even at 175-180 °C. Similar promotion effect of aqueous ammonia treatment of Pd/CA₂ was observed.¹⁵

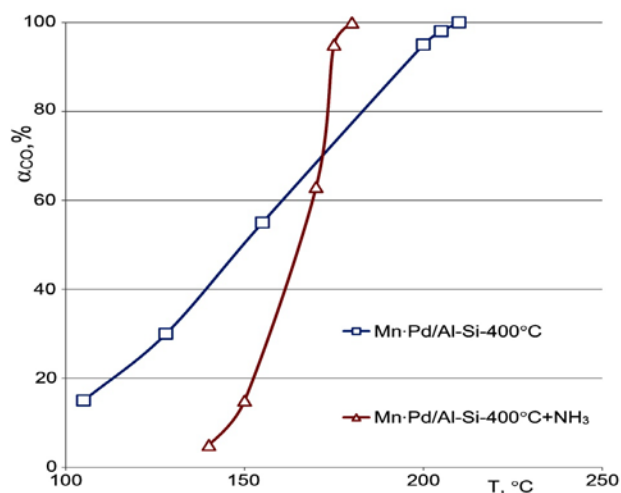
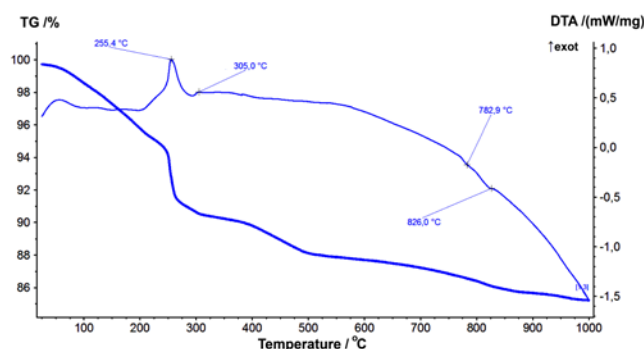
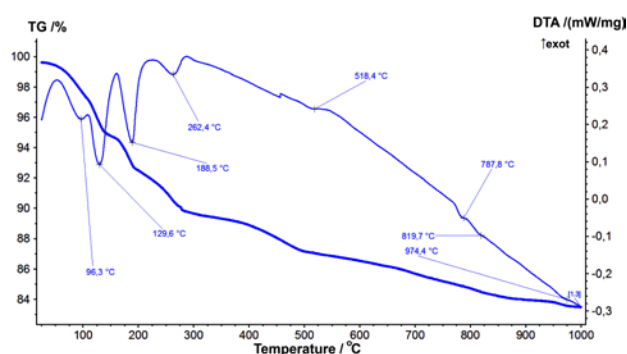


Figure 2. Dependence of Pd-MnO_x/cordierite catalyst activity with and without aqueous ammonia treatment on the temperature in the CO oxidation ($G_{\text{cat}} = 1.0$ g, composition of reaction mixture: 1.0 vol. % of CO+air, volume rate of the gas $W = 15.10^3$ h⁻¹).

The treatment of the catalyst by ammonia water can lead to the formation of ammine-palladium complexes which can decompose with formation of catalytically active palladium black.^{16,17}



a)



b)

Figure 3. Curves of thermal analyses (DTA and TG) of the catalyst Pd-MnO_x/cordierite treated with aqueous ammonia (a) and without treatment of aqueous ammonia (b)

Comparison of the decomposition curves of Pd-MnO_x/cordierite catalyst with and without treatment by aqueous ammonia, shows the exoeffect on the DTA curve at the temperatures: 255 and 305 °C which is indicative of the phase decomposition. This can only be observed in the aqueous ammonia treated sample.

CONCLUSIONS

Activity of the Pd-MnO_x/cordierite catalyst is similar with the activity of Pd-MnO_x/CaO.2Al₂O₃ catalyts in the CO oxidation reaction. Treatment of catalyst with aqueous ammonia has positive influence on the completion of the active surface species of the catalyst and reduces the temperature needs for total oxidation of carbon monoxide.

ACKNOWLEDGEMENTS

This work was supported by Shota Rustaveli National Science Foundation of Georgia (SRNSFG) (Grant № 18-750)

REFERENCES

- ¹Ioseliani, D., Bakhtadze, V., Investigation in the field of heterogenic catalysis, *Khim. Khim. Technol. Akad. Nauk. Gruzii, Sbornik Trudov, Metsniereba*, Tbilisi, **2001**, 120-133.
- ²Bakhtadze, V., Mosidze, V., Janjgava, R., Chochishvili, N., Dzanashvili, D., Kharabadze, N., Pajishvili, M. Preparation of efficient catalysts – adsorbents for cleaning gases from sulfur compounds, *Eur. Chem. Bull.*, **2014**, *3(1)*, 46-49. DOI: <http://dx.doi.org/10.17628/ecb.2014.3.46-49>
- ³Popova, N., Dosumov, K., Zheksenbaeva, Z., Komashko, L., Grigor'eva, V., Sass, A., and Salakova, R., Thermally stable multicomponent manganese catalyst for the deep oxidation of methane to CO₂, *Kinet. Catal.*, **2006**, *47(6)*, 935-944. <https://doi.org/10.1134/S0023158406060140>
- ⁴Tsikoza, L., Ismagilov, Z., Ushakov, V., Spojakina, V., and Ovsyanikova, I., Fuel Combustion Reactions and Catalysts: XXI. Synthesis and Characterization of Modified Mn–Al–O Catalysts for High-Temperature Oxidation, *Kinet. Catal.*, **2003**, *44(6)*, 806-812. <https://doi.org/10.1023/B:KICA.0000009058.43038.94>
- ⁵Decarne, C., Bokova, M., Abi-Aad, E., Pryakhin, A., Lunin, V., and Aboukais, A., Effects of Ozone on Catalytic and Physicochemical Properties of Cu–Ce–Al–O Catalysts for Soot Combustion, *Kinet. Catal.*, **2003**, *44(5)*, 677-681. <https://doi.org/10.1023/A:1026102408243>
- ⁶Shigapov, A., Dubkov, A., Ukropec, R., Carberry, B., Graham, G., Chun, W., and McCabe, R., Development of PGM-Free Catalysts for Automotive Applications, *Kinet. Catal.*, **2008**, *49(5)*, 756-764. <https://doi.org/10.1134/S0023158408050224>
- ⁷Bakhtadze, V., Mosidze, V., ICESI 2019 International Conference on Engineering, Science and Industrial Applications. Proc., 22-24 August, 2019, Tokyo University of Science, Tokyo, Japan.
- ⁸Bakhtadze, V., Mosidze, V., Kartvelishvili, D., Janjgava, R., Kharabadze, N., *Katal. Promysl.*, Modification of γ -, χ -Al₂O₃ alumina support by calcium oxide for the preparation of oxidation of CO and hydrocarbons commercial catalysts, *Katal. Promysl.*, **2012**, *2*, 56-63.
- ⁹Bakhtadze, V., Kharabadze, N., Moroz, E., Supported Modified Mn-Pd Catalysts of the MPK-1 Series for CO Oxidation *Katal. Promysl.*, **2007**, *3*, 115-120
- ¹⁰Bakhtadze, V., Mosidze, V., Kharabadze, N., Chochishvili, N., Fajishvili, M., Janjgava, R., Effect of SO₂ on the activity and physical-chemical properties of Mn-Pd catalyst for CO oxidation, *Slovak Int. Sci. J.*, **2017**, *1(7)*, 14-17. <https://doi.org/10.5089/9781475587937.002>
- ¹¹Bakhtadze, V., Mosidze, V., Kharabadze, N., Dzanashvili, D., Janjgava, R., Fajishvili, M., Chochishvili, N., Dispersity and activity of palladium in CO oxidation catalysts, *Khim. Zh. Gruzii*, **2014**, *14(1)*, 100-103.
- ¹²Ivanova, A., Slavinskaya, E., Stonkus, O., Zaikovskii, V., Danilova, I., Gulyaev, R., Bulavchenko, O., Tsibulya, S., Boronin, A., Low-Temperature Oxidation of Carbon Monoxide over (Mn_{1-x}M_x)O₂ (M=Co, Pd) Catalysts, *Kinet. Catal.*, **2013**, *54(1)*, 81-94. <https://doi.org/10.1134/S0023158413010084>
- ¹³Savonkina, M., Kupcha, L., Yegizarov, Yu., Potapovich, A., Zhizhenko, G., Zaretsky, M., Physico-chemical study of palladium-manganese catalysts based on aluminum oxide, *Vestnik Akad. Navuk BSSR, ser. Khim.*, **1986**(3), 58-62.
- ¹⁴Farrauto, R., Heck, R., Honeycomb Catalysts: Present and Future, *Kinet. Catal.*, **1998**, *39(5)*, 646-652..
- ¹⁵Bakhtadze, V., Mosidze, V., Kharabadze, N., Dzanashvili, D., Janjgava, R., Fajishvili, M., Chochishvili, N. Effect of Pd concentration and reductants on the activity of CO oxidation catalysts, *Khim. Zh. Gruzii*, **2015**, *15(1)*, 66-68.
- ¹⁶Platinum metals., *A Guide to Preparative Inorganic Chemistry*, Edited by G. Brauer., Izdatinlit, **1956**, 723-726.
- ¹⁷Chernyaev, I., About diamminitrochloropalladium [Pd(NH₃)₂NO₂Cl], *Complex compounds of transition metals, Selected Works*, Moscow, Science, **1973**, 177-184.

Received: 01.12.2019.

Accepted: 04.03.2020.