UDC 542.924:544.47

T. Batakliev, S. Rakovsky, G. Zaikov,
V. Georgiev, M. Anachkov, Kh. Abzaldinov

CATALYTIC ACTIVITY OF TITANIA-SUPPORTED MANGANESE OXIDE CATALYST IN OZONE DECOMPOSITION. PART 2

Keywords: ozone, titania, manganese oxide, decomposition, activation energy.

A titania-supported Mn oxide system made by incipient wetness impregnation method was investigated in the reaction of heterogeneous catalytic decomposition of ozone. The catalyst was characterized by TPR, XRD, AFM, FT-IR spectroscopy and surface measurements. A catalytic cycle of ozone decomposition on MnOx/TiO2 catalyst was proposed.

Ключевые слова: озон, диоксид титана, оксид марганца, разложения, энергия активации.

В реакции гетерогенного каталитического разложения озона исследована система оксида марганца на титановом носителе, полученная методом пропитки до начальной влажности. Катализатор охарактеризован методами температурно-программируемого восстановления (ТПВ), рентгеноструктурного анализа (РСА), атомно-силовой микроскопии (АСМ), ИК-Фурье спектроскопии (ИКС) и измерения поверхностей. Предложен каталитический цикл разложения озона на катализаторе MnOx/TiO_2.

Introduction

Ozone is widely used in the industrial and environmental processes such as semiconductor manufacturing, deodorization, disinfection and water treatment [1]. The residual ozone must be removed because on the ground level it is an air contaminant [2]. Ozone is highly toxic in concentrations greater than 0.1 mg/m3 and it could harm the human health [3]. An effective method for purification of waste gases containing ozone is the heterogeneous catalytic decomposition [4]. Manganese oxide catalysts are of interest due to their applicability to catalytic reactions such as selective catalytic reduction of NO_x with ammonia [5], CO oxidation [6] and combustion of organic compounds [7] in gaseous phase and selective oxidation of organic compounds [8] in liquid phase. Manganese oxide catalysts are also useful for the decomposition of ozone in gas streams [9]. Titanium dioxide is already known as catalyst support [10, 11] and also has been used as catalyst for several chemical reactions including decomposition of aqueous ozone [12, 13], photocatalytic decomposition of ozone [14] and catalytic ozonation of naproxen and carbamazepine [15]. X-ray diffraction (XRD) [16], IR spectroscopy [17], temperature programmed reduction (TPR) [18] and atomic force microscopy (AFM) [19] are popular techniques that have been used to characterize bulk, modified and supported manganese oxides.

The aim of present study is to investigate the catalytic activity of titania-supported manganese oxide system during heterogeneous catalytic decomposition of ozoneand to determine its composition and surface properties using different physical methods for analysis.

Experimental

Manganese oxide catalysts (6, 8 and 10 wt%) were prepared using aqueous solutions of manganese acetate ($Mn(CH_3.COO)_2.4H_2O$, BDH Chemicals>99.99%). For support it has been used TiO_2 (Degussa, Aeroxid P25). The synthesized catalytic samples contained 5.5, 7.4 и 9.3% molar percentages respectively on the TiO_2 support. These values were calculated on the basisof assumption that MnO_2 was formed on the support surface. At every synthesis the support was impregnated with precursor solution to the point of incipient wetness determined in separate measurements. After impregnation, all samples were heated at 393 K for 6 hours and calcinated at 773 K for 6 hours to produce MnO_x/TiO_2.

The catalysts were granulated and contained cylindrical grains with diameter of about 9 mm and thickness of 3 mm.

IR studies were performed in the transmittance mode using a Nicolet 6700 FT-IR spectrometer (Thermo Electron Corporation). A mixture of KBr and manganese oxide catalyst (100:1) was milled in an agate mortar manually before the preparation of pellets. The spectra were obtained by averaging 50 scans with 0.4 cm^{-1} resolution.

A typical TPR experiment is done by passing a H_2 stream over a catalyst while it is heated linearly and monitoring the consumption of H_2 with a thermal conductivity detector or mass spectrometer. In our study a 10% H_2/Ar mixture was used and the consumption of H_2 was monitored using a thermal conductivity detector. A linear heating rate of 0.17 K s^{-1} was used for the experiment.

X-ray diffraction (XRD) analysis was used to determine the crystalline metal oxide phases for the supported catalyst. A Bruker D8 Advance powder diffractometer with Cu $K\alpha$ radiation source and SolX detector was used. The samples were scanned from 2θ angles of 10° to 80° at a rate of 0.04° s^{-1}. The X-ray power operated with a current of 40 mA and a voltage of 45 kV.

FT-IR studies were performed in the transmittance mode using a Nicolet 6700 FT-IR spectrometer (Thermo Electron Corporation). A mixture of KBr and manganese oxide catalyst (100:1) was milled in an agate mortar manually before the preparation of pellets.

Atomic force microscopy (AFM) measurement was carried on Veeco Multimode scanning probe microscope instrument in taping mode.

Results and Discussion

The X-ray analysis results for the investigated catalyst are shown in Fig. 1. The diffractogram for the MnOx/TiO_2 sample showed peaks with large intensities at different values of 2θ angle. The peaks at 23°, 33°, 45.1° and 65.6° correspond to manganese oxide phase Mn_2O_3. The diffraction features at 27.5°, 35.9°, 41.2 and 54.4° are indicative of rutile TiO_2. The catalyst sample at 25.3° is due to another mineral form of TiO_2-anatase.

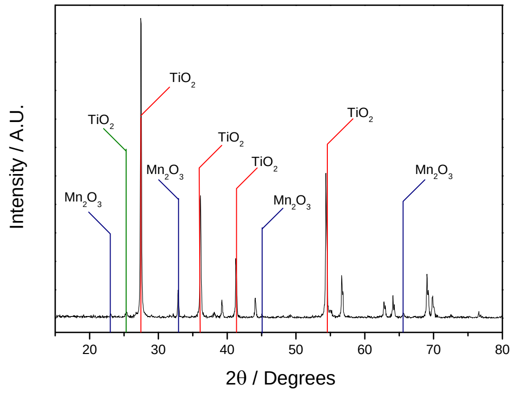


Fig. 1 - X-ray diffraction of MnOx/TiO2 catalyst

The reducibility of the supported manganese oxide catalyst and the influence of the support over the catalyst were found by TPR experiment. The peak temperatures of reduction in Fig. 2 are 444 K, 596 K and 745 K for the supported catalyst and 824 K for the pure support. This shows that MnOx is well dispersed on the support and the oxide-support interaction is moderate.

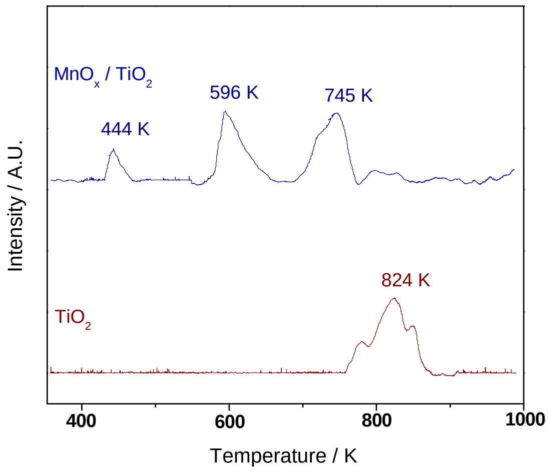
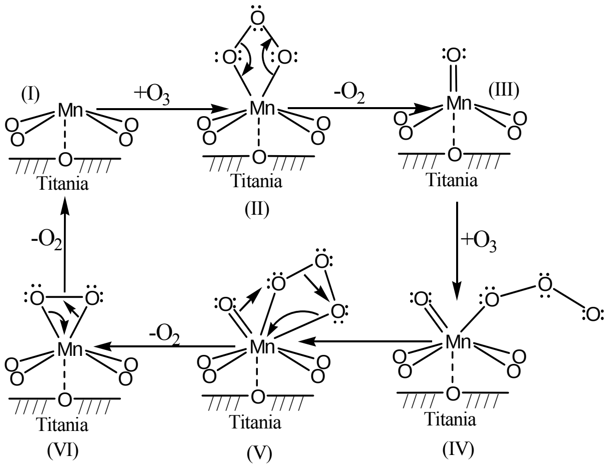


Fig. 2 - TPR spectra of MnOx/TiO2 catalyst and pure TiO2 support

FT-IR spectra of the manganese-oxide catalyst before ozone decomposition (a) and after ozone decomposition (b) are presented in Fig. 3. The spectra are almost identical, showing that the catalyst structure is not altered during the catalytic reaction. The broad adsorption band at 3446 cm^{-1} appears from the stretching vibration of hydrogen bonded hydroxyl groups [20]. The adsorption band at 1628 cm^{-1} is due to the vibrations of water molecules [21]. The intensive band at 650 cm^{-1} appears at higher manganese concentrations and, in accordance with literature, can be attributed to well-defined metal oxide phase [16].

A catalytic cycle of ozone decomposition on MnOx/TiO2 catalyst is proposed in scheme.



This cycle is based on a probable mechanism of catalytic ozone decomposition described notably in paper [10] and also in several articles [22, 23]. The transformation of the manganese site from species (I) to (III) is indicative of an oxidation reaction. The structure numbered (II) is likely a transition state for this first step in the ozone decomposition process. The transformation of species (III) to species (VI) in the proposed catalytic cycle is represented by the redox reaction: $O_3 + Mn^{4+} + O_2- \rightarrow O_2 + O_2^{2-} + Mn^{4+}$. The transition states for this reaction are species (IV) and (V) presented in the catalytic cycle. Finally, the transformation of species (VI) to (I) in the catalytic cycle is a desorption step and the redox reaction for this step is: $Mn^{4+} + O_2^{2-} \rightarrow O_2 + Mn^{2+}$.

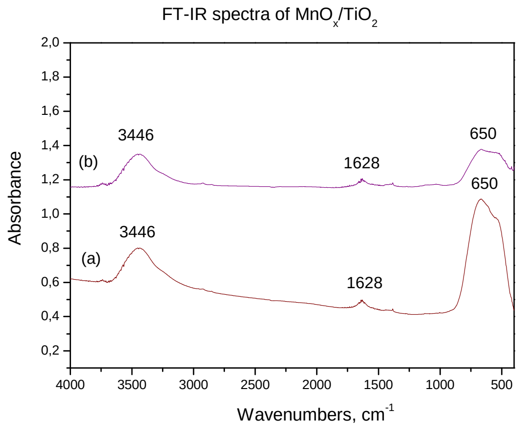
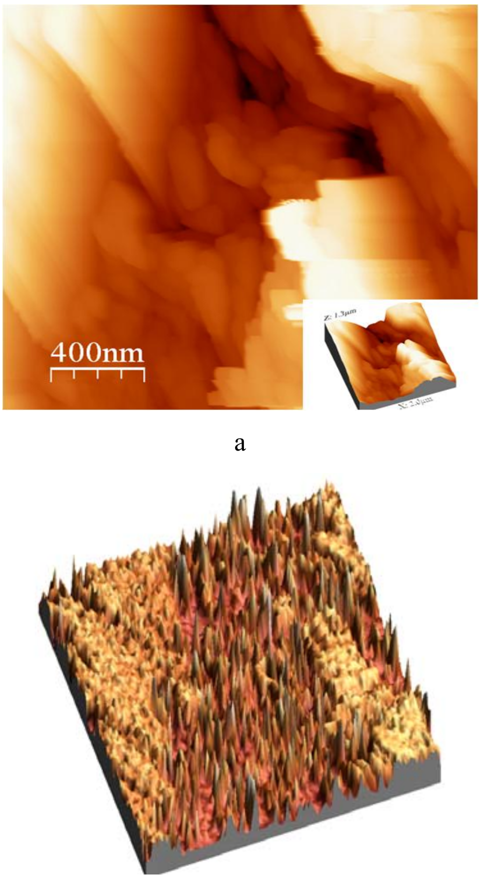


Fig. 3 - FT-IR spectra of MnOx/TiO_2 catalyst

In Figures 4A and 4B we show 2D and 3D AFM images of the 8 wt% MnOx/TiO_2 catalyst thermally treated at 773 K for 2 hours in air atmosphere. The AFM results presented here give an estimation of the catalyst surface roughness. The images demonstrate the validity of our preparation method for the synthesis of heterogeneous catalysts for ozone decomposition with advanced pores and active sites distribution. Surface roughness increases the effective surface area of the material. Fig. 4A reveals the morphology of the modified titanium dioxide obtained by the AFM. The sample is composed of tightly packed regular particles, stacked in a very rough catalytic surface.



a

b

Fig. 4 - AFM image of 8 wt% MnOx/TiO_2 catalyst: a) 2D, b) 3D

Conclusions

1. The TPR spectra show that manganese oxide is well dispersed on the support and the oxide–support interaction is moderate.

2. The metal oxide phases in catalyst are identified using XRD analysis and the stability of the catalyst structure is proved with FT–IR analysis.

3. The proposed catalytic cycle reveals the important role of the peroxide species in ozone decomposition process.

4. Studies of atomic force microscopy (AFM) evidenced strong influence of preparation methods and pre-treatment conditions on the structural and catalytic properties of the samples.

References

1. S. Rakovsky, G. Zaikov, Kinetic and Mechanism of Ozone Reactions with Organic and Polymeric Compounds in Liquid Phase, monograph (second edition), Nova Science Publishers Inc., New York, 2007, pp. 1-340.
2. S. T. Oyama, Chemical and Catalytic Properties of Ozone, Catal. Rev. Sci. Eng., 42, 279 (2000).
3. T. L. Brown, H. E. Lemay JR., B. E. Bursten, J. R. Burdge [1977], "22", in Nicole Folchetti Chemistry: The Central Science, 9th Edition (in English), Pearson Education, 2003, pp. 882-883.
4. B. Dhandapani, S. T. Oyama, Gas Phase Ozone Decomposition Catalysts, J. Appl. Catal. B: Environmental, 11, 129 (1997).
5. W. S. Kijlstra, D. S. Brands, E. K. Poels, A. Bliek, Mechanism of the Selective Catalytic Reduction of NO by NH3 over MnOx/Al2O3, J. Catal., 171, 208 (1997).
6. J. Ma, G. K. Chuah, S. Jaenicke, R. Gopalakrishnan, K. L. Tan, Catalysis by manganese oxide monolayers part 1: alumina and magnesia supports, Ber.Bunsenges. Phys. Chem., 100,585 (1995).
7. L. S. Puckhaber, H. Cheung, D. L. Cocke, A. CLearfield: Reactivity of copper manganese oxides, Solid State Ionics, 32/33,206 (1989).
8. R. Ghosh, Y.–C. Son, V. D. Makwana, S. L. Suib, Liquid-phase epoxidation of olefins by manganese oxide octahedral molecular sieves, Journal of Catalysis, 224,288 (2004).
9. P. Hunter, S.T. Oyama, Control of Volatile Organic Compound Emissions, Conventional and Emerging Technologies, Wiley, New York, 2000.
10. 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).
11. H. Einaga, A. Ogata, Benzene oxidation with ozone over supported manganese oxide catalysts: Effect of catalyst support and reaction conditions, J. Hazard. Mater., 164, 1236(2008).
12. J. Lin, A. Kawai, T. Nakajima, Effective catalysts for decomposition of aqueous ozone, J. Appl. Catal. B: Environmental, 39,157 (2002).
13. M. Muruganandham, S. H. Chen, J. J. Wu, Evaluation of water treatment sludge as a catalyst for aqueous ozone decomposition, Catalysis Communications, 8,1609 (2007).
14. B. Ohtani, S. Zhang, S. Nishimoto and T. Kagiya, Catalytic and photocatalytic decomposition of ozone at room temperature over titanium (IV) oxide, J. Chem. Soc., Faraday Trans., 88,1049 (1992).
15. R. Rosal, A. Rodriguez, M. S. Gonzalo, E. Garcia-Calvo, Catalytic ozonation of naproxen and carbamazepine on titanium dioxide, J. Appl. Catal. B: Environmental, 84,48 (2008).
16. F. Buciuman, F. Patcas, R. Craciun, D. R. T. Zhan, Vibrational spectroscopy of bulk and supported manganese oxides, Phys. Chem. Chem. Phys., 1,185 (1998).
17. F. Fillaux, C. H. Cachet, H. Ouboumour, J. Tomkinson, C. Lévy-Clément and L. T. Yu, Inelastic scattering study of the proton dynamics in manganese oxides I - γ-MnO2 and manganite, J. Electrochem. Soc., 140,585 (1993).
18. F. Kapteijn, A. D. Van Langeveld, J. A. Moulijn, A. Andreini, M. A. Vuurman, M. A. Turek, J. M. Jehng, I. E. Wachs, Alumina-supported manganese oxide catalysts, J. Catal., 150,94 (1994).
19. W. Gac, The influence of silver on the structural, redox and catalytic properties of the cryptomelane-type manganese oxides in the low-temperature CO oxidation reaction, Applied Catalysis B: Environmental, 75,107 (2007).
20. C. Subrahmanyam, D. Bulushev, L. Kiwi-Minsker, Dynamic Behaviour of Activated Carbon Catalysts during

Ozone Decomposition at Room Temperature, J. Appl. Catal. B: Environmental, 61,98 (2005).

21. M. Stoyanova, 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).
22. Y. Xi, C. Reed, Y.-K. Lee, S.T. Oyama, Acetone oxidation using ozone on manganese oxide catalysts, J. Phys. Chem. B, 109,17587 (2005).
23. C. Reed, Y. Xi, S.T. Oyama, Distinguishing between reaction intermediates and spectators: a kinetic study of acetone oxidation using ozone on a silica-supported manganese oxide catalyst, J. Catal., 235,378 (2005).

© **T. Batakliev –** PhD, Assistant Professor of Institute of Catalysis, Bulgarian Academy of Sciences, **S. Rakovsky -** PhD, Professor, Director of Institute of Catalysis, Bulgarian Academy of Sciences, **G. Zaikov -** Doctor of Chemical Sciences, Professor of the Plastics Technology Department of Kazan National Research Technological University,**V. Georgiev -** PhD, Assistant Professor of Institute of Catalysis, Bulgarian Academy of Sciences, **M. Anachkov –** PhD, Associate Professor of Institute of Catalysis, Bulgarian Academy of Sciences, **Kh. Abzaldinov**– Candidate of Chemical Sciences, Docent of the Plastics Technology Department of Kazan National Research Technological University, ov_stoyanov@mail.ru.