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

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Abstract. The titania-supported Mn oxide system made by incipient wetness impregnation method was investigated in the reaction of heterogeneous catalytic decomposition of ozone. The catalytic activity of the catalysts containing 6, 8 and 10 wt % manganese oxide was found using the decomposition coefficient γ which is proportional to ozone decomposition rate. It was established that all catalytic samples are active towards ozone decomposition but the catalyst possessing

10 t % MnOx/TiO2 was the most active. The calculated values of γ were in the range of 0.05×10^{-4}–0.4×10^{-4}. The experiments were performed at the temperature range of 258 K to 313 K in a tube glass reactor. It was determined that the activation energy of the process is 11 kJ/mol. 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.

Key words: ozone, titania, manganese oxide, decomposition, activation energy.

Introduction

Ozone is widely used in the industrial and environmental processes such as semiconductor manufacturing, deodorization, disinfection and water treatment [16]. 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 [13]. 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 [11], CO oxidation [6] and combustion of organic compounds [17] 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 [19]. Titanium dioxide is already known as catalyst support [10, 14] and also has been used as catalyst for several chemical reactions including decomposition of aqueous ozone [12, 19], 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 ozone and 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 %). TiO_2 (Degussa, Aeroxid P25) has been used to support it. The synthesized catalytic samples contained 5.5, 7.4 and 9.3 % molar percentages respectively on the TiO_2 support. These values were calculated on the basis of 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 (Fig. 1).

The catalysts were granulated and contained cylindrical grains with diameter of about 9 mm and thickness of 3 mm. The kinetic measurements were carried out in a glass tube reactor (10×125 mm) filled in with 0.3-0.6 g of catalyst. Fig. 2 shows the scheme of the experimental set-up for all kinetics.

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. Ozone concentration about 1 mM was obtained at 15-20 kV. 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 m^2/g) was measured by N_2 adsorption-desorption isotherms at 77 K using BET method in a FlowSorb 2300 instrument (Micromeritics Instrument Corporation). 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 manually in an agate mortar before the preparation of pellets. The spectra were obtained by averaging 50 scans with 0.4 cm^{-1} resolution.

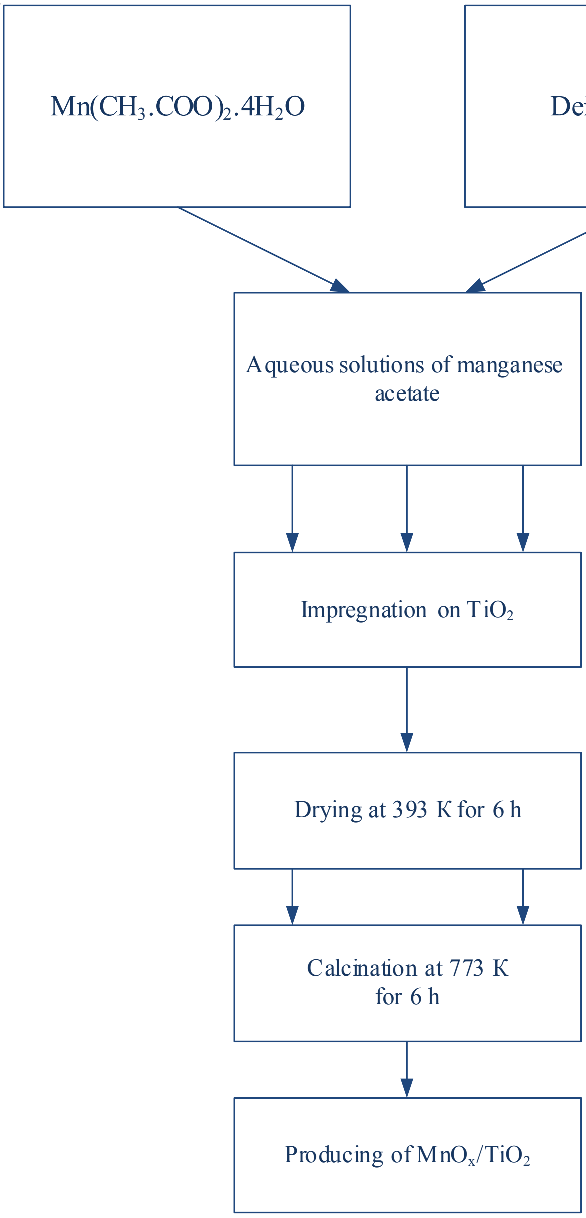

Fig. 1. Synthesis of MnO_x/TiO_2catalyst

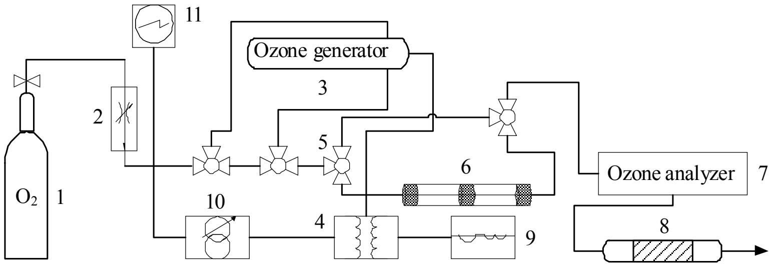

Fig. 2. Experimental set-up of reaction system for catalytic decomposition of ozone:

1 –oxygen; *2* – flow controller; *3* – ozone generator; *4* – transformer; *5* – three way turn cock; *6* – reactor charged with catalyst sample; *7* – Ozone analyzer; *8* – reactor for decomposition of residual ozone; *9* – current stabilizer; *10* – autotransformer; *11* – voltmeter

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 Ka radiation source and SolX detector was used. The samples were scanned from 2q 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.

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

Results and Discussion

The catalytic activity was evaluated on the basis of the coefficient γ [20] that is proportional to ozone decomposition rate and to catalyst efficiency. It has been already used in other studies [21, 22]:

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

where ω is the flow rate, V_t – specific heat rate of ozone molecules, S – geometrical surface of catalyst sample and $[O_3]_0$ and $[O_3]$ – inlet and outlet ozone concentrations, respectively.

Fig. 3 presents the comparative activities of 6, 8 and 10 wt% manganese oxide catalysts on support TiO_2 during the decomposition of ozone produced from pure oxygen under dry conditions. The experiments were carried out with ozone flow rate in the range 6–24 l h^{-1} at room temperature.It was found that all three types of catalytic samples are active in the process of ozone decomposition. However we can see that the catalyst which contains 10 wt% manganese oxide showed the highest catalytic activity whereas the results for the other two catalysts are inconsistent and we could not say which one is more effective in ozone decomposition. The total ozone flow influence on catalytic activity concerning the 8 wt% MnO_x/TiO_2 catalyst is lower compared to the other two catalysts where the increase of ozone decomposition activity with total ozone flow enhancement was observed.

On Fig. 4 the changes in the decomposition coefficient γ values in dependence on temperature of the catalytic reaction are shown. The ozone was decomposed over 10 wt% manganese oxide supported on titanium dioxide. The total ozone flow in all experiments was 6 l h^{-1} and the temperature range – from 258 K to 313 K.The graphic is presented in Arrhenius coordinates because we would like to find the activation energy of the process of ozone decomposition. On this graphic we could see a stable catalytic activity of the samples and growth of that activity with the growth of the temperature. The measured activation energy of the process of ozone decomposition over manganese oxide catalyst supported on titanium dioxide is 11 kJ/mol. This value is very close to some literature data [10] for similar catalytic samples.

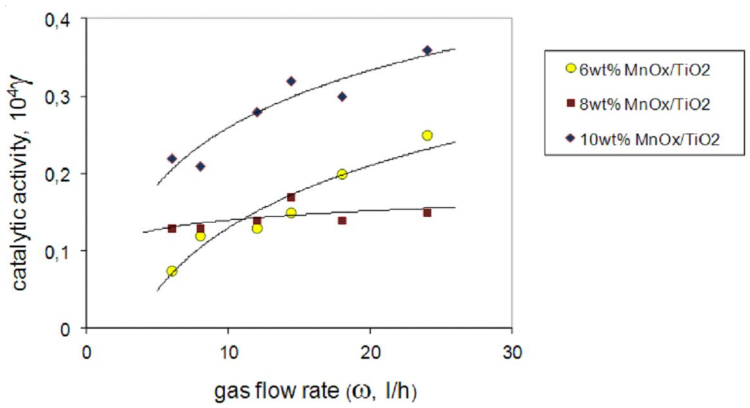

Fig. 3. Catalytic activity of 6, 8 and 10 wt% MnO_x/TiO_2 in ozone decomposition

The X-ray analysis results for the investigated catalyst are shown in Fig. 5. The diffractogram for the MnO_x/TiO_2 sample showed peaks with large intensities at different values of 2q angle. The peaks at 23°, 33°, 45.1° and 65.6° correspond to manganese oxide phase Mn2O3. 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.

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. 6 are 444 K, 596 K and 745 K for the supported catalyst and 824 K for the pure support. This shows that MnO_x is well dispersed on the support and the oxide-support interaction is moderate.

FT-IR spectra of the manganese-oxide catalyst before ozone decomposition (a) and after ozone decomposition (b) are presented in Fig. 7. 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 [21]. The adsorption band at 1628 cm^{-1} is due to the vibrations of water molecules [22]. 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 MnO_x/TiO_2 catalyst is proposed in Fig. 8. This cycle is based on a probable mechanism of catalytic ozone decomposition described notably in paper [10] and also in several

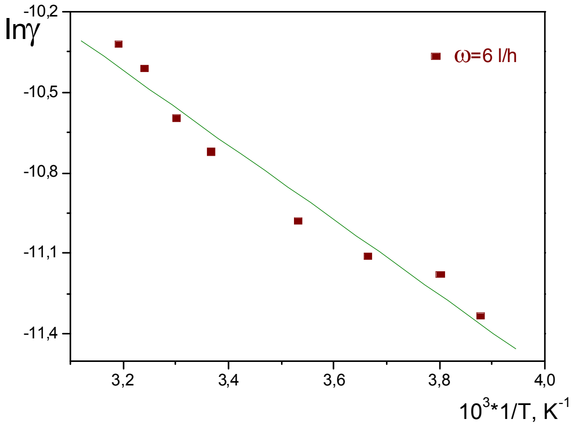

Fig. 4. Temperature dependence of catalytic activity at dry conditions in presence of 10 wt % manganese oxide supported on titanium dioxide, temperature range 258-313 K, O_3/O_2 flow rate 6 l h^{-1}

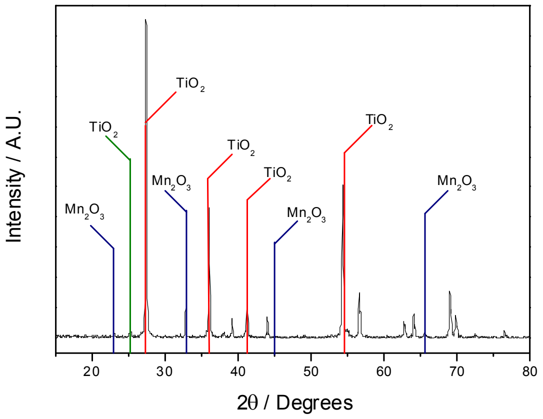

Fig. 5. X-ray diffraction of MnO_x/TiO_2 catalyst

articles [23, 24]. The transformation of the manganese site from species (I) to (III) is indicative of an oxidation reaction. The structure numbered (II) in Fig 8 is probably 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: $Mn^{4+} + O_2^{2-} \rightarrow O_2 + Mn^{2+}$.

In Figures 9A and 9B 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. 9A 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.

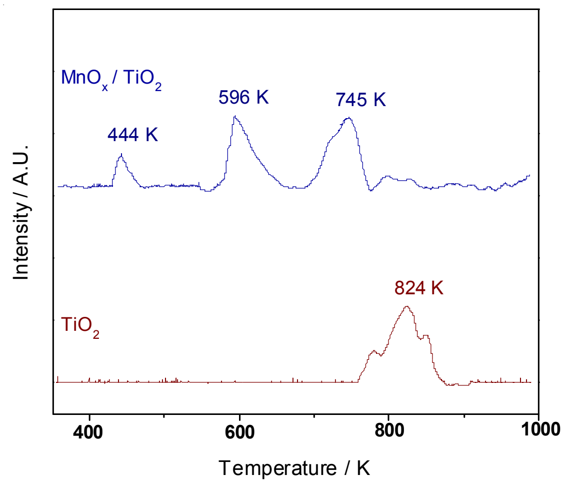

Fig. 6. TPR spectra of MnO$_x$/TiO$_2$ catalyst and pure TiO$_2$ support

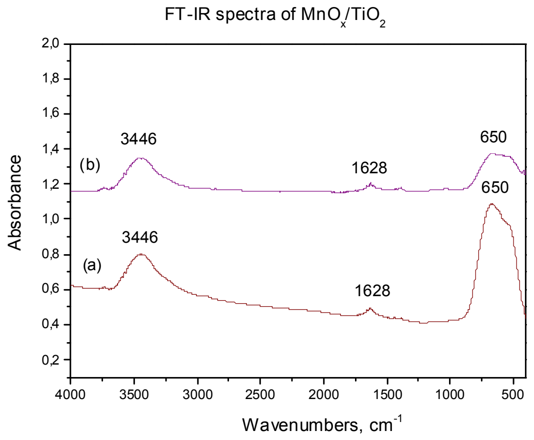

Fig. 7. FT-IR spectra of MnO$_x$/TiO$_2$ catalyst

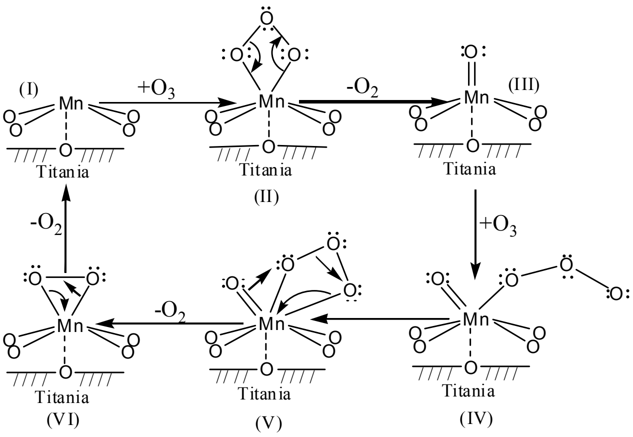

Fig. 8. Catalytic cycle of ozone decomposition on MnO_x/TiO_2 catalyst

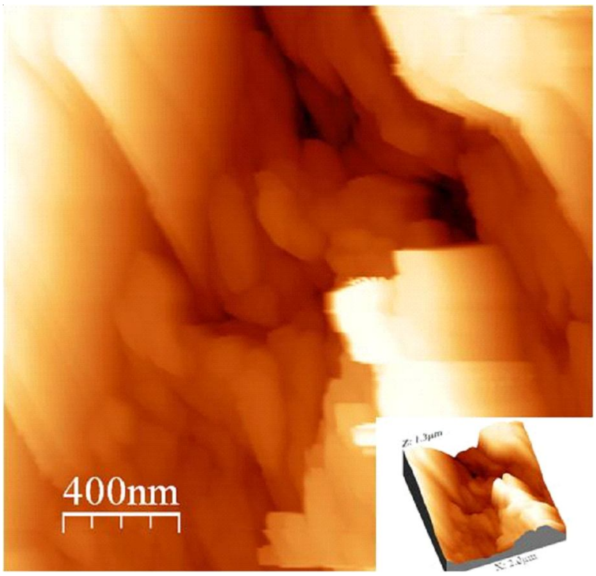

Fig. 9A. AFM image of 8 wt% MnO_x/TiO_2 catalyst

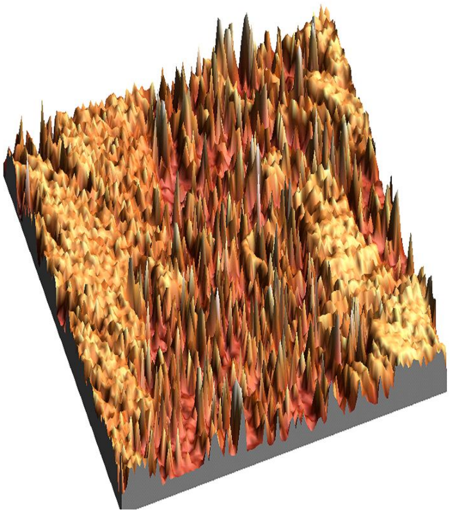

Fig. 9B. 3D AFM image of 8 wt% MnO_x/TiO_2 catalyst

Conclusions

1. The catalyst owns high activity that is not change dramatically by varying temperature and flow rates.

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

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

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

5. 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.

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АКТИВНОСТЬ ТИТАНОВОГО КАТАЛИЗАТОРА ОКСИДА МАГНИЯ ПРИ РАЗЛОЖЕНИИ ОЗОНА

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Аннотация. Авторами было установлено, что каталитическая активность всех образцов зависела от скорости разложения озона, но самым активным был катализатор, обладающий MnOx/TiO2. Расчетные значения были в диапазоне $0.05\times10^{-4}\times10^{-4}$. Эксперименты проводились в температурном диапазоне от 258 к до 313 K. Было установлено, что энергия активации процесса составляет 11 кДж/моль.

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