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CATALYTIC ACTIVITY OF TITANIA-SUPPORTED MANGANESE OXIDE CATALYST IN OZONE DECOMPOSITION. PART 1

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 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 have activity towards ozone decomposition but most active was the catalyst possessing 10 wt% MnOx/TiO₂. The calculated values of γ were in the range 0.05×10^{-4} – 0.4×10^{-4} . The experiments were performed in 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.

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

В реакции гетерогенного каталитического разложения озона исследована система оксида марганца на титановом носителе, полученная методом пропитки до начальной влажности. Каталитическая активность катализаторов, содержащих 6, 8 и 10 мас% оксида марганца была найдена с использованием коэффициента разложение γ , который пропорционален скорости разложения озона. Было установлено, что все образцы катализаторов имеют активность к разложению озона, но наиболее активным был катализатор, содержащий 10% масс. MnOx/TiO₂. Расчетные значения γ находились в диапазоне 0.05×10^{-4} – 0.4×10^{-4} . Эксперименты проводились в диапазоне температур от 258 K до 313 K в трубчатом стеклянном реакторе. Установлено, что энергия активации процесса составляет 11 кДж / моль.

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].

The aim of present study is to investigate the catalytic activity of titania-supported manganese oxide system during heterogeneous catalytic decomposition of ozone.

Experimental

Manganese oxide catalysts (6, 8 and 10 wt%) were prepared using aqueous solutions of manganese acetate (Mn(CH₃COO)₂·4H₂O, BDH Chemicals >99.99%). For support it has been used TiO₂ (Degussa, Aeroxid P25). The synthesized catalytic samples contained 5.5, 7.4 и 9.3% molar percentages respectively on the TiO₂ support. These values were

calculated on the basis of assumption that MnO₂ 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 MnOx/TiO₂ (Fig. 1).

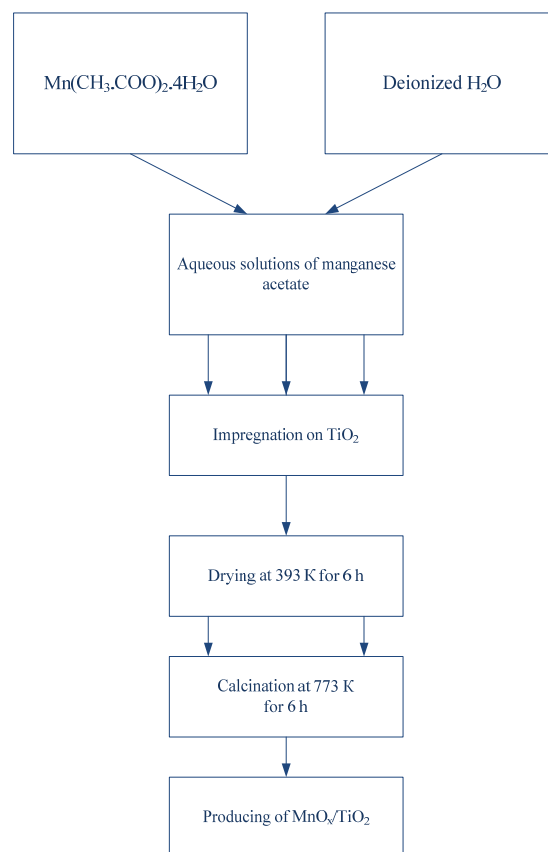


Fig. 1 - Synthesis of MnOx/TiO₂ catalyst

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 schematic of the experimental set-up for all kinetics.

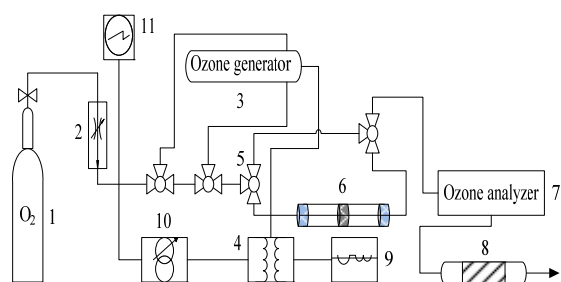


Fig. 2 - Experimental set-up of reaction system for catalytic decomposition of ozone: 1 - oxygen; 2 - flow controller; 3 - ozone generator; 4 - transformer; 5 - three way turn cock; 6 - reactor charged with catalyst sample; 7 - Ozone analyzer; 8 - reactor for decomposition of residual ozone; 9 - current stabilizer; 10 - autotransformer; 11 - voltmeter

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 N₂ 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 [16] 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, 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 TiO₂ 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 is more effective in ozone decomposition. The total ozone flow influence on catalytic activity concerning the 8 wt% MnOx/TiO₂ catalyst is lower compared to the other two catalysts where it was observed increase of ozone decomposition activity with total ozone flow enhancement.

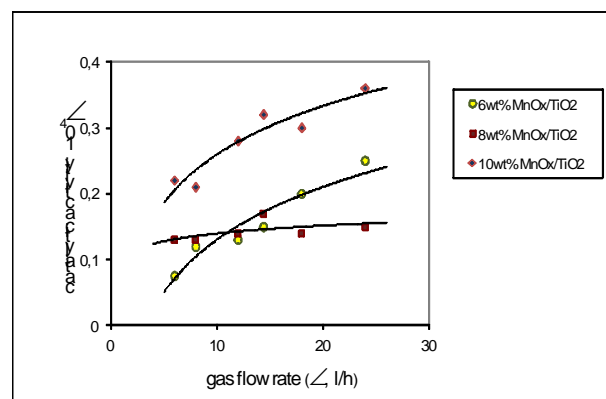


Fig. 3 - Catalytic activity of 6, 8 and 10 wt% MnOx/TiO₂ in ozone decomposition

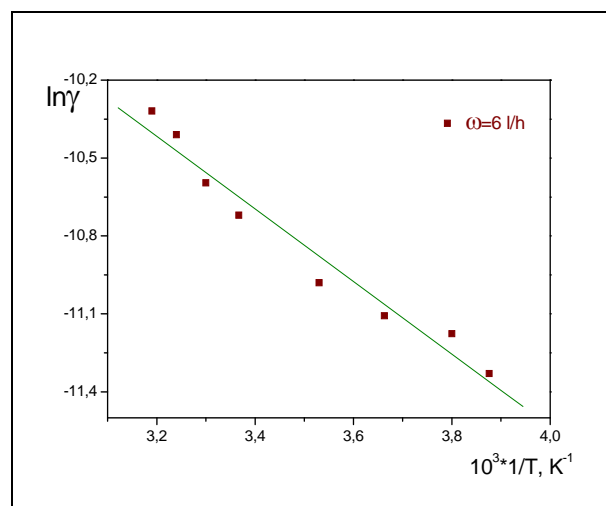


Fig. 4 - Temperature dependence of catalytic activity at dry conditions in presence of 10 wt% manganese oxide supported on titanium dioxide, temperature range 258-313 K, O₃/O₂ flow rate 6 l h⁻¹

On Fig. 4 are shown changes in the decomposition coefficient γ values in dependence on temperature of the catalytic reaction. 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.

Conclusions

The catalyst owns high activity that doesn't change dramatically by varying temperature and flow rates.

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