UDC 542.924:544.47

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OZONE DECOMPOSITION ON THE SURFACE OF METAL OXIDE CATALYST. PART 2

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 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 temperature programmed reduction and IR-spectroscopy. The phase composition of the metal oxide catalyst was determined by X-ray diffraction. 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. Реакцию изучали в присутствии термически модифицированных каталитических образцов, работающих при различных температурах и расходах озона. Изменения катализатора исследованы методом температурно программиируемого восстановления и ИК-спектроскопии. Фазовый состав катализатора из оксида металла был определен с помощью рентгеновской дифракции. Смесь катализаторов показала высокую активность при разложении озона на влажных и сухих смесях газов О3/О2. 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 $\Delta H0298$=−138 kJ/mol and free energy of reaction of $\Delta G0298$=−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. 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 Kα 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.

Results and Discussion

A popular technique used to characterize manganese oxide containing catalyst and to determine the identity of the manganese oxide phase at high loadings (>6%) has been X-ray diffraction (XRD) [19, 20]. The X-ray diffraction results for the cement-containing metal oxide catalyst are presented on Fig. 1. The diffractogram for the catalyst sample showed peaks with a certain number of large intensities at different 2θ values. The peaks at 39° and 35.5° correspond to copper oxide (CuO). The diffraction features for the catalyst at 33° and 55.1° are indicative of bixbyite-o (Mn_2O_3). The metal oxide catalyst sample peaks at 43°, 37.2° and 62.9° are due to nickel oxide (NiO). The catalyst diffraction peaks at 36.1°, 32.4° and 59.9° correspond to hausmannite (Mn_3O_4). Finally, the cement diffraction peaks at 20°, 25.5° and 29.5°, 47.5° are due respectively to grossite ($CaAl_4O_7$) and calcite ($CaCO_3$). In conclusion, the information which can be deduced from the X-ray diffractogram for this catalyst is that there are three metal oxides as the manganese oxide is present in two forms- Mn_2O_3 and Mn_3O_4. It could also be seen that the cement support of the catalyst is build mainly by two components- $CaAl_4O_7$ and $CaCO_3$.

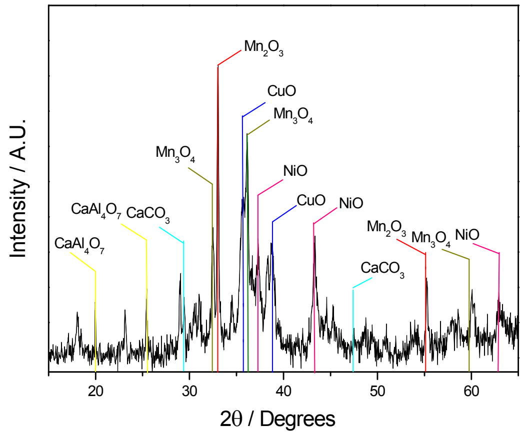

Fig. 1 - XRD of MnOx/CuO/NiO catalyst supported on cement

The TPR experiment was carried out for the supported on cement metal oxide catalyst (Fig. 2).

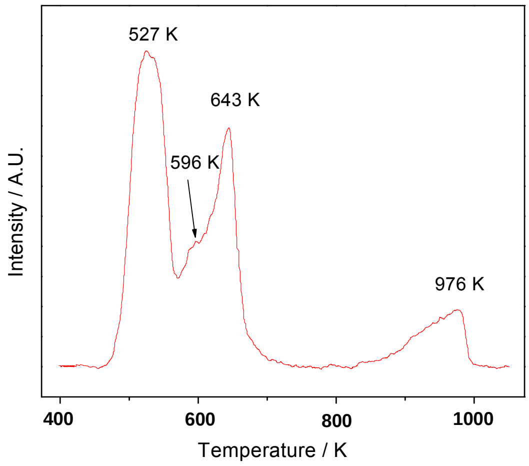

Fig. 2 - TPR of MnOx/CuO/NiO catalyst supported on cement

The H_2 consumption was monitored by thermal conductivity detector in the course of time. Manganese‒containing catalyst was already studied using TPR [21]. The peak temperatures of reduction on Fig. 2 are 527 K, 596 K, 643 K and 976 K or the reduction temperature of the catalyst was in the range 527-976 K. The bulk reduction peaks at 596 K and 643 K can be identified for the manganese oxide in the cement-containing metal oxide mixture while the peak at 976 K can be related with reduction of the nickel oxide [8, 21].

The most possible mechanism [6, 7] of catalytic ozone decomposition can be presented as follows:

$$O_3 + {*} \longrightarrow O_2 + O^* \qquad (1)$$

$$O_3 + O^* \longrightarrow O_2^* + O_2 \qquad (2)$$

$$O_2^* \longrightarrow O_2 + {*} \qquad (3)$$

where the symbol * was used to denote surface sites. In step (1) ozone decays and the finding that the adsorbed ozone does not desorbs ascertains the irreversibility of steps (1) and (2). Further peroxide particles are formed in accordance with step (2) and then oxygen is desorbed from the catalytic surface - step (3). The finding that the peroxide species could not be formed from molecular oxygen at any conditions shows the irreversibility of step (3).

The FT-IR spectra of the catalyst before and after ozone decomposition are shown in Fig. 3. The two similar spectra indicate that the catalyst does not change practically during the reaction. A broad band at 3415-3425 cm-1 and also the band at 1410-1430 cm-1 are associated with the vibrations of water molecules [15, 22]. The intensive bands at 515-530 cm-1 in accordance with literature [23], were assigned to the stretching vibration of the surface metal-oxygen bond.

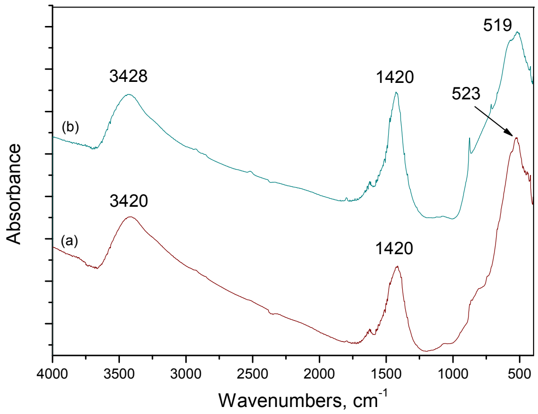

Fig. 3 - FT-IR spectra of MnOx/CuO/NiO catalytic samples obtained before ozone decomposition (a) and after ozone decomposition for 8 h (b)

The FT-IR spectra of cement-oxide catalyst after dry ozone decomposition (a) and after humid ozone decomposition (b) are presented in Fig. 4. The spectra are almost identical, showing that the catalyst structure is not altered during the humid catalytic reaction. The broad adsorption band at 3430 cm-1 appears from the stretching vibration of hydrogen bonded hydroxyl groups [15]. The adsorption band at 1635 cm-1 is due to vibrations of water molecules [14].

The intensive band at 520-530 cm-1 appears at higher manganese concentrations and, in accordance with literature, can be attributed to well-defined Mn2O3 phase [20].

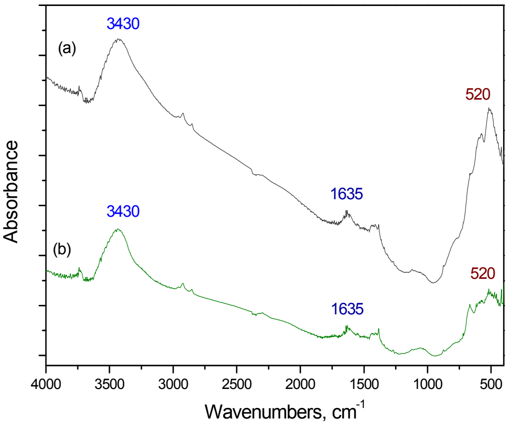

Fig. 4 - FT-IR spectra of cement-oxide catalyst after dry ozone decomposition (a) and after humid ozone decomposition (b)

Conclusions

1. XRD analysis has proven to be a useful tool for the identification of all metal oxide phases in catalyst mixture. The temperature programmed reduction of the catalyst denotes its high reducibility.
2. The FT-IR spectral band at 526 cm-1 shows that the catalyst stays unchangeable during the ozone decomposition for about 8 h.
3. The FT-IR spectra after humid ozone decomposition indicates that even decomposing ozone in humid conditions the catalyst structure does not change practically during the reaction.

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