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Supported catalysts containing δ-MnO_2 in low-temperature catalytic formaldehyde oxidation reaction

P.A. Rumyantsev, V.V. Dutov, O.V. Vodyankina

Tomsk State University, Tomsk, Russia

rumyantsev9@gmail.com

HCHO removal from air attracts much attention due to the high toxicity and carcinogenic properties of formaldehyde. This process is utterly important for human health and environment protection. Formaldehyde sources are materials made from polyvinyl chloride, lacquered furniture, plastics based on phenol-formaldehyde resins, etc. Birnessite (δ-MnO_2) exhibits catalytic activity in low-temperature oxidation reactions of volatile organic compounds via the Mars - Van Krevelen mechanism. In contrast to α-, β- and γ-modifications, δ-MnO_2 possesses a layered structure consisting of two-dimensional sheets of MnO_6 octahedra with a basal interplanar distance of about 0.7 nm in which alkali metal ions Li^+, Na^+, K^+ and water molecules are intercalated [1]. Due to structural features and high reaction ability toward oxidative process, δ-MnO_2 is a good candidate for the development of catalyst composition used to eliminate formaldehyde from air at RT.

In the present work, manganese-containing catalysts with birnessite structure supported on silica gel and carbon materials were synthesized and studied.

MnO_x over carbon material catalysts were prepared via hydrothermal method using an aqueous solution of $KMnO_4$. A silver-containing MnOx catalyst (5 % wt Ag) was prepared as follows. $AgNO_3$ solution was added to a solution of $KMnO_4$ immediately before the hydrothermal synthesis. MnO_x supported on silica gel catalysts were prepared with the use of deposition-precipitation method [2], precipitation method [3], and redox reaction between oxalic acid and $KMnO_4$ on the surface of support [4]. The porosity, specific surface, phase composition and properties of the catalysts obtained were determined by low-temperature adsorption of nitrogen, Raman spectroscopy, X-ray phase analysis, TPx methods.

Testing of catalytic properties was carried out under the following conditions: temperature was 23-25 °C, flow rate was 300 ml / min, formaldehyde content in the gas flow was 60 - 90 ppm, catalyst mass was 0.0625 g. Analysis of inlet and outlet flows was performed by high-effective liquid-phase chromatography with using of DNPH formaldehyde derivatives.

Synthesized samples showed a degree of formaldehyde removal of about 90 % wt. from the gas flow. In the course of experiment the removal degree was reduced from 90 up to 20-30 % wt within 120 min. Among the tested samples, catalysts prepared with the use of carbon carriers and carbon-containing composites as supports were the most active and stable. It was a catalyst based on carbon material with a 14.8 % wt δ-MnO_2; carbon-based catalyst containing 49.8 % wt δ-MnO_2 and 2.4 % wt Ag; a catalyst based on silica gel with an inverted carbon structure containing δ-MnO_2 and silver similar to previous catalyst. After 120 min the degree of removal of formaldehyde from the gas flow was 35.3; 20.4; 15.5 % wt for the above-titled samples, respectively.

Decrease in the HCHO removal efficiency may be due to the formation of alkali metal carbonates stable on the catalyst surface at the experimental temperature and/or the low reoxidation ability at the reaction conditions. Subsequent studies will be devoted to identification of these factors as well as their elimination.

References

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