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Tuning the performance of Mn/Beta in ozone catalytic oxidation of VOCs by variation of Mn content and its localization in the zeolite structure

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Catalyst preparation

A BEA-type zeolite (Beta, Zeolyst, Si/Al = 20, (NH_4^+-form, S_{BET} = 680 m^2/g) was used as catalyst supports. The 0.6%Mn/Beta sample was prepared by ion-exchange of parent Beta with an aqueous solution of $Mn(NO_3)_2 \cdot 4H_2O$ (≥97%,Sigma-Aldrich, the United States) at room temperature for 6 h. After washing and drying, the sample was calcined in air flow at 550°C for 4 h. The Mn/Beta sample containing 3 wt %Mn was prepared by combination of ion exchange and impregnation with an aqueous solution of $Mn(NO_3)_2 \cdot 4H_2O$ (≥97%,Sigma-Aldrich, the United States). The Mn/Beta sample containing 10 wt %Mn was prepared by incipient-wetness impregnation with an aqueous solution of $Mn(NO_3)_2 \cdot 4H_2O$ (≥97%,Sigma-Aldrich, the United States). The impregnated materials were dried in air for 12 h and then calcined at 550°C for 4 h. The resulted powder was pressed, crushed and sieved to obtain an appropriate particle size for the catalytic tests (0.4 - 1 mm).

Catalyst characterization

X-ray diffraction (XRD). The crystallographic structure of the catalysts was characterized by X-ray powder diffraction (XRD) using a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) with Bragg–Brentano geometry, Ni-filtered CuKα radiation, and LYNXEYE detector. The XRD patterns were recorded in the 2θ range 5–75º (scan rate 1.2º/min). Crystallographic parameters were calculated using the Rietan-FT software, which uses the Rietveld method.

H_2-temperature programmed reduction (H_2-TPR). The experiment was conducted on a USGA-101 instrument (Unisit, Moscow, Russia). The catalyst sample (100 mg) was pre-treated in Ar flow at 325°C for one hour and then cooled down to RT. The H_2-TPR was carried out in a 5% H_2/Ar

mixture at a flow rate of 30 mL/min. The temperature was increased in a linear fashion from RT to 700°C at a rate of 10°C per minute. The data were processed using the Data Treatment software of the USGA-101 instrument. The quantity of hydrogen consumed was quantified using CuO (99.999%, Sigma Aldrich, St. Louis, MO, USA) and NiO (99.99%, Sigma Aldrich, St. Louis, MO, USA) standards. The H_2-TPR pattern of the Mn/BEA catalyst was normalized using the H_2-TPR profile of the parent zeolite as a background.

Electron paramagnetic resonance (EPR). EPR spectra of powdered samples were recorded on a Jeol JES-FA200 X-band spectrometer at 25°C. Spectra were recorded in a single scan for 4 minutes with a modulation of 0.2 mT at 100 kHz and a power of 2.39 mW.

Catalytic tests

Catalytic tests were carried out on a setup equipped with a flow-type tubular quartz reactor (d_{in} =10 mm) with a fixed catalyst bed (200 mg; a fraction of 0.4‑1.0 mm) operating at atmospheric pressure (Fig S1). The hydrocarbon (n-C_4H_{10}) was supplied from a cylinder with 0.98% *n*-C_4H_{10}/N_2 (Linde Gas Rus, Russia). Ozone was generated from O_2 (99.999%, Linde Gas Rus, Russia) using a YOTA-60-01 ozone generator (MedOzon, Russia). Depending on the reaction under study, a mixture of 100 ppm n-C_4H_{10}, 450 or 1600 ppm O_3, 20% O_2, and 2% H_2O in N_2 was supplied to the reactor. The total flow rate of the mixture was 750 mL/min. The experiments were carried out under conditions of a temperature increase from 30 to 150ºC at a heating rate of 5ºC/min. Ozone content at the inlet and outlet of the reactor was measured by ozone analyzer Medozone 254/5 (Medozone, Russia) with an accuracy of 2%. The concentration of *n*-C_4H_{10} was determined using a Gasmet DX4000 FTIR spectrometer (Temet Instruments Oy, Finland). To prevent residual ozone from entering the spectrometer cell, a trap with a saturated aqueous solution of KI was installed at the outlet of the reactor. The activity of the catalysts was evaluated from the conversions (X) of n-C_4H_{10} and O_3 calculated according to the following equation:

$$X = \frac{C_{in} - C_{out}}{C_{in}} \times 100\%$$

where C_{in} and C_{out} are the concentrations of *n*-C_4H_{10} or O_3 at the inlet and outlet, respectively.

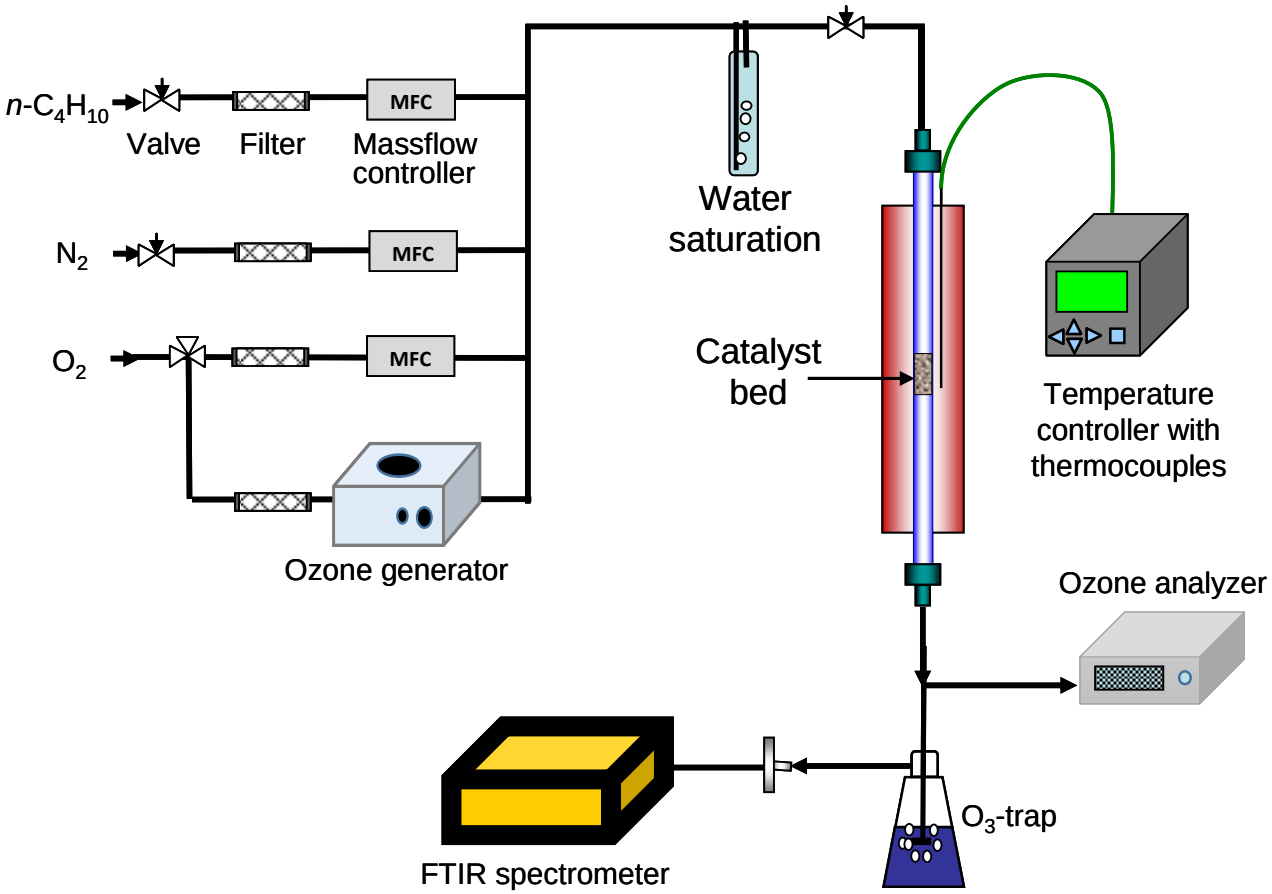

Figure S1. Experimental setup