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Location, stability, and reactivity of oxygen species generated by N_2O decomposition over Fe-ZSM-5 and Fe-Beta zeolites

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ABSTRACT

Reactivity of oxygen species generated by N_2O decomposition over Fe-ZSM-5 and Fe-Beta zeolites was investigated using oxygen isotopic exchange as test reaction. The generated species are very stable up to 300 °C in the absence of the organic traces or residual N_2O in the gas phase. The reactivity of the oxygen species towards organics depends on the size of the organic molecules and their ability to penetrate into the zeolite pores. For example, in case of Fe-ZSM-5 zeolite, the oxygen species react readily with toluene, but stay intact with more bulky 1,3,5-trimethylbenzene.

1. Introduction

N_2O decomposition over Fe-containing zeolites can be used to generate a very efficient surface oxidant. This process has been suggested to proceed over special complexes of Fe^{2+} stabilized in the micropore space of the zeolite matrix [1–22]. N_2O decomposition over the Fe^{2+} sites results in formation of reactive surface oxygen species called "α-oxygen" [23–31]. This oxygen can oxidize methane and benzene to form methanol and phenol even at room temperature [23,32–37] similar to the enzymatic catalysis by methane monooxygenase (MMO) [38,39]. The stoichiometric reactions of α-oxygen with organic substrates are very informative to elucidate the role of this species in catalytic hydroxylation. One of such catalytic reactions, oxidation of benzene to phenol with N_2O, has received considerable attention because of its potential to replace the current cumene process. Fe-ZSM-5 zeolites were shown to be excellent catalysts for this reaction giving selectivity to phenol close to 100% [40–43].

Furthermore, catalytic selective oxidation of various (substituted) aromatic compounds over ZSM-5 zeolites has been studied using nitrous oxide as oxidant. Thus, benzonitrile was oxidized to hydroxybenzonitriles with a selectivity of 73% [44]. Phenol was found to oxidize with a selectivity of 97% to dihydroxybenzenes [45]. Oxidation of toluene by N_2O led to formation of *p*-cresol with selectivity of about 20% [46]. The comparatively low selectivity in the last case was explained by diffusion limitations for the product, which resulted in deeper oxidation. Really, diffusion inside the zeolite pores has to be kept in mind when choosing a substrate for reactions catalyzed by zeolites.

It is suggested that the majority of active sites responsible for N_2O decomposition are located inside the micropores of zeolites. Pirutko et al. [47] investigated a silylation effect on the catalytic properties of Fe-ZSM-11 in benzene oxidation by nitrous oxide. It was shown that SiO_2 deposition on the external surface of the zeolite affects practically neither the rate of benzene oxidation nor the selectivity to phenol. Ribera et al. [22] studied the oxidation of 1,3,5-trimethylbenzene with N_2O over Fe-ZSM-5 zeolite and revealed that this organic substrate is too large to fit inside the zeolite channels and thus no reaction was observed. So, when estimating the reactivity of the active oxygen species towards organic molecules, combination of two factors should be taken into account. First is a real reactivity of the oxygen species. Second is an ability of the organic molecules to reach the active oxygen.

The present work is devoted to the properties of α-oxygen generated by N_2O decomposition on two zeolite matrixes with different diameter of pores, ZSM-5 and Beta zeolites. ZSM-5 has a 10-ring channels system with apertures of 0.51 nm × 0.55 nm and 0.53 nm × 0.56 nm, while Beta has 12-ring apertures of 0.66 nm × 0.67 nm and 0.56 nm × 0.56 nm [48,49]. A set of organic molecules of different size, such as toluene, *m*-xylene and 1,3,5-trimethylbenzene, was involved in the reaction with α-oxygen.

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The ability of these molecules to react with active surface oxygen species was studied using O_2 isotope exchange (OIE) method.

Isotope exchange between oxygen in the gas phase and a solid oxide is a powerful tool to discriminate between oxygen species of different reactivity. In the case of Fe-containing zeolites, a significant effect of α-oxygen on the rate of O_2 exchange was shown [1,2,15,50]. Gas phase oxygen is able to exchange with surface α-oxygen even at room temperature and OIE can be used for quantitative estimation of the amount of the active surface oxygen species.

2. Experimental

Fe-ZSM-5 ($SiO_2/Al_2O_3 = 80$, 0.56 wt.% Fe) and Fe-β ($SiO_2/Al_2O_3 = 38$, 0.53 wt.% Fe) zeolites were obtained by calcination of their NH_4^+ precursors (CBV 8014 and CP 814C, respectively, from Zeolyst International) in air at 550 °C for 6 h, followed by ion exchange with 0.05 M $FeCl_3$ (4 ml per 2 g of zeolite sample) during 24 h at room temperature. The samples were washed with deionized water, and dried overnight at room temperature. Then the obtained samples were activated by calcination in air at 115 °C for 3 h and then at 550 °C for 5 h.

All adsorption and isotope exchange experiments were carried out in a vacuum static setup. The setup was made of stainless steel with a small quartz reactor and was described elsewhere [2]. The setup was equipped with an on-line mass-spectrometer (Stanford Research Systems RGA 200) to analyze the gas phase composition. The pressure of gases in the reaction volume was in the range of 0.1–2.0 Torr and was measured by Baratron capacitance manometer (MKS Instruments). A catalyst sample (0.5 g) was placed in a quartz microreactor, which can be isolated from the rest of the setup. Before each experiment the sample was pretreated in vacuum and then in oxygen at 550 °C.

The experiments included four steps that were performed in the following sequence:

(1) α-oxygen loading;
(2) adsorption of organic substrate over zeolite;
(3) evacuation of the excess organic material from the gas phase;
(4) oxygen isotope exchange.

α-Oxygen was loaded by N_2O decomposition at 250 °C as described in [1,2]. After α-oxygen deposition the reactor was isolated from the rest of the reaction volume and cooled to the experiment temperature. Gas in the reaction volume was replaced with an organic vapor which was contacted with the catalyst for 10–15 min. The excess organic material was removed by evacuation and then 0.2 Torr of labeled $^{36}O_2$ with 84% of isotope ^{18}O was introduced into the system. The exchange parameters were determined from the experimentally obtained time dependence of the isotope composition of the molecular oxygen ($^{36}O_2$, $^{34}O_2$ and $^{32}O_2$). The fraction of the ^{18}O isotope in the molecular oxygen (α) calculated as

$$\alpha = \frac{1/2\,C_{34} + C_{36}}{C_{32} + C_{34} + C_{36}}$$

was used to characterize the oxygen isotope exchange. Number of exchangeable surface oxygen atoms, N_s, was calculated from the material balance:

$$\alpha^{\circ} * (N_g) = \alpha^{\infty} * (N_g + N_s)$$

$$N_s = N_g * \left(\frac{\alpha^{\circ}}{\alpha^{\infty}} - 1\right)$$

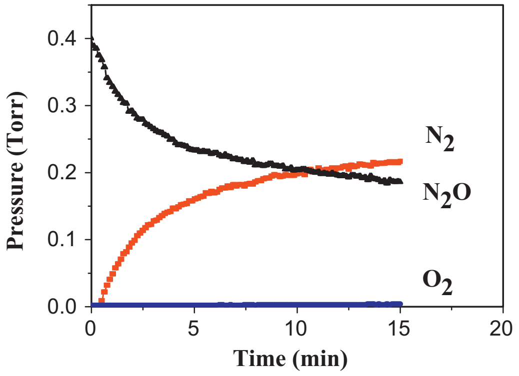

Fig. 1. N_2O decomposition over FeZSM-5 at 250 °C.

where N_g – number of oxygen atoms in the gas phase, α° and α^{∞} – the initial and equilibrium values of α.

3. Results and discussion

3.1. N_2O decomposition and temperature-programmed desorption

N_2O decomposition on the Fe-ZSM-5 sample at 250 °C and N_2O initial pressure of 0.4 Torr is presented in Fig. 1. The reaction proceeds with evolution of only N_2 and formation of surface oxygen atom, $(O)_\alpha$, according to reaction (1):

$$N_2O + (\,)_\alpha \rightarrow N_2 + (O)_\alpha \qquad (1)$$

These surface oxygen species are stable at 250 °C and can be removed from the surface by temperature increasing. Fig. 2 shows temperature-programmed desorption experiment after N_2O decomposition at 250 °C. Two neighboring surface $(O)_\alpha$ can recombine with evolution of molecular oxygen into the gas phase:

$$2(O)_\alpha \rightarrow O_2 + 2(\,)_\alpha \qquad (2)$$

It is seen that desorption of O_2 begins above 315 °C, and the molecular oxygen is the only desorption product. The amount of the molecular oxygen desorbed is half of the amount of N_2O decomposed at 250 °C. So, the total amount of oxygen atoms adsorbed on the active surface sites as well as the concentration of these sites can be determined by the calculation of the amount of N_2O decomposed or the amount of O_2 desorbed in TPD experiment.

The time of N_2O decomposition shown in Fig. 1 is 15 min. After such decomposition only surface oxygen species are obtained with evolution only molecular oxygen in TPD experiment. The picture is different if time of N_2O decomposition is much longer. Fig. 3 shows

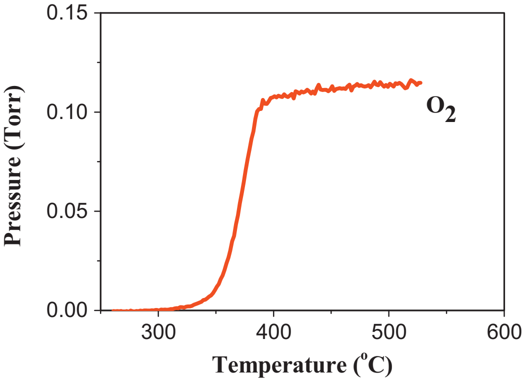

Fig. 2. TPD after N_2O decomposition for 15 min over FeZSM-5 at 250 °C.