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N_2O Decomposition over Dehydroxylated HZSM-5 Zeolites

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N_2O decomposition over dehydroxylated HZSM-5 zeolite resulting in chemisorption of O-atoms and formation of new Z–O* sites has been observed; oxidation of H_2, CH_4, C_2H_6 and CO over these sites at room temperature has been studied using IR diffuse-reflectance spectroscopy.

The H-forms of zeolites are known to be classic acid-type catalysts, and exhibit activity in some redox-type reactions.[1–5] Radical centres of a different nature or transition metal impurities[4,5] are usually considered to be active sites responsible for these reactions.

In previous work, N_2O decomposition over dehydroxylated HZSM-5 zeolite resulting in chemisorption of O-atoms on this zeolite and the formation of N_2 has been reported.[6] A similar effect has been monitored for Fe-containing HZSM-5 zeolites using mass spectrometry.[4,7] This short communication presents some new results obtained using UV and IR spectroscopy on HZSM-5 zeolite with a relatively low level of iron impurities.

The H-form of ZSM-5 (100 mg, Si/Al = 20, 0.04 mass% Fe_2O_3) was heated at 3 K min^{-1} to 1120 K *in vacuo* and then held for 4 h at this temperature. The D-form of ZSM-5 zeolite was prepared by H–D exchange with D_2 at 770 K. The UV and IR diffuse-reflectance spectra were recorded using ‘Hitachi-340’ and ‘Perkin Elmer 580 B’ spectrometers, respectively

The decomposition of N_2O at 520 K over HZSM-5 zeolite preheated at 1120 K leads to the formation of N_2 and chemisorption of 10^{19} O-atoms per g of zeolite according to Scheme 1.

$$N_2O + Z \xrightarrow{520\text{ K}} Z\text{–}O^* + N_2, \quad Z\text{-zeolite}$$

Scheme 1

Simultaneously, absorption bands at 360 and 590 nm appear in the UV spectrum. Evacuation of the sample at a temperature

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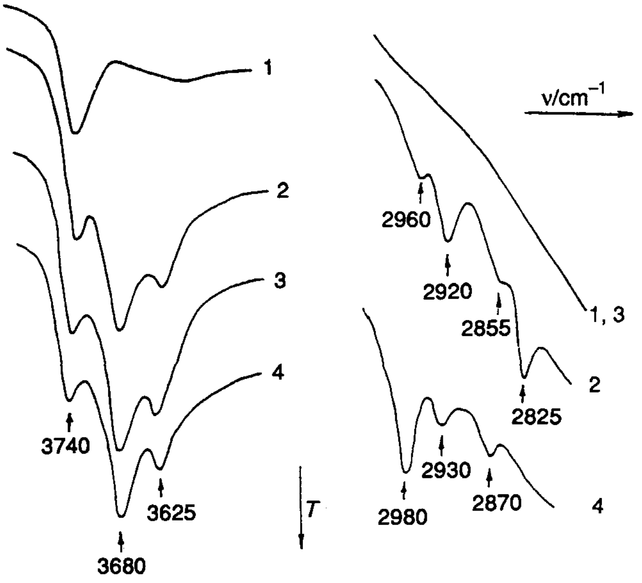

Fig. 1 IR spectra of dehydroxylated D-ZSM-5 zeolite treated with N_2O at 520 K (1) followed by adsorption of H_2; (2), CH_4; (3), C_2H_6; (4) at 300 K

above 620 K results in the desorption of O_2 and the disappearance of the bands at 360 and 590 nm, Scheme 2.

$$2Z\text{–}O^* \xrightarrow{>620\ K} 2Z + O_2$$

Scheme 2

Repeated treatment of the HZSM-5 zeolite in N_2O at 520 K is again accompanied by chemisorption of atomic oxygen and the appearance of the absorbance bands at 360 and 590 nm.

Adsorption of CO at 300 K on dehydroxylated HZSM-5 zeolite treated with N_2O at 520 K results in CO oxidation to CO_2 ($\nu = 2370\ cm^{-1}$). Simultaneously, the UV bands of chemisorbed oxygen at 360 and 590 nm disappear. Adsorption of H_2, D_2, CH_4 and C_2H_6 at room temperature leads to their oxidation with the formation of new OH-groups ($\nu = 3680$ and $3620\ cm^{-1}$) or OD-groups ($\nu = 2710$ and $2675\ cm^{-1}$). In the case of adsorption of hydrocarbons in addition to OH-groups new CH_x fragments also form after their interaction with chemisorbed oxygen (Fig. 1). Therefore, R–H molecules dissociate on the Z–O* sites forming hydroxyl radicals and O–R fragments.

Oxygen chemisorption on ZSM-5 zeolites has previously been attributed to iron impurities.[4,7] In the present work, however, when HZSM-5 with relatively low iron concentration was activated at 720 K, no oxygen chemisorption and subsequent oxidation of CO, H_2 and CH_4 were observed. The formation of Z–O* sites was observed only for HZSM-5 zeolites dehydroxylated at a temperature above 770 K and no oxygen consumption during N_2O adsorption was observed on HY, mordenites, amorphous silica–alumina or H-ferrisilicates. It is possible that Z–O* sites are active in the catalytic oxidation of C_6H_6[5,8] and CH_4.[2,3]

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