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Unusual forms of molecular Hydrogen adsorption by Cu^{+1} ions in the Copper-modified ZSM-5 zeolite

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DRIFT and IR transmittance spectra of H_2 adsorbed at 77 K or at room temperature by the copper-modified ZSM-5 zeolite pre-evacuated or pre-reduced in CO at 873 K indicated several unusual forms of adsorbed hydrogen. H–H stretching frequencies of adsorbed species at 3075–3300 cm^{-1} are by about 1000 cm^{-1} lower than in the free hydrogen molecules. This indicates unusually strong perturbation of adsorbed hydrogen by reduced Cu^{+1} ions that has been never before reported neither for hydrogen nor for adsorption of other molecules by any cationic form of zeolites or oxides.

KEY WORDS: Cu loaded ZSM-5 zeolite; molecular hydrogen adsorption; IR spectra of adsorbed hydrogen.

1. Introduction

The most interesting feature of the copper modified ZSM-5 zeolites is their activity in NO decomposition or in Selective Catalytic Reduction (SCR) of NOx by hydrocarbons resulting in molecular nitrogen [1–3]. It is believed that these reactions involve mutual redox transformations of Cu^{+2} and Cu^{+1} ions [4–6]. Therefore, the properties of Cu^{+1} ions in the copper modified high-silica zeolites have been studied using UV–VIS spectroscopy, luminescence [7–9] or carbon monoxide adsorption as a molecular probe [5,9] by different research groups. It was also reported in Refs. [9–13] that reduced Cu^{+} ions very strongly adsorb CO and nitrogen. In Ref. [13] these findings were confirmed by quantum chemical calculations. In the present study we for the first time report unusually strong adsorption by Cu^{+} ions of molecular hydrogen both at 77 K and at room temperature.

2. Experimental

Copper containing ZSM-5 samples were prepared by triple wet ion exchange of ammonium form of SN-25 zeolite from “Alsi-Penta” with 0.02 M copper acetate aqueous solution. After the third exchange the material was washed and dried at 380 K. As detected by the AAS analysis, the copper content in the samples was equal to 2.5%. The hydrogen form of ZSM-5 was obtained by decomposition of ammonium form in flowing oxygen at 770 K.

Similar to our previous studies [14–17], DRIFT spectra of adsorbed molecular hydrogen adsorbed at 77 K were measured using a Nicolet “Impact 410” spectrophotometer equipped with a home-made diffuse reflectance attachment. For this purpose the zeolite grains with the particle size of ca. 0.5 mm were transferred into quartz part of the optical cell that was immersed into quartz Dewar flask filled with liquid nitrogen. All DRIFT spectra were transformed into Kubelka–Munk units assuming that the reflective ability of the samples at 5000 cm^{-1} was equal to 0.9 units. After that the background created by the zeolite was subtracted.

The transparence IR spectra of hydrogen adsorption by the thin pellet pressed from the powder of the copper modified zeolite were recorded at room temperature through the CaF_2 windows. The background created by the zeolite in this case was also subtracted from the overall spectrum.

3. Results and discussion

DRIFT spectra of OH groups in the hydrogen form of ZSM-5 zeolite and in the copper–modified zeolite reduced in CO at 873 K are shown in figure 1(a) and (b), respectively. Their comparison indicates that ion exchange results in substitution of about 60% of protons by copper. On the other hand, according to the AAS analysis the copper content in the ion-exchanged sample was equal to 2.5 weight percent. For the zeolite with the Si/Al ratio of 25 this value just corresponds to substitution of about 60% of hydroxyl groups by the Cu^{+1} ions, while substitution of 60% of OH groups by the bivalent copper would result in a twice lower copper content only of 1.25 weight percent. Therefore, there is no doubt that after reduction in CO, the predominant part of copper was transformed into Cu^{+} ions. This conclusion also well agrees with the previously reported literature data on self-reduction of

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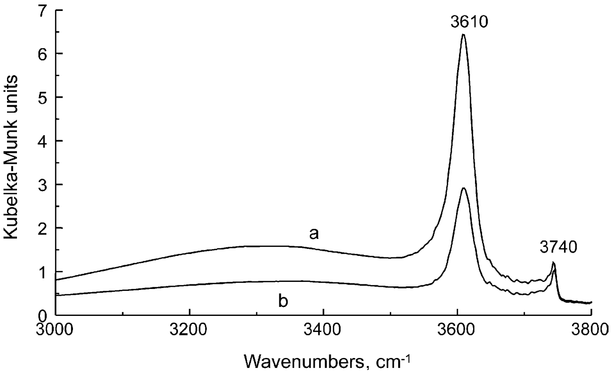

Figure 1. DRIFT spectra of OH groups in the hydrogen form of ZSM-5 (a) and in the copper modified zeolite after reduction in CO at 873 K (b) DRIFT measurements at room temperature.

bivalent copper after vacuum treatment at high temperature or reduction in CO [9–13].

The results obtained in the present study for hydrogen adsorption by reduced samples were quite surprising since they indicated absolutely unusual forms of adsorbed molecular hydrogen. This follows from figure 2 that shows DRIFT spectra of hydrogen adsorbed at 77 K by the Cu/ZSM-5 after different pretreatments.

The bands at 4105 and 4125 cm^{-1} were earlier also observed after hydrogen adsorption at 77 K on the non-modified hydrogen form of ZSM-5. Therefore they belong to hydrogen adsorption by acidic and silanol hydroxyl groups respectively [14–17]). In contrast, the low-frequency bands at 3075, 3125, 3300 and 2635 cm^{-1} are due to hydrogen molecules perturbed by Cu^{+1} ions, since they appeared only after hydrogen adsorption by the reduced copper-modified sample. The low-frequency shifts of H–H stretching vibrations are unusually large indicating a very strong perturbation of adsorbed hydrogen molecules.

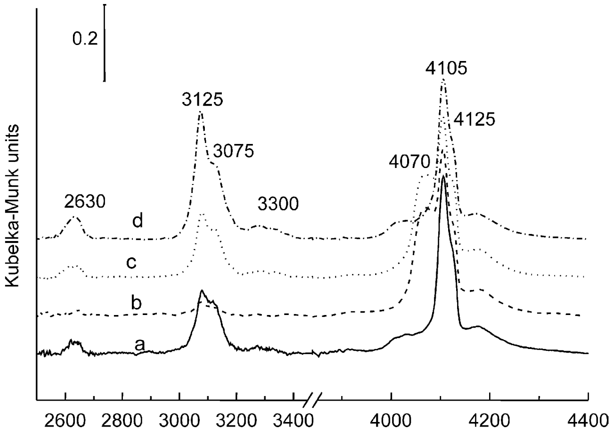

Figure 2. DRIFT spectra of molecular hydrogen adsorbed by the CuZSM-5 sample at 77 K at the pressure of 1.33×10^4 Pa after different pretreatments: (a) the sample pre-reduced in CO was evacuated for 2 h at 873 K; (b) sample (a) was subsequently calcinated in oxygen at 773 K and evacuated at room temperature; (c) sample (b) was evacuation at 873 K; (d) sample (c) was reduced in CO at 600 °C and subsequently evacuated at this temperature.

There is no doubt that hydrogen adsorption occurs on the reduced copper cations. This conclusion is supported by increasing intensities of the above-mentioned DRIFT bands after reduction of the copper-modified sample in CO atmosphere at 873 K with subsequent evacuation of carbon monoxide at this temperature (figure 2(d)). In contrast, the copper sites of hydrogen adsorption were destroyed by calcination in oxygen at 773 K figure 1(b)). Instead a new band of adsorbed molecular hydrogen with the much higher H–H stretching frequency appears at 4070 cm^{-1}. It should be ascribed to the hydrogen adsorption either by Cu^{+2} or $[Cu^{+2}\text{-O-}Cu^{+2}]^{+2}$ oxo-species resulting from oxidation of the pairing Cu^{+1} cations localized at aluminum atoms in the next nearest positions [5]. After evacuation figure 2(c)) or reduction of the oxidized sample in CO at 873 K figure 2(d)) the band at 4070 cm^{-1} was eliminated, while the strongly low–frequency shifted bands of hydrogen perturbed by reduced Cu^{+1} ions were regenerated.

Preliminary adsorption by reduced copper-modified zeolites of carbon monoxide or nitrogen at room temperature eliminates DRIFT bands of adsorbed hydrogen. This also confirms hydrogen adsorption by Cu^{+} ions, since both these molecules are also adsorbed in CuZSM-5 by univalent copper.

The similar DRIFT spectra of adsorbed hydrogen were also observed at room temperature (figure 3). This indicates a much stronger adsorption of molecular hydrogen by reduced copper ions in comparison with alkaline or bivalent transition metal cations that adsorb hydrogen only at 77 K [14–17]. However, position of the most intense band at 3082 cm^{-1} at room temperature is slightly different. This band is also not as well resolved

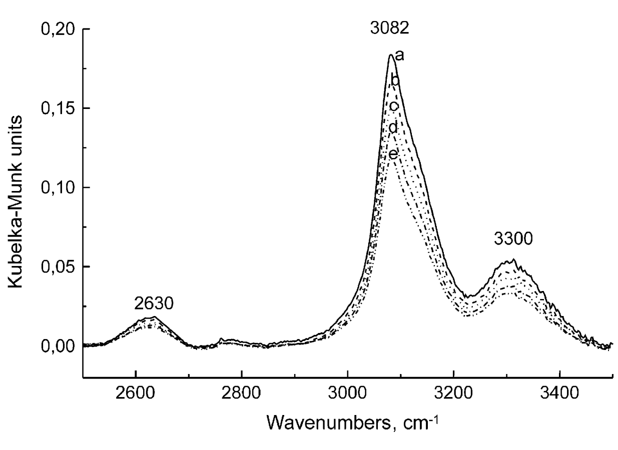

Figure 3. DRIFT spectra of molecular hydrogen adsorbed at room temperature at different pressures by reduced CuZSM-5 sample: (a) 2.66×10^4 Pa; (b) 1.33×10^4 Pa; (c) 0.67×10^4 Pa; 0.33×10^4 pa; 0.13×10^4 Pa.

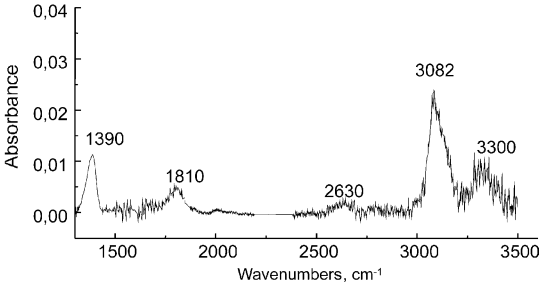

Figure 4. Transmittance IR spectrum of H_2 adsorbed by CuZSM-5 at room temperature at the equilibrium pressure of 0.67×10^4 Pa.

into two components as in the low-temperature spectrum and the relative intensity of the band at 3300 cm^{-1} is somewhat higher in comparison with the main absorption at 3082 cm^{-1}. These differences most likely indicate inhomogeneity of reduced copper sites that are differently populated by adsorbed hydrogen molecules 77 K or room temperature. The different relative intensities of the bands from adsorbed hydrogen with the maxima at 3075 and 3125 cm^{-1} are also evident in the spectra (a), (c) and (d) in figure 2. Thus, it looks like there are at least two or three different copper sites of molecular hydrogen adsorption with the different H–H stretching frequencies of 2630, 3075 and 3125 cm^{-1}.

In order to expand the spectral range of our IR measurements toward lower frequencies, we also studied adsorption of molecular hydrogen at room temperature by the transmittance technique. The corresponding IR spectrum obtained for the thin semi-transparent pellet pressed from the powder of the copper modified zeolite pre-reduced in carbon monoxide at 873 K is shown in figure 3. In this case the H–H stretching bands of adsorbed hydrogen above 2500 cm^{-1} practically coincide with those in the above-discussed DRIFT spectra. In addition, due to the less intense light scattering at lower frequencies, we also succeeded in observation of two additional IR bands from adsorbed hydrogen at 1390 and 1810 cm^{-1}. They were removed by evacuation at room temperature simultaneously with removal of the H–H stretching bands of adsorbed H_2. Therefore, they most likely belong to vibrations of the non-dissociated hydrogen molecules relative to the copper adsorption sites.

Thus, the present study indicates unusually strong perturbation of adsorbed molecular hydrogen by Cu^+ ions. The low-frequency shifts of H–H stretching vibrations are extremely large being equal to about 25% of the fundamental frequency. In this case it is even difficult to distinguish weather one deals with adsorbed hydrogen molecule or with the copper dihydride with the very strong interaction between hydrogen atoms. For the cationic forms of zeolites or for oxide catalysts such extremely strong perturbation of adsorbed H_2 has been never reported before. The similar very strong perturbation of molecular hydrogen has been reported only for complexes of noble metals in solutions [18].

Observation for adsorbed hydrogen of several stretching bands also demonstrated that Cu^{+1} adsorption sites are inhomogenous most likely due to the different environment in the zeolite structure. Our results also indicated that perturbation of adsorbed molecular hydrogen by Cu^{+2} or $[Cu\text{-}O\text{-}Cu]^{+2}$ oxo-ions is very much weaker than that by Cu^{+1} cations.

Acknowledgments

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