

QUANTITATIVE CHARACTERIZATION OF ZEOLITES BY FTIR SPECTROSCOPY OF ADSORBED CO

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The most important application of IR spectroscopy to the studies of catalysts is the ability to provide information on the nature of active sites, their strength and concentration. The strength usually correlates with the frequency shifts of test molecules on adsorption, although these data can be distorted by lateral interactions in the adsorbed layer if surface coverage is high enough. As to the site concentration, its estimation based on the measurements of band intensities is complicated by the necessity to know the absorption coefficient ϵ of test molecules, which can be influenced by adsorption.

CO has certain advantages as a test molecule for oxide adsorbents. The frequency of the only vibration changes regularly in the electric field of non-transition metal cations, reflecting the strength of Lewis acid sites. However, the data on the absorption coefficient of adsorbed CO are rather contradictory [1–4].

Mordenite-type zeolites are widely used in catalysis and for environmental protection. The catalytic properties of mordenites depend on $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio and the nature of charge compensating cations. In H-mordenites, the most important characteristic is the distribution of acidic OH groups, which depends on the number and distribution of Al-tetrahedra in the framework. In [5], the number of Lewis and Brønsted acid sites, as well as the number of silanol groups, were estimated by IR spectra of adsorbed CO, while the content of aluminum was measured from NMR data. The correspondence was not bad, but IR measurements were based on the ϵ values for CO or OH groups obtained for other zeolites, although it was known that even for the same mordenite structure the bridged Brønsted hydroxyls are not equivalent, and differ in their position.

Here we report the results of measurements of the integrated extinction coefficients and adsorption enthalpy for different CO species adsorbed on mordenite with $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio ~ 15.0 . The shift of the band of zeolitic OH groups from 3613 to 3290 cm^{-1} is accompanied by the growth of adsorbed CO band at 2175 cm^{-1} (fig. 1). Further addition of gas at $-196\text{ }^\circ\text{C}$ results in the band at 2137 cm^{-1} , which, as we believe, is due to the side-on complexes with siloxane bridges [6]. Following the procedure described in [3], we measured the quantity of adsorbed CO from the pressure increase on raising the sample from the bottom of cell to ambient temperature. The resulting ϵ value was $1.77 \pm 0.09\text{ cm}/\mu\text{mol}$ for the band at 2175 cm^{-1} and $2.0 \pm 0.1\text{ cm}/\mu\text{mol}$ for that at 2137 cm^{-1} .

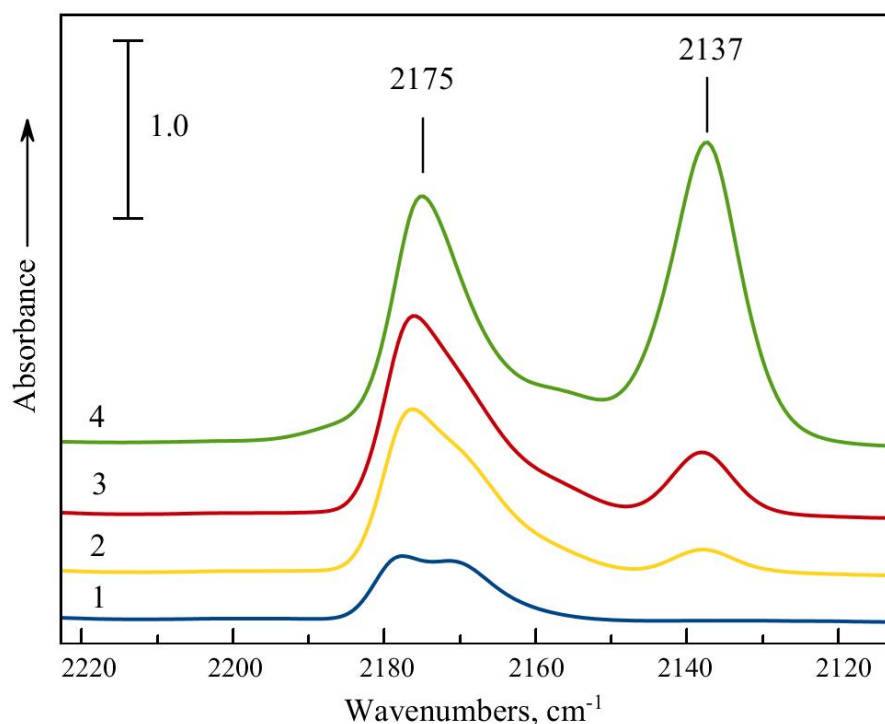


Fig. 1. FTIR spectrum of H-MOR-15.0, pretreated at 450 °C, after adsorption of 390 (1), 780 (2), 1060 (3) and 2120 (4) $\mu\text{mol/g}$ of CO

Simultaneous observation of OH band perturbation enabled us to obtain the value of ϵ for the acidic hydroxyls from the volumetric measurements of the quantity of adsorbed CO. This gave the values of 5.87 and 30.0 $\text{cm}/\mu\text{mol}$ for the bands of free and perturbed OH groups, respectively. After ammonia adsorption the OH groups are converted into ammonium NH_4^+ ions, whose band near 1450 cm^{-1} is usually present in the spectrum of mordenite sample before the pretreatment. From the comparison of band intensities of the hydroxyls and ammonium ions the ϵ value of the latter was also obtained and was found to be $11,5 \pm 0,5\text{ cm}/\mu\text{mol}$. For nitrogen, which shifts the band of OH groups from 3613 to 3490 cm^{-1} the band of induced absorption occurs at 2333 cm^{-1} , the estimated ϵ value was $0,05\text{ cm}/\mu\text{mol}$.

Using the values obtained herewith we can upgrade the data presented in [5]. The concentration of Brønsted sites for H-MOR-15.0 sample, determined basing on the OH intensity and ϵ value from [7] was much higher than that one estimated from CO band intensity and even greater than the concentration of Al in the sample from NMR measurements. Now it is below the latter, as one could expect, since certain part of aluminum exists in extraframework state.

Variable temperature spectroscopy enables us to study thermodynamics of surface processes, e.g. to measure the enthalpy of CO adsorption on the acidic OH groups of mordenite from simultaneous registration of gas pressure and temperature providing certain surface coverage (certain intensity of the corresponding band of adsorbed CO). Figure 2 shows the plot of $\ln(p)$ versus the reciprocal temperature for the 2175 cm^{-1} band. From the slope of this graph we ob-

tain the value of $\Delta H^0 = 26 \pm 3$ kJ/mol for the coverage about 0.2 of maximum. The value seems to decrease slightly with coverage increase, apparently, demonstrating some heterogeneity of the site strength. For the band at 2137 cm^{-1} , not saturable in the condition of experiment the same procedure leads to the value $\Delta H^0 = 21 \pm 2$ kJ/mol.

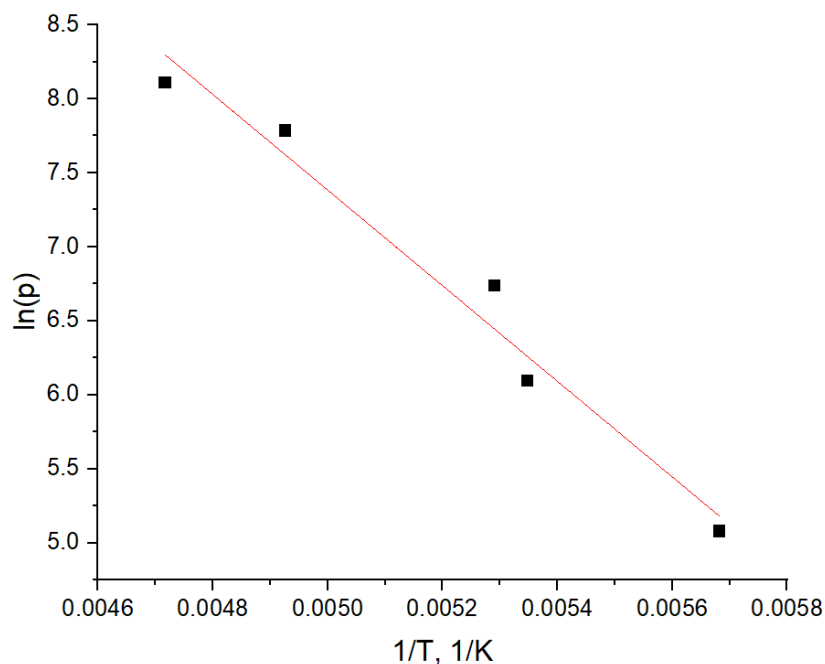


Fig. 2. The plot of $\ln(p)$ versus $1/T$ for the 2175 cm^{-1} band of CO adsorbed on H-MOR-15.0 zeolite for the intensity ~ 0.2 of maximum

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