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Journal of Catalysis 216 (2003) 192–202

JOURNAL OF CATALYSIS

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Localization of bivalent transition metal ions in high-silica zeolites with the very broad range of Si/Al ratios in the framework probed by low-temperature H_2 adsorption

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Received 12 September 2002; revised 16 October 2002; accepted 25 October 2002

Abstract

H_2 adsorption at 77 K with DRIFT control of H–H stretching frequency was used as a molecular probe for the study of MOR and ZSM-5 modified with Co^{2+}, Zn^{2+}, or Ni^{2+} ions. The obtained results indicated localization of these transition metal ions in the zeolites with the very broad range of Si/Al ratios at several different sites. Moderate red shifts of H–H stretching frequencies of H_2 adsorbed by Zn^{2+} in the aluminum-rich ZSM-5 are close to those for hydrogen adsorption by ZnY. Therefore it is suggested that similar to HY the moderately perturbing adsorbed hydrogen bivalent cations are localized in the five- or six-membered rings of the pentasil framework with two negatively charged aluminum-occupied oxygen tetrahedra per ring. In contrast, the fraction of the sites of the strongest perturbation of adsorbed hydrogen with the low-frequency shifts of H–H stretching frequency over 200 cm^{-1} is the highest at the highest Si/Al ratios. In this case aluminum ions are distantly separated from each other. Therefore, the bivalent transition metal ions are localized at the singly negatively charged aluminum-centered oxygen tetrahedra. The excessive positive charge of cations at such sites is compensated by the electrostatic interaction with the surrounding negatively charged $[AlO_2]^-$ tetrahedra with cationic vacancies. In ZSM-5 such acid–base pairs with the distantly placed Zn^{2+} cations and basic oxygen dissociatively adsorb molecular hydrogen at room temperature or at the moderately elevated temperatures. Formation of the active sites with the excessive positive charge of transition metal ions explains the unusually strong perturbation of adsorbed hydrogen and unusual catalytic properties of the high-silica zeolites modified by transition metal ions.

Keywords: High-silica zeolites; Sitting of Zn^{2+}, Ni^{2+}, and Co^{2+}; H_2 molecular probe; Hydrogen adsorption; DRIFT

1. Introduction

High-silica zeolites modified with transition metal ions exhibit unique catalytic properties that are quite different from those of the low-silica zeolites modified with the same cations. For instance, ZnZSM-5 or GaZSM-5 for a long time were known as the active catalysts for aromatization of light paraffins [1,2]. Modification of ZSM-5 with Co^{2+} or Cu^{2+} ions results in the catalysts of selective NO reduction with methane, or of NO and N_2O decomposition with formation of molecular nitrogen [3,4]. CoZSM-5 is active in amoxidation of ethane into acetonitryl [3], etc. Therefore, the study of the localization in the high-silica zeolites of modifying transition metal ions is by no means of great interest. However, this is a rather difficult task due to the random distribution and to the low concentration of aluminum and the compensating transition metal ions in these materials.

Indeed, direct XRD data on localization of transition metal ions in pentasils are absent. The main information on this subject has been obtained in an indirect way from UV–VIS spectra, fluorescence, XAFS, or IR control of perturbation of adsorbed probing molecules. In the present work we also used for the study of the state of Zn^{2+}, Co^{2+}, and Ni^{2+} ions in HM and high-silica HZSM-5 a similar approach of molecular probes. However, the probe itself—H_2 adsorption at 77 K—was quite unusual. The choice of hydrogen was connected with its extremely high resolving power for discrimination of different cationic adsorption sites that has been demonstrated in our previous work on the study of alkaline and alkaline earth forms of faujasites [5].

Another important feature of our work was the very broad Si/Al ratios in the zeolites under study. Most researchers ignored this factor whereas we considered only the influence

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doi:10.1016/S0021-9517(02)00117-3

on localization of transition metal ions of the geometry of different windows in the zeolite framework [6,7]. However, as will be shown later, the role of aluminum distribution is even more important.

2. Experimental

Initial hydrogen forms of ZSM-5 and mordenite were obtained by decomposition of ammonium forms in vacuo at 773 K followed by calcination in flowing oxygen at 793 K. Below the Si/Al ratios in the zeolites under the study are indicated in brackets. MOR(5), ZSM-5(41), and ZSM-5(80) were obtained from Shell, ZSM-5(15) from Akzo Chemical, and ZSM-5(25) from Alsi Penta. Modification of most of the samples with transition metal ions was carried out by incipient wetness impregnation of the corresponding hydrogen forms with the aqueous solutions of nitrates [8–10]. The content of transition metal ions in the samples was equal to 1 wt%. This was estimated from the preparation procedure, and for some of the samples it was also checked by AAS analysis. Modification of HZSM-5(25) by reaction with zinc vapor was carried out at 720 K for the sample that was preevacuated at this temperature for 4 h.

The impregnated samples of the zeolites were dried at 473 K, calcined in flowing oxygen at 700 K for 1 h and then evacuated for 4 h at several gradually increasing intermediate temperatures, which are indicated in the figure legends. DRIFT spectra of hydroxyl groups and those of adsorbed molecular hydrogen were recorded for each of the pretreatment temperatures.

As in our previous work [8–10], DRIFT measurements were carried out in quartz ampoules using a Nicolet Impact 410 Fourier transforming spectrophotometer equipped with a homemade diffuse reflectance unit. DRIFT spectra of hydroxyl groups were recorded at room temperature whereas those of adsorbed molecular hydrogen were taken at 77 K. For cooling the samples we used a quartz Dewar vessel filled with liquid nitrogen. Molecular hydrogen was adsorbed at an equilibrium pressure of 1.33×10^4 Pa (100 Torr). All DRIFT spectra were transformed into Kubelka–Munk units using a standard program assuming that the reflective ability of the samples at 5000 cm^{-1} was equal to 0.9 kM units. After that the backgrounds created by zeolites were subtracted.

3. Results

3.1. *Dehydroxylation of the initial hydrogen forms*

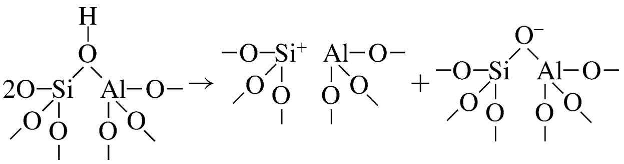
Dehydroxylation of high-silica zeolites was controlled in two different ways: by monitoring directly DRIFT spectra of hydroxyl groups or using low-temperature hydrogen adsorption as a molecular probe.

As shown in Fig. 1a, upon increasing the dehydration temperature of HZSM(41) from 570 to 920 K, the intensity of the DRIFT band from acidic hydroxyl groups at 3610 cm^{-1} decreased by about 25%. As seen in Fig. 1b, the results similar to HMOR(5) were obtained. Thus, in agreement with previously published results, high-temperature vacuum pretreatment of high-silica zeolites results in partial dehydroxylation. This conclusion was also confirmed by low-temperature hydrogen adsorption as a molecular probe.

Figs. 2a and 3a display evolution of DRIFT spectra of molecular hydrogen adsorbed at 77 K by the same samples of HMOR(5) and HZSM(41) dehydroxylated at the same temperatures as those in Fig. 1. The spectra of hydrogen adsorbed by HZSM-5 in Fig. 3a contain two unresolved H–H stretching bands with the maxima at 4105 and at about 4125 cm^{-1}, respectively from H_2 perturbed by the acidic hydroxyls and by silanol groups. The low-intensity high-frequency band with the maximum at 4182 cm^{-1} has been attributed to the high-frequency satellite, i.e., to a combination mode of the H–H stretching vibrations with oscillations of adsorbed molecular hydrogen relative to the Brønsted acidic sites [5]. DRIFT spectra in Fig. 2a of H_2 adsorbed by the dehydroxylated mordenite are very similar to those of the dehydroxylated HZSM-5; however, the bands from hydrogen adsorbed by the silanol groups are not resolved.

Both for HMOR and HZSM-5 the intensities of the low-frequency bands with the maxima at about 4030 cm^{-1} monotonically increased upon increasing temperature of vacuum pretreatment. In contrast, the bands from hydroxyl groups decreased. Therefore, in agreement with our previous studies [9], we ascribed the new low-frequency strongly shifted bands to hydrogen molecules perturbed by adsorption sites resulting from the high-temperature dehydroxylation of the corresponding hydrogen forms.

Such Lewis lattice sites are most likely formed by removal of two bridging hydroxyl groups according to the following equation:



$+ H_2O$. (1)

For both zeolites this mechanism is supported by a much lower intensity of DRIFT bands from the silanol groups in comparison with the bridging hydroxyls. Therefore, dehydroxylation obviously could not result from the recombination of the bridging OH groups with SiOH groups. In addition, the intensities of the bands from the silanol groups in both zeolites practically do not decrease upon dehydroxylation.

It is also possible that the band with the maximum at 4030 cm^{-1} is connected with H_2 adsorption by the extra lattice AlO^+ ions which are formed by subsequent

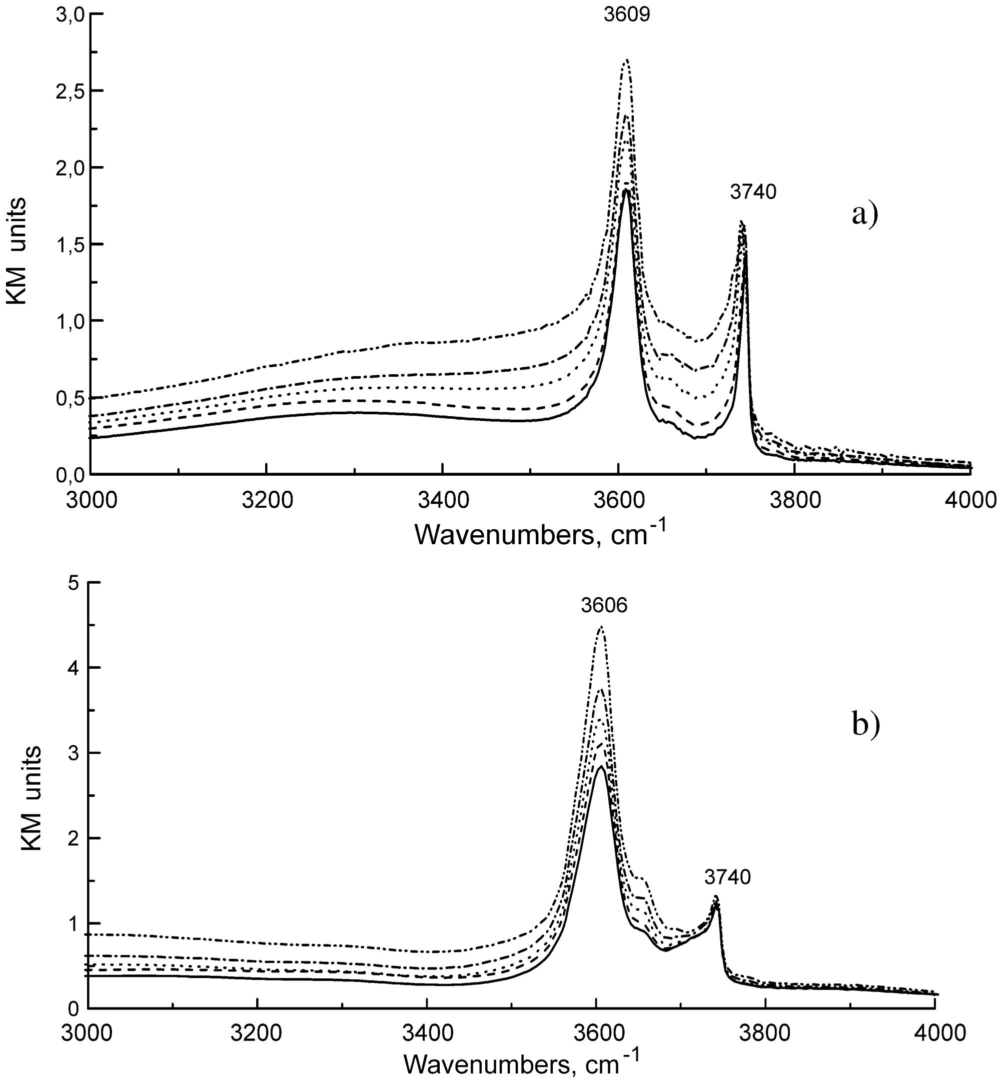
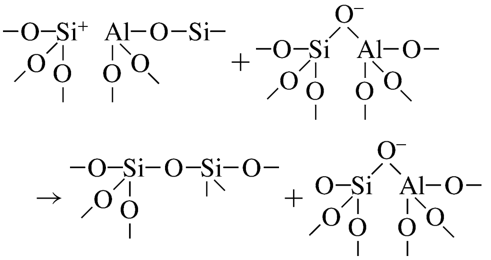


Fig. 1. Evolution of DRIFT spectra of OH groups in the HZSM-5(41) zeolite (a) and in HM(5) (b) upon different vacuum pretreatments: pretreated in vacuum at 300 °C (-···-), 400 °C (-·-·-), 500 °C (· · ·), 600 °C (- - -) or 650 °C (—). DRIFT measurements at 298 K.

dealumination of the dehydroxylated zeolite according to Eq. (2):



$$-O-\overset{+}{Si}(O)(O)\quad Al(O)(O)-O-Si- \;+\; -O-Si(O)(O)\overset{O^{-}}{}Al(O)(O)-O- \;\rightarrow\; -O-Si(O)(O)-O-Si-O- \;+\; O-Si(O)(O)\overset{O^{-}}{}Al(O)(O)-O- \;+ AlO^{+} + H_2O. \qquad (2)$$

3.2. Dehydroxylation of HM and ZSM-5 zeolites modified with Co^{2+} or Ni^{2+} ions

The main difference in dehydroxylation of the pure hydrogen forms of high-silica zeolites and of those modified with Co^{2+} or Ni^{2+} ions consists in appearance for the latter of several new DRIFT bands from adsorbed hydrogen with the much larger low-frequency shifts of H–H stretching vibrations [11]. These bands were ascribed to H_2 molecules adsorbed by the modifying transition metal ions. In addition, after dehydroxylation of the modified samples the intensities of the bands from acidic hydroxyl groups and of those from the hydrogen adsorbed by these hydroxyl groups were decreasing somewhat stronger than for the corresponding hydrogen forms. Therefore, we concluded that modification results in partial substitution of acidic hydroxyl groups by transition metal ions creating the new sites of low-temperature hydrogen adsorption.

As one can see by comparing Fig. 2b with Figs. 3b and 4a, the proportion between intensities of different bands of hydrogen adsorbed by cobalt ions depends on the Si/Al ratio in the zeolite framework (see also [11]). Indeed, for the aluminum-rich CoHMOR(5) three H–H stretching bands with the poorly resolved maxima are evident in DRIFT spectra of adsorbed hydrogen at 3965, 3920, and 3890 cm^{-1}

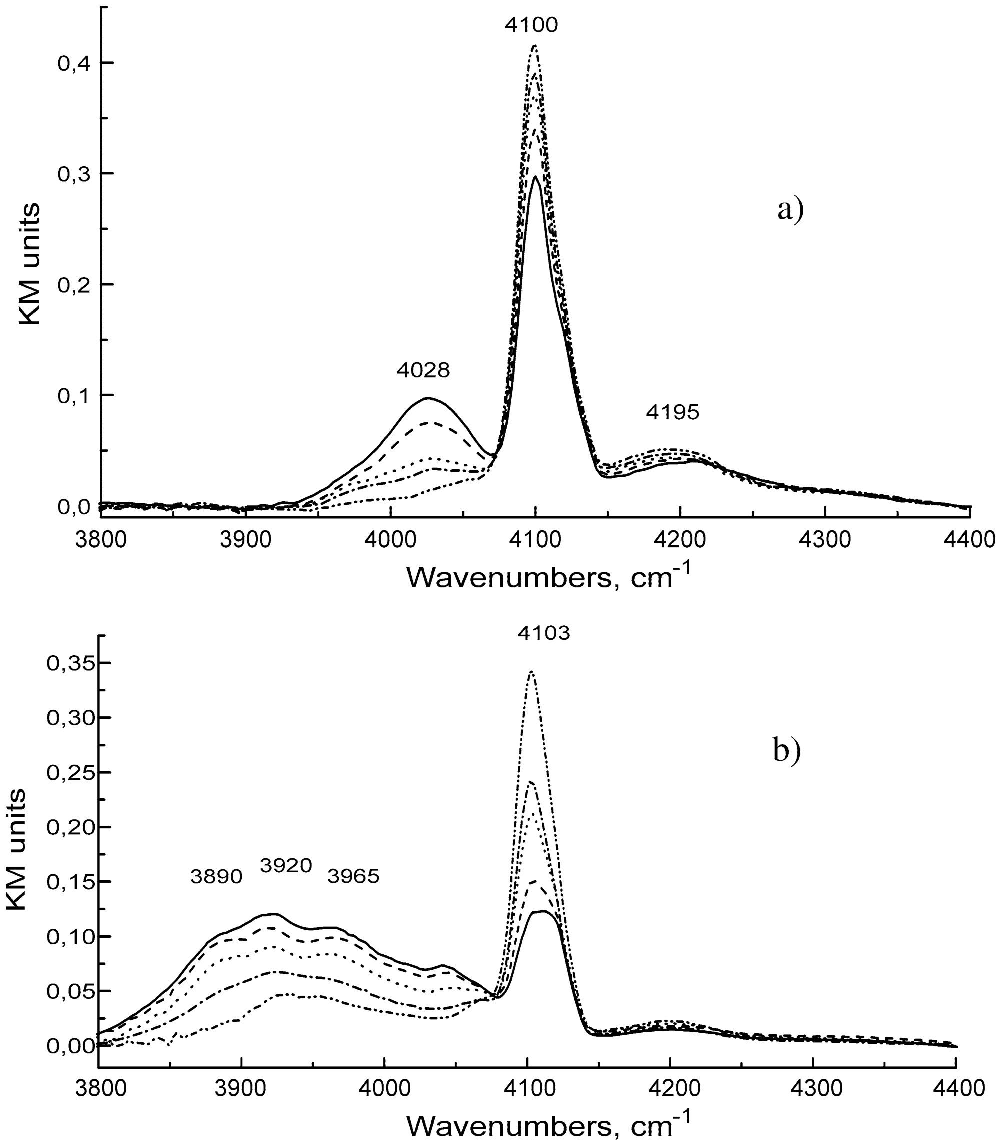


Fig. 2. DRIFT spectra of H_2 adsorbed at 77 K by the same zeolites as in Fig. 1 measurements at 77 K. (a) HMOR. (b) CoHMOR.

with the poorly resolved maxima. With the increasing Si/Al ratios, the number of different sites connected with Co^{2+} decreases in favor of the sites of the strongest hydrogen perturbation with the lowest H–H stretching frequency of 3896 cm^{-1} (Fig. 3b). (The band at 4927 cm^{-1} in this figure belongs to either hydrogen adsorption by the extra lattice AlO^+ ions or the lattice Lewis sites.) The summary of H–H stretching frequencies of hydrogen adsorbed by Co^{2+} ions in the zeolites with the different Si/Al ratios in the framework is given in Table 1.

Results obtained for ZSM-5 modified with Ni^{2+} are quite similar. This is evident from comparison of the spectra in Figs. 4a and 4b. However, the low-frequency H–H stretching shifts of adsorbed hydrogen for the nickel are larger. Therefore, the resolution of the H–H stretching bands is better and one can better discriminate three different sites of low-temperature molecular hydrogen adsorption.

3.3. High-silica zeolites modified with Zn^{2+} ions

The results for hydrogen adsorption by ZnHZM-5 or ZnHMOR which were also prepared by incipient wetness impregnation are similar to those for cobalt or nickel [9,10]. However, due to the somewhat smaller red shifts of the H–H stretching bands, resolution of the spectra for the zinc modified samples is worse and instead of three different sites only two sites of Zn^{2+} localization could be discriminated (see Figs. 5 and 6 and Table 1). Also similar to the ZSM-5 modified with Co or Ni the relative intensity of the most strongly red shifted band increases at the higher Si/Al ratios. In contrast, the relative intensity of the band from the moderately perturbed adsorbed hydrogen decreases (Figs. 5b and 6a and 6b). Thus, the conclusion about the existence in high-silica zeolites of several different sites of localization of bivalent transition metal ions is quite general. Moreover,

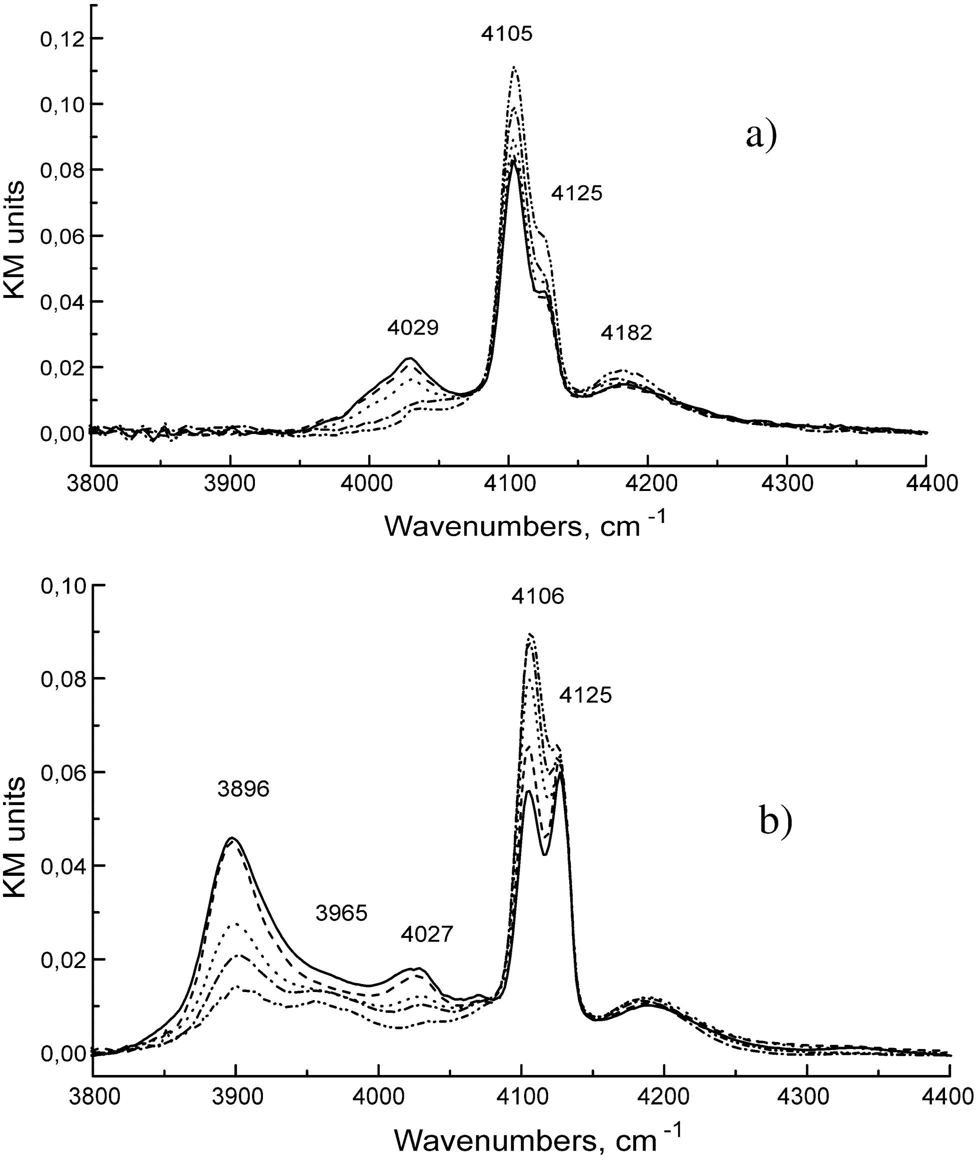


Fig. 3. DRIFT spectra of molecular hydrogen adsorbed at 77 K by HZSM-5(41) (a) and by CoZSM-5(41) (b). Pretreatment temperatures are the same as those in Fig. 1.

low-temperature hydrogen adsorption indicated that for all three transition metal ions the fraction of the sites of the strongest hydrogen perturbation strongly increases at the higher Si/Al ratios.

Unfortunately, the incipient wetness impregnation results only in partial substitution of protons by transition metal ions. Indeed, as one can see from Figs. 2–6, the extent of proton replacement by different bivalent cations was in our experiments only about 30–50%. Therefore, at the constant loading of 1 wt% the resting modifying bivalent cations form small clusters of corresponding oxides in amounts depending on the Si/Al ratio in the zeolite framework [11]. For a more complete substitution of protons by zinc ions, we also tried to modify HZSM-5(25) by high-temperature reaction with zinc vapor results similar to those published earlier for HY in [12]. In this case the obtained results indicated that substitution of protons by Zn^{2+} ions was practically complete.

This conclusion follows from DRIFT spectra of hydroxyl groups which are shown in Fig. 7a. The solid line in this figure corresponds to the spectrum of the initial HZSM-5(25) pretreated in vacuum at 720 K. As shown by the dashed line, after reaction with zinc vapor at 720 K, the band from the acidic hydroxyls with the maximum at 3610 cm^{-1} almost completely disappeared. This indicates quantitative substitution of protons by zinc ions. In contrast, the intensity of the band with the maximum at 3740 cm^{-1} did not change. Therefore, the silanol groups are not involved in reaction with zinc vapor.

Quantitative substitution of protons by zinc ions also follows from the DRIFT spectrum of adsorbed hydrogen that is shown in Fig. 7b. In agreement with Fig. 7a, the

Table 1
Experimental stretching frequencies of H_2 adsorbed at 77 K ZSM-5 and HY with different Si/Al ratios in the framework modified with Zn^{2+}, Co^{2+}, and Ni^{2+} ions in amount of 1 wt%

Zeolites	ν_1	ν_2	ν_3	Reference
ZnY		4037 (123)		[8]
ZnHMOR	3967 (193)		3928 (232)	[Kazansky et al., submitted for publication]
ZnHZSM-5(15)	4003 (157)		3964 (196)	
ZnHZSM-5(25)	4005 (155)		3948 (222)	[Kazansky et al., submitted for publication]
ZnHZSM-5(40)	4010 (150)		3936 (224)	
ZnHZSM-5(80)	4010 (150)		3934 (226)	
ZnZSM-5(25)	4010 (159)		3938 (222)	This paper
CoHMOR	3965 (195)	3920 (240)	3890 (270)	[11]
CoHZSM-5(15)	4007 (153)	3965 (195)	3905 (255)	
CoHZSM-5(25)	4010 (150)	3980 (180)	3904 (256)	[11]
CoHZSM-5(40)	—	3980 (180)	3903 (357)	
CoHZSM-5(80)	—	3965 (195)	3896 (264)	
NiHZSM-5(25)	3967	3928	3866 (294)	This paper

Si/Al ratios and the low frequency shifts of H–H stretching vibrations relative to the stretching frequency of free hydrogen are given in brackets.

band of H_2 adsorbed by the bridging protons is practically absent, whereas the intensity of the most strongly low-frequency shifted band with the maximum at 3938 cm^{-1} is about two times stronger than that for hydrogen adsorbed by the ZnHZSM-5(25) sample prepared by incipient wetness impregnation (compare Figs. 6a and 7b).

Earlier we reported that the most strongly perturbing H–H stretching frequency Zn^{2+} ions dissociatively adsorb hydrogen at room temperature. In [10] this conclusion was made in an indirect way from the weaker adsorption of molecular hydrogen at 77 K after hydrogen adsorption at room temperature. This result was explained by the blocking of the low-coordinated Zn^{2+} ions by hydrides resulting from the dissociative hydrogen adsorption:

$$Z^-–Zn^{2+}–Z^- + H_2 \rightarrow Z^-–Zn^{2+}–H^- + Z–H^+. \qquad (3)$$

In the present work, due to the more selective preparation of ZnZSM-5 zeolite via reaction with zinc vapor, such dissociative hydrogen adsorption was observed directly by appearance of DRIFT bands from the hydroxyls and zinc hydrides (Figs. 8a and 8b).

The maximum of the OH band at 3610 cm^{-1} in Fig. 8b indicates that dissociative adsorption results in formation of the same bridging hydroxyl groups as in the initial HZSM-5. In contrast, the stretching frequency of zinc hydride of 1934 cm^{-1} that is formed in parallel with hydroxyl groups is somewhat unusual: it is more than by 200 cm^{-1} higher than that for the hydrides resulting from dissociative hydrogen adsorption on ZnO of 1710 cm^{-1} [11].

According to Eq. (3), the number of hydroxyl groups resulting from heterolytic dissociative adsorption of hydrogen should be equal to one half of the number of protons in the initial sample. In reality the amount of hydroxyls regenerated after dissociative adsorption of hydrogen in Fig. 8a is about 30% of the bridging hydroxyl groups in Fig. 7a. Thus, the zinc ions resulting from reaction of protons with zinc vapor are only partially involved in dissociative hydrogen adsorption. In agreement with our results published earlier in [10], this should be explained by the weaker perturbation of hydrogen by that part of Zn^{2+} ions which results in the moderate perturbation of adsorbed hydrogen with the stretching frequency of 4010 cm^{-1}.

4. Discussion

As one can see from Table 1 and Figs. 5 and 6, our results on low-temperature molecular hydrogen adsorption indicated localization of Zn^{2+} cations in mordenite and ZSM-5 at two different sites and Co^{2+} and Ni^{2+} ions at three different sites (the band with the maximum at 4027 cm^{-1} in some of these figures belongs to hydrogen adsorption on the framework Lewis acid sites). As already discussed, the proportions of the amounts at these sites depend on the Si/Al ratio in the ZSM-5 framework.

According to Table 1, low-frequency stretching shifts of hydrogen adsorbed by the weaker Zn^{2+} sites in ZSM-5 zeolites for all Si/Al ratios in the zeolite framework are equal to ~ 155 cm^{-1}. This is close to the shift of 123 cm^{-1} that has been reported earlier in [8] for hydrogen adsorption by Zn^{2+} ions at S_{II} sites in ZnY. Therefore, it is highly probable that similar to ZnY, the sites with the moderate red shifts of adsorbed hydrogen are represented by Zn^{2+} ions in the six-membered rings of the ZSM-5 framework which contain two Al atoms per the ring. The similar localization of Zn^{2+} ions in the five-membered rings is also quite probable; however, since the bands at ca. 4010 cm^{-1} are not resolved, discrimination between five- and six-membered rings is not possible.

It is also very likely that the sites of moderate perturbation of adsorbed hydrogen with the close shifts of H–H stretching vibrations correspond to the localization of cobalt and nickel in the five- or six-membered rings of the zeolite framework with two aluminum atoms per ring. For nickel, resolution of the corresponding bands is much better than it is for cobalt.

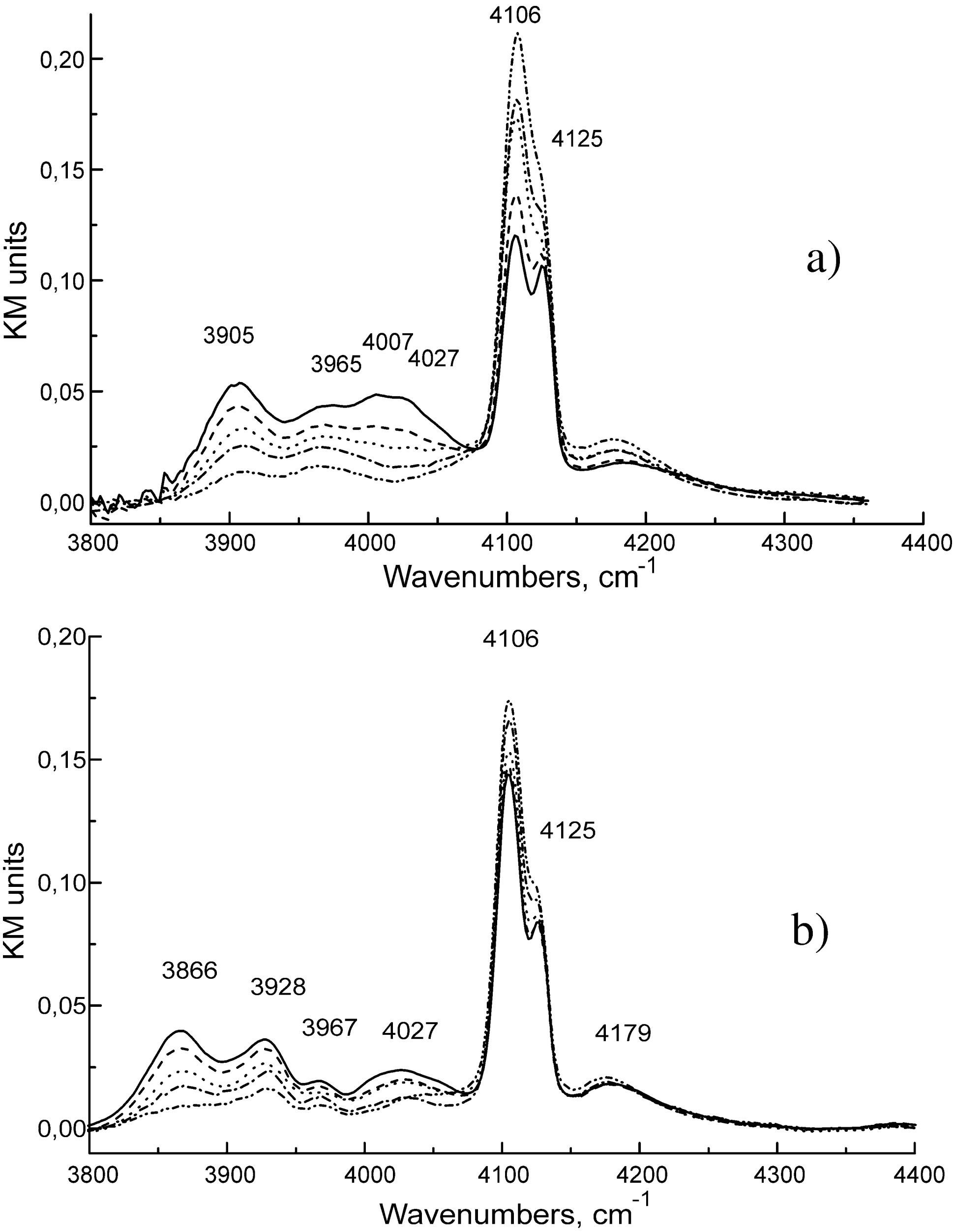


Fig. 4. DRIFT spectra of molecular hydrogen adsorbed at 77 K by CoZSM-5(25) (a) and by NiZSM-5(25) (b). Pretreatment temperatures are the same as those in Fig. 1.

The possible positions of bivalent cations in the zeolites with the very high Si/Al ratios in the framework have been discussed in a number of previously published papers. In all of them it was postulated that similar to the aluminum-rich zeolites the bivalent cations, are localized at two negatively charged aluminum-centered tetrahedra in the next nearest positions. The number of such sites should decrease at higher Si/Al ratios. In this connection, several attempts have been made to predict the distribution of Al atoms in the silicon-rich zeolites.

Stochastic simulations of Al distribution have been performed by Feng and Hall [13] and by Rice et al. [14]. The latter authors discussed also the effects of the nonrandom distribution of Al in the zeolite frameworks [15]. It was demonstrated in these papers that at the very high Si/Al ratios the probability of finding two Al ions in the same rings of the pentasil framework is very low. Therefore, for the random aluminum distribution that follows from ^{29}Si MAS NMR experiments [16], localization of bivalent cations at the sites with the distantly placed Al ions should be also considered.

Since the number of the pairing aluminum sites in ZSM-5(25) is certainly much less than the total aluminum content, our results on quantitative substitution of protons by Zn^{2+} ions for the first time present the direct experimental evidence of localization of bivalent transition metal cations at the single lattice negative charges.

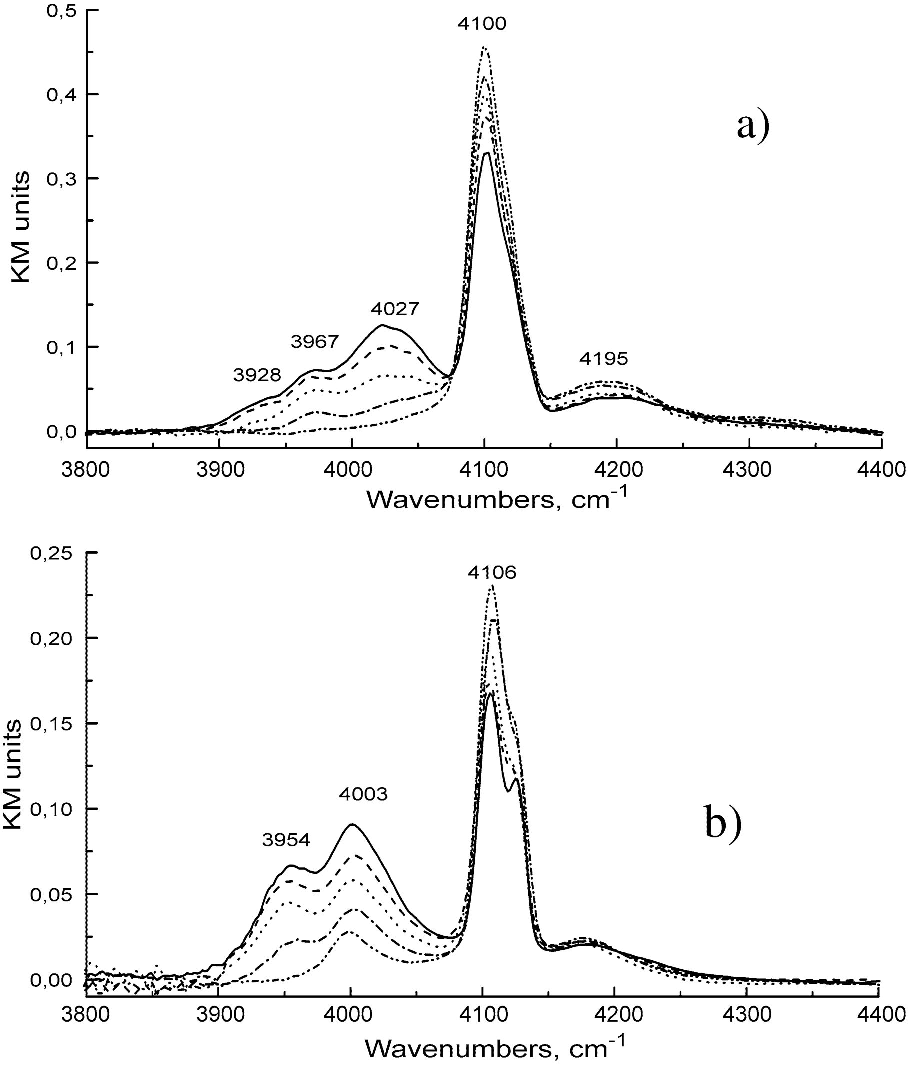


Fig. 5. DRIFT spectra of molecular hydrogen adsorbed at 77 K by ZnMOR (a) and by ZnZSM-5(15) (b). Pretreatment temperatures are the same as those in Fig. 1.

Indeed, there are many examples of substitution in high zeolites of monovalent cations by others. Probably the best known example of such is the preparation of ammonium forms by ion exchange of sodium forms with ammonium ions:

$$Z^{-}\text{–}H^{+} + NH_4Cl \rightarrow Z^{-}\text{–}NH_4^{+} + HCl. \tag{4}$$

Complete substitution of protons by the monocharged cations is also possible via reactions with vapors of zinc or gallium chlorides. For instance, for zinc chloride,

$$Z^{-}\text{–}H^{+} + ZnCl_2 \rightarrow Z^{-}\text{–}ZnCl^{+} + HCl. \tag{5}$$

For zinc vapor a similar reaction should result in the substitution of protons by monovalent Zn^{1+} ions:

$$Z^{-}\text{–}H^{+} + Zn^{0} \rightarrow Z^{-}\text{–}Zn^{+} + \tfrac{1}{2}H_2. \tag{6}$$

However, this is not the case since it is well known that reaction of zinc with acids results in the bivalent zinc ions and hence requires two protons. In addition to this argument based on the general experience of inorganic chemistry, formation in our experiments of bivalent zinc ions is supported by the same stretching frequencies of H_2 adsorbed both by the samples prepared by reaction with zinc vapor and by impregnation with bivalent zinc nitrate. In other words, reaction with zinc vapor results in substitution by a single bivalent zinc cation of two distantly placed protons:

$$2Z^{-}\text{–}H^{+} + Zn^{0} \rightarrow Z^{-}\text{–}Zn^{2+} + Z^{-} + \tfrac{1}{2}H_2. \tag{7}$$

Localization in high-silica zeolites at such sites of the bivalent cations most likely corresponds to the structures with alternating positive and negative electric charges. In this case one half of the bivalent cations is stabilized at the single negatively charged isolated aluminum-occupied oxygen tetrahedra creating the sites with the excessive positive charges. The negative charge of the rest of aluminum-centered tetrahedra with the cationic vacancy is then compensated in an indirect way by electrostatic interaction with the surrounding biva-

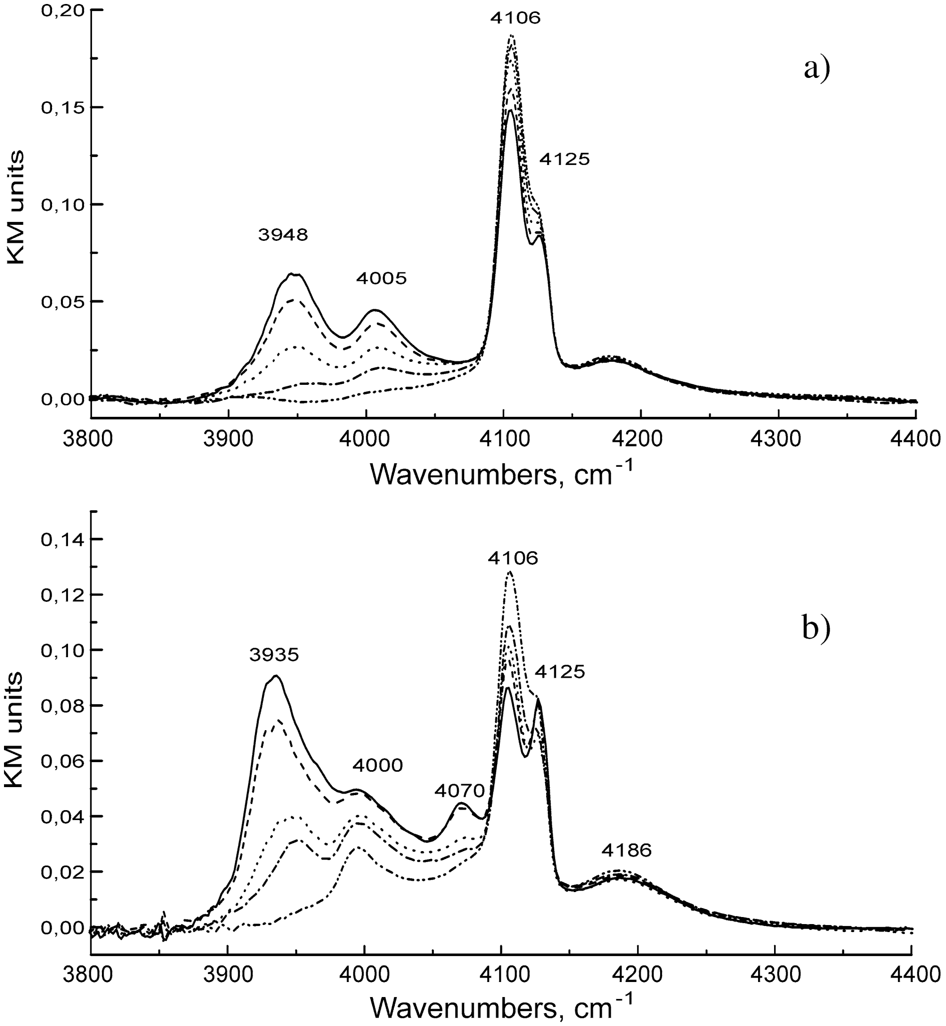


Fig. 6. DRIFT spectra of molecular hydrogen adsorbed at 77 K by ZnZSM-5(25) (a) and by ZnZSM-5(80) (b). Pretreatment temperatures are the same as those in Fig. 1.

lent cations. For localization in high-silica zeolites of multivalent cations such structures are quite unusual. However, the structures similar to those of local alternating excessive positive and negative electric charges of cations and lattice oxygen in the framework have been well known for a long time for a large number of simple and mixed oxides with different electric charges of cations and lattice oxygen. A well-known example of such a structure is the crystal structure of spinels.

The important feature of such a charge alternation model should be the stronger perturbation of adsorbed molecules by the bivalent cations with only partially compensated positive charges than by the same cations at two aluminum atoms in the next nearest positions. This explains our observation in the present study and in our previous work [9–11] concerning the unusually large low-frequency shifts of molecular hydrogen adsorbed by bivalent cations in the zeolites with very high Si/Al ratios in the framework when the charge alternation model with the distant placing of aluminum ions is most probable. The properties of adsorbed species resulting from heterolytic dissociative hydrogen adsorption also support this model.

Indeed, the unusually high stretching frequency of zinc hydrides resulting from hydrogen dissociative adsorption of 1930 cm^{-1} is more than 200 cm^{-1} higher than that for those resulting from hydrogen adsorption on zinc oxide [17]. This also confirms the unusual properties of zinc ions in the zeolites with the very high Si/Al ratios. The unusually high stretching frequency of hydrides is, however, quite naturally explained by the excessive positive charge of the zinc ions localized at the singly negatively charged aluminum-centered oxygen tetrahedra.

The stretching frequency of the bridging protons resulting from heterolytic dissociative hydrogen adsorption of 3610 cm^{-1} also fits well in the model of the acid–base pairs with the distantly placed zinc ions and basic oxygen atoms. Indeed, it is the same as that for the isolated bridging acidic hydroxyl groups in the initial HZSM-5. For the hydroxyl groups closely adjacent to zinc ions this should be hardly expected.

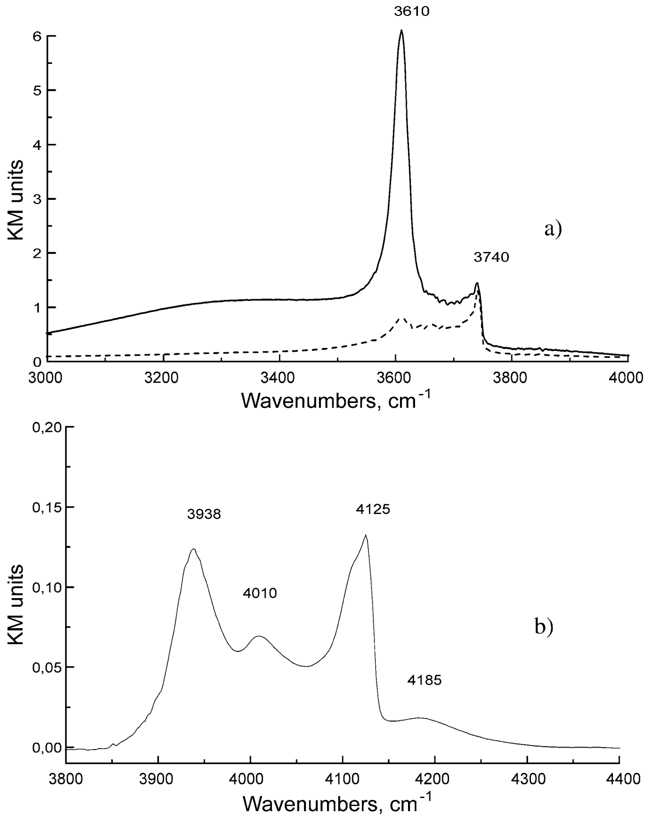


Fig. 7. (a) Solid line—DRIFT spectra of hydroxyl groups in HZSM-5(25). Dashed line—DRIFT spectra of hydroxyl groups in the same sample after reaction with zinc vapor at 720 K. DRIFT measurements are at room temperature. (b) DRIFT spectrum of hydrogen adsorbed by ZnHZSM-5 prepared by reaction with zinc vapor. Measurement is at 77 K.

Last, but not least, the unusual state of Zn^{2+} and the other bivalent transition metal ions at the sites with the distantly placed aluminum atoms explains the unusual catalytic properties of high-silica zeolites recently reported in the literature.

5. Conclusions

Localization of bivalent transition metal ions in pentasils with high-aluminum content in the five- or six-membered with two aluminum atoms per ring is similar to that in faujasites. In contrast at the very high Si/Al ratios the main part of bivalent transition metal cations is localized at the sites with the distantly placed aluminum atoms. This results in the acid–base pairs with the positively charged cations and negatively charged oxygen atoms separated from each other. Formation of such acid–base sites explains unusually strong perturbation and heterolytic dissociation of molecular hydrogen. Such a charge alternation model of the active sites with the distant placing of cations and basic oxygen also explains well the unusual catalytic properties of high-silica zeolites recently reported in the literature for a number of different reactions.

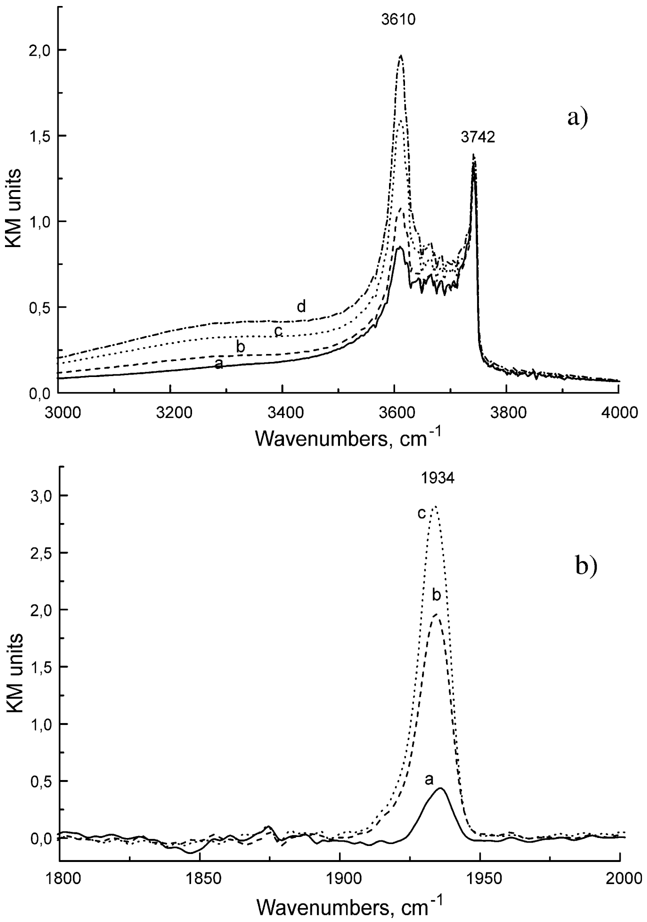


Fig. 8. Dissociative adsorption of H_2 at the pressure of 100 Torr on ZnZSM-5 prepared by reaction with zinc vapor at 720 K. DRIFT measurements are at 293 K. (a) DRIFT spectra of hydroxyl groups. Initial spectrum (a); adsorption at 293 K (b); at 373 K (c), and at 473 K (d). DRIFT spectra of zinc hydrides. Adsorption at 293 K (a); at 373 K (b); and at 473 K (c).

Acknowledgments

The Dutch Science Foundation and the US Civilian and Research Development Foundation are gratefully acknowledged for the financial support of Projects 99003288 and CRDF RC-1 2204. The author is also grateful to Prof. R.A. van Santen and Prof. A.T. Bell, who participated in different parts of this work.

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