

Nature of the sites of dissociative adsorption of dihydrogen and light paraffins in ZnHZSM-5 zeolite prepared by incipient wetness impregnation

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A DRIFT study of ZnHZSM-5 zeolites with Si/Al ratios of 15 or 41 and a Zn loading of 0.8 wt% revealed a high thermal stability of bridging OH groups that was practically the same as in the pure hydrogen forms. It was concluded that the incipient wetness impregnation of NH₄ZSM-5 zeolite with zinc nitrate and the subsequent high-temperature treatment results only in a minor amount of ion exchange. A considerable part of the modifying zinc forms nanometric ZnO clusters inside the channels of the zeolite. The use of the low-temperature adsorption of dihydrogen as a probe indicated the appearance, after high-temperature vacuum pretreatment, of three different Lewis acid sites connected with coordinatively-unsaturated Zn²⁺ ions. The strongest Lewis sites, with an H–H stretching frequency of adsorbed molecular hydrogen of 3940 cm⁻¹, dissociatively adsorbed hydrogen, methane and propane at both room and elevated temperatures. These sites are represented either by Zn²⁺ ions on the walls of the main channels of the zeolite (α sites according to Mole et al.) or by Lewis-base pairs on the surface of nanometric clusters of zinc oxide.

Keywords: ZnHZSM-5 zeolites, DRIFT spectra of adsorbed dihydrogen, dissociative adsorption, nanometric ZnO clusters

1. Introduction

HZSM zeolites modified with Zn²⁺ ions are active catalysts for the aromatization of light paraffins. These materials can be prepared by wet ion exchange, by impregnation or by solid ion exchange. It is believed that zinc increases the rate and selectivity of aromatization by increasing the rate of propane and propene dehydrogenation [1–7].

The state of zinc in ZSM-5 zeolites has been studied in several publications to date. It was studied by IR spectroscopy [8,9], by thermodesorption or thermoreduction [6,9,10], and by EXAFS [9].

The proposed models suggest that zinc is introduced in those materials as either Zn²⁺ ions [8–10] or as ZnOH⁺ ions [6], or that Zn²⁺ replaces two protons in the neighboring aluminum–oxygen tetrahedra resulting in formation of binuclear (Al–O–Zn²⁺–O–Zn²⁺–O–Al) bridging fragments [9]. However, none of these models explains all of the available experimental data. For instance, the bands of ZnOH⁺ species have never been directly observed in IR spectra. In addition, the substitution of protons by Zn²⁺ ions does not agree well with the high concentration of bridging hydroxyl groups that remains on HZSM-5 zeolites after high-temperature pretreatment [9]. Further, for ZSM-5 zeolites with high silica-to-aluminum ratios, the formation of binuclear structures is rather unlikely [10].

Although ZnZSM-5 zeolites are known to activate paraffins, the sites responsible for dissociative adsorption of paraffins have yet not been directly observed by any spectral technique. In this context, we tried to detect these sites

via carbon monoxide and low-temperature hydrogen adsorption as molecular probes using highly sensitive DRIFT spectroscopy. The first of these molecules has been widely used for testing of different coordinatively-unsaturated surface cations, while the second probe has been more recently introduced for this purpose in our previous work [11–15]. The adsorption of molecular hydrogen was proven to be very adept at resolving the nature of different cations. For instance, molecular hydrogen adsorption is even able to discriminate between sodium ions in faujasites at S_{II} sites in six-membered rings that contain different numbers of aluminum atoms in the ring [15]. This is possible because adsorbed molecular hydrogen is not only a probe for the cations alone but is also rather sensitive for acid–base pairs that contain the low coordinated cations and the adjacent basic oxygen atoms. The effectivity of adsorbed hydrogen as a molecular probe was also demonstrated earlier in the study of ZnHY zeolite [16].

2. Experimental

Ammonium forms of ZSM-5 zeolites with framework Si/Al ratios of 15 or 41 were prepared from the sodium forms by triple ion exchange with 1 M aqueous solution of NH₄NO₃ at room temperature. The Si/Al ratios of these samples are indicated in parentheses in the text that follows. The degree of sodium exchange by protons was equal to 95% as measured by AAS of Na⁺.

The Zn/HZSM(15) and Zn/HZSM(41) samples with a Zn content of 0.80 and 0.81 wt%, respectively, were prepared from the ammonium form by incipient wetness impregnation with 1 M aqueous $\text{Zn}(\text{NO}_3)_2$ solutions. The actual zinc content and Si:Al ratios in the framework of both zeolites were measured by AAS analysis. After ion exchange the samples were dried at 390 K in flowing nitrogen for 45 min followed by calcination in a flow of oxygen at 820 K for 4 h.

Thermovacuum pretreatment of both hydrogen and Zn-containing forms was performed in the same sapphire ampoules that were then used for recording of Fourier transform IR diffuse reflectance (DRIFT) spectra. Prior to spectral measurements the ampoule-encapsulated samples were heated in vacuum at 570, 670, 770, 870 or 920 K for 2 h. The rate of preliminary temperature increase was equal to 5 K min⁻¹.

DRIFT spectra of the powdered zeolites were measured using a Nicolet Impact 410 spectrophotometer with a home-made DR unit. The spectra of the hydroxyl groups and of adsorbed CO were recorded at room temperature. Those of adsorbed molecular hydrogen were measured at 77 K using a quartz Dewar vessel filled with liquid nitrogen for cooling of the samples. All DRIFT spectra were transformed into Kubelka–Munk units assuming that the reflectivity of the samples at 5000 cm⁻¹ was equal to 0.9 units.

Molecular hydrogen was adsorbed at 77 K at an equilibrium pressure of 1.33×10^4 Pa. Adsorption of CO was performed at room temperature at an equilibrium pressure of 2.66×10^3 Pa. In both cases DRIFT measurements were carried out in the presence of gaseous molecules. Propane and methane adsorption was performed at different temperatures at a pressure of 2.66×10^3 Pa.

3. Results

3.1. H forms of ZSM-5 zeolites

Figure 1 shows DRIFT spectra of the hydroxyl groups of an HZSM(41) zeolite dehydrated in vacuum at different temperatures. The spectra contain narrow absorption bands at 3610 and at 3740 cm⁻¹ which correspond to isolated bridging acidic hydroxyls and to silanol groups, respectively. The additional broad absorption with a maximum in the range of 3290–3360 cm⁻¹ is attributed to either hydrogen-bonded acidic OH groups or to residual adsorbed water that was not completely removed by vacuum pretreatment at lower temperatures. The increase of the dehydration temperature from 570 to 920 K resulted in a disappearance of this broad band. At the same time the intensity of the 3610 cm⁻¹ band did not decrease by more than 30%.

Figure 2 displays the spectra of molecular hydrogen adsorbed on an HZSM(41) sample at 77 K and at an equilibrium pressure of 1.33×10^4 Pa. After dehydration at 570 K the spectra contained two unresolved stretching bands with maxima at 4105 and 4125 cm⁻¹. These bands correspond to the stretching vibrations of hydrogen molecules adsorbed on acidic hydroxyls and on silanol groups, respectively [17]. The low-intensity band at 4180 cm⁻¹ is attributed to a satellite, i.e., to a combination mode of the H–H stretching vibration with the oscillations of adsorbed molecular hydrogen relative to the Brønsted acidic sites. Similar bands have been observed earlier for H₂ adsorption on NaA, NaX and NaY zeolites [14]. The intensity of the very weak, low-frequency band at 4030 cm⁻¹ increased monotonically as the temperature of the vacuum pretreatment was increased. Therefore, in accordance with our

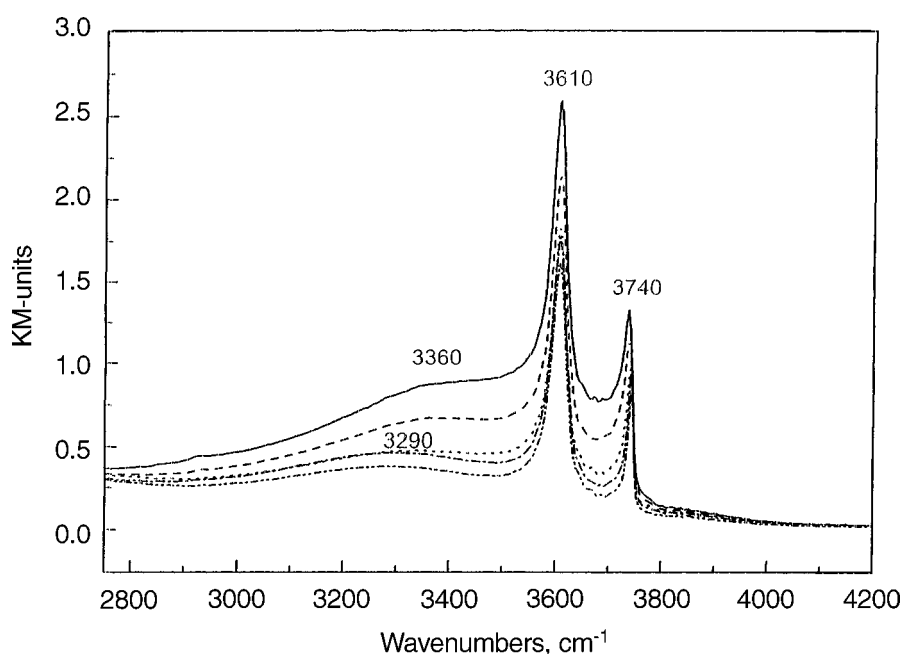


Figure 1. DRIFT spectra of the OH groups of an HZSM(41) zeolite dehydrated in vacuum at 570 (—), 670 (---), 770 (···), 870 (— · —) or 920 K (— · — · —).

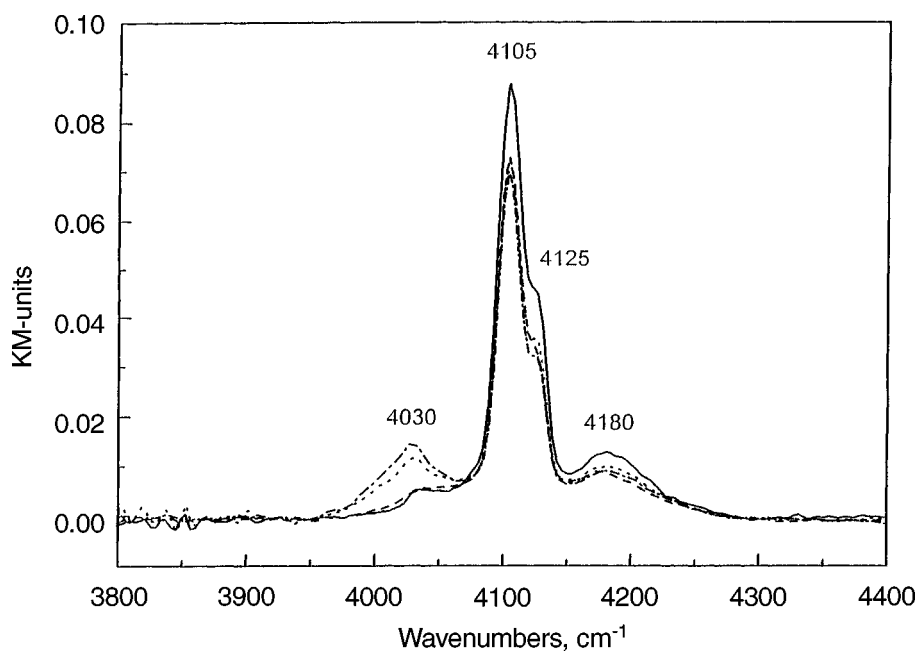


Figure 2. DRIFT spectra of molecular hydrogen adsorbed at 77 K and at an equilibrium pressure of 13.3 kPa on an HZSM(41) sample dehydrated at 570 (—), 670 (---), 770 (···) or 920 K (-·-·-).

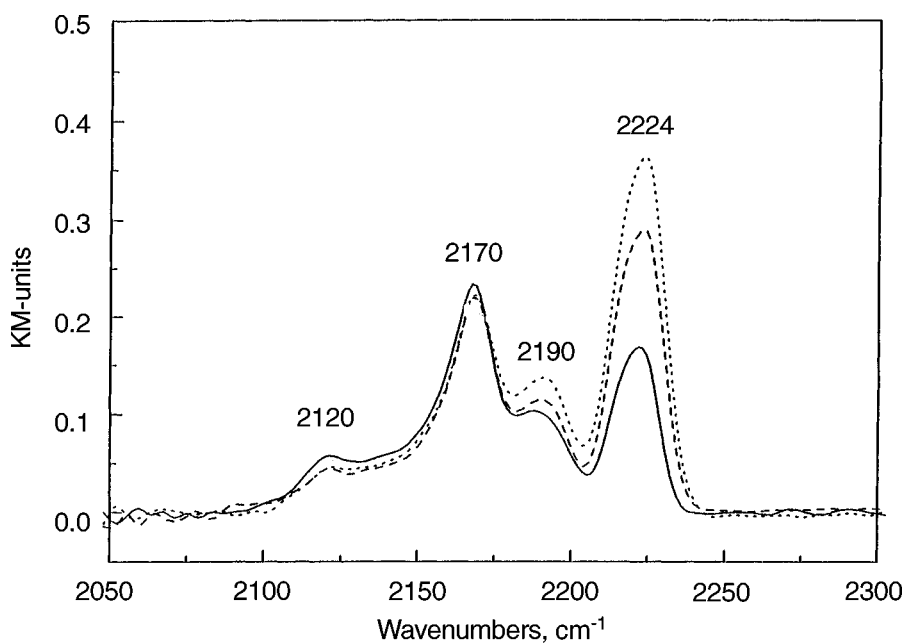


Figure 3. DRIFT spectra of carbon monoxide adsorbed at room temperature and at an equilibrium pressure of 2.66 kPa on an HZSM(41) sample dehydrated at 670 (—), 770 (---) or 920 K (···).

previous studies [18], this band has been assigned to hydrogen molecules perturbed by Lewis acidic sites resulting from the dehydroxylation of the zeolite.

The formation of Lewis acid sites upon zeolite dehydroxylation was also confirmed by the DRIFT spectra of adsorbed CO which contained bands at 2120, 2170, 2190 and 2220–2224 cm^{-1} (figure 3). The first two of these bands were reported earlier for CO adsorption on both alkaline and hydrogen forms of faujasites [19]. The intensities of these bands did not depend on the temperature of pre-

liminary vacuum pretreatment. By contrast, the intensities of the high-frequency bands at 2190 and 2220–2224 cm^{-1} increased with increasing dehydration temperature. Therefore, similar to the low-frequency bands in the spectra of adsorbed hydrogen, these bands belong to CO molecules either coordinated by extra-lattice aluminum or by lattice Lewis sites [20].

HZSM(15), despite having a lower Si/Al ratio than the previous sample, showed similar spectra for hydroxyl groups, for adsorbed hydrogen and for adsorbed CO mole-

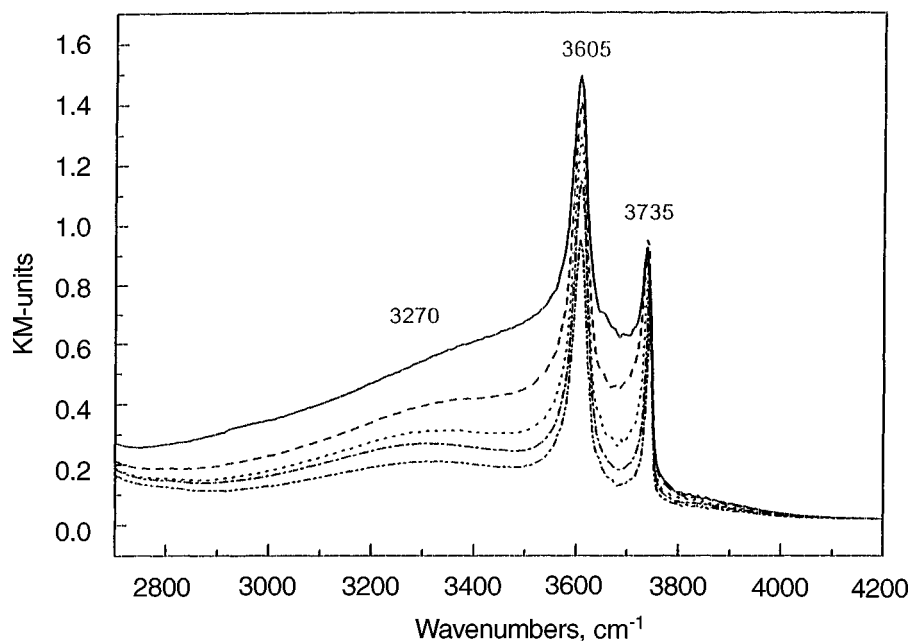


Figure 4. DRIFT spectra of OH groups of a ZnHZSM(41) sample dehydrated in vacuum at 570 (—), 670 (---), 770 (···), 870 (— · —) and 920 K (— · — · —).

cules and a similar evolution of corresponding bands with increasing zeolite dehydration temperature. The main difference observed in the DRIFT spectra of the OH groups consisted in the appearance of an additional weak and narrow band at 3690 cm^{-1} after high-temperature dehydration which most likely belongs to hydroxyls connected with extra-lattice aluminum species. The thermal stability of the acidic OH groups in the HZSM(15) sample was therefore somewhat lower than that of the HZSM(41) sample. This follows from the slightly faster increase in the intensity of the band due to bridging acidic hydroxyls at 3610 cm^{-1} upon dehydroxylation of the former sample at high temperatures.

3.2. Zn-containing zeolites

Let us start with the spectral data obtained for the Zn/HZSM(41) zeolite with a higher Si to Al ratio. The spectra of hydroxyl groups of this zeolite dehydrated at different temperatures are depicted in figure 4. They are quite similar to those of HZSM(41) pretreated under similar conditions. No additional IR bands due to isolated hydroxyls attached to zinc cations were observed. After high-temperature vacuum pretreatment the intensity of the bands due to silanol and to bridging hydroxyl groups decreased in a similar manner as that observed for the corresponding hydrogen form.

Figure 5 shows the spectra of molecular hydrogen adsorbed on this Zn/HZSM(41) sample. The bands at 4105 and 4125 cm^{-1} , and that of the high-frequency satellite at 4185 cm^{-1} are quite similar to those for the corresponding hydrogen form. However, after evacuation of Zn/HZSM(41) at 570 K or at higher temperatures,

new bands with unresolved maxima at $4005\text{--}4030\text{ cm}^{-1}$ strongly shifted to lower frequency appeared and a band with the maximum at 3940 cm^{-1} appeared. The intensities of all of these bands strongly increased with the temperature of the sample. Upon increasing temperature of the sample dehydration the intensities of both these bands strongly increased.

As measured in the hydrogen form of HZSM(41), the bands at 4105 , 4125 and 4185 cm^{-1} belong to hydrogen adsorption on acidic hydroxyls and on silanol groups. The bands at 3940 and 4005 cm^{-1} , which are absent in the spectra of hydrogen adsorbed on HZSM(41) zeolite but appeared after dehydration at elevated temperatures, should be attributed to adsorbed H_2 molecules perturbed by Zn^{2+} cations. As indicated by low-temperature molecular hydrogen adsorption, the number of these sites increased with increasing temperature of vacuum pretreatment. Thus, the introduction of Zn^{2+} ions into ZSM-5 by incipient wetness impregnation creates new Lewis acid sites, presumably containing coordinatively unsaturated Zn^{2+} ions.

Figure 6 displays the DRIFT spectra of CO adsorbed on the same ZnHZSM(41) sample dehydrated at different temperatures. A comparison of figures 3 and 6 reveals that after high-temperature vacuum pretreatment the intensity of the band at 2227 cm^{-1} , due to adsorbed CO on the Zn-containing zeolite increased more rapidly than for the HZSM(41) sample, indicating removal of water or oxygen from zinc-containing adsorption sites.

On the other hand, comparison of figures 3 and 6 also indicates that the spectra of adsorbed CO are almost insensitive to the nature of Lewis acid sites. Indeed, the position of the bands from adsorbed CO with a maximum at $2224\text{--}2227\text{ cm}^{-1}$ is practically identical for both the hydrogen

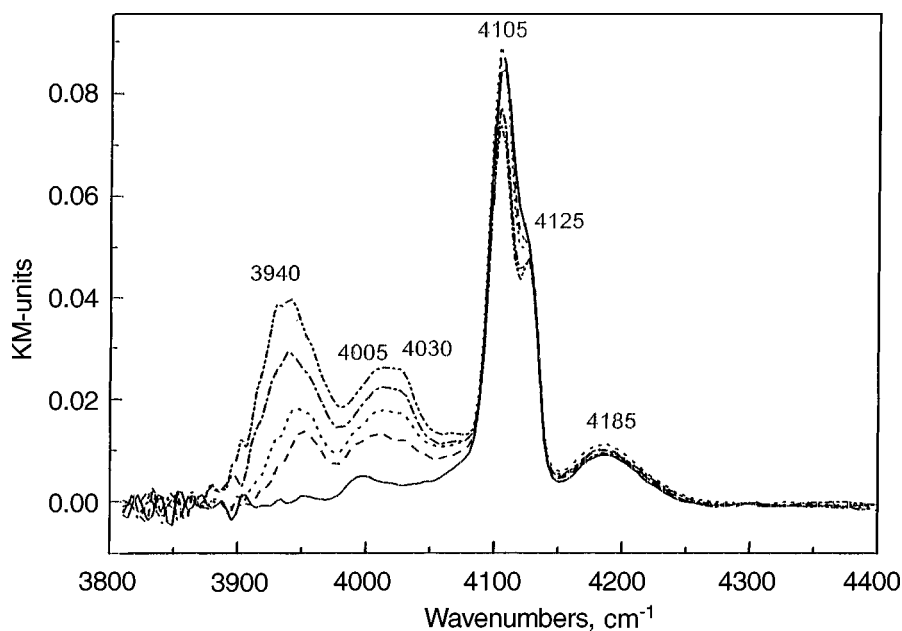


Figure 5. DRIFT spectra of molecular hydrogen adsorbed at 77 K and at an equilibrium pressure of 13.3 kPa on a ZnHZSM(41) sample dehydrated in vacuum at 570 (—), 670 (---), 770 (···) or 920 K (-·-·-).

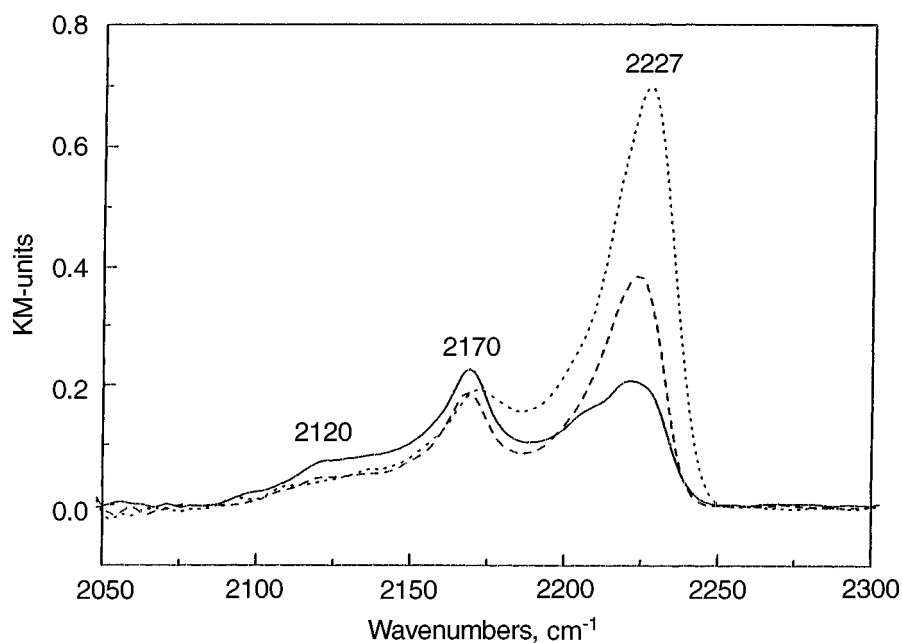


Figure 6. DRIFT spectra of carbon monoxide adsorbed at room temperature and at an equilibrium pressure of 13.3 kPa on a ZnHZSM(41) sample dehydrated in vacuum at 570 (—), 670 (---) or 920 K (···).

and the zinc forms. By contrast, the corresponding bands of molecular hydrogen adsorbed on Zn/HZSM5(41) are well resolved into two components with maxima at 3940 and at about 4005 cm^{-1} , respectively (see figure 5).

The band at 4005–4030 cm^{-1} probably has an even more complicated nature and most likely represents a combination of two unresolved bands (maxima at 4005 and 4030 cm^{-1}). Both of them definitely result from hydrogen adsorbed on coordinatively-unsaturated Zn^{2+} ions. This clearly demonstrates the advantage of hydrogen as a mo-

lecular probe. The reason is that adsorbed molecular hydrogen is not only perturbed by the coordinatively-unsaturated cations, but also by the adjacent basic oxygen atom of the zeolite framework [14]. Therefore, unlike carbon monoxide, probing with adsorption of molecular hydrogen also gives some information on the environment close to the Lewis sites.

The evolution of the DRIFT spectra of hydrogen adsorbed at 77 K on the Zn/HZSM(15) sample dehydrated at different temperatures is depicted in figure 7. Compar-

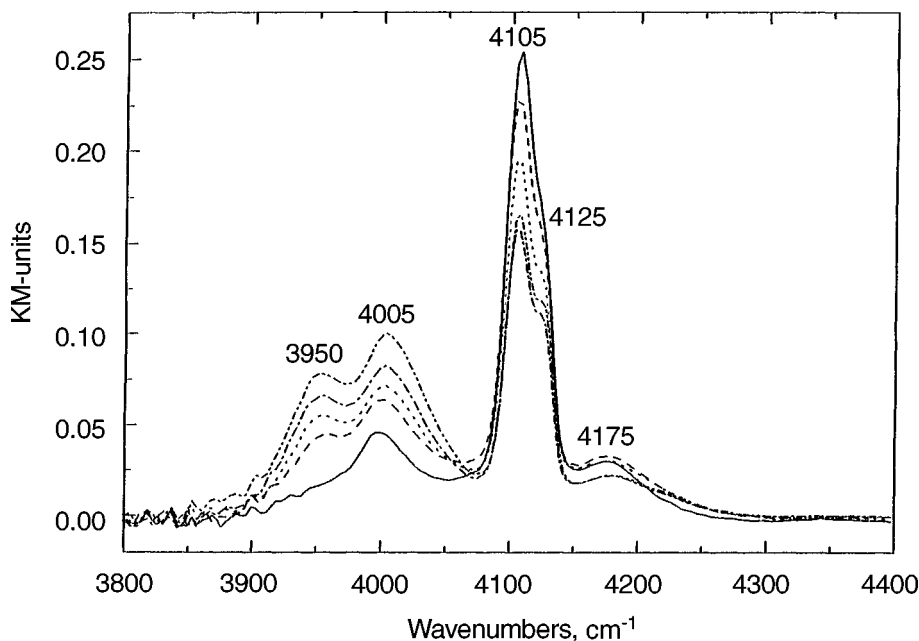


Figure 7. DRIFT spectra of molecular hydrogen adsorbed at 77 K and at an equilibrium pressure of 13.3 kPa on a ZnHZSM(15) sample dehydrated in vacuum at 570 (—), 670 (---), 770 (···), 870 (— · —) or 920 K (— · — · —).

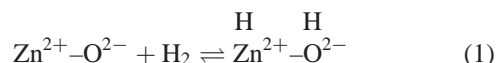
ison of these results with those presented in figure 5 for H_2 adsorption on HZSM(41) confirms that the thermal stability of acidic OH groups in the Zn/HZSM(15) sample is somewhat lower than those in the Zn/HZSM(41). The thermal stability of both zinc-containing samples is lower than of the H forms of both zeolites. This follows from the faster intensity decrease of the 4105 cm^{-1} band upon dehydroxylation at high temperatures due to hydrogen adsorbed on isolated acidic hydroxyls for the sample with the lower Si/Al ratio.

Another difference between the Zn-containing zeolites with different Si/Al ratios is the different relative amounts of Lewis sites that result from the high-temperature dehydroxylation. In the Zn/HZSM(15) zeolite the sites connected with the band of adsorbed hydrogen at 4005 cm^{-1} predominate. By contrast, the proportion of those sites in Zn/HZSM(41) is lower. This indicates different relative amounts of the corresponding Lewis sites. In addition, for both samples the positions of these bands are also slightly different.

3.3. Adsorption of hydrogen and paraffins on Zn forms of ZSM5 zeolites

We also observed that, after prolonged storage of the Zn/HZSM(41) zeolite in a hydrogen atmosphere at room temperature, or after heating of samples of this zeolite in hydrogen at 400 K for 1 h, the 3940 cm^{-1} IR band of molecular hydrogen adsorbed at 77 K significantly decreased in intensity. By contrast, the band with a maximum at 4105 cm^{-1} remained unchanged (figure 8). A similar phenomenon was reported earlier in [14]. It was explained

by heterolytic dissociative adsorption of hydrogen on acid-base $\text{Zn}^{2+}\text{--O}^{2-}$ pairs:



It was suggested that such adsorption blocks the adsorption sites and in this way decreases the subsequent adsorption of molecular hydrogen.

The present experiments should be explained in a similar way. Unfortunately, neither resulting hydrides nor additionally-formed hydroxyl groups were directly observed in the DRIFT spectra, since the stretching frequency of the hydride species is too low for the direct DRIFT detection and while observation of additional hydroxyls is difficult due to the existence of intense O–H bands. Anyway, it is quite remarkable that only the Zn^{2+} ions with the strongest polarization ability are able to dissociate molecular hydrogen at room and at elevated temperatures. By contrast, the Lewis sites connected with the bands of adsorbed molecular hydrogen at $4005\text{--}4030\text{ cm}^{-1}$ are not involved in dissociative adsorption.

Our results also indicated that at high temperatures the sites of dissociative hydrogen adsorption are able to dissociatively adsorb paraffins. This follows from similar poisoning experiments in which low-temperature molecular hydrogen adsorption was performed after a preliminary heating of ZnHZSM(41) or ZnHZSM(15) samples in methane or propane atmosphere. For instance, figure 9 illustrates the complete disappearance of the low-frequency band from adsorbed hydrogen (at 3940 cm^{-1}) after propane adsorption at 470 K. Such dissociative adsorption of propane proceeds on both ZnZSM(41) and ZnZSM(15) samples. However, on the sample with the

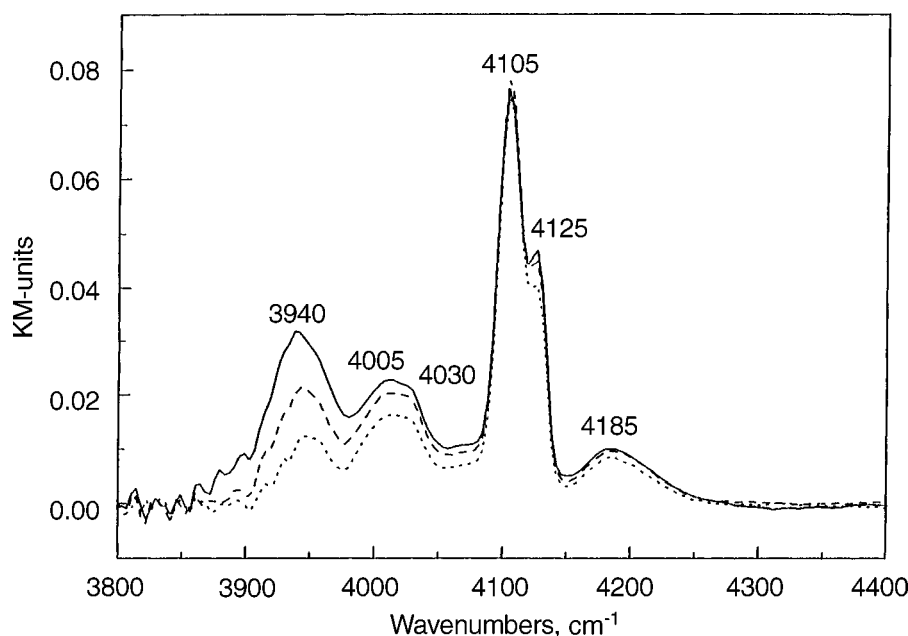


Figure 8. DRIFT spectra of molecular hydrogen adsorbed at 77 K and at an equilibrium pressure 13.3 kPa on a ZnZSM(41) sample dehydrated in vacuum at 873 K (—) and then kept overnight in hydrogen atmosphere (---) or heated for 1 h in hydrogen at 393 K at the pressure 13.3 kPa (···).

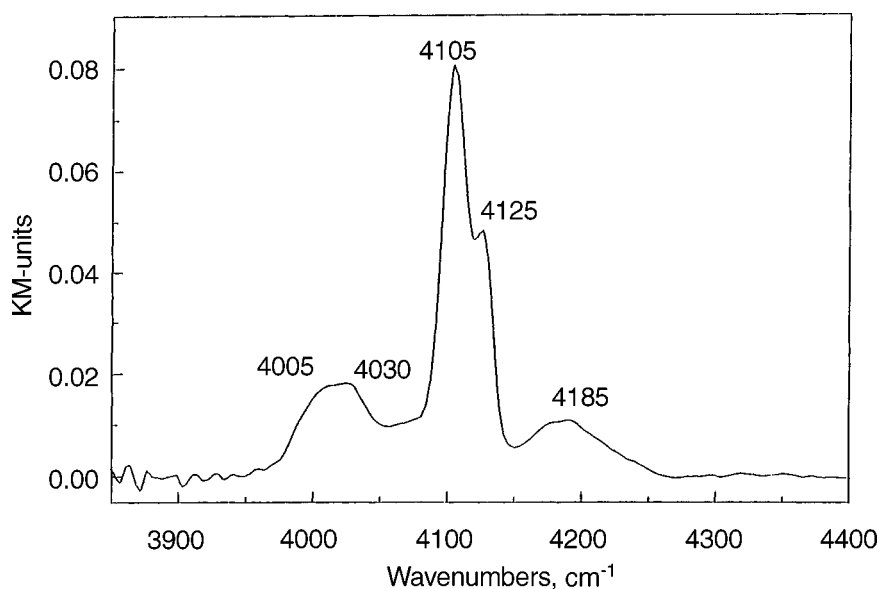


Figure 9. DRIFT spectra of molecular hydrogen adsorbed at 77 K on a ZnZSM(41) sample after pretreatment with propane at 470 K. The pretreatment temperature in vacuum was equal to 873 K.

lower Si/Al ratio it occurs at a somewhat higher temperature.

4. Discussion

The most important finding of this work certainly is the observation of three different sites for molecular hydrogen adsorption and of the sites of dissociative adsorption of hydrogen and paraffins resulting from modification of ZSM-5 zeolites with zinc ions. In this connection, let us discuss the possible location of zinc in the framework of ZSM-5 zeolite.

The corresponding information is unfortunately very limited. This is connected with the absence of reliable X-ray data for high-silica zeolites due to the low concentration of the extraframework cations and to the poor ordering of these ions in the framework. Therefore, the main source of information concerning different sites of localization of bivalent cations in MFI, FER and MOR is supplied by UV-VIS spectra, by luminescence studies and by ESR spectra of transition metal ions [1,21]. The first of these techniques was mainly applied to the cobalt-exchanged, high-silica zeolites while the latter two were applied to the copper forms of these materials. Neither of them was used to investi-

gate zinc-containing zeolites. Nevertheless, there should be some common features in the location of bivalent transition metal ions in high-silica zeolites. These are summarized below.

According to analysis by Mortier for mordenite [24] and to optical studies by Wichterlova [25], one can discriminate between the following sites for Co^{2+} , Cu^{2+} or Cu^+ in MFI, FER and MOR that are able to adsorb small molecules:

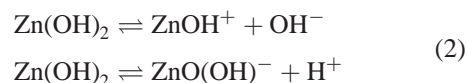
- (i) Metal ions situated on the walls of the main channels in a square planar coordination in distorted six-membered rings (α sites according to Wichterlova or E sites according to Mortier). The bivalent cations at these sites exhibit an open coordination sphere and a positive charge that is balanced by a low-density negative charge on the framework. In the case of Co^{2+} ions, these sites exhibit a preference for the formation of dinitrosyls confirming that they have an open coordination. Cu^{2+} ions at these sites could be easily reduced to Cu^+ and exhibited a high catalytic activity for NO decomposition or for the selective reduction of NO by paraffins.
- (ii) Bivalent ions in a hexagonal coordination in distorted eight-membered rings (β sites according to Wichterlova or A sites according to Mortier). The copper ions at these sites did not cause formation of dinitrosyls upon NO adsorption and were not readily reduced. The positive charge of these ions is most likely balanced by a higher negative charge of the zeolite framework in comparison with cations at α positions, i.e., it is compensated by two framework Al atoms.
- (iii) Cations in boat-shape, five-membered rings (γ sites according to Wichterlova or C sites according to Mortier).

In the present work we also observed three different sites for hydrogen adsorption that were connected with zinc ions. It is therefore quite reasonable to assign them to the three similar types of Zn^{2+} ions locations in the ZSM-5 framework. The stretching frequencies of adsorbed hydrogen equal to 4005 and 4030 cm^{-1} are close to the stretching frequency of 4037 cm^{-1} for hydrogen adsorption on Zn^{2+} ions in hexagonal windows at S_{II} sites of ZnY zeolite reported by us earlier [16]. These sites most likely belong to β or γ sites with distorted hexagonal or pentagonal coordinations. By contrast, the dissociative adsorption of hydrogen on ZSM-5 with the lowest H–H stretching frequency of adsorbed hydrogen molecules equal to 3940 cm^{-1} that was not observed for hydrogen adsorption on S_{II} sites in faujasites most likely occurs on Zn^{2+} ions at α sites in a planar square coordination. According to Wichterlova, these sites have much higher chemical activity. This explains the large low-frequency shift of the H–H stretching vibration and the dissociative adsorption of hydrogen and paraffins.

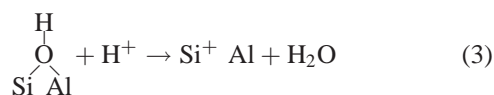
Another alternative explanation involves the dissociative adsorption of hydrogen on small zinc oxide particles that

are formed upon incipient wetness impregnation and subsequent high-temperature treatment of the zeolite. Indeed, dissociative adsorption of molecular hydrogen on zinc oxide has been reported in [23–25], while formation of ZnO microclusters in ZSM-5 zeolites is supported by the following arguments:

- (i) The wet ion exchange of protons in high-silica zeolites by zinc ions is a difficult process [9,10]. Therefore, a considerable part of Zn^{2+} ions introduced in ZSM-5 by incipient wetness impregnation forms after high-temperature treatment zinc oxide particles. They could be either encapsulated in the micropores of the zeolite as nanometric zinc oxide clusters or be localized on the external surface of the zeolite grains as larger particles.
- (ii) For ZnHZSM(41) zeolite, the amount of Zn^{2+} ions introduced by the incipient wetness impregnation was sufficient for substitution of about 60% of ammonium ions. However, we did not observe any noticeable decrease in the amount of bridging hydroxyls due to the substitution of protons by zinc ions. Therefore, we have to conclude that ion exchange took place only in a minor extent. In contrast, the major part of zinc nitrate introduced in the initial ammonium form by incipient wetness impregnation transforms after high-temperature treatment into zinc oxide microclusters.
- (iii) Formation in ZnHZSM-5 zeolite prepared by impregnation of nanometric zinc oxide particles has been reported by Biscardi [9]. For a sample with a Si : Al ratio equal to 14.5, the amount of zinc ions that resulted in the formation of ZnO particles and the amount that was stabilized by the zeolite framework were approximately equal. In our case the amount of zinc oxide particles was probably higher due to the much lower aluminum content.
- (iv) Formation of zinc oxide particles is also supported by the amphoteric nature of zinc hydroxide, which can dissociate both into hydroxyl ions and protons:



The first of these reactions favors ion exchange. It should result in a faster dehydration of the hydrogen form of ZSM-5 zeolite modified with zinc due to interaction of the protons with the basic hydroxyl ions. By contrast, the second reaction would not strongly influence the rate of dehydroxylation that should proceed via interaction of protons with bridging hydroxyls, in a manner similar to that which occurs in the pure hydrogen form:



Thus, the slow rate of dehydration observed in the present study should be also considered as an argument in favor of formation of zinc oxide microclusters.

Indeed, earlier we studied the dehydration of ZnY zeolite prepared by ion exchange in [15]. It was then concluded that this process starts with formation of bridging protons and proceeds via intermediate hydrolyzed zinc oxide particles. During the course of subsequent dehydration at higher temperature these species reacted with each other, while the resulting Zn^{2+} ions were stabilized at S_{II} sites inside large cavities of the zeolite framework. This resulted in a much faster dehydration of ZnY zeolite in comparison with the hydrogen form.

By contrast, in the present study we did not observe any noticeable difference in dehydroxylation of the ZnHZSM-5 zeolite at elevated temperatures in comparison with the pure hydrogen form. This indicates that dehydroxylation mainly results from interaction of protons with hydroxyls rather than from a reaction of acidic protons with basic ZnOH^+ species.

Thus, the results of the present paper definitely indicate that dehydroxylation of zinc forms of Y and ZSM-5 zeolites proceeds quite differently. In the first case the high-temperature vacuum treatment results in replacement of protons by Zn^{2+} ions and in their stabilization at S_{II} sites in the big cavities of the framework. By contrast, in ZSM-5 samples prepared by the incipient wetness impregnation, zinc ions substitute only a small fraction of acidic protons, while the main part of modifying zinc ions forms microclusters of zinc oxide.

This difference is most likely connected with different content of aluminum in the frameworks of high-silica zeolites and faujasites. Indeed, the stabilization energy of bivalent cations in the six-membered rings of faujasites with two aluminum atoms per ring is rather high. By contrast, due to the much lower density of aluminum atoms in the framework of ZnHZSM-5, stabilization of Zn^{2+} ions at the sites with only one aluminum atom per site is energetically much less favorable. Instead, decomposition of the modifying zinc nitrate results in the formation of ZnO microclusters in parallel with ion exchange.

Thus, there is no doubt concerning the possibility that the formation of ZnO nanometric microparticles in ZSM-5 could be involved in the dissociative adsorption of molecular hydrogen. One has, however, to bear in mind that the H–H stretching frequency of adsorbed hydrogen that is the precursor of dissociative adsorption of 3940 cm^{-1} is considerably lower than that of 4019 cm^{-1} reported for molecular hydrogen adsorption on zinc oxide [23–25]. This difference could certainly be attributed to the very small size of the nanometric zinc oxide clusters inside the micropores of the ZSM-5 zeolite in comparison with those in the zinc oxide powder. However, the possibility that dissociative hydrogen adsorption occurs on Zn^{2+} ions at α sites with

an unusual coordination and a poorly-compensated positive charge cannot be excluded at present. The final choice between these alternatives requires, however, an additional more detailed study.

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