The Sites of Molecular and Dissociative Hydrogen Adsorption in High-Silica Zeolites Modified with Zinc Ions. III DRIFT Study of H2 Adsorption by the Zeolites with Different Zinc Content and Si/Al Ratios in the Framework

Citation for published version (APA):
Kazansky, V. B., Serykh, A. I., Anderson, B. G., & Santen, van, R. A. (2003). The Sites of Molecular and Dissociative Hydrogen Adsorption in High-Silica Zeolites Modified with Zinc Ions. III DRIFT Study of H2 Adsorption by the Zeolites with Different Zinc Content and Si/Al Ratios in the Framework. *Catalysis Letters*, *88*(3-4), 211-217. https://doi.org/10.1023/A%3A1024026225712, https://doi.org/10.1023/A:1024026225712

DOI:
10.1023/A%3A1024026225712
10.1023/A:1024026225712

Document status and date:
Published: 01/01/2003

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Catalysis Letters Vol. 88, Nos. 3–4, June 2003 (© 2003)

The sites of molecular and dissociative hydrogen adsorption in high-silica zeolites modified with zinc ions. III DRIFT study of H_2 adsorption by the zeolites with different zinc content and Si/Al ratios in the framework

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Received 24 September 2002; accepted 3 April 2003

DRIFT study of dihydrogen adsorbed at 77 K by the zinc-modified hydrogen forms of mordenite and ZSM-5 zeolites with the different Si/Al ratios in the framework indicated the existence of several adsorption sites connected with the modifying zinc ions. The fraction of the sites of the strongest perturbation of adsorbed molecular hydrogen with the H–H stretching frequency of *ca.* 3930–3950 cm^{-1} is the highest at the highest Si/Al ratios of 41 or 80. These sites dissociatively adsorb hydrogen at moderately elevated temperatures. Adsorption of hydrogen with the higher H–H stretching frequency of about 3970–4000 cm^{-1} predominates at the lower Si/Al ratios. It does not result in the dissociation of adsorbed molecules. It was concluded that the most active sites are most probably connected with the zinc ions, which compensate two distantly separated negatively charged $[AlO_4]^-$ tetrahedra localized in the adjacent five- or six-membered rings on the walls of the large channels of the pentasil's framework. The sites of the weaker perturbation of adsorbed hydrogen are most probably connected with Zn^{+2} ions at the conventional exchangeable cationic positions with two aluminum atoms in the same five- or six-membered ring.

KEY WORDS: high-silica zeolites; modification with Zn^{+2}; H_2 adsorption; DRIFT.

1. Introduction

HZSM-5 zeolites modified with Zn^{+2} ions are known as active catalysts for aromatization of light paraffins. Therefore, the study of the state of zinc in these materials has been a subject of numerous recent publications [1–10]. However, in any of them the modifying zinc ions responsible for adsorption of paraffins or hydrogen and for subsequent activation of these molecules were directly observed by spectral techniques. This has been done only in our previous publications [11,12] using low-temperature dihydrogen adsorption as a molecular probe. Perturbation resulting from hydrogen adsorption by the modifying zinc ions was followed in these articles by DRIFT spectroscopy.

The present paper is a continuation of this study. Similar to our previous works, the zinc-modified hydrogen forms of ZSM-5 zeolite and mordenite were investigated by measuring DRIFT spectra following adsorption of dihydrogen at 77 K. The silica-to-aluminum ratio in the framework ZnHZSM-5 was changed over a very broad range. The results obtained allowed a more convincing assignment of the sites resulting from modification of the pentasils with zinc than was done in our previous publication [12].

2. Experimental

Initial hydrogen forms of ZSM-5 and mordenite were obtained by decomposition of ammonium forms in the flowing oxygen at 793 K. In the text below, the Si/Al ratios of the zeolites under 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." The compositions of the different parent zeolites that were used for modification with zinc of hydrogen forms as the starting materials are listed in table 1. Incipient wetness impregnation of hydrogen forms was described earlier in references [11,12]. Wet ion exchange of the hydrogen form of mordenite with zinc nitrate was carried out in the conventional way from an aqueous solution of zinc nitrate. Zinc content in the modified zeolites was measured by AAS analysis.

Similar to our previous publications, DRIFT spectra of hydroxyl groups and of the adsorbed molecular hydrogen were recorded using a Nicolet "Impact 410" spectrophotometer equipped with a home-made DR unit. DRIFT measurements of hydrogen adsorption at 77 K were carried out using a quartz Dewar vessel filled with liquid nitrogen for cooling the samples. All DRIFT spectra were transformed to Kubelka–Munk units using a standard program with the assumption that the reflective ability of the samples at 5000 cm^{-1} was equal

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Table 1
List of zeolites studied in the present paper

No	Zeolite	Si/Al	Zn content weight (%)	
1	HMOR	5	0	0
2	HMOR	5	1	~0.05
3	HZSM-5	15	1	~0.14
4	HZSM-5	15	0	0
5	HZSM-5	25	1	~0.23
6	HZSM-5	25	1.2	0.2
7	HZSM-5	25	0	0
8	HZSM-5	41	1	~0.38
9	HZSM-5	41	2	~0.76
10	HZSM-5	41	4	1.5
11	HZSM-5	41	0	0
12	HZSM-5	80	1	~0.77
13	HZSM-5	80	0	0

to 0.9 units. After that, the background created by the zeolites was subtracted.

Molecular hydrogen was adsorbed at 77 K at an equilibrium pressure of $1.33 \cdot 10^4$ Pa. DRIFT measurements were carried out either in the presence of gaseous hydrogen or after evacuation of H_2 at room temperature. Dissociative adsorption of hydrogen was studied at room temperature by transmittance IR spectroscopy in a glass cell with CaF_2 windows. The transmittance technique broadened the spectral range of IR measurements towards lower wavenumbers and thus made possible the direct observation of zinc hydrides or hydroxyl groups resulting from the dissociative adsorption of molecular hydrogen or deuterium.

3. Results

3.1. DRIFT spectra of dihydrogen adsorbed by HMOR and the ZnHMOR samples of different preparations

Similar to the previously studied HZSM-5, high-temperature pretreatment of HMOR resulted in partial dehydroxylation. In the present work, it was controlled both directly by DRIFT spectra of OH groups and by low-temperature adsorption of molecular hydrogen by observing the bands with the H–H stretching frequencies of 4105 and 4125 cm^{-1} resulting from H_2 interacting with hydroxyl groups. It was found that the high-temperature dehydroxylation generates new sites of molecular hydrogen adsorption with a lower H–H stretching frequency equal to 4030 cm^{-1}. In contrast to hydrogen adsorbed by hydroxyl groups, the intensity of these bands increases with increasing temperatures of vacuum pretreatment (figure 1). These new adsorption sites resulting from dehydroxylation have been earlier ascribed either to formation of the framework Lewis sites or to the extralattice AlO^+ ions generated by the subsequent dealumination of the dehydroxylated zeolite [11,12]. The main difference in the behavior of HZSM-5 and HMOR upon such high-temperature vacuum pretreatment is that for HMOR the H–H stretching band from the hydrogen perturbed by the framework Lewis sites or by the extralattice AlO^+ ions is somewhat more intense than that for the HZSM-5.

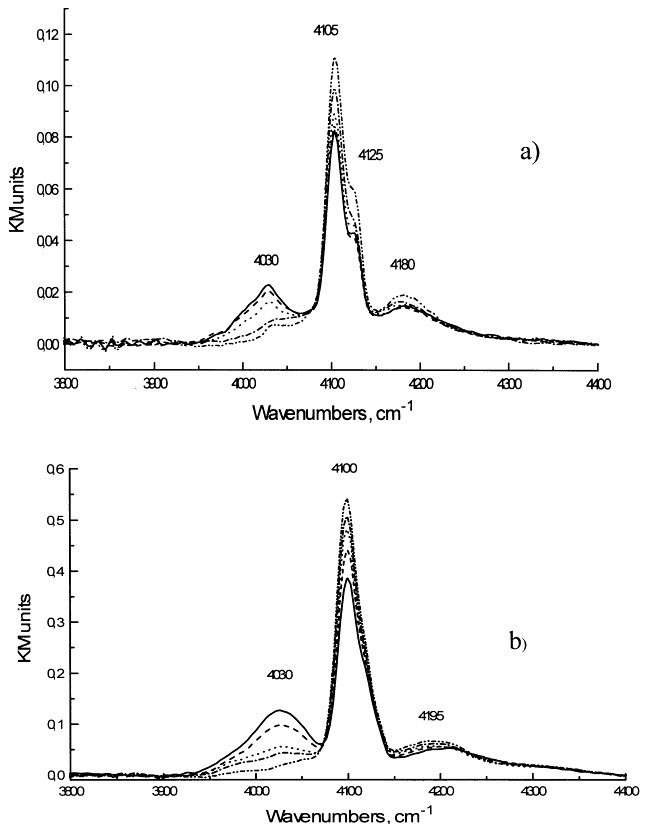

Figure 1. DRIFT spectra of H_2 adsorbed at 77K by HZSM-5(41) (a) and HMOR(5) (b) pretreated in vacuum at 300 °C (–··–··–··), 400 °C (–·–·–·–·–), 500 °C (..........), 600 °C (- - - - - -) or 650 °C (————). DRIFT measurements at 77 K.

DRIFT spectra of hydrogen adsorbed by the zinc-modified HMOR prepared by incipient wetness impregnation or by ion exchange of the hydrogen form of mordenite are shown in figure 2. Modification with zinc resulted in several new more strongly red-shifted IR bands from the adsorbed hydrogen with the poorly resolved maxima at about 3930, 3970 and 4022 cm^{-1}. The latter band is probably a superposition of the band from the hydrogen adsorbed by the Lewis sites of the dehydroxylated HMOR and a new band arising from the hydrogen perturbed by the modifying zinc ions. The DRIFT spectra are only weakly dependent on the way of HMOR modification by zinc, thus indicating the similar nature of adsorption sites in the samples of different preparation.

3.2. DRIFT spectra of dihydrogen adsorbed by HZSM-5 zeolite with different content of modifying zinc ions

In our previous publications [11,12], low temperature adsorption of molecular hydrogen was studied only for

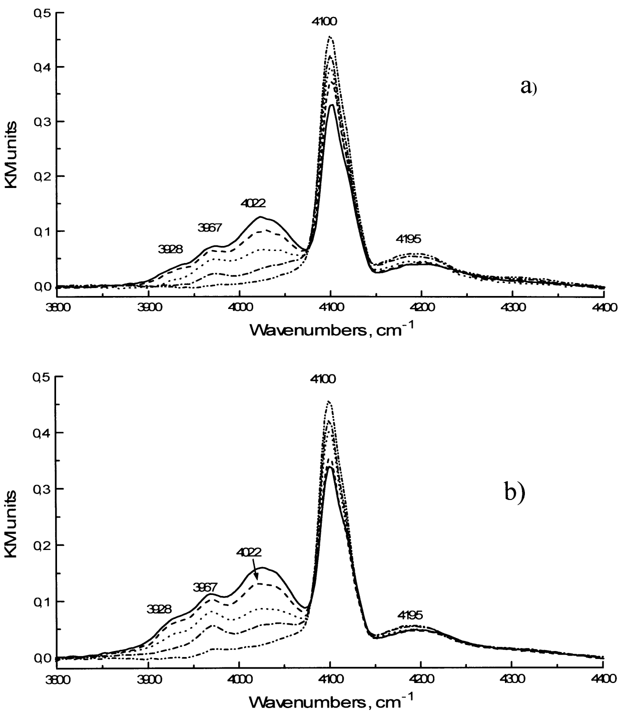

Figure 2. DRIFT spectra of H_2 adsorbed at 77 K on 1% Zn-modified HMOR(5) prepared by the ion exchange (a) or incipient wetness impregnation (b) of hydrogen form of mordenite pretreated in vacuum at 300 °C (–··–··–··), 400 °C (–·–·–·–·–), 500 °C (..........), 600 °C (------) or 650 °C (———) DRIFT measurements at 77 K.

the HZSM-5 zeolite with the constant silicon-to-aluminum ratio in the framework equal to 41 and zinc loading only of about 0.8 wt%. This amount of modifying zinc ions was about 2.5 times less than the total number of Al atoms or of the OH groups in the corresponding samples. Therefore, for such low zinc loading, it was difficult to notice the influence of modification with zinc on the number of the bridging hydroxyl groups when substitution of protons by zinc ions was occurring.

In the present paper, we studied the same ZSM-5(41) zeolite as in references [11,12] with the higher zinc loadings of 2 or 4 wt%. These amounts of the modifying zinc ions were either comparable with those of the acidic hydroxyl groups or were about twice higher than the number of OH groups, respectively. In figure 3, DRIFT spectra of hydroxyl groups in such ZnZSM-5 samples pretreated in vacuum at 920 K are compared with the spectrum of the initial HZSM-5 zeolite recorded after similar pretreatment.

As one can see from figure 3, the number of the bridging acidic hydroxyl groups remaining in the HZSM-5(41) samples strongly decreased at higher temperatures of the vacuum pretreatment. For a zinc content of 2 wt%, when the amount of the zinc ions was comparable with that of the hydroxyl groups, the intensity of the OH bands decreased by about 40%, whereas for the sample with the 4 wt% of zinc the decrease of intensity was about 50%. This obviously indicates that modification of ZSM-5 with zinc and subsequent high-temperature pretreatment results in the replacement of a considerable part of the hydroxyl groups by Zn^{+2} ions. Of course, some of the modifying zinc ions could also form small zinc oxide particles inside micropores of the zeolite framework or on the external surface of the zeolite grains. Therefore, the relationship between the amount of the modifying zinc ions and the number of the bridging hydroxyl groups deviates from the linear shape, this deviation being stronger for the higher zinc loadings.

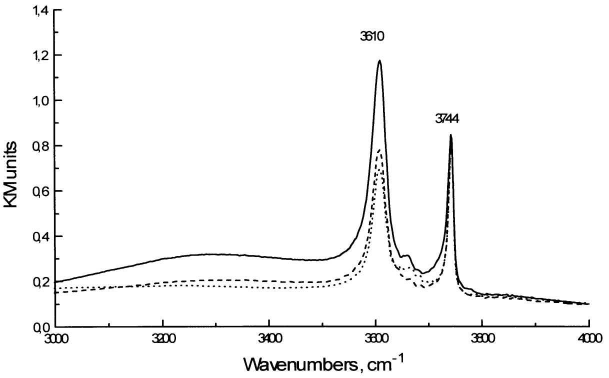

Figure 3. DRIFT spectra of hydroxyl groups in HZSM-5(41) (solid line) and the samples of this zeolite loaded with 2% of Zn (dashed line) and 4% of Zn (dotted line) pretreated in vacuum at 923 K. DRIFT measurements at room temperature.

3.3. DRIFT spectra of dihydrogen adsorbed by the ZnHZSM-5 zeolites with different silica-to-aluminum ratios in the framework

In the present paper, we also studied the influence on modification of HZSM-5 by zinc of different Si/Al ratios in the zeolite framework. The corresponding DRIFT spectra of H_2 adsorbed at 77 K by the ZnHZSM-5 zeolites with the constant zinc loading of 1 wt% are shown in figures 4–7.

For the zeolites with the Si/Al ratios equal to 15 or 25, adsorption of hydrogen discriminated two main sites of localization of the modifying zinc ions. They correspond to the stretching frequencies of the adsorbed hydrogen equal to about 3930–3950 and 4005 cm^{-1}. For the sample with $Si/Al = 15$, the intensity of the H–H stretching band at 4003 cm^{-1} predominates. In contrast, for the sample with $Si/Al = 25$, the intensity of the band at 3948 cm^{-1} is higher than that of the band at 4005 cm^{-1} (figures 4 and 5).

Thus, the nature of the sites of hydrogen adsorption resulting from the modification of the HZSM-5 zeolite with zinc ions depends on the aluminum content in the zeolite framework. For the high-silica samples, the relative intensity of the most strongly low-frequency shifted band is the highest. Moreover, for the sample with the Si/Al ratio of 80, the H–H stretching band with the band with the maximum at about 3940 cm^{-1}

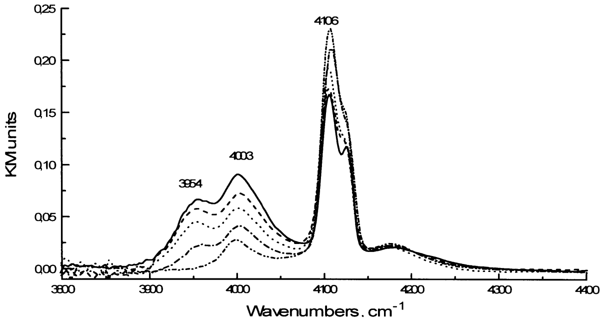

Figure 4. DRIFT spectra of hydrogen adsorbed at 77 K by HZSM-5(15) with 1% of modifying Zn ions pretreated in vacuum at 300 °C (–··–··–), 400 °C (–·–·–·–), 500 °C (..........), 600 °C (- - - - - -) or 650 °C (———). DRIFT measurements at 77 K.

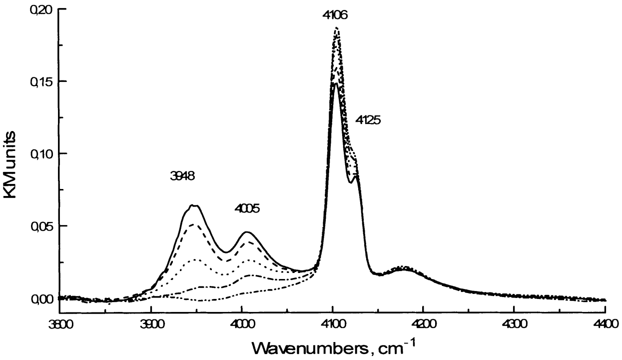

Figure 5. DRIFT spectra of hydrogen adsorbed at 77 K by HZSM-5(25) with 1% of modifying Zn ions pretreated in vacuum at 300 °C (–··–··–··), 400 °C (–·–·–·–), 500 °C (..........), 600 °C (- - - - -) or 650 °C (———). DRIFT measurements at 77 K

predominates, whereas intensities of other bands resulting from modification with zinc ions are much lower (figure 7).

We also made several attempts to reduce the modifying zinc ions by hydrogen or carbon monoxide pretreatment at 773 K. To control the state of the modifying zinc ions, DRIFT spectra of hydrogen adsorbed before and after reduction were used as a molecular probe. In accordance with the previously published results, reduction of Zn^{+2} ions did not occur either for the lower, or for the higher Si/Al ratios in the zeolite framework.

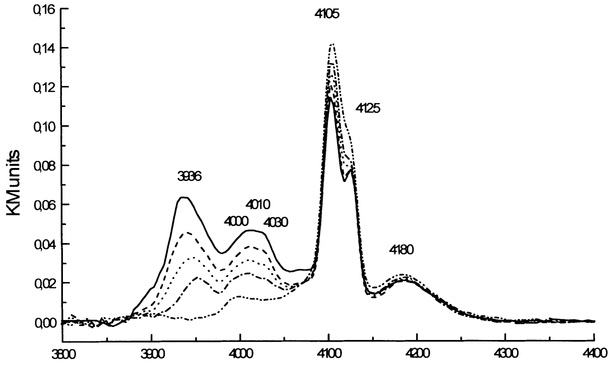

Figure 6. DRIFT spectra of hydrogen adsorbed at 77 K by HZSM-5(41) with 1% of modifying Zn^{+2} ions pretreated in vacuum at 300 °C (–··–··–··), 400 °C (–·–·–·–), 500 °C (..........), 600 °C (- - - - -) or 650 °C (———). DRIFT measurements at 77 K.

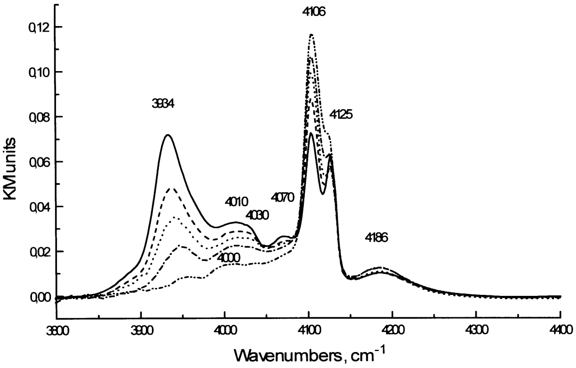

Figure 7. DRIFT spectra of hydrogen adsorbed at 77 K by HZSM-5(80) with 1% of modifying Zn ions pretreated in vacuum at 300 °C (–··–··–··), 400 °C (–·–·–·–), 500 °C (..........), 600 °C (- - - - -) or 650 °C (———). DRIFT measurements at 77 K.

3.4. *Dissociative adsorption of molecular hydrogen by the modifying zinc ions*

Earlier we reported in reference [11] that the prolonged storage of the ZnHZSM-5(41) zeolite in hydrogen atmosphere at room temperature or heating in hydrogen at 400 K for 1 h results in a lowering of the intensity of the 3935 cm^{-1} IR band from the molecular hydrogen subsequently adsorbed at 77 K. This was explained by the heterolytic dissociative adsorption of hydrogen, which blocks the acid–base Zn^{+2}-O^{-2} pairs created in ZnHZSM-5 by the modifying zinc ions and in this way decreases the subsequent molecular hydrogen adsorption:

$$-\mathrm{Zn}^{+2}\text{–}\mathrm{O}^{-2}- + \mathrm{H}_2 \rightarrow \overset{\mathrm{H}^{\delta-}}{\mathrm{Zn}^{+2}}\text{–}\overset{\mathrm{H}^{\delta+}}{\mathrm{O}^{-2}}- \tag{1}$$

Unfortunately, in that work neither resulting hydrides nor the additionally formed hydroxyl groups were directly observed in DRIFT spectra. The reason for that is the low stretching frequency of the hydride species that was too low for a direct DRIFT detection. On the other hand, observation of the hydroxyl groups additionally generated by the dissociative hydrogen adsorption was also difficult due to the intense IR bands from the bridging hydroxyl groups already existing in the ZnHZSM-5 zeolite. Therefore, in the text below we study dissociative adsorption of hydrogen and deuterium by the IR transmittance technique, which allows a better registration of IR absorption bands at wavelengths below 2000 cm^{-1}. In this case, both observation of hydrides and of the new hydroxyl groups resulting from hydrogen dissociative adsorption was possible.

This is demonstrated by figure 8, where after prolonged storage of the ZnHZSM-5 zeolite in hydrogen or deuterium atmosphere at room temperature the new bands from zinc hydrides at 1936 cm^{-1} and those from the hydroxyl groups at 3612 cm^{-1} appeared. The stretching frequency of the OH groups is very close to that of 3610 cm^{-1} for the acidic bridging hydroxyls in the initial hydrogen form of the zeolite. As an independent check of hydrogen dissociation, we also studied dissociative adsorption of molecular deuterium. The transmittance IR spectrum obtained in this case is shown in figure 8 by the broken line, whereas the corresponding stretching frequencies of ZnD and OD groups are equal to 1394 and 2664 cm^{-1}, respectively.

The stretching frequencies of ZnH and ZnD species are quite remarkable: they are considerably higher than the corresponding values of 1706 to 1708 and 1231 cm^{-1} earlier reported for dissociative adsorption of hydrogen or deuterium by the massive zinc oxide [13,14]. Therefore, we concluded that the dissociative adsorption of hydrogen or deuterium does not take place on the nanometric zinc oxide particles encapsulated in the channels of the zeolite framework, as was earlier suggested in [12], but occurs on the modifying zinc ions. A similar conclusion also follows from the different stretching frequencies of OH and OD groups resulting from the dissociative adsorption of hydrogen on ZnHZSM-5 and ZnO (3612 and 2664 cm^{-1} for HZSM-5, and 3495 and 2585 cm^{-1} for the ZnO, respectively). Finally, one more argument in favor of this conclusion is presented by the H–H and D–D stretching frequencies of molecular hydrogen and deuterium adsorbed by the ZnHZSM-5 zeolites that are equal to 3934 and 2824 cm^{-1}, respectively. These values are also quite different from those for H_2 and D_2 adsorption by ZnO, which are equal to 4017 and 2886 cm^{-1}, respectively [14].

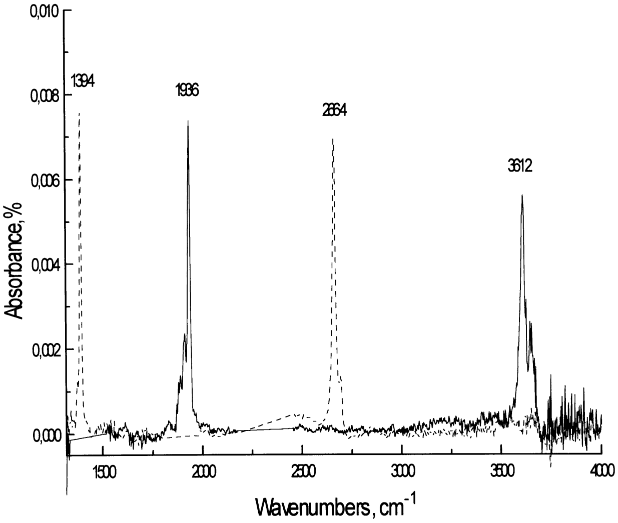

Figure 8. Transmittance IR spectra of H_2 (solid line) and D_2 (dashed line) adsorbed on HZSM-5 with Si/Al = 41 modified with 4% of Zn^{+2}ions at room temperature and equilibrium pressure of 50 Torr.

4. Discussion

Experimental results obtained in the present paper indicate that modification of high-silica zeolites with zinc results in the appearance of several new sites for molecular hydrogen adsorption. As has been earlier demonstrated in reference [11], H_2 adsorbed by zinc at 77 K with the stretching frequency of about 3930–3950 cm^{-1} is dissociatively adsorbed at moderately elevated temperatures. Therefore, the corresponding Zn^{+2} ions most likely act as the dehydrogenating active sites in the aromatization of light paraffins.

The sites of the weaker perturbation of adsorbed molecular hydrogen are also connected with the modifying zinc ions. They correspond to the broader H–H stretching bands with the maxima at about 3970 and 4022 cm^{-1} for mordenite and *ca.* 4005 cm^{-1} for ZSM-5. These bands are probably of a complicated nature, each of them connected with several different kinds of Zn^{+2} ions. However, the poor resolution of the spectra does not permit a more precise interpretation. Interaction with these sites does not result in heterolytic dissociation of adsorbed hydrogen.

Similar to previous publications, of other authors [8,9], our results also indicated that the sites resulting from the modification of HZSM-5 by zinc are formed in the high-silica zeolites by replacement of acidic hydroxyl groups. In principle, substitution of the bridging hydroxyl groups by the bivalent zinc ions could occur in several different ways. One of the possibilities is the ion exchange of two protons localized in the same five- or six-membered ring of the zeolite framework. Such mechanism of ion exchange is well known for faujusites, where the probability of finding two oxygen tetrahedra occupied by Al^{+3} ions in the same six-membered ring is quite high. A similar conventional ion exchange is also most probable for mordenite or for the aluminum-rich ZSM-5 with Si/Al = 15. In this case, the most intense bands of adsorbed hydrogen correspond to the H–H stretching frequencies of 4022 cm^{-1} for mordenite and to 4005 cm^{-1} for ZSM-5. This is only slightly lower than the frequency of 4037 cm^{-1} that has been earlier reported by us for hydrogen adsorption by Zn^{+2} ions in the six-membered rings of Y zeolite [18]. Such a difference is most probably connected with the higher exposure of Zn^{+2} ions in the five-membered rings of pentasils in comparison with the six-membered rings of faujusites. On the other hand, the difference in the stretching frequencies of hydrogen adsorbed by the ion-exchanged Zn^{+2} in the ZnHM and ZnHZSM-5 could be explained by a somewhat different geometry of the framework of these zeolites. Thus, the sites of the moderate perturbation of adsorbed hydrogen are most probably connected with the zinc ions localized in the five- or six-membered rings with two aluminum atoms per ring.

The nature of the sites of the strongest molecular and dissociative adsorption of hydrogen with the stretching H–H frequency of $3940\,cm^{-1}$ is most intriguing. Our experimental results indicated that the fraction of these sites is the highest for the ZSM-5 with the highest Si/Al ratios equal to 41 or 80. According to the theoretical treatment performed in references [10,15,16] and to ^{29}Si MAS NMR data [17], aluminum atoms in the framework of high-silica zeolites are rather far separated from each other. Therefore, in this case the conventional ion exchange is less probable. This puts forward the problem of a possible explanation of neutralization of two strongly separated negative electric charges by the single bivalent zinc ions.

One of the possibilities is substitution of two protons in the adjacent five- or six-membered rings of the zeolite framework by the bridging $[Zn\text{-}O\text{-}Zn]^{+2}$ oxo-ions. Formation of such species in the high-silica zeolites has been discussed and reported by several authors mainly for the iron-loaded (see reviews [19,20] and references therein) and the copper-loaded zeolites [21,22].

For the zinc-modified high-silica zeolites, formation of the bridging oxo-complexes has been also discussed by Bell and van Santen by means of quantum-chemical calculations in references [15,24]. The conclusions of these papers are, however, rather controversial. On the one hand, Bell and coworkers concluded that formation of the oxo-ions from two ZnOH groups according to the reaction:

$$2\ Z - ZnOH \rightarrow Z\text{–}Zn\text{–}O\text{–}Zn\text{–}Z + H_2O \qquad (2)$$

is a strongly endothermic process and therefore is rather improbable [15,16]. On the other hand, the quantum-chemical calculations performed by van Santen's group indicated that such species should be highly active in heterolytic dissociation of hydrogen and light paraffins [24,25].

At first glance, dissociative adsorption of molecular hydrogen at moderately high temperature observed in the present study could be considered as an indication of the formation of binuclear oxo-species. However, the products of the dissociative hydrogen adsorption are not consistent with the existence of the bridging oxo-ions. Indeed, according to the following equation:

$$Z - Zn\text{–}O\text{–}Zn\text{–}Z + H_2 \rightarrow Z\text{–}ZnH + HO\text{–}Zn-Z \qquad (3)$$

the heterolytic dissociative adsorption of molecular hydrogen involving bridging oxo-ions should result in the formation of zinc hydrides and the ZnOH groups. However, instead, we observed the formation of zinc hydride and of the hydroxyl group with the stretching frequency of $3612\,cm^{-1}$ that is very close to the one for the bridging acidic hydroxyls in hydrogen forms of the initial zeolites. Therefore, this result is not consistent with formation of the oxo-ions.

Another alternative that better explains our results on dissociative hydrogen adsorption, corresponds to the localization of Zn^{+2} ions with stretched zinc–oxide binds at the two distantly separated negatively-charged aluminum occupied tetrahedra. Such a possibility has been already mentioned before by a number of authors. We also discussed it in a more definite way in references [25–27].

It was suggested that Zn^{+2} ions are localized in the five- or six-membered rings of the zeolite structure with only one aluminum atom per ring. This creates a Lewis acid site with only partially compensated positive charges. The negatively charged aluminum-occupied oxygen tetrahedra localized in the adjacent five- or six-membered ring remains then only partially compensated by coulomb interaction with adjacent zinc cations. The resulting acid–base pairs correspond to the distantly separated excessively positively charged zinc ions and the negatively charged aluminum–occupied oxygen tetrahedra with the cationic vacancies:

$$2[AlO_2]^- + Zn^{+2} \rightarrow [AlO_2]^-\ Zn^{+2} + [AlO_2]^- \qquad (4)$$

The attractive feature of this charge-alternating model is a very strong perturbation by the Lewis sites with only partially neutralized positive electric charges of adsorbed H_2. This explains the very large low-frequency shifts of H–H stretching frequency and the easy heterolytic dissociation of adsorbed hydrogen. In reference [27], the heterolytic dissociation of molecular hydrogen adsorbed by such is supported by quantum-chemical calculations.

Earlier in reference [12] we suggested that the sites of the strongest perturbation and dissociative adsorption of molecular hydrogen in ZnHZSM-5 zeolites could be connected with the low-coordinated zinc ions located on the surface of nanometric ZnO clusters, which are formed in the channels of the zeolite framework upon incipient wetness impregnation and subsequent high-temperature pretreatment. The results of the present study on only partial substitution of hydroxyl groups by zinc ions confirmed formation of such nanometric zinc oxide clusters at high zinc loadings. However, our results on the different nature of the sites of dissociative hydrogen adsorption in zeolites with different Si/Al ratios in the framework definitely indicate that modification by zinc could not be explained by purely matrix effects that are connected only with the size of the zeolite micropores.

Acknowledgment

The financial support from the Dutch Science Foundation in the collaborative Russian–Dutch research project 047-005-011 NWO is gratefully acknowledged.

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