Catalysis Letters Vol. 83, Nos. 3–4, November 2002 (©2002)

Siting of Co^{2+} ions in cobalt-modified high-silica zeolites probed by low-temperature molecular hydrogen adsorption

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Received 26 April 2002; accepted 28 June 2002

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy was used to characterize the effects of introducing cobalt into the zeolites ZSM-5 and mordenite. Aqueous impregnation of the hydrogen form of the zeolite and subsequent *in vacuo* treatment at temperatures up to 920 K results in partial exchange of protons in bridging hydroxyl groups by Co^{2+} cations. These changes are evidenced by a decrease in intensity of the bands at 3606–3609 cm^{-1} characteristic of Brønsted acid sites. DRIFT spectra of hydrogen adsorbed at 77 K also confirm the exchange of protons for Co^{2+} cations, as evidenced by a decrease in the intensity of the band at 4106 cm^{-1} for H_2 adsorbed on protons. By contrast, the bands at ~3905, ~3965, and ~4010 cm^{-1} for H_2 adsorbed on the Co^{2+} cations increase in intensity. With increasing Si/Al ratio at a constant Co loading of 1 wt% the intensity of the band at 3905 cm^{-1} for H-ZSM-5 strongly increases in intensity relative to the other bands. This feature is attributed to Co^{2+} cations interacting with two adjacent cation-exchange sites located in a 10-membered ring. It is hypothesized that the Lewis acidity of Co^{2+} cations in such environments is higher than that of Co^{2+} cations associated with oxygen atoms in individual five- or six-membered rings containing two Al atoms, because the Co^{2+} cation can interact with only two of the four basic oxygen anions located in the ring. It is proposed that Co^{2+} cations in the latter type of sites are identified by the bands at 3965 cm^{-1} and 4010 cm^{-1} for adsorbed H_2.

KEY WORDS: high-silica zeolites; Co^{2+}; H_2 molecular adsorption; DRIFT.

1. Introduction

High-silica zeolites containing Co^{2+} cations are known to be active catalysts for selective catalytic reduction (SCR) of NO by methane [1–4], N_2O decomposition to nitrogen and oxygen [5], and ammoxidation of ethane to acetonitrile [6]. Therefore, understanding the state of cobalt ions in these materials is of considerable interest. Because of the low concentration of Co^{2+} cations and their random distribution in high-silica zeolites, no information about the location of these cations relative to the zeolite framework can be obtained from XRD. To date, the main source of such information has been UV-Visible spectroscopy of the cations [7–10]. The results of these studies suggest that Co^{2+} cations introduced into high-silica zeolites (*e.g.*, MFI, MOR) are localized in three types of sites designated as α, β and γ. Co^{2+} cations in α sites are coordinated to four oxygen atoms located on the walls of the straight channels, whereas Co^{2+} in β sites are coordinated to the oxygen atoms in distorted six-membered rings located at the intersection between the straight and sinusoidal channels. The Co^{2+} cations in γ sites are in "boat-shaped" pockets located on the walls of the sinusoidal channels. Population of the three sites depends on the extent of the cation exchange. The β sites are most highly occupied at low cobalt loading, whereas the α sites are more highly occupied at high cobalt loading. The γ sites accommodate only a minor fraction of the Co^{2+} cations in ZSM-5. It should be noted, however, that the proposed interpretation of Co^{2+} cation placement was based on ZSM-5 samples with Si/Al ratios below 25 and did not account for the distribution of Al in the zeolite framework. Recent investigations of the distribution of framework Al atoms has shown that the fraction of charge-exchange sites located in single five- and six-membered rings capable of accommodating divalent cations decreases rapidly as the Si/Al ratio of the framework increases [11–14]. In addition, recent quantum chemical calculations of Co^{2+} cation in ferrierite show several different types of charge-exchange sites exhibiting features which fall within the range reported for α, β and γ sites [15].

In the present study, Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy of H_2 adsorbed at 77 K was used to probe the local environment of Co^{2+} cations introduced into H-ZSM-5 and H-MOR. This technique has been used successfully to study the local environment of alkaline and alkaline earth cations exchanged into zeolites with different Si/Al ratios in the framework [16–27]. An objective of particular interest for the present investigation was to establish the effects of Si/Al ratio and Co loading on the environment of Co^{2+} cations in the zeolites with very high silica to aluminum ratios.

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2. Experimental

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 numbers given in parenthesis after each zeolite is the Si/Al ratio. The hydrogen forms of ZSM-5 and mordenite were prepared by decomposition of the ammonium forms in vacuum at 773 K, followed by calcination in flowing oxygen at 793 K. Cobalt was introduced by incipient-wetness impregnation of the hydrogen forms of the zeolites with a cobalt nitrate solution in a manner similar to that described previously for zinc-modified zeolites [22–24]. Variations in the cobalt content were achieved by changing the concentration of the cobalt nitrate solution used for impregnation of the hydrogen forms. The impregnated samples were dried at 473 K and calcined in flowing oxygen at 700 K for 1 h. The amount of cobalt introduced into the zeolites was estimated from the preparation procedure and for some of the samples was also confirmed by AAS analysis.

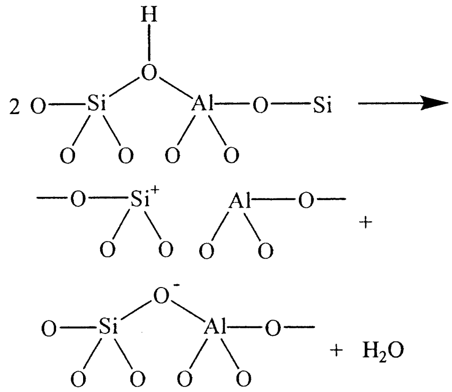
DRIFT spectra of hydroxyl groups and of adsorbed molecular hydrogen were recorded using a Nicolet "Impact 410" spectrophotometer equipped with a home-made diffuse reflectance attachment. Spectra were recorded either at room temperature or at 77 K. DRIFT measurements of H_2 adsorbed at 77 K were carried out using a quartz cell immersed in a Dewar filled with liquid nitrogen. Molecular hydrogen was adsorbed at 77 K 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 reflectivity of the samples at $5000\,\mathrm{cm}^{-1}$ was equal to 0.9 KM units. The background created by the zeolite was subtracted from the spectrum of adsorbed H_2.

3. Results

It is well known that high-temperature vacuum pretreatment of high-silica zeolites in their hydrogen form results in dehydroxylation of these materials. In the present study this process was monitored by taking DRIFT spectra of the hydroxyl groups and spectra of H_2 adsorbed at 77 K. Figure 1(a) shows DRIFT spectra of the hydroxyl groups in H-ZSM-5(41) zeolite dehydrated in vacuum at different temperatures. The spectra contain narrow absorption bands with maxima at 3609 and $3740\,\mathrm{cm}^{-1}$ corresponding to isolated bridging acidic hydroxyls and silanol groups, respectively [21]. The additional broad absorption in the range of 3200–$3600\,\mathrm{cm}^{-1}$ is attributed to either residual adsorbed water or to hydrogen-bonded acidic OH-groups. Upon increasing the dehydration temperature from 570 to 920 K, this feature gradually disappears. At the same time, the intensity of the band at $3609\,\mathrm{cm}^{-1}$ decreases by less than 30%. Figure 1(b) displays similar results for dehydroxylation of H-MOR(5). Thus, in agreement with the previously published results, high-temperature vacuum pretreatment of the hydrogen forms of high-silica zeolites results in partial dehydroxylation of these materials. This conclusion was also confirmed using low-temperature hydrogen adsorption as a molecular probe.

Figure 2 displays spectra of H_2 adsorbed at 77 K and an equilibrium pressure of 1.33×10^4 Pa on the same samples of H-ZSM-5(41) and H-MOR(5) as those shown in figure 1. After dehydration at 570 K the spectra of H_2 adsorbed by H-ZSM-5 contain two unresolved stretching bands with the maxima at $4105\,\mathrm{cm}^{-1}$ and at about $4125\,\mathrm{cm}^{-1}$. These bands result from the H–H stretching vibrations of adsorbed hydrogen perturbed by the acidic bridging hydroxyls and by the silanol groups, respectively [21]. The low-intensity band at $4180\,\mathrm{cm}^{-1}$ is attributed to a high-frequency satellite that is a combination of the H–H stretching vibrations and oscillations of the adsorbed H_2 relative to the Brønsted acidic sites. Similar bands have been earlier observed for H_2 adsorption by NaA, NaX and NaY zeolites [16–22].

Upon increasing the temperature of evacuation, the intensity of the bands due to H_2 adsorbed by bridging OH groups decreases due to dehydroxylation of the zeolite. At the same time, a new, much weaker band centered at about $4030\,\mathrm{cm}^{-1}$ appears and increases in intensity monotonically. In accordance with our previous studies [25–27], this band is assigned to H_2 perturbed by Lewis acid sites resulting from the high-temperature dehydroxylation of the zeolite framework. Such lattice sites are most likely formed by the removal of two bridging hydroxyl groups according to the following scheme:



(1)

For H-MOR this mechanism is supported by the much lower intensity of the DRIFT band for the silanol groups in comparison to the bridging hydroxyls. Therefore, dehydroxylation could not result from recombination of bridging OH groups with SiOH groups. Consistent with this idea, the bands for the silanol groups decrease upon zeolite dehydroxylation to a much lesser degree than the bands for the bridging OH groups. Thus, taken together, these observations indicate

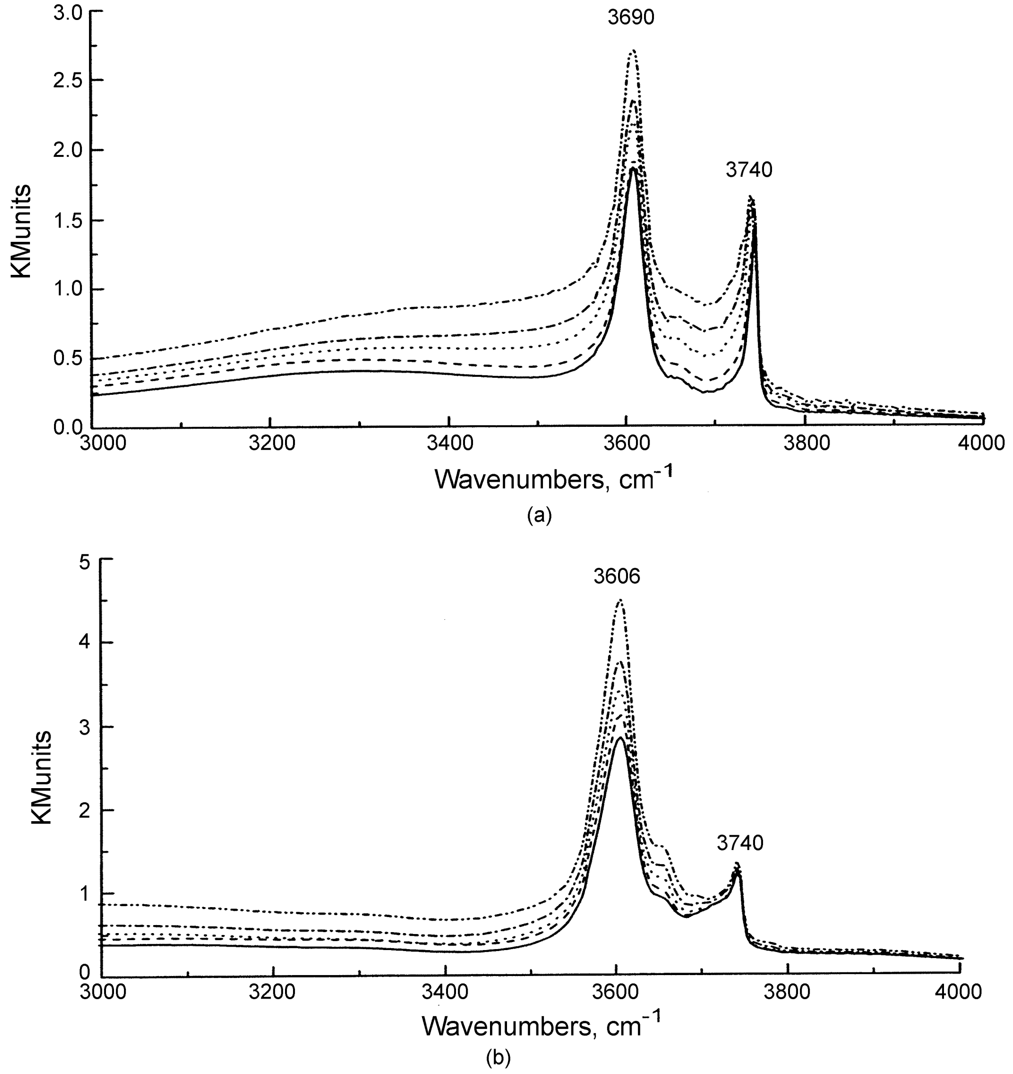
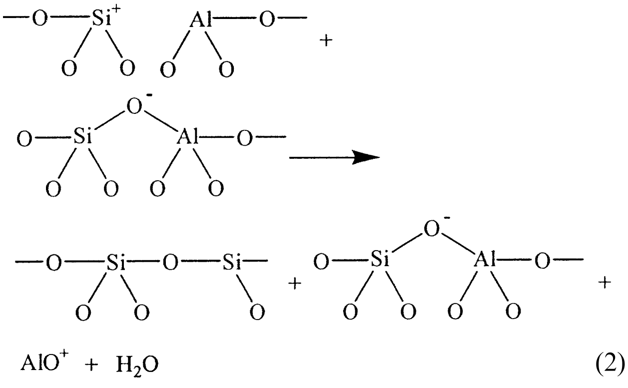


Figure 1. Evolution of DRIFT spectra of OH groups in the H-ZSM-5(41) zeolite (a) and in H-MOR(5) (b) upon different vacuum pretreatments: pretreated in vacuum at 573 K (– · · –), 673 K (– · –), 773 K (·······), 873 K (– – –), and 923 K (——). DRIFT measurements at 77 K.

that the formation of water occurs via condensation of two bridging hydroxyls. It is also possible that the new adsorption sites in the form of AlO^+ are produced via subsequent dealumination of the dehydroxylated zeolite framework according to reaction (2):


(2)

The main difference in the behavior of H-ZSM-5 and H-MOR upon high-temperature vacuum pretreatment is the somewhat greater extent of dehydroxylation and dealumination of the latter zeolite. This is evident both from the somewhat stronger decrease in the DRIFT bands of the hydroxyl groups and from the DRIFT spectra of H_2 adsorbed at 77 K on H-MOR dehydroxylated at different temperatures. The more facile dealumination of H-MOR in comparison with H-ZSM-5 is most likely due to the higher density of the bridging hydroxyl groups in the former case.

Figure 3 shows DRIFT spectra of the O–H stretching region for ZSM-5(41) samples with cobalt loadings of 2 and 4 wt%, pretreated in vacuum at 920 K. For comparison, the spectrum is shown for H-ZSM-5 after similar pretreatment. It is evident that the introduction of Co into H-ZSM-5 by incipient wetness impregnation strongly decreases the number of bridging hydroxyl groups remaining in the samples after high-temperature pretreatment relative to that observed for the corresponding hydrogen forms. For example, for a cobalt content of 2 wt%, for which the concentration of

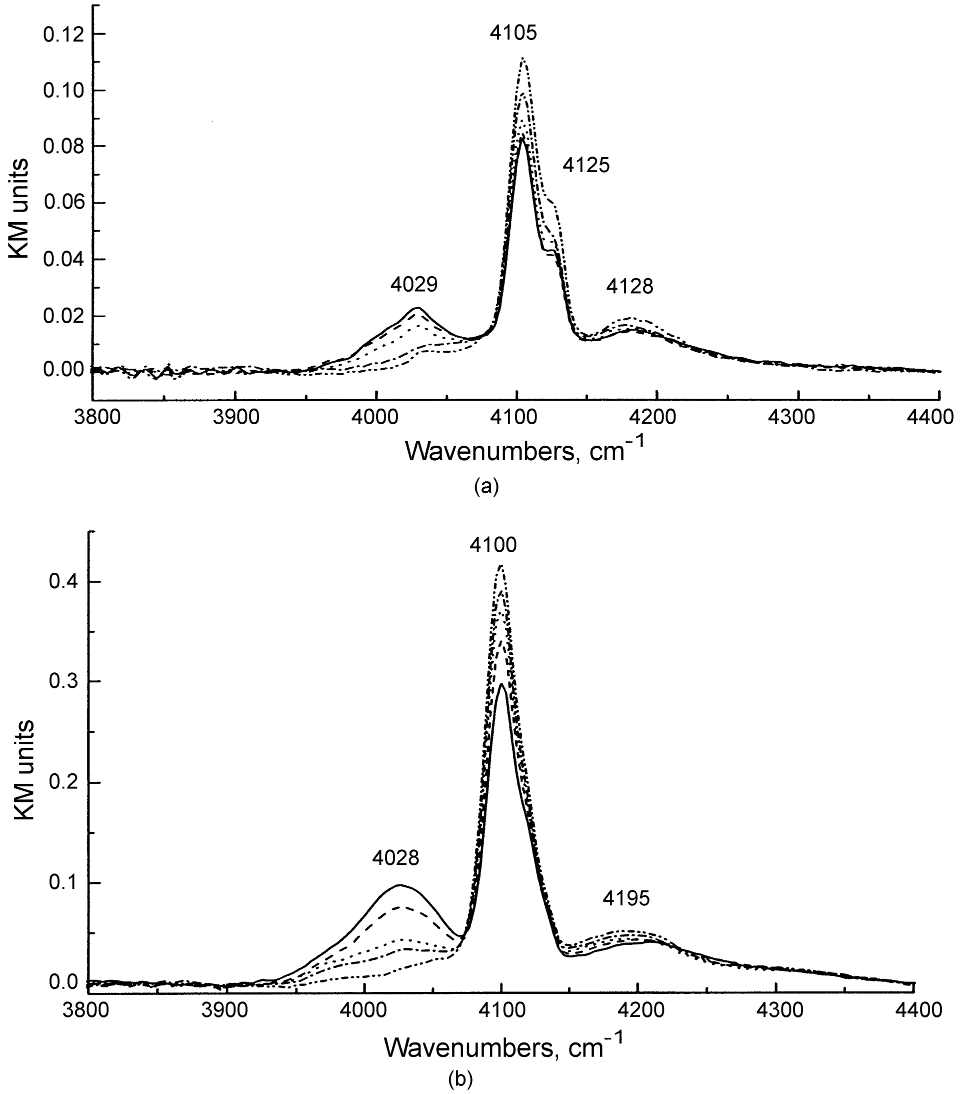


Figure 2. DRIFT spectra of H_2 adsorbed at 77 K by the same zeolites as those in figure 1 pretreated in vacuum at 573 K (– · · –), 673 K (– · –), 773 K (·······), 873 K (– – –), and 650 °C (——). DRIFT measurements at 77 K.

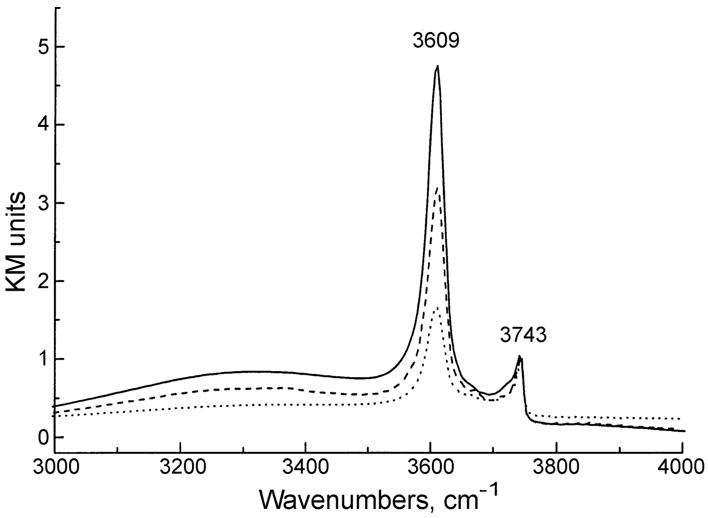


Figure 3. DRIFT spectra of hydroxyl groups in H-ZSM-5(41) zeolite (solid line) and of the samples of this zeolite loaded with 2% of Co (dashed line) and 4% of Co (dotted line) pretreated in vacuum at 923 K. DRIFT measurements at room temperature.

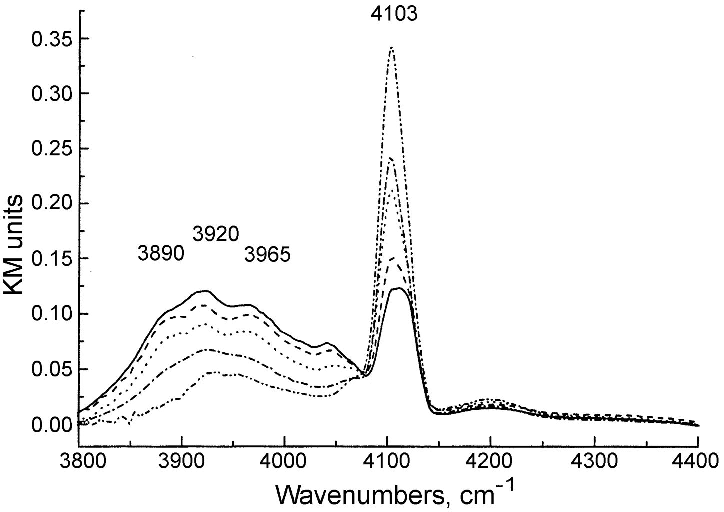


Figure 4. DRIFT spectra of hydrogen adsorbed at 77 K by H-MOR(5) loaded with 5% of modifying Co cations pretreated in vacuum at 573 K (– · · · –), 673 K (– · –), 773 K (·······), 873 K (– – –), and 923 K (——). DRIFT measurements at 77 K.

cobalt ions is nearly the same as the concentration of Al, the intensity of the OH bands decreases by about 40 wt%. By contrast, for the sample with 4 wt% cobalt, for which the concentration of Co^{2+} cations is about twice high as that of Al, the intensity of the OH band decreases by about 75%. It is also quite remarkable that the presence of cobalt has no influence on the intensity of the bands for the silanol groups. This obviously indicates that upon modification of H-ZSM-5 with cobalt and subsequent high-temperature pretreatment, a considerable part of the bridging hydroxyl groups is replaced by Co^{2+} ions. Since the Co/Al ratios are ~1 and ~2 for the cases of H-ZSM-5 containing 2 and 4 wt% Co, respectively, it is possible that some of the modifying cobalt ions could also form the small cobalt oxide particles inside micropores of the zeolite framework or on the external surface of the zeolite grains. The relationship between the amount of Co^{2+} introduced into the zeolite and the decrease in the intensity of the bridging hydroxyl groups is discussed below in more detail.

High-temperature vacuum pretreatment of the cobalt modified H-MOR or H-ZSM-5 results not only in a decrease in the number of bridging hydroxyl groups, but also in the appearance of new Lewis acid sites associated with the cobalt cations. Adsorption on these sites perturbs the H–H vibrations of H_2 to a much greater degree than adsorption of H_2 on the Lewis acid sites resulting from dehydroxylation of the zeolite.

The effects of cobalt addition on H-MOR are illustrated in figure 4. In addition to the band at about 4027 cm^{-1} for H_2 adsorbed on the Lewis sites in the zeolite framework, three new bands associated with the presence of cobalt cations are clearly visible. The positions of these bands are at about 3890, 3920 and 3965 cm^{-1}. It is also noted that modification with cobalt strongly reduces the intensity of the band at 4103 cm^{-1} for H_2 adsorbed on bridging hydroxyl groups in a manner similar to that observed for H-ZSM-5(41) in figure 3.

Figures 5–8 present DRIFT spectra for H_2 adsorbed on cobalt-modified H-ZSM-5 with Si/Al ratios of 15–80. As for cobalt-modified H-MOR, stretching bands below about 4050 cm^{-1} are due to H_2 interacting with cobalt cations in various environments. The relative intensities of the bands in this region are strongly dependent on the cobalt loading and the Si/Al ratio of the zeolite. Of particular note is the observation that for a fixed Co loading of 1 wt% the relative intensity of the band at 3905 cm^{-1} strongly increases with increasing Si/Al ratios.

4. Discussion

The results presented in figures 4–8 demonstrate that incipient-wetness impregnation of cobalt into H-MOR or H-ZSM-5 and subsequent calcination results in the loss of Brønsted acid sites and the appearance of Lewis acid sites associated with Co^{2+} cations. The loss of Brønsted acid sites is evidenced by the decrease in the intensity of both the bands at 3606–3609 cm^{-1} for O–H stretching vibrations and the bands at 4106 cm^{-1} for H–H vibrations of H_2 adsorbed at 77 K by bridging hydroxyl groups. With increasing calcination temperature and cobalt loading the degree of substitution of Co^{2+} for H^+ increases.

There is certainly no doubt that the introduction of Co^{2+} by incipient-wetness impregnation results in parallel with the ion exchange in the formation of cobalt oxide particles with the amount of the latter increasing with increasing Si/Al ratio. For example, for ZSM-5(41) containing 1 wt% Co, the amount of Co^{2+} is one-half that of Al. Assuming that Co^{2+} exchanges with two Brønsted acid protons, one would expect all

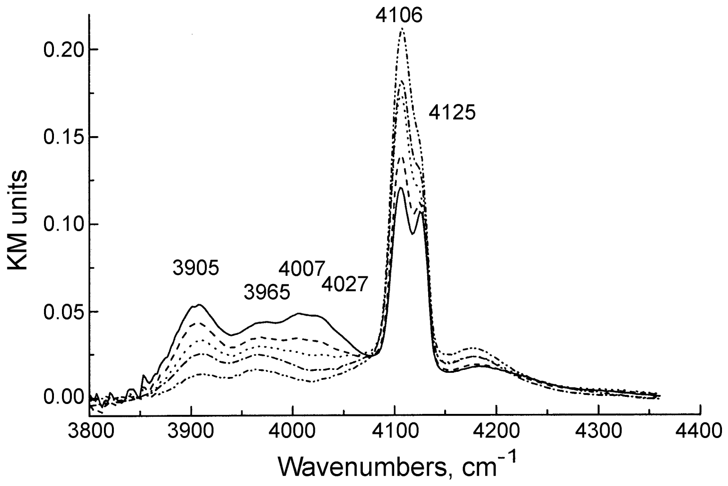


Figure 5. DRIFT spectra of hydrogen adsorbed at 77 K by H-ZSM-5(15) with 1% of modifying Co ions pretreated in vacuum at 300 °C (–··–), 400 °C (–·–), 500 °C (·······), 600 °C (– – –), or 650 °C (——). DRIFT measurements at 77 K.

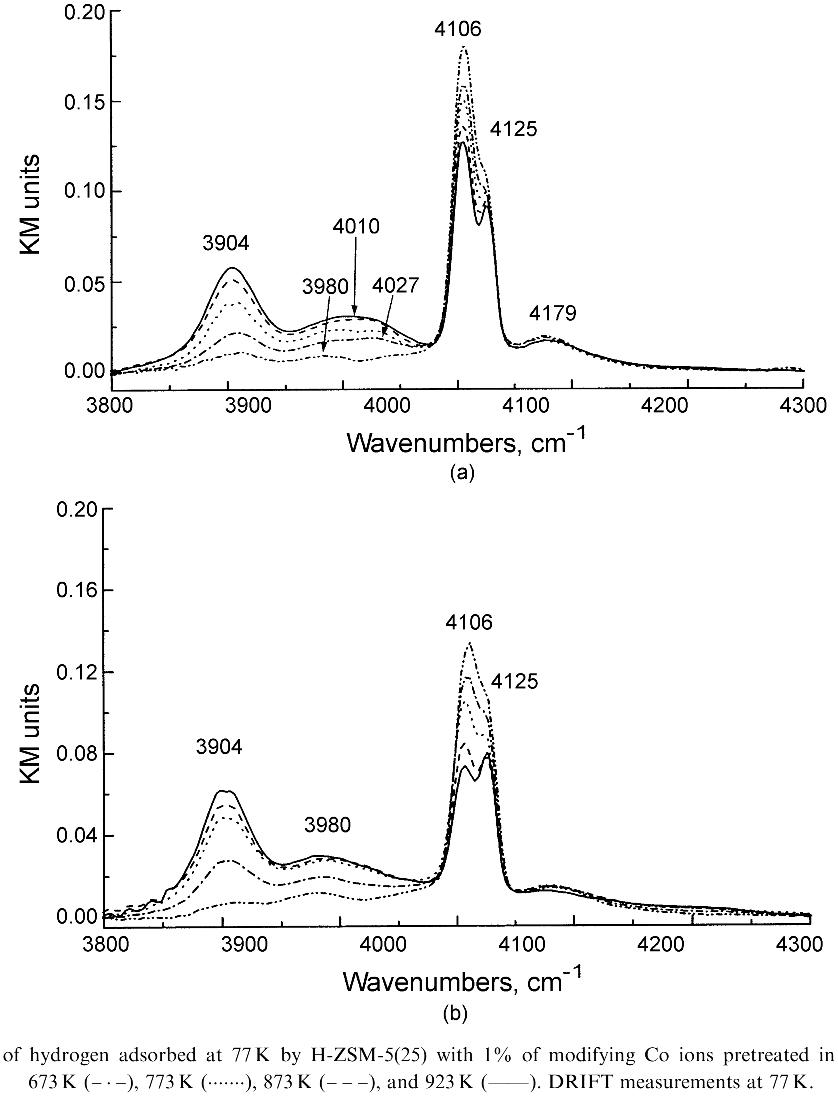


Figure 6. DRIFT spectra of hydrogen adsorbed at 77 K by H-ZSM-5(25) with 1% of modifying Co ions pretreated in vacuum at 300 °C (–··–), 673 K (–·–), 773 K (·······), 873 K (– – –), and 923 K (——). DRIFT measurements at 77 K.

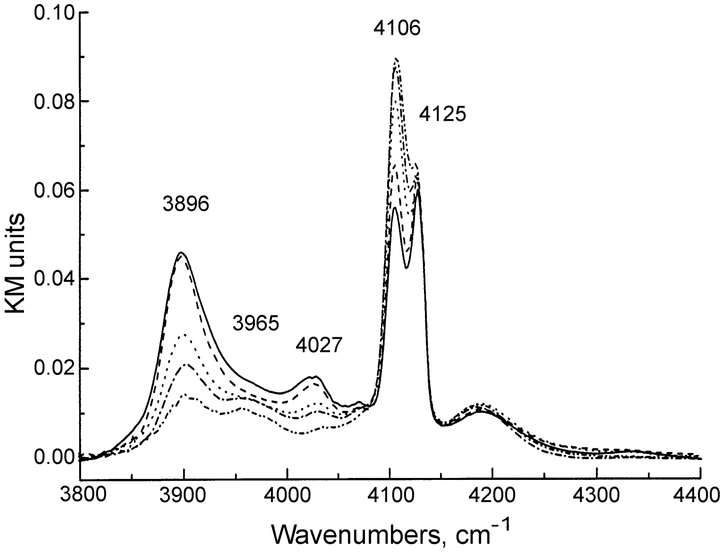


Figure 7. DRIFT spectra of hydrogen adsorbed at 77 K by H-ZSM-5(41) with 1% of modifying Co cations pretreated in vacuum at 573 K (– · · · –), 673 K (– · –), 773 K (·······), 873 K (– – –), and 923 K (——). DRIFT measurements at 77 K.

of the bridging hydroxyl groups to be displaced. In reality, the intensity of the DRIFT band for bridging hydroxyl groups decreases upon modification by cobalt by less than 50% (figure 7). Thus, for ZSM-5(41) loaded by 1 wt% of Co about 50% of the cobalt ions introduced into the zeolite are converted to cobalt oxide particles. For H-ZSM-5(80) modified with 1 wt% Co, the amount of cobalt oxide is twice as high because for the same Co loading the Al content is half of that in ZSM-5(41).

The opposite situation holds for mordenite modified with 5 wt% of Co. In this case, the amount of cobalt is approximately one-third that of Al. On the other hand, as follows from figure 4, the intensity of the DRIFT band for the bridging hydroxyl groups drops after modification with cobalt by two-thirds. Assuming again the displacement of two protons by each exchanged Co^{2+} cation leads to the conclusion that almost all of the Co introduced could be placed into charge-exchange sites, without the formation of cobalt oxide particles. It is also quite clear that the samples with the intermediate Si/Al ratios correspond to a gradual transition from the ion exchange to the formation of cobalt oxide particles in an amount comparable to the ion exchange.

Figures 5–8 also show that the introduction of Co into H-ZSM-5 results in the appearance of new bands in the spectrum of H_2 adsorbed at 77 K. As noted earlier, these bands are associated with Lewis acid centers that are different from those formed by the condensation of zeolite hydroxyl groups or by expulsion of Al from the zeolite framework. Comparison of the spectra of adsorbed H_2 observed for H-MOR and H-ZSM-5 modified with Co strongly suggests that the Lewis acid sites are associated only with Co^{2+} cation in cation-exchange

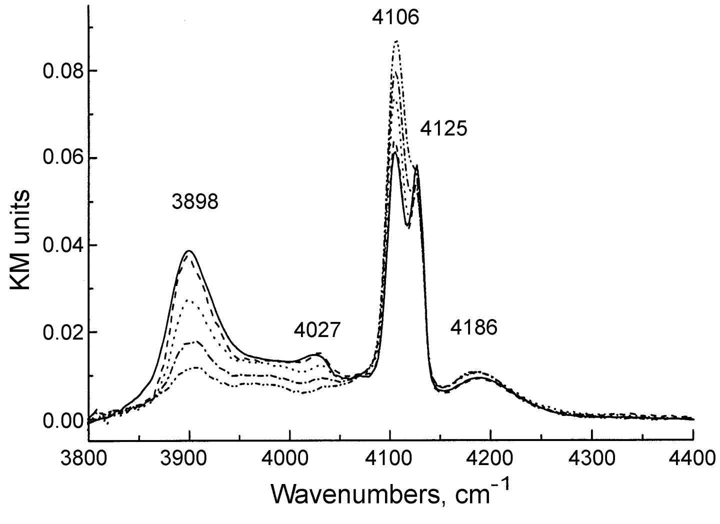


Figure 8. Transmittance IR spectra of H_2 (solid line) and D_2 (dashed line) adsorbed at room temperature and equilibrium pressure of 50 Torr on H-ZSM-5 with Si/Al = 41 and with 4% modifying Zn ions.

positions, and not with Co^{2+} associated with particles of cobalt oxide. Since the frequencies of the H–H stretching vibrations associated with the Co^{2+}-based Lewis acid sites are lower than those formed in the absence of Co, the Lewis acidity of the former sites is assumed to be stronger. The best-defined band for H_2 adsorbed on Co^{2+} cations is that appearing at 3905 cm^{-1}. The relative intensity of this band increases with the nominal Si/Al ratios up to 80.

The bands for H_2 adsorbed on Co^{2+} can be assigned to specific cation exchange environments by the following logic. It is assumed that the differences in vibrational frequencies for these features are attributable to differences in the Lewis acidity of the Co^{2+} cations located at different cation-exchange positions in the zeolite, and that the most Lewis acidic Co^{2+} cation causes the largest red shift in the H–H vibrational frequency. It is further assumed that the Lewis acidity of Co^{2+} will increase with increasing distance of the cation from the zeolite framework O atoms bonded to the Al atoms. The logic here is that an isolated Co^{2+} cation should exhibit the highest Lewis acidity and that the cation Lewis acidity should decrease as the cation interacts more and more strongly with the negatively charged O atoms at the cation exchange site. Since the zeolite framework is a soft base, association of the oxygen anions with Co^{2+} will result in charge flow to the cation, thereby reducing its Lewis acidity. DFT calculations by Rice *et al.* [13] show that Co^{2+} cations are preferably situated in rings containing five T atoms, two of which are Al. Furthermore, flat five-membered (F5) rings present in the straight channels of the zeolite are preferred over bent five-membered (B5) rings present in the sinusoidal channels. Stabilization of Co^{2+} in six-membered (F6 and B6) rings is also possible, and here again flat rings are preferred over bent rings. For a given ring conformation, the M–O bond distances are 0.02–0.04 A longer for the six- *versus* the five-membered rings.

Based on the considerations presented above, one would predict that the Lewis acidity should decrease in the order B6 > F6 > B5 > F5. Calculations of the distribution of Al in ZSM-5 for Si/Al ratios of 15–25 show that the maximum value of Co^{2+} that can be accommodated in five- and six-membered rings corresponds to a Co/Al ratio of 0.25–0.15 [12]. This suggests that the bands observed at 3965 and 4106 cm^{-1} are attributable to H_2 interacting with Co^{2+} cations interacting with five- and six-membered rings containing two Al atoms, respectively. The band at 3898–3905 cm^{-1}, attributed to H_2 adsorption on the most Lewis acidic Co^{2+}, is most intense for the ZSM-5 samples with Si/Al ratio of 41 and 80. For such high values of the Si/Al ratio, the maximum Co/Al ratio that can be achieved with all of the Co^{2+} cations sited in five- and six-membered rings containing two Al atoms is 0.1–0.05. Since the nominal Co/Al ratio for these samples exceeds this ratio, some of the Co^{2+} cations are likely to be associated with other types of sites. A possible candidate is shown in figure 9. Illustrated here is a 10-membered ring containing two Al atoms in next-nearest-neighbor sites. Quantum chemical calculations show that for this environment, because of geometric constraints, the Co^{2+} cation can interact with only two of the four basic O atoms in the ring. The weaker compensation of the positive charge on the Co^{2+} cation should, therefore, lead to a higher Lewis acidity for Co^{2+} cations located in the type of environment shown in figure 9.

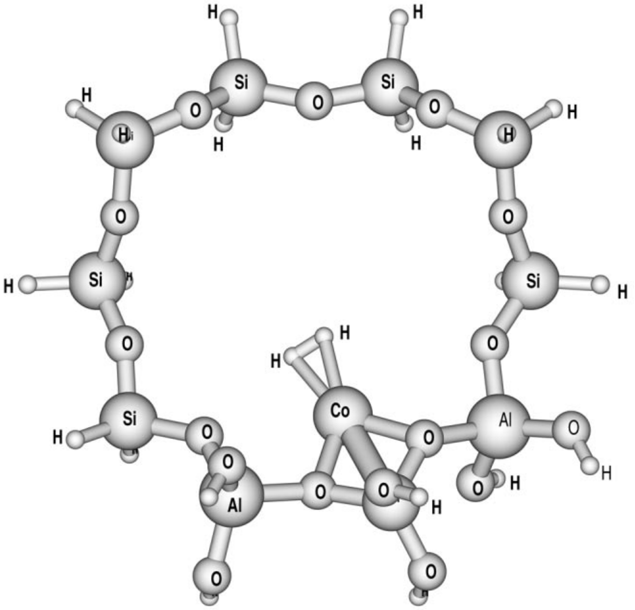


Figure 9. An illustration of the positioning of a Co^{2+} cation in a 10-membered ring containing two Al atoms in next-nearest-neighbor positions.

The possibility that H_2 adsorption could occur on dioxo metal cations of the form $[Co–O–Co]^{2+}$ was also considered, since such structures have been reported based on EXAFS studies conducted with Zn, Cu and Fe containing ZSM-5 [28–32]. However, recent density functional theory calculations indicated that the formation of such structures via the process

$$2Z^{-}[Co{-}OH]^{+} \rightarrow Z^{-}[Co{-}O{-}Co]^{2+}Z^{-} + H_2O \quad (3)$$

is highly endothermic [12]. Consistent with this, EXAFS experiments conducted with Co–ZSM-5 show no evidence for dioxo cobalt cations [33]. For this reason the adsorption of H_2 on $[Co–O–Co]^{2+}$ cations was taken to be unlikely.

5. Conclusions

Hydrogen adsorbed at liquid nitrogen temperature is an effective probe for the Co^{2+} cations ion-exchanged into the acid forms ZSM-5 and mordenite. The exchange of Co^{2+} cations for Brønsted acid protons is observed by the decrease in intensity of the H–H vibrational band at

4105 cm^{-1} for H_2 adsorbed on bridging OH groups and the simultaneous appearance of bands at 4610, 3965 and 3905 cm^{-1} for H_2 adsorbed on Co^{2+} cations. The last of these three features is particularly prominent in ZSM-5 samples with Si/Al ratios of 41 and 80. The red shift in the H–H vibrational frequency for H_2 adsorbed on Co^{2+} is attributed to the Lewis acidity of the cation, and the lower the frequency the higher the Lewis acidity. It is proposed that the Lewis acidity of Co^{2+} increases with increasing distance of the cation from the zeolite framework. Based on this consideration and taking into account the effect of Si/Al ratio on the distribution of Al atoms in the zeolite, the bands at 4610 and 3965 cm^{-1} are assigned to H_2 adsorbed on Co^{2+} associated with two cation exchange sites present in either a five- or six-membered ring. The band at 3905 cm^{-1} is assigned to Co^{2+} interacting with a pair of cation exchange sites located in a 10-membered ring.

Acknowledgment

This work was supported by the US Civilian Research and Development Foundation through Award RC1–2204.

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