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Fourier Transform-Infrared Investigation of Adsorption of Methane and Carbon Monoxide on HZSM-5 and Mo/HZSM-5 Zeolites at Low Temperature

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The low-temperature (173 K) methane adsorption and coadsorption of methane and CO on HZSM-5 and Mo/HZSM-5 were investigated by FT-IR spectroscopy. Five distinct bands of adsorbed methane at 3008, 3002, 2900, 2890, and 1303 cm^{-1} were observed for HZSM-5 zeolite. The assignments of these bands are the ν_1 (2900, 2890 cm^{-1}), ν_3 (3008, 3002 cm^{-1}), and ν_4 (1303 cm^{-1}) modes of methane, respectively. The infrared inactive ν_1 mode (2917 cm^{-1}) of free methane became active and shifted to lower frequencies when methane was adsorbed on the zeolite sample. The weakness of the C–H bond of methane caused by distortion of the methane molecule via its interaction with the zeolite surface is possibly the first step in methane activation. Very possibly the bands at 3002 and 2890 cm^{-1} are due to the methane that interacts with the hydroxyl groups, whereas the band at 2900 cm^{-1} is from the methane that interacts with the oxygen anion species formed by dehydroxylation HZSM-5 zeolite. Three strong bands of adsorbed CO at 2173, 2162, and 2138 cm^{-1} were detected for HZSM-5. The 2173 cm^{-1} band was assigned to the CO that interacts with surface Lewis acidic sites, whereas the band at 2162 cm^{-1} is attributed to the CO that interacts with hydroxyl groups and the band at 2138 cm^{-1} originates from the weakly adsorbed CO. The introduction of molybdenum into HZSM-5 considerably reduces the amount of adsorbed methane and CO because molybdenum may eliminate the surface hydroxyl groups and block the Lewis acidic sites available for methane and CO adsorption.

INTRODUCTION

The activation and conversion of methane are two of the most challenging and toughest subjects in catalysis science because of the inert property of the methane molecule. Considerable attention has been paid to the investigation of reaction mechanisms for the oxidative coupling and partial oxidation of methane (1, 2) as well as the conversion of methane over supported metals (3–5) and superacid (6, 7) under nonoxidizing conditions. However, it is difficult to gain insight into the reaction mechanisms because of the lack of experimental data on methane interaction with catalyst surfaces possibly due to the short lifetime of adsorbed methane and reaction intermediates at high temperature. One effective way to understand the mechanisms of methane activation and conversion is to investigate methane adsorption on catalyst surfaces. Sheppard and Yates have studied the physical adsorption of methane on porous silica glass (8). The adsorption of methane on various zeolites such as NaX, NaA, NaZSM-5, and HZSM-5 has also been reported (9–16). However, the attention of these investigators was focused largely on the changes in absorption bands after methane adsorption. Less attention was paid to the behavior of the interaction between methane and solid surface. Recently, we have investigated the adsorption of methane on CeO_2, MgO, and Al_2O_3 at 173 K by FT-IR spectroscopy (17–19). Direct information about the interaction of methane with oxide surface has been obtained. The active species that interact with methane vary with different oxides. The surface oxygen species O^- and the surface lattice oxygen are the active species on CeO_2, whereas the surface oxygen anions and the Lewis acid–base pairs are responsible for the adsorption of methane on MgO. The methane adsorbed on Al_2O_3 is formed mainly via the interaction of methane with both surface hydroxyls and coordinately unsaturated surface oxygen anions.

CO is a useful probe molecule for the characterization of Lewis acidic sites on oxides and zeolites (20–24). For the HZSM-5 zeolite, the IR bands at 2138, 2198, 2222, and 2232 cm^{-1} of adsorbed CO are observed at low temperature (20). The 2138 cm^{-1} band is ascribed to the physically adsorbed CO, the absorbed CO that interacts with bridging hydroxyls exhibits a band at 2175 cm^{-1}, and the 2232, 2222, and 2198 cm^{-1} bands are attributed to CO adsorbed on nonskeletal aluminum species. In an attempt to characterize the active sites in the HZSM-5 and Mo/HZSM-5 samples and to discriminate the sites responsible for the

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adsorption of methane and CO, the adsorption and coadsorption of methane and CO at low temperature (173 K) were investigated in this study.

The recent development of nonoxidative methane conversion over HZSM-5 and Mo/HZSM-5 catalysts has attracted much interest (21, 25–28). As these catalysts are solid acid in nature, it has been speculated that the reaction mechanism may be quite different from those of the oxidative coupling of methane (OCM) and the partial oxidation of methane. Therefore, a study of the interaction of methane with HZSM-5 zeolite surface is important to an understanding of the new route of methane conversion and also is complementary to our former studies on methane adsorption (17–19).

EXPERIMENTAL

HZSM-5 and NaZSM-5 zeolites with SiO_2/Al_2O_3 ratios of 50 were obtained from Nankai University (China). Mo/HZSM-5 was prepared by impregnating HZSM-5 with a given amount of aqueous ammonium heptamolybdate solution (pH 6, 0.025 g of Mo metal/ml), then drying at 393 K for 10 h and calcining in air at 993 K for 12 h. All Mo/HZSM-5 samples with Mo loadings of 1–5% were well crystallized (29). The tested sample was pressed into a self-supporting wafer with a weight of about 20 mg (the sample thickness was always about 0.15 mm) for IR study. The quartz IR cell was connected to a vacuum system and gas reservoirs. Details of this cell and the system are described elsewhere (17–19). A Mo–Si sample, which was synthesized according to Ref. (27) in the absence of aluminum species, was used to clarify the role of aluminum in the adsorption of methane and CO. The structure of this sample was confirmed by X-ray diffraction (XRD). It can readily be seen in Fig. 1 that this material has a structure similar to that of ZSM-5 zeolite.

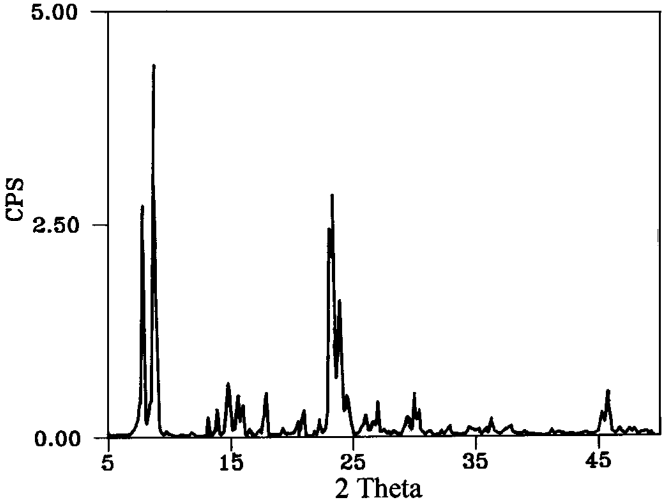


FIG. 1. XRD pattern of the calcined Mo–Si sample.

The procedure for the measurement of methane and CO adsorption is as follows. The sample was outgassed under a vacuum of about 2×10^{-5} Torr for half an hour at 873 K; then the temperature was slowly decreased to 173 K followed by the admission of methane or CO. The IR spectra were recorded in the presence of gaseous methane and/or CO, and the pressure of both methane and CO was about 12 Torr in this study unless otherwise specified. The coadsorption of methane and CO was performed by introducing CO into the sample with preadsorbed methane, or vice versa, at 173 K. The purities of methane and CO were higher than 99.99% and they were further purified by a liquid nitrogen trap before introduction into the IR cell.

IR spectra were recorded on a Perkin–Elmer 1800 double-beam FT-IR spectrometer equipped with a liquid nitrogen-cooled mercury–calcium–telluride (MCT) detector, with four scans and a resolution of 4 cm^{-1}. All IR spectra of adsorbed species are difference spectra obtained by subtracting the background spectra at the corresponding temperatures.

RESULTS

Adsorption of Methane

No adsorbed methane can be detected if HZSM-5 zeolite is outgassed below 573 K. This is possibly due to the presence of adsorbed water, which cannot be removed at low temperature. Figure 2 illustrates the IR spectra of adsorbed methane on HZSM-5 outgassed at various temperatures from 573 to 873 K. The band of free methane at 3016 cm^{-1} is always detectable because of the presence of gaseous methane. Five strong bands at 3008, 3002, 2900, 2890, and 1303 cm^{-1} were observed for the adsorbed methane. The assignments of these bands are listed in Table 1. The bands at 3008 and 3002 cm^{-1} are ascribed to the ν_3 mode of methane, and the bands at 2890 and 2900 cm^{-1} are attributed to the ν_1 mode (8). The fact that the infrared-forbidden ν_1 mode of methane became active and shifted to lower frequencies (2890 and 2900 cm^{-1}) indicates that the adsorption of methane on HZSM-5 is quite strong. Other evidence for methane adsorption is the abatement of the methane rotation structure bands caused by the decrease in methane's rotation freedom after interaction with the zeolite surface. However, the broading of the bands around 3000 cm^{-1} possibly infers that methane still retains some rotational freedom (9). It is interesting that two hydroxyl absorption bands at 3648 and 3510 cm^{-1} and a reverse band at 3622 cm^{-1} appeared after methane adsorption. The strong band at 3510 cm^{-1} was very likely due to the shift of the band at 3622 cm^{-1} because of the perturbation of surface bridging hydroxyl groups by adsorbed methane. This is a strong indication of the interaction of methane with the hydroxyl groups of HZSM-5. This interaction caused the weakening of the hydroxyl group band at 3622 cm^{-1}; as a

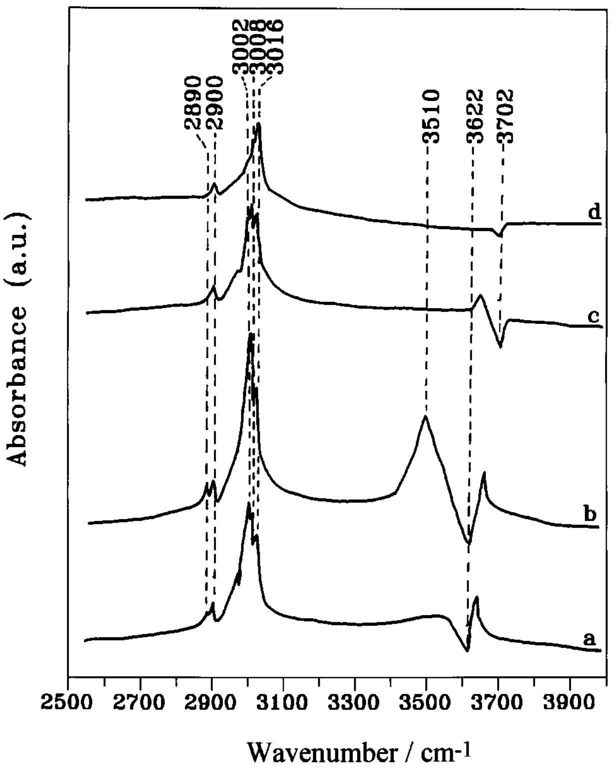


FIG. 2. IR spectra of adsorbed methane at 173 K on HZSM-5 outgassed at various temperatures: (a) 573 K, (b) 673 K, (c) 773 K, (d) 873 K.

result, a negative band at 3622 cm^{-1} appeared in the IR differential spectra. No noticeable negative band for the silanol groups, which showed an IR band at 3740 cm^{-1}, was detected. This means that interaction of the silanol groups with methane did not take place or this interaction was too weak to be detected. The sample pretreatment conditions of the HZSM-5 zeolite also exert significant influence on methane adsorption. It can be seen that maximum adsorption of methane occurred over the HZSM-5 outgassed at 673 K. With an increase in outgassing temperature, the bands of adsorbed methane at 3008, 3002, 2900, and 2890 cm^{-1} attenuated. The simple reason for this attenuation is that more hydroxyls were dehydroxylated and fewer hydroxyl groups remained when the zeolite was outgassed at a higher temperature. Based on the above results, it is concluded that the bridging hydroxyl groups of HZSM-5 play an important role in methane adsorption.

Figure 3 shows the IR spectra of adsorbed methane on HZSM-5 and Mo/HZSM-5 of different molybdenum content. It is interesting to note that the band intensities of the adsorbed methane at 3008, 3002, and 2890 cm^{-1} on HZSM-5 were weakened by the addition of molybdenum. As molybdenum content reached 5%, the adsorbed methane was hardly detected. Another change was observed for the bands of the hydroxyl groups with the addition of molybdenum. The reverse band at 3622 cm^{-1}, which represents the interaction between the surface hydroxyl groups and the adsorbed methane as we see above, gradually disappeared with the increase in molybdenum content. This possibly was a result of the elimination of hydroxyl groups of zeolite by molybdenum species (30). Therefore, the interaction of methane with the hydroxyl groups was substantially decreased. Noteworthy is the influence of molybdenum content on the 2900 cm^{-1} band of adsorbed methane. No matter what the molybdenum content was, this band was always exhibited, and only the band intensity decreased with the increase in the molybdenum content. Very possibly the band at 2900 cm^{-1} is produced from the adsorbed methane which interacts with the surface unsaturated oxygen anions of HZSM-5 zeolite.

For the Mo–Si sample in the absence of aluminum, the bands of adsorbed methane at 2890 and 3002 cm^{-1} were not observed and only the bands at 3008 and 1303 cm^{-1} and a very weak band at 2900 cm^{-1} appeared (Table 1). By comparing this result with those of HZSM-5 and 3% Mo/HZSM-5, it is suggested that the bands at 2890, 2900, and 3002 cm^{-1} are due to the adsorbed methane which interacts with both the hydroxyl groups and the surface

TABLE 1

Vibrational Modes of CH_4 and Detected IR Bands of Adsorbed CH_4 on Outgassed HZSM-5, Mo/HZSM-5, Mo–Si, and NaZSM-5 (in cm^{-1})

Vibrational mode	Gas phase, methane	Methane adsorbed on			
		HZSM-5	3% Mo/HZSM-5	Mo–Si	NaZSM-5
ν_1, sym. stretch.	2917^a	2890 2900	2890 2900	2900^b	2890
ν_2, deg. deform	1533^a	^{c}	^{c}	^{c}	^{c}
ν_3, deg. stretch.	3019	3008 3002	3008 3002	3008	3008
ν_4, deg. deform.	1306	1303	1303	1303	1303

[a] Infrared inactive.

[b] Very weak peak.

[c] Not observed.

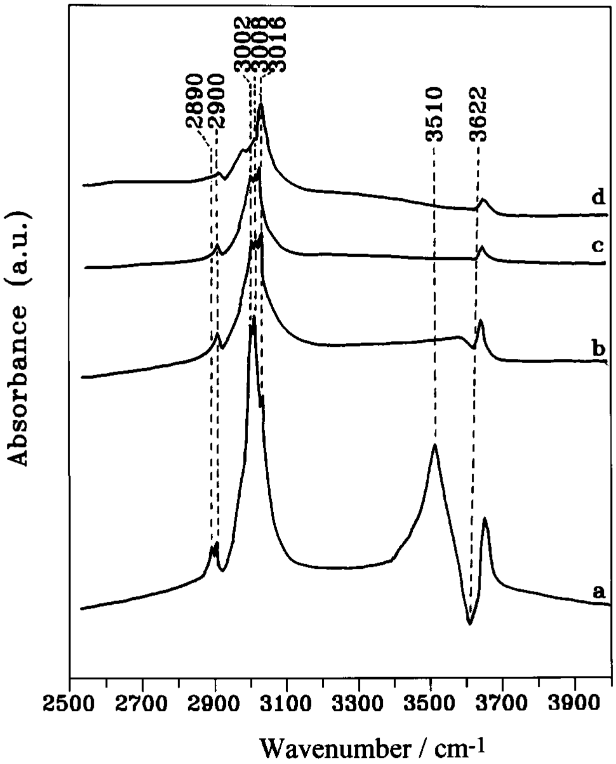


FIG. 3. Influence of molybdenum content on the IR spectra of adsorbed methane at 173 K. Molybdenum content in HZSM-5: (a) 0%, (b) 1%, (c) 3%, (d) 5%.

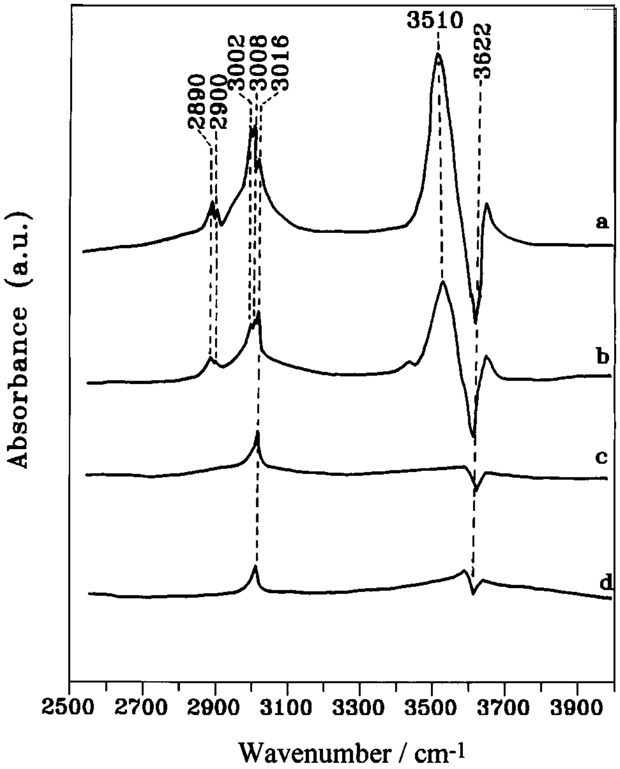


FIG. 4. Temperature dependence of IR spectra of adsorbed methane on HZSM-5. $P_{CH_4} = 1.2$ Torr. (a) 173 K, (b) 183 K, (c) 213 K, (d) 243 K.

unsaturated oxygen anion species related to the aluminum species in the HZSM-5 zeolite, whereas the band at 3008 cm^{-1} can be attributed to the adsorbed methane which interacts mainly with the silanol groups or physically adsorbed species.

The adsorption temperature is a very important factor which influences methane adsorption. It was found that significant adsorption of methane can be observed only at temperatures lower than 213 K (Fig. 4). With the increase in adsorption temperature, the amount of adsorbed methane on all the tested samples decreased considerably. It is also noteworthy that the hydroxyl group band at 3510 cm^{-1} and the reverse band at 3622 cm^{-1} changed synchronously with the changes in methane adsorption. This result further substantiates the conclusion that the adsorbed methane really interacts with the bridging hydroxyl groups of HZSM-5 zeolite.

Adsorption of Carbon Monoxide

Gaseous CO exhibits only two indistinguishable bands near 2138 and 2156 cm^{-1} at 173 K. One way to illustrate the occurrence of CO adsorption is to examine if shifts in CO absorption bands or the appearance of new bands can be observed. The IR spectra in Fig. 5 clearly reveal that adsorption of CO took place on the HZSM-5 samples that were outgassed at temperatures from 573 to 873 K. The IR spectrum of adsorbed CO on HZSM-5 outgassed at 473 K showed only a weak band at 2138 cm^{-1}, which possibly corresponded to the condensed or physically adsorbed CO in zeolite channels. For the HZSM-5 outgassed at 573 and 673 K, three strong bands at 2173, 2162, and 2138 cm^{-1} were observed. It is interesting to note that the intensity of the band at 2173 cm^{-1} increased and that of the band at 2162 cm^{-1} declined with the elevation of outgassing temperature. The 2162 cm^{-1} band almost disappeared when the outgassing temperature exceeded 873 K. From these facts, we can make the assignments of the bands of adsorbed CO at 2173, 2162, and 2138 cm^{-1} as follows. The 2138 cm^{-1} band can be attributed to the weakly adsorbed or condensed CO on the surface or in the zeolite channels because the intensity of this band is strongly dependent on the CO pressure as shown in Fig. 6. The bands at 2162 and 2173 cm^{-1} were rather persistent as the CO pressure decreased. This implies that these two bands resulted from the strongly adsorbed CO. The band at 2162 cm^{-1} possibly resulted from the CO that interacted with the hydroxyls in HZSM-5, as the intensity of this band decreased significantly with an increase in outgassing temperature, and furthermore, this band disappeared when the zeolite was severely dehydroxylated. The band at 2173 cm^{-1} is attributed to the adsorbed CO that interacted with the coordinately unsaturated surface aluminum or silicon cations which were formed in the

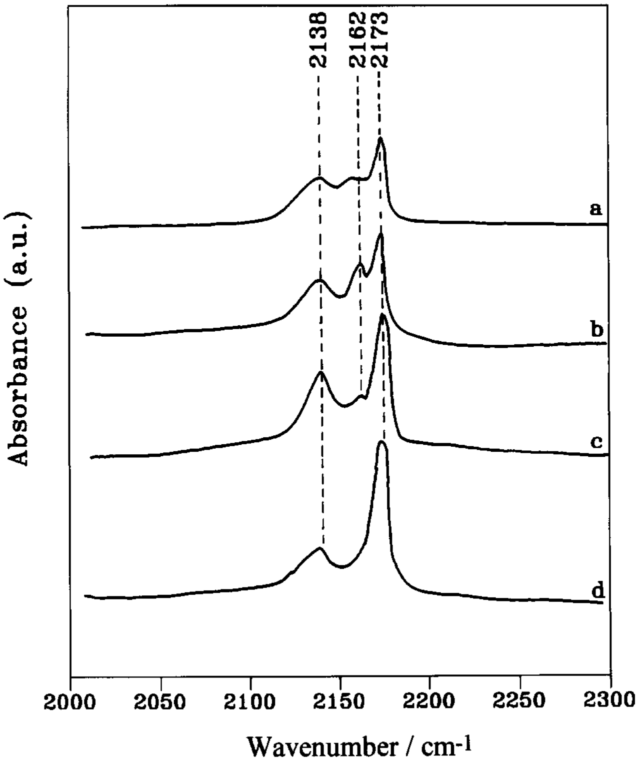


FIG. 5. IR spectra of adsorbed CO at 173 K on HZSM-5 outgassed at various temperatures. $P_{CO} = 1.2$ Torr. (a) 573 K, (b) 673 K, (c) 773 K, (d) 873 K.

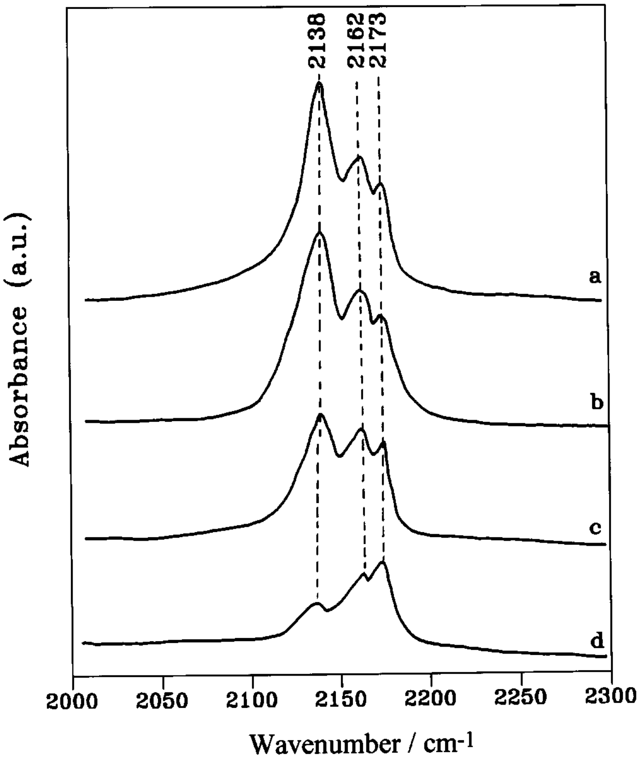


FIG. 6. Pressure dependence of IR spectra of adsorbed CO at 173 K on HZSM-5. P_{CO} (Torr): (a) 8.4, (b) 4.1, (c) 0.9, (d) 0.02.

outgassing process at high temperatures (20), because the intensity of this band increased sharply with the extent of dehydroxylation of the zeolite. The feasibility of these assignments can be confirmed by taking into account the fact that the more severe the dehydroxylation, the smaller the amount of hydroxyl groups remaining and the larger the amount of aluminum or silicon cations formed.

Figure 7 gives the IR spectra which display the influence of molybdenum content in Mo/ZSM-5 on CO adsorption. Just as seen in Fig. 6, there are also three bands of adsorbed CO at 2173, 2162, and 2138 cm^{-1}. However, the band at 2173 cm^{-1} almost disappeared when even only 1% molybdenum was introduced into the zeolite. The bands at 2162 cm^{-1} attenuated significantly with the increase in molybdenum loading. According to the aforementioned assignments of CO absorption bands, it is suggested that molybdenum in HZSM-5 zeolite prevented the formation of aluminum or silicon cations and destroyed some of the hydroxyl groups of the zeolite. Therefore, the amount of adsorbed CO was decreased.

To investigate the role of aluminum species of HZSM-5 in CO adsorption, CO adsorption on the Mo–Si sample was carried out. It can be seen that the IR spectrum of adsorbed CO on the Mo–Si sample exhibited only one broad band centered at 2138 cm^{-1}. By comparing this spectrum with that for HZSM-5, it is deduced that the 2173 and 2162 cm^{-1}

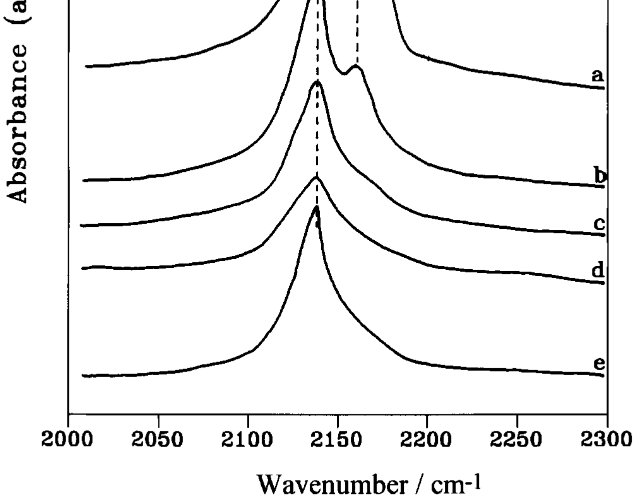


FIG. 7. IR spectra of adsorbed CO at 173 K on HZSM-5 (a), Mo/HZSM-5 with different molybdenum contents [(b) 1%, (c) 3%, (d) 5%], and Mo–Si zeolite (e).

bands were contributed mainly by the adsorbed CO which interacted with the coordinately unsaturated surface aluminum or silicon cations and the bridging hydroxyl groups of HZSM-5 zeolite.

Coadsorption of Methane and CO

To differentiate the sites responsible for methane and CO adsorption, the coadsorption of methane and CO on HZSM-5 and 3% Mo/HZSM-5 samples was performed at 173 K. If methane was adsorbed on HZSM-5 zeolite first, then CO was introduced, the presence of CO caused the disappearance of the band at 2890 cm^{-1} and the partial attenuation of the bands at 3008 and 3002 cm^{-1} of adsorbed methane (Fig. 8a). This result demonstrates that the band at 2890 cm^{-1} possibly originated from the methane that interacted with the sites on which CO could adsorb; thus, CO adsorption would compete with methane adsorption on these sites. Therefore, the previously adsorbed methane was partly substituted by CO. Most possibly these sites were the bridging hydroxyl groups of the HZSM-5 zeolite. The presence of CO showed little effect on the bands of adsorbed methane at 3008 and 3002 cm^{-1}. This result probably means that the 3008 and 3002 cm^{-1} bands did not originate solely from the methane that interacted with the hydroxyls; contributions from other species such as oxygen anion species were also possible. The 2900 cm^{-1} band of adsorbed methane was intact in the presence of CO. This fact leads us to suggest that there exist some sites on which CO could not adsorb. Very possibly these sites were the surface oxygen anion species produced by the dehydroxylation of the zeolite at high temperature. When the adsorption of CO on HZSM-5 was achieved first, the introduction of methane had hardly any influence on CO adsorption (Fig. 8b). The attenuation of the band at 2138 cm^{-1} was probably a result of the dilution of the CO concentration by methane. The absorption band at 2173 cm^{-1} did not change because this band originated from the CO that interacted with the cationic aluminum and/or silicon species, while methane could not adsorb on these sites alone.

On the other hand, the influence of the preadsorbed methane on the adsorption of CO was found to be the same as the influence of introducing methane into the sample preadsorbed with CO, and vice versa. The same influences were observed for the preadsorbed CO on the adsorption of methane and that of introducing CO into the sample preadsorbed with methane. These results suggest that there are three kinds of sites on the dehydroxylated HZSM-5 zeolite. One interacts with methane only, the other interacts with CO only, and the third one can interact with both methane and CO.

For the molybdenum-containing HZSM-5 samples, the results of the coadsorption of CO and methane are displayed in Fig. 9. As part of the hydroxyl groups of HZSM-5 were eliminated by the molybdenum species, the adsorption of both CO and methane was suppressed. If CO was admitted to the 3% Mo/HZSM-5 preadsorbed with methane,

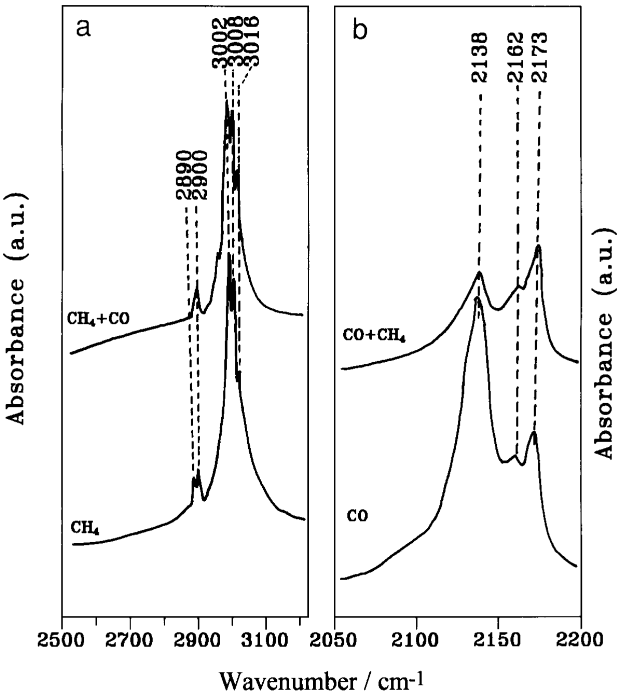


FIG. 8. IR spectra of coadsorbed methane and CO at 173 K on HZSM-5. (a) Methane first, (b) CO first.

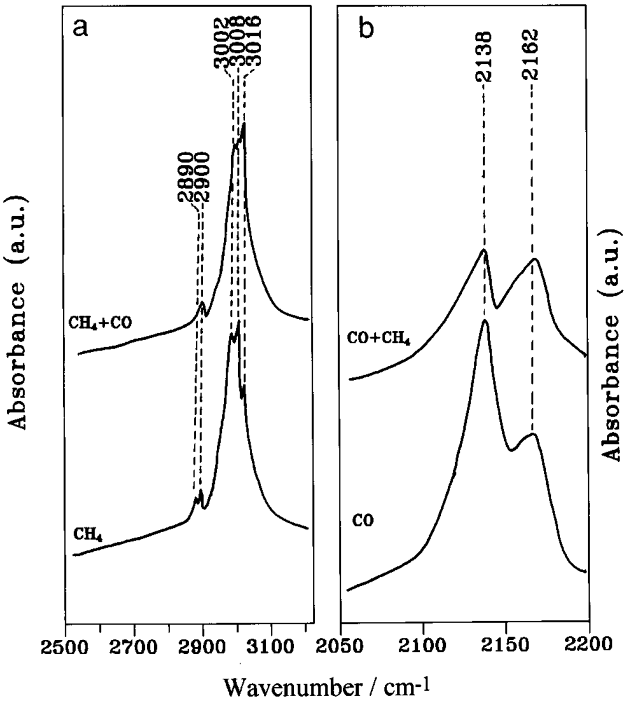
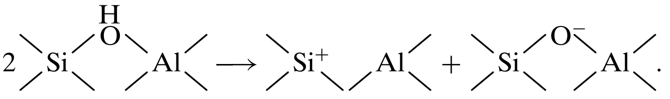


FIG. 9. IR spectra of coadsorbed methane and CO at 173 K on 3% Mo/HZSM-5. (a) Methane first, (b) CO first.

the absorption band of adsorbed methane at 3002 cm^{-1} decreased considerably, whereas other bands were almost intact in the presence of CO (Fig. 9a). This result indicates that the 3002 cm^{-1} band of adsorbed methane on the 3% Mo/HZSM-5 sample possibly resulted from the methane that interacted with the hydroxyl groups of the zeolite.

DISCUSSION

The investigation on the interaction of methane with the catalyst surface is of significance to the fundamental understanding of methane activation and conversion. The interaction patterns of adsorbed methane on different surfaces differ greatly. Two types of adsorbed methane are formed on well-outgassed CeO_2 (17): one interacts with the surface lattice oxygen anions, and the other interacts with the O^{-1} species. Over MgO, the surface oxygen anions as well as the Lewis acid–base pair sites are responsible for the adsorption of methane (18), whereas over the acidic alumina, both the surface hydroxyls and the surface oxygen anion species play crucial roles in the adsorption of methane (19). A conclusion similar to that in the case of acidic alumina can be drawn from the results of methane adsorption on HZSM-5. The data in this study provide strong evidence for the interaction of methane with the surface hydroxyl groups and the surface oxygen anion species on the dehydroxylated HZSM-5 sample. The appearance of a new hydroxyl band at 3510 cm^{-1} and a reverse band at 3622 cm^{-1} reveals the interaction of methane with the bridging hydroxyl groups in HZSM-5 zeolite. The simultaneous disappearance of the hydroxyl band at 3510 cm^{-1} and the reverse band at 3622 cm^{-1} with the elimination of adsorbed methane when the temperature was increased (Fig. 4) is other direct evidence. When the HZSM-5 zeolite was outgassed at a high temperature, partial dehydroxylation occurred. Two hydroxyl groups were removed from the zeolite framework as postulated by Kazansky (15):



[1]

Therefore, the oxygen anion species are formed via the outgassing of HZSM-5 at high temperature. However, if the outgassing temperature is too high, severe dehydroxylation will eliminate most of the hydroxyl groups. As a result, the amount of adsorbed methane will be substantially decreased. The occurrence of reaction [1] well interprets the results of methane adsorption experimentally observed under our conditions.

Based on the results of methane adsorption and those of the coadsorption of methane and CO, we attribute the bands at 3002 and 2890 cm^{-1} to the adsorbed methane that interacts with the bridging hydroxyl groups. The gaseous CO competes with methane adsorption to the hydroxyl groups. As a result, methane adsorption is diminished in the presence of CO. The band at 2900 cm^{-1} possibly originates from the adsorbed methane that interacts with surface anion species. Because CO interacts mainly with the hydroxyl groups and the Lewis acidic sites, the Lewis basic sites (the oxygen anion species (produced via reaction [1]) will interact with methane only. Therefore, the adsorbed methane that interacts with oxygen anions is intact in the presence of CO (Fig. 8) It is speculated that the interaction of methane with both the bridging hydroxyl groups and the oxygen anions of the zeolite surface is very strong because the absorption bands of adsorbed methane were very persistent to a strong evacuation. The T_d symmetry of free methane was greatly altered after adsorption, perhaps turned to C_{3v}, C_{2v}, or C_s symmetry as suggested previously (18). This symmetry change breaks down the infrared selection rule so that the infrared inactive mode (ν_1) 3016 cm^{-1} of methane becomes infrared active and shifts to lower frequencies (2890 and 2900 cm^{-1}). The weakness of at least one of the C–H bonds of methane via its interaction with the zeolite surface is possibly the first important step for methane activation.

The assignments of the three absorption bands of CO adsorbed on HZSM-5 at 2173, 2162, and 2138 cm^{-1} are as follows. The 2173 cm^{-1} band resulted from the interaction of CO with the cationic aluminum and silicon species both in the framework and in the extraframework of HZSM-5. The 2162 cm^{-1} band originated from the CO that interacted with the hydroxyls via the formation of H bonds, and the last one at 2138 cm^{-1} originated from the physically adsorbed CO because it is very close to the bands of free CO in the gas phase. After taking into account the occurrence of reaction [1] at high temperature, it is easy to understand the decline in the intensity of the band at 2162 cm^{-1} and the increase in that at 2173 cm^{-1} with the increase in outgassing temperature (Fig. 5).

With the introduction of molybdenum into HZSM-5, the adsorption of both methane and CO was suppressed. The 3008, 2900, and 2890 cm^{-1} bands of adsorbed methane were noticeably diminished. On the other hands, only the bands of adsorbed CO at 2173 and 2162 cm^{-1} were disturbed to a great extent with the increase in molybdenum content in HZSM-5 zeolite. As the molybdenum content increased to 5%, no adsorbed methane was detected and the only observable band of adsorbed CO was at 2138 cm^{-1}. A simple explanation for these results is that some of the hydroxyl groups of HZSM-5 zeolite were eliminated by molybdenum species, as in the cases in which molybdenum was introduced into alumina or silica (31, 32). The higher the molybdenum content, the smaller the number of the hydroxyl groups remaining. Furthermore, the introduction of molybdenum also impeded the occurrence of reaction [1] so that the amount of Lewis basic sites of oxygen anions active for methane adsorption was greatly decreased. Therefore, the amounts of both adsorbed methane and CO decreased with the increase in molybdenum content in the HZSM-5 zeolite.

CONCLUSIONS

At 173 K, five bands of adsorbed methane were observed at 3008, 3002, 2900, 2890, and 1303 cm^{-1} on the HZSM-5 zeolite which was outgassed at temperatures greater than 573 K. It was demonstrated that the bridging hydroxyl groups and the surface oxygen anion species are the active sites for methane adsorption on outgassed HZSM-5 zeolite. The infrared inactive ν_1 mode (2917 cm^{-1}) of free methane became active and shifted to lower frequencies (2890 and 2900 cm^{-1}) when methane adsorbed to the zeolite samples. The weakness of the C–H bond caused by distortion of the methane molecule via its interaction with the zeolite surface is possibly the first important step in methane activation. Possibly the bands at 3002 and 2890 cm^{-1} are due to the adsorbed methane that interacts with the bridging hydroxyl groups, whereas the band at 2900 cm^{-1} results from the adsorbed methane that interacts with the oxygen anion species of the HZSM-5 zeolite.

Three strong bands of adsorbed CO at 2173, 2162, and 2138 cm^{-1} appear for HZSM-5 at 173 K. The 2173 cm^{-1} band is assigned to the CO that interacts with the surface Lewis acidic sites, the band at 2162 cm^{-1} is attributed to the CO that interacts with the hydroxyl groups, and the band at 2138 cm^{-1} originates from the condensed or physically adsorbed CO.

The introduction of molybdenum into HZSM-5 considerably attenuates the adsorption of both methane and CO. Elimination of the surface hydroxyl groups and inhibition of the formation of surface oxygen anion species as well as the Lewis acidic sites caused by molybdenum species in HZSM-5 zeolite are possibly responsible for the suppression of methane and CO adsorption.

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