Interaction of methane with surfaces of silica, aluminas and HZSM-5 zeolite. A comparative FT-IR study

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Infrared investigations on the interaction of methane with silica, aluminas (η, γ and α) and HZSM-5 zeolite have been carried out. At low temperature (173 K), methane adsorption was observed over these oxides and HZSM-5 zeolite. Our findings featured that the infrared inactive ν_1 band (2917 cm^{-1}) of a gaseous methane molecule became active and shifted to lower frequencies (2900 and 2890 cm^{-1}) when it adsorbed on the surfaces of these adsorbents. Our results also demonstrate that hydroxyl groups played a very important role in methane adsorption over the acidic oxides and the HZSM-5 zeolite. When interaction between the hydroxyl groups and methane took place, the band shift of the hydroxyl groups varied with different oxides. The strength of the interaction decreased according to the following sequence, Si-OH-Al > Al-OH > Si-OH, which is in accordance with the order of their acidities. At higher temperatures, methane interacted quite differently with various oxides and HZSM-5 zeolite. It has been observed that the hydroxyl groups of silica, γ-alumina and HZSM-5 zeolite could exchange with CD_4 at temperatures higher than 773 K, while those on η-alumina could exchange at a temperature as low as 573 K. Another interesting observation was the formation of formate species over Al_2O_3 (both η and γ) at temperatures higher than 473 K. The formate species would decompose to CO_2, or produce carbonate at much higher temperatures. Formation of formate species was not observed over silica and HZSM-5 under similar conditions. α-Al_2O_3 did not adsorb or react with methane in any case.

Keywords: methane; adsorption; hydroxyl groups; H–D exchange reaction

1. Introduction

The activation of methane in the oxidative coupling reactions to form ethylene as well as in the partial oxidation reactions to yield formaldehyde or methanol is of

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great practical interest. Considerable attention has been concentrated on the screening of catalysts and the optimization of reaction conditions. However, information on the interaction of methane with the catalyst surfaces, which is by no means less important, is relatively deficient. The reason is probably due to the failure of a large number of physical methods in obtaining this kind of information, since it is very difficult to adsorb methane molecules on the catalyst surfaces at the operating temperatures of these reactions, which are usually higher than 973 K.

More recently, it has been found that FT-IR is a powerful technique for the study of methane adsorption at low temperatures, and for the investigation of methane interaction with oxide surfaces as well. Based on the results obtained in our laboratories, we have proposed that the surface oxygen species O^- and the surface lattice oxygen are the active species on CeO_2 [1], whereas the surface oxygen anions and the Lewis acid–base pairs are responsible for the adsorption of methane over MgO [2], and the adsorbed methane on Al_2O_3 is formed mainly via the interaction of methane with both of the surface hydroxyls and the cus oxygen anions [3]. So far, the most intensively studied oxides are basic oxides, which can provide good selectivity for the desired products in the oxidative coupling of methane. However, very little attention has been paid to the interaction of methane with acidic oxides. In fact, acidic oxides and zeolites are of significance in the conversion of methane as well as in the separation of natural gas components [4]. They play a more and more important role in C_1 chemistry as catalyst supports, especially in methane steam reforming, methane reforming with CO_2, methane partial oxidation to syngas, and so on. Furthermore, discrepancy seemed to exist between the information obtained at low temperatures and that at high temperatures. The information at high temperature is more desirable.

Therefore, we present briefly in this paper the results of comparative studies on methane interactions with the surfaces of silica, alumina (η, γ and α) and HZSM-5 zeolite at both low (173 K) and high temperatures.

2. Experimental

Commercial silica (Degussa, BET surface area 210.2 m^2/g), HZSM-5 zeolite ($SiO_2/Al_2O_3 = 38$, BET surface area 311.2 m^2/g), MgO powder (Emerck Co., BET surface area 40 m^2/g) and three aluminas (η, γ and α) were used in this work. The forms of these aluminas were further confirmed by XRD. Their BET surface areas were 271.9, 237.5 and 0.8 m^2/g, respectively. These powders were pressed into self-supporting wafers with a weight of about 20 mg each for IR studies. A specially designed quartz cell, in which the sample wafer can be treated in various ways at a wide temperature range from 100 to 1000 K, was used. Prior to the adsorption of methane or deuterated methane (CD_4), the sample wafer was outgassed at a high temperature (773 or 873 K), treated in oxygen or hydrogen if needed, then cooled down to 173 K or any other desired temperatures. The purity of the methane was better than 99.99%, and was further purified by a liquid nitrogen trap. Deuterated methane with an isotopic purity (D) of 99.6% was obtained from ISOTEC Inc., USA.

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

3. Results and discussion

3.1. METHANE ADSORPTION AT LOW TEMPERATURE

3.1.1. On silica

Silica (quartz) is an important material utilized in catalytic and chemical reaction studies as reactor material, due to its inert property for most of the reactions. However, it is reported that the methane oxidative coupling (MOC) reaction took place to a great extent in an empty quartz reactor in addition to the occurrence of homogeneous reactions [5]. This implied that SiO_2 was a catalytically active material under MOC reaction conditions. In fact, the interaction of methane with silanol groups at 173 K was observed by FT-IR spectroscopy in this work. The silica outgassed at 773 K showed one IR band at 3750 cm^{-1} (fig. 1), which can be easily

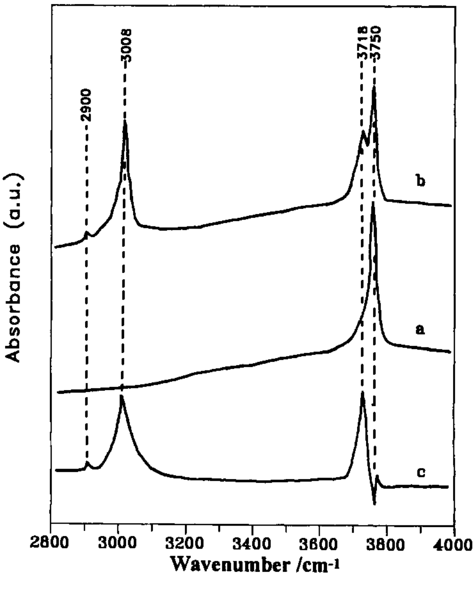

Fig. 1. IR spectra of silica at 173 K (a) outgassed at 773 K (b) after exposure to 12 Torr of CH_4. (c) The difference spectrum of (b) and (a).

ascribed to the vibration of the surface silanol groups. After the introduction of methane at 173 K, two bands at 3008 and 2900 cm^{-1} for the adsorbed methane appeared. Similar bands attributed to adsorbed methane had also been observed by Sheppard and Yates [6]. According to our previous papers [1–3], the 3008 cm^{-1} band was assigned to the ν_3 mode of the methane C–H vibration at 3019 cm^{-1}, with a shift of 11 cm^{-1}, and the 2900 cm^{-1} band was assigned to the ν_1 mode at 2917 cm^{-1}, with a shift of 17 cm^{-1}. The fact that the infrared-forbidden ν_1 mode (2917 cm^{-1}) became active and shifted to lower frequency (2900 cm^{-1}) demonstrated that the adsorption of methane occurred over silica. It is interesting to note that a new band at 3718 cm^{-1} appeared, and in the meanwhile the intensity of the band at 3750 cm^{-1} attenuated. This new band at 3718 cm^{-1} most probably resulted from the disturbed hydroxyl groups with a down shift of 32 cm^{-1} from 3750 cm^{-1} via the formation of a hydrogen bond with methane. The suggestion that methane interacts with the surface silanol groups, not siloxane groups, can be substantiated by the results of the adsorption of deuterated methane. Bands for the adsorbed CD_4 were registered at 2251 and 2091 cm^{-1}. In addition, the same effect on the IR absorption band in the hydroxyl region was displayed just as in the case of methane adsorption. No new band for OD groups was observed. Therefore, it was deduced that only the silanol groups interacted with methane, and the interaction was so weak that the cleavage of a C–H bond at 173 K was not possible. With the elevation of the adsorption temperature to 213 K, or with the decrease of the methane pressure to less than 1 Torr, the bands for adsorbed methane completely disappeared, while the band for the hydroxyl groups restored as undisturbed. These results further demonstrated the occurrence of an interaction between methane and the silanol groups at 173 K, and also implied that this interaction was very weak, and very probably was physical adsorption in nature.

3.1.2. On η-, γ- and α-alumina

The low temperature adsorption of methane on γ-alumina was reported previously [3]. In this study, however, more attention was paid to the changes of the hydroxyls after methane adsorption. Moreover, comparative investigation results on methane adsorption on η-, γ- and α-aluminas were furnished. Similar absorption bands for adsorbed methane were observed on η- and γ-alumina. However, particular attention has been paid to γ-Al_2O_3, which is extensively used in catalysis studies and in industrial processes. Fig. 2 illustrates the IR spectra before and after the exposure of methane to the γ-alumina outgassed at 773 K. Four strong bands at 3008, 3000, 2900 and 1305 cm^{-1} attributed to adsorbed methane were observed. These bands strongly indicated that the adsorption of methane on γ-Al_2O_3 was very strong. Four distinct bands of hydroxyl groups of the γ-Al_2O_3 outgassed at 773 K appeared at 3760, 3731, 3674 and 3585 cm^{-1}. According to Peri [7] and Knözinger [8], these bands correspond to the hydroxyl groups in different environments. After the intervention of methane at 173 K, the intensity of the band at 3760 cm^{-1} decreased, while the band at 3674 cm^{-1} shifted to 3667 cm^{-1}. It is appar-

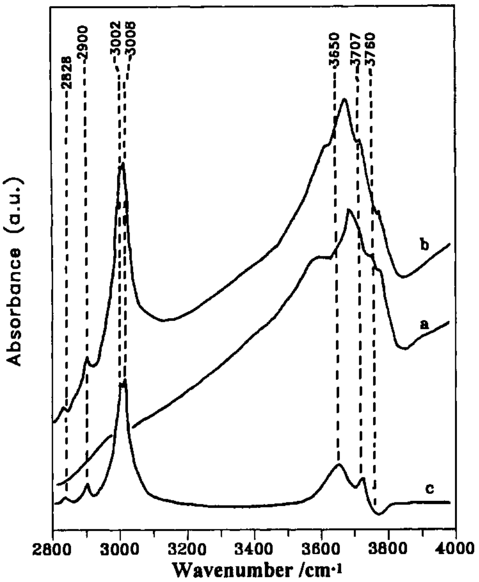

Fig. 2. IR spectra of γ-alumina at 173 K (a) outgassed at 773 K (b) after exposure to 12 Torr of CH_4. (c) The difference spectrum of (b) and (a).

ent that the higher frequency hydroxyl bands are more sensitive to adsorbed methane. Based on either the model proposed by Peri [7] or by Knözinger [8], we can conclude that the hydroxyl groups with a larger number of near-neighbor negative oxygen ions interacted easily with methane. The larger shift of the band at 3760 cm^{-1} to 3707 cm^{-1} ($\Delta\nu$=53 cm^{-1}) indicated that the interaction of methane with these Al-OH groups was rather strong. The 3650 cm^{-1} band probably resulted from the interaction of methane with other types of hydroxyl groups on alumina, or from the formation of a new kind of hydroxyls by the interaction of methane with the surface oxygen anions. A careful comparison of the intensities of the absorption bands at 3008 and 2900 cm^{-1} demonstrated that the amount of adsorbed methane on η-alumina was about twice of that on γ-alumina. The well crystallized α-alumina did not adsorb methane at all. The difference in the adsorption of methane over these different forms of alumina can be better interpreted after taking into account their differences in the hydroxyl region. The transitional phases η- and γ-Al_2O_3 possess a large number of surface hydroxyl groups, while the number of hydroxyl groups on α-Al_2O_3 is rather small [8]. It is interesting to note that the amount of adsorbed methane on these aluminas followed the sequence of η- > γ- > α-Al_2O_3, which is in good coincidence with the order of the numbers of their surface hydroxyl groups.

3.1.3. On HZSM-5 zeolite

The adsorption of methane on the HZSM-5 zeolite at low temperature is rather evident (fig. 3). Five distinct bands at 3008, 3002, 2900, 2890 and 2828 cm^{-1} depict-

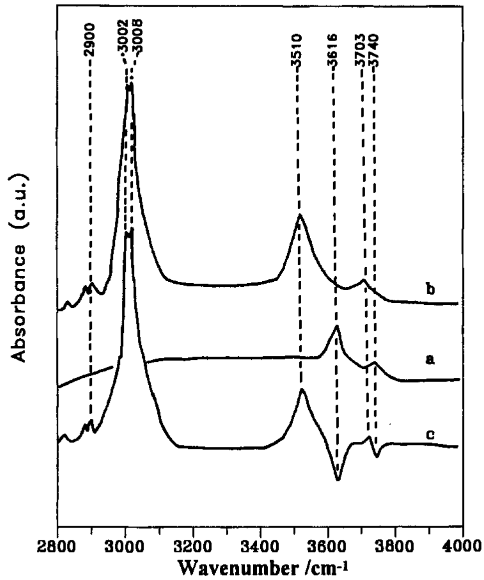

Fig. 3. IR spectra of HZSM-5 at 173 K (a) outgassed at 773 K (b) after exposure to 12 Torr of CH_4. (c) The difference spectrum of (b) and (a).

ing the adsorbed methane were observed. It is noteworthy that another new band at 2890 cm^{-1} appeared, and the intensities of the other bands of adsorbed methane were higher than those over SiO_2 and Al_2O_3. This indicates that the interaction of methane with HZSM-5 was even stronger. The HZSM-5 zeolite outgassed at 773 K showed two absorption bands at 3740 and 3616 cm^{-1} which are attributed to the hydroxyl groups of the Si-OH and the Si-OH-Al type, respectively. The data are consistent with those reported in the literature [9]. After the adsorption of methane at 173 K, it can be seen from fig. 3 that the band at 3740 cm^{-1} shifted to 3703 cm^{-1}, whereas the 3616 cm^{-1} band shifted to 3510 cm^{-1}. The former one changed in a manner similar to the situation of silica, and was due to the interaction of methane with the Si-OH type of the hydroxyl groups of the HZSM-5 zeolite. The influence of methane on the Si-OH-Al type hydroxyl groups was much more pronounced, as compared to that of the Si-OH type. The band at 3616 cm^{-1} almost vanished, and a new broad band at 3510 cm^{-1} appeared. A similar phenomenon was observed in the interaction of carbon monoxide with the Si-OH-Al type hydroxyl groups on HZSM-5 [9]. The shift of this band was as large as 106 cm^{-1}, which was much larger than those in the cases of the Si-OH and Al-OH type hydroxyl groups.

The fact that all the changes in the absorption bands of the hydroxyl groups disappeared with the elimination of the adsorbed methane once again demonstrated the existence of the interaction of methane with the hydroxyl groups. Thus, the important conclusion that hydroxyl groups play a crucial role in methane adsorption at low temperature can be drawn. In previous studies, the strength of the interactions of methane, hydrogen and carbon monoxide with the surface of the acidic oxides and zeolites was used to measure the surface acidity [9,10]. The evaluation of the interaction strength was based on the shift in the absorption band of the hydroxyls. The results in this study showed that the band shifts of the hydroxyl groups after interaction with methane are $\Delta\nu_{(\text{Si-OH})} = 32\,\text{cm}^{-1}$, $\Delta\nu_{(\text{Al-OH})} = 53\,\text{cm}^{-1}$ and $\Delta\nu_{(\text{Si-OH-Al})} = 106\,\text{cm}^{-1}$. Therefore, according to the shifts of the OH groups, the surface Brønsted acidities of the hydroxyl groups on silica, alumina and HZSM-5 decreased in the following sequence: Si-OH-Al > Al-OH > Si-OH. It is apparent that the low temperature adsorption of methane can be a useful method for measuring acid strength on solid acid catalysts.

3.2. INTERACTION OF METHANE AT HIGH TEMPERATURE

3.2.1. *With silica*

The interaction of methane with the surfaces of acidic oxides at low temperature is evident, and the behavior of the oxides are somewhat similar. However, discrepancy may exist between the data obtained at low temperatures and these at high temperatures. As we have seen, the low temperature adsorption results cannot be used to differentiate the surface heterogeneity of the oxides, which really deviated significantly. It is known that reactions for the conversion of methane are mostly conducted at high temperatures. Therefore, studies on the interaction of methane with oxides at high temperatures are more meaningful for the understanding of methane activation and reaction mechanism.

In earlier studies concerning the exchange of methane with hydroxyl groups of acidic oxides, Hall [11] and Amenomiya [12] have found that the exchange reaction did not occur over silica gel below 873 K. The IR result in our study, however, indicated that the exchange of CD_4 with hydroxyl groups commenced at temperatures higher than 773 K. Fig. 4 illustrates the difference spectra before and after contacting with methane (or CD_4). It can be seen from fig. 4a that only one peak at $3016\,\text{cm}^{-1}$ with a shoulder at $3008\,\text{cm}^{-1}$ appeared in the C–H stretching vibrational region. The band at $3016\,\text{cm}^{-1}$ is easily assigned to the ν_3 vibrational mode of free methane. It is interesting to note that the intensity of the shoulder peak at $3008\,\text{cm}^{-1}$ increased with the increase of temperature, but we cannot surely assign this band to adsorbed methane, due to the fact that the same band (a rather weak peak at $3008\,\text{cm}^{-1}$) was observed in the difference spectrum when using an empty cell. The $3008\,\text{cm}^{-1}$ band might very probably be resulted from a temperature effect. Nevertheless, the interaction of methane with the silanol groups at high temperatures was demonstrated by the change in the hydroxyl region. In order to get further evidence for this conclusion, we also carried out similar experiments by using deuterated methane. The simultaneous appearance of the band for OD groups at $2752\,\text{cm}^{-1}$ and the decrease of the band at $3735\,\text{cm}^{-1}$ led to the conclusion that the interaction and exchange reaction of deuterated methane with the silanol groups occurred at temperatures higher than 773 K. Although the exchange of CD_4

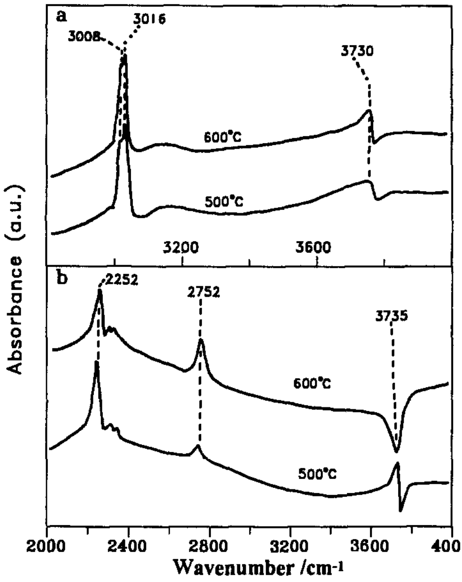

Fig. 4. IR difference spectra over silica after and before contacting with 12 Torr of CH_4 (a) or CD_4 (b) at high temperature.

with the silanols was obvious by IR study, the extent of the exchange was rather small. That is, only a very small fraction of the silanols exchanged with CD_4. This may well interpret the discrepancy of our results with those of Hall and Amenomiya [11,12]. The exchange reaction of CD_4 with the silanols indicated that silanol groups are indeed reactive at high temperatures. Therefore, caution should be taken in the explanation of reaction mechanism when using SiO_2 as support.

3.2.2. With η-, γ- and α-alumina

It has been proven that different forms of alumina exhibit different catalytic performances [13]. The surface hydroxyl groups and Lewis acid sites of alumina are of importance in catalysis. However, when various aluminas are used as supports, their effects on the catalytic performances are usually neglected. Only a few studies discussed the roles they play [14]. Kazansky has observed the adsorption of methane over η- and γ-aluminas by using diffuse reflectance spectroscopy [15]. However, we failed to obtain any information of adsorbed methane over alumina at high temperatures using an IR transmission spectroscopy. The reasons of the discrepancy of our results with that of Kazansky might be due to the use of transmission spectroscopy, the severe pretreatment of the alumina before exposure to methane and the high temperature applied in our work. Nevertheless, interesting results were obtained when transmission spectroscopy was used for these studies, and some of the results are given and discussed below. It is not unexpected that α-alumina did not show any reactivity. However, it is quite interesting that both the η- and γ-alumina reacted evidently with methane (figs. 5 and 6). Two new bands

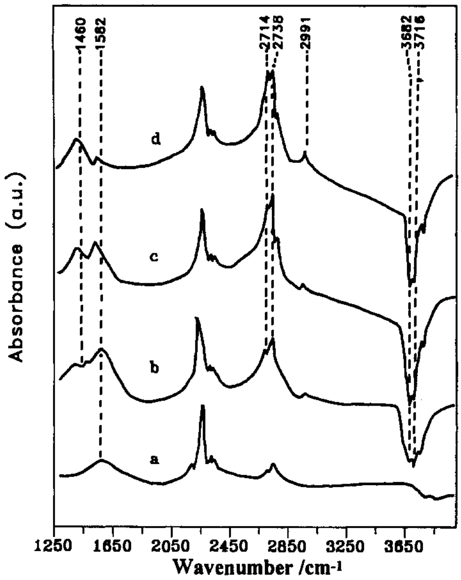

Fig. 5. IR difference spectra over η-Al_2O_3 after contacting with CD_4 for 10 min at (a) 573 K, (b) 673 K, (c) 773 K, (d) 873 K (CD_4 pressure was 13.5 Torr at 473 K).

centered at about 1582 and 1468 cm^{-1} appeared at temperatures above 473 K. These bands were not observed over SiO_2 under the same pretreatment conditions. There has been certain controversy in the literature on the assignment of the bands

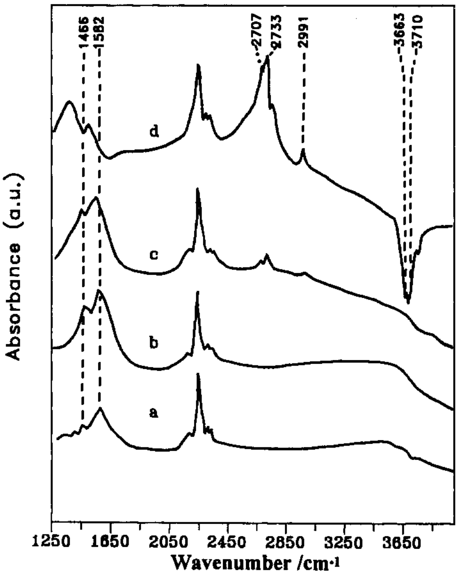

Fig. 6. IR difference spectra over γ-Al_2O_3 after contacting with CD_4 for 10 min at (a) 573 K, (b) 673 K, (c) 773 K, (d) 873 K (CD_4 pressure was 13.5 Torr at 473 K).

near 1580 and 1460 cm^{-1}. The band near 1580 cm^{-1} can be assigned to either the C=C stretching of aromatics or to the asymmetric C–O vibration in a carboxylate, while the band near 1460 cm^{-1} can be assigned to symmetric C–O vibration in carboxylate or to C–H deformation vibration. Eisenbach [16] and Goodwin [17] observed similar bands in their studies on coke deposition over HY zeolite, and they assigned these bands to the aromatic coke. In an IR study of coke deposition from acetylene over Al_2O_3 and Ni/Al_2O_3, Galuszka and Amenomiya reported the similar bands, and they also attributed the bands to aromatic species [18]. However, due to the difficulty in the coupling of methane to a C=C bond in the absence of any oxidant, the formation of aromatic species from methane over Al_2O_3 is extremely difficult. Assigning of these bands to surface formate species seemed more reasonable. Indeed, this assignment can be substantiated by the results of the adsorption of methanol and formate acid on Al_2O_3 under similar conditions. Apparently, the bands near 1580 and 1460 cm^{-1} cannot be assigned to the methoxide, which shows bands at 1483 and 1416 cm^{-1}. Adsorbed formate acid exhibited bands at 1586 and 1468 cm^{-1}. Therefore, it is quite reasonable to assign the bands near 1580 and 1460 cm^{-1} to surface formate species. Recent results from the literature also support this assignment. In the IR study of coke on Al_2O_3, Eischens and coworkers [19,20] confidently attributed the bands at 1580 and 1460 cm^{-1}, which resulted from the exposure of Al_2O_3 to acetylene at 523 K, to carboxylate species. In fact, early IR studies on alcohol and $(CF_2H)_2O$ adsorption over alumina by Greenler [21], Kagel [22] and Yates [23] revealed that similar bands were from surface carboxylate species. The surface formate species possibly originated from the interaction of methane with the surface lattice oxygen and the hydroxyl groups. As a matter of fact, the oxidative property of alumina has been proven by the pervious work of Eischens and Amenomiya [18–20]. As the temperature was increased to above 873 K, the surface formate species decomposed to gaseous CO_2, and surface carbonate species were produced. These species were quite stable under vacuum or inert atmosphere, and decomposed to CO_2 in the presence of oxygen. These results are in agreement with that of methane interaction with a cuprous oxide [24].

Aside from the formation of formate species, another interesting result is the exchange of CD_4 with the surface hydroxyl groups. It can be seen from figs. 5 and 6 that the hydroxyls on η-Al_2O_3 could be exchanged with CD_4 at temperatures as low as 573 K. However, the exchange reaction over γ-Al_2O_3 took place at a much higher temperature. The exchange of CD_4 with the hydroxyls over Al_2O_3 was observed previously [11,12]. Unfortunately, the exact form of the alumina used was not stated. As we have already known, the commencing temperature and the extent of H–D exchange differed greatly with different forms of alumina. According to Larson and Hall [11], methane will dissociatively adsorb on a pair of sites consisting of exposed aluminum and O^{2-} ions to form $Al-CH_3$ and OH groups. They preferred a group of sites where the nearest neighbors of an isolated OH group are all aluminum ions. Such a model can be used to explain the difference of exchange reaction over η- and γ-Al_2O_3. More OH groups are removed from η-Al_2O_3 if they are evacuated under similar conditions. Therefore, more exposed aluminum and O^{2-} ions will be produced on η-Al_2O_3.

3.2.3. With HZSM-5 zeolite

More recently, the reports on methane conversion over HZSM-5 zeolite and HZSM-5 supported catalysts attract much interest [25–28]. Only a few papers discussed the role of Brønsted acid in methane activation. It was proposed by Iglesia [28] and Wang [4] that methane activation occurs via a heterolytic C–H bond dissociation process involving protonic sites. However, no such direct evidence for this process has been reported so far. Although the adsorption of methane on HZSM-5 zeolite has been testified by using the gas chromatography pulse technique [29] and the diffuse reflectance IR spectroscopy [30,31]. Unfortunately, we cannot identify any adsorbed species of methane on HZSM-5 at temperatures up to 873 K by FT-IR transmission spectroscopy. This was perhaps due to the fact that the concentration of these species was below the limit of detection, as reported over Ni/SiO_2 [32] and Rh/SiO_2 [33], or it was difficult to differentiate the adsorbed CH_x species from CH_4 by IR transmission spectroscopy.

The low temperature experiments showed that methane adsorption over HZSM-5 zeolite occurred mainly via the formation of hydrogen-bonding with the hydroxyl groups. In order to clarify whether these hydroxyl groups also played an important role in the activation of methane at high temperatures, the adsorption of deuterated methane (CD_4) was carried out. The spectra are illustrated in fig. 7.

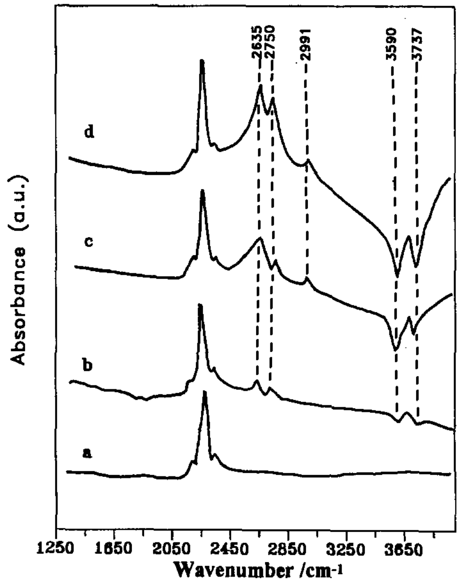

Fig. 7. IR difference spectra depicting the exchange of CD_4 with the OH groups of HZSM-5. (a) 673 K, (b) 773 K, (c) 873 K, 5 min and (d) 873 K, 20 min.

The bands in the range of 2000–2400 cm^{-1} are assigned to the gas phase CD_4. It is noteworthy that the reverse bands at 3737 and 3590 cm^{-1} and the new bands at 2750 and 2635 cm^{-1} appeared simultaneously when the temperature was higher than 773 K. It is reasonable that the O–D band at 2750 cm^{-1} resulted from the exchange of the terminal silanol hydrogen atom with the deuterium atom in CD_4, while the O–D band at 2635 cm^{-1} was from the exchange of CD_4 with the bridging hydroxyl groups at 3590 cm^{-1}. No bands that can be attributed to formate or carbonate species, as in the case of Al_2O_3, were observed over the HZSM-5 zeolite.

Recent studies suggested that the activation of methane occurs on superacid catalysts [34], as well as on Hg-based organometallic complexes [35] at low temperature via a heterolytic cleavage of a C–H bond. In the case of HZSM-5 zeolite, it is also plausible that methane is activated by interacting with a proton to form an intermediate CH_5^+, and this species either decomposes to CH_3^+, which initiates a reaction, or goes back to methane [34]. During the interaction, the C–D bond breaks first, then followed by the exchange with hydroxyl groups present on the HZSM-5. The conclusion that the protons in HZSM-5 play a crucial role in the C–H bond cleavage can be further substantiated by the fact that no band which could be attributed to O–D vibration was observed during the reaction of CD_4 with NaZSM-5 (which contains almost no Brønsted acid protons) even at 873 K. However, since the protonation of methane is very difficult, other factors which may influence the activation of methane possibly exist. It is interesting to note that the sequence of Si-OH-Al > Al-OH > Si-OH cannot be applied to the exchange of OH with CD_4 at high temperatures. This implies that the acidity of the OH groups is really not the only factor, and perhaps the environment of the OH groups also plays an important role in the H–D exchange reaction. Theoretical study results revealed that the exchange reaction is a concerted acid–base reaction, with a transition state which is different from the adsorbed carbonium ion [36]. Combining with the fact that the surface formate species were not formed over silica and HZSM-5 zeolite, it is suggested that an assembly of adjacent aluminums is important for formate formation and exchange reaction of OH groups with CD_4.

4. Conclusions

The adsorption of methane at low temperatures over acidic silica, alumina and HZSM-5 zeolite was observed. The surface OH groups played an important role in methane adsorption, and the sequence of the strength of interaction of methane with OH groups is Si-OH-Al > Al-OH > Si-OH, which agrees well with the strength of their acidities. The low temperature adsorption of methane can be a useful method for measuring acid strength on solid acid catalysts. Discrepancy exists between the information of methane interaction with oxides and HZSM-5 zeolite at low temperatures and that at high temperatures. At high temperatures, formate species were produced over Al_2O_3 (both η and γ forms), while they could not be formed over silica and HZSM-5 zeolite. Meanwhile, the exchange reaction of CD_4 with the OH groups was observed over silica, alumina and HZSM-5 zeolite. The exchange reaction commenced at temperatures higher than 573 K over η-Al_2O_3, while it occurred at a much higher temperature over γ-Al_2O_3, HZSM-5 and SiO_2. The extent of the exchange of CD_4 with the OH groups over silica was rather small even at 873 K, whereas almost all of the OH groups over alumina (both η and γ) and the OH groups of the Al-OH-Si type on HZSM-5 could exchange with CD_4.

Acknowledgement

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