

Adsorption of methane on zeolite studied by FT-IR spectroscopy*

LI Can (李 灿), LI Guoqiang (李国强), LIU Zhongmin (刘中民)
and XIN Qin (辛 勤)

(State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China)

Received October 8, 1993

Keywords: methane adsorption, CO adsorption, FT-IR, zeolite, catalysis, surface vibrational spectroscopy.

The activation of methane is regarded as one of the challenges in catalysis and chemistry. Much effort has been made for the selective oxidation and oxidative coupling of methane in catalysis; however, at fundamental level the activation of methane on catalyst surface is still poorly understood. Experimentally, it is difficult to get insights into the interaction mechanism between methane and catalyst because methane is chemically most a stable molecule which cannot be easily captured on the surface of catalyst. To explore the interaction and activation of methane on catalyst, a quartz-made IR cell combined with a reaction system was made specially for IR study in a wide temperature range from 130 to 1000 K. In our previous work the adsorptions of methane on CeO_2 ^[1, 2] and MgO ^[3] at 173 K were studied by FT-IR spectroscopy. It was found that several types of adsorbed methane could be formed on these catalysts and the formation of adsorbed methane strongly depends on the kind and the surface state of catalyst. Weakly adsorbed methane gives two IR peaks of ν_3 and ν_4 which are similar to those of gas phase except for a slight red shift in frequency. But for strongly adsorbed methane, not only the ν_3 and ν_4 peaks were observed but also the infrared-forbidden vibration of ν_1 appeared and shifted to lower frequency. In the present study, methane adsorption on zeolites has been investigated with an intention to understand the interaction of methane with an acidic surface. This note shows that methane interacts strongly with surface oxygen anion, hydroxyls and Lewis acidic sites in forming the adsorbed state.

1 Experimental

IR spectra were recorded on a Perkin-Elmer 1800 FT-IR spectrometer with scans of 4 and at a resolution of 4 cm^{-1} . HZSM-5 and mordenite zeolites obtained from commercial source were used in this work. The zeolite samples were pressed into a

* Project supported by the National Natural Science Foundation of China.

self-supporting disc which was placed in a quartz-made IR cell for IR study. The sample in IR cell was outgassed at 773 K and then cooled to 173 K prior to the adsorption of methane or CO. IR spectra were presented as absorbance which was calculated from the ratio of IR spectra recorded before and after introducing CH₄ or CO. CH₄ and CO used in this study were 99.99% in purity and were purified further through a liquid-nitrogen trap. A detailed experimental aspect was described in a previous paper^[2].

2 Results and discussion

IR spectra of adsorbed CH₄ formed on outgassed HZSM-5 and mordenite zeolite are almost similar, i.e. common IR peaks can be observed at 3 008, 3 002, 2 990, 2 890 and 1 305 cm⁻¹ for adsorbed CH₄ on the two samples at 173 K. The peaks at 3 008 and 3 002 cm⁻¹ are assigned to ν_3 mode, 1 305 cm⁻¹ to ν_4 mode and 2 900 and 2 890 cm⁻¹ to ν_1 mode of the adsorbed CH₄^[2, 3]. In comparison with the IR spectra of gaseous CH₄, the ν_1 and ν_3 modes of adsorbed CH₄ shift to lower frequencies, indicating that the C—H bonds of adsorbed CH₄ are weakened somewhat because the two modes are stretch vibrations of the C—H bonds. It is noteworthy that the appearance of the peaks at 2 990 and 2 890 cm⁻¹ reflects a strong interaction of methane with surface that causes a distortion in structure of Td-point group since the two modes in Td symmetry are infrared-forbidden vibrations. The symmetry distortion induced by surface breaks down the infrared selection rule of CH₄; as a result, the infrared-forbidden vibration could be observed by infrared spectroscopy. In addition, the two peaks at 2 890 and 2 990 cm⁻¹ are indicative of two types of adsorbed methane formed on the zeolite surfaces. A very interesting phenomenon is that the IR peaks of surface hydroxyls are changed very much when CH₄ is adsorbed.

As an example, fig. 1 shows IR spectra of adsorbed methane on mordenite in which IR peaks at 3 008, 3 002, 2 902 and 2 890 cm⁻¹ are readily attributed to the adsorbed CH₄. Upon the methane adsorption, several reverse IR peaks at 3 740, 3 670, and 3 615 cm⁻¹ are produced and meanwhile a broad peak appears at around 3 505 cm⁻¹. These peaks are just located in the vibrational region of surface hydroxyls. Obviously the appearance of the reverse peaks accounts for the surface hydroxyls which are perturbed by adsorbed methane and accordingly the perturbed hydroxyls give IR peaks at lower frequencies near $\sim 3 505$ cm⁻¹. This can be explained in terms of strong hydrogen-bonding existing between CH₄ and surface OH which participates in the formation of adsorbed CH₄. The adsorbed CH₄ can be partly removed by an outgassing at 173 K but some adsorbed methane species persist on the surface even after a prolonged evacuation indicating that the adsorption of methane on zeolites is relatively strong.

Figure 2 gives the IR spectra of coadsorbed CH₄ and CO on mordenite at 173 K. In much the same way as the methane adsorption, CO was introduced into the CH₄

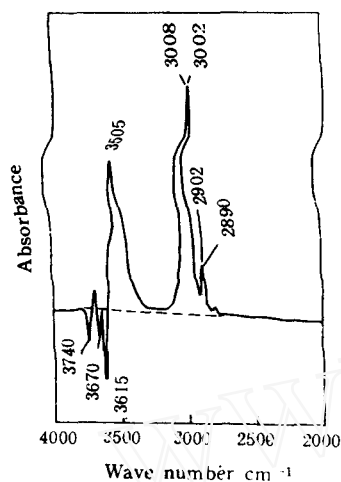


Fig. 1 IR spectra of adsorbed CH_4 on mordenite at 173 K.

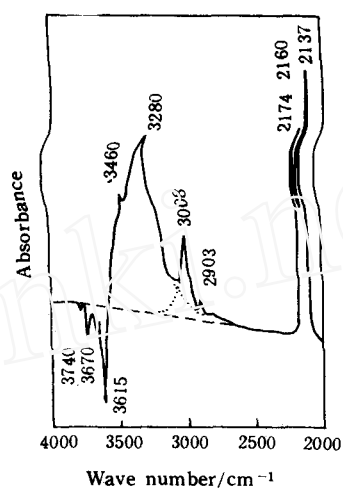


Fig. 2 IR spectra of coadsorbed CH_4 and CO on mordenite at 173 K.

mordenite system after an equilibrium adsorption of methane was reached. There are three IR peaks appearing at 2174, 2160 and 2137 cm^{-1} for the CO adsorption. These peaks suggest that CO is adsorbed on Lewis acid sites of mordenite surface^[4,5]. The three distinct peaks may correspond to three or more kinds of surface Lewis sites. With the development of peaks at 2174, 2160 and 2137 cm^{-1} the peaks of adsorbed CH_4 are weakened meanwhile, and finally the peaks at 3002 and 2890 cm^{-1} disappear. This result demonstrates that the portion of the adsorbed methane can be replaced by the coadsorbed CO . The shift of the IR peak at 3505 to 3280 cm^{-1} for the CO adsorption corroborates newly formed hydrogen-bonding between surface hydroxyls and CO which substitutes for adsorbed CH_4 . But those adsorbed methane without the hydrogen-bonding are not affected by the coadsorbed CO . On the basis of the above observation, the adsorbed methane on mordenite can be classified into at least two types of species, denoted as α (3002, 2890 and 1305 cm^{-1}) and β (3008, 2900 and 1305 cm^{-1}) species. The α species is the adsorbed CH_4 interacting with surface oxygen anion, hydroxyls and Lewis acid sites, which can be replaced by the coadsorbed CO . However, β species is formed mainly via the interaction of CH_4 with surface oxygen anions and hydroxyls. The α species has a stronger interaction than the β species because the former shows a larger red shift of C—H vibration than the latter.

The amount of adsorbed methane is relatively small for air-contaminated zeolites but it increases with outgassing temperatures and reaches a maximum at outgassing temperatures around 773 K. When the outgassing temperature of the zeolites is elevated further, the amount of adsorbed methane decreases. The enhancement of adsorbed methane with outgassing temperature can be interpreted as the outgassing removing the surface contaminant covering the surface oxygen anions and Lewis acid

sites which are available for the methane adsorption. A high temperature outgassing may cause a severe dehydroxylation that leads to a decrease of methane adsorption.

The information obtained from the methane adsorption is very important to understanding methane activation and reaction on zeolites. It can be speculated that the adsorbed species observed at low temperatures may be the precursors of reaction at high temperatures where the lifetime of reaction intermediate is so short that it is difficult to detect by the conventional techniques. It is supposed that the distortion in symmetry of methane on surface may be the primary factor which changes the degeneration of LUMO and HOMO levels of methane, and accordingly one of the C—H bonds is of preferable to be weakened and even cleaved.

3 Conclusions

The methane adsorption on mordenite and HZSM-5 zeolites has been studied at 173 K by *in situ* FT-IR spectroscopy. The zeolites can adsorb a considerable amount of methane and the adsorbed methane can be classified into two types of surface species according to their interaction extent with surface. α species can be replaced by the coadsorbed CO but β species are not influenced by the coadsorption of CO. α species interact with surface hydroxyls, oxygen anions and Lewis acid sites while β species are formed through the interaction with surface oxygen anions and hydroxyls.

References

- 1 Li Can, Xin Qin, Direct observation of chemisorbed methane on cerium (IV) oxide by FTIR spectroscopy, *J. Chem. Soc., Chem. Commun.*, 1992, (10):782.
- 2 Li Can, Xin Qin, FT-IR spectroscopic investigation of methane adsorption on cerium oxide, *J. Phys. Chem.* (in Chinese), 1992, 96:7714.
- 3 Li Can, Li Guo-qiang, Xin Qin, FT-IR spectroscopic studies of methane adsorption on magnesium oxide, *J. Phys. Chem.*, 1994, 98:1933.
- 4 Ferrnandea, A., Leyrer, J., Gonzalez-Elipse, A. R. *et al.*, Spectroscopic characterization of TiO₂/SiO₂ catalysts, *J. Catal.*, 1988, 112:489.
- 5 Zaki, M. I., Knozinger, H., Carbon monoxide—a low-temperature infrared probe for the characterization of hydroxyl group properties on metal oxide surfaces, *Materials Chem. and Phys.*, 1987, 17:210.