The first observation of the broad-range DRIFT spectrum of methane adsorbed on H-mordenite

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This paper presents the first observation of the broad-range NIR DRIFT spectrum of CH_4 adsorbed on HM zeolite including different combinations of C–H bending and stretching vibrations and overtones of those vibrations. The obtained results indicate that adsorption of methane results in the strongest perturbation of the combinations of ν_2 and ν_4 C–H bending frequencies with each other and with the ν_3 asymmetric stretching frequency. Therefore, it is suggested that those combinations could be used as a better index of methane perturbation and of the reaction coordinate of methane protolytic dehydrogenation than the fundamental frequencies commonly used for this purpose.

KEY WORDS: methane adsorption; mordenite; NIR spectra; reaction coordinate

1. Introduction

Transmittance IR spectra of methane adsorbed on cationic forms of zeolites have been studied in [1–5]. The authors of these papers reported only the fundamental symmetric ν_1, and asymmetric, ν_3, stretching frequencies or the ν_2 and ν_4 bending frequencies of C–H bonds in adsorbed CH_4. The reported results indicate that the asymmetric stretching frequency ν_3 exhibits upon adsorption a low-frequency shift of about 20 cm^{-1}, while the symmetric stretching frequency ν_1 that is observed in the gas phase only in Raman spectra, becomes IR active and is also red shifted by 20–25 cm^{-1}. In some cases additional splittings of both of these lines, due to the lowering of the symmetry of adsorbed methane, were also reported. The red shifts of ν_2 and ν_4 bending vibrations are much less than those of the stretching frequencies. In contrast to cationic forms, the IR spectra of methane adsorbed on hydrogen forms of zeolites have not yet been reported.

Our previous DRIFT study of molecular hydrogen (see [6], and references therein) and carbon dioxide [7] adsorption on different cationic forms of zeolites demonstrated the advantage of DRIFT spectroscopy for measurements in the NIR spectral range. It was also shown that this technique is much more suitable for observation of overtones and different combinations of stretching and bending vibrations than traditional transmittance IR spectroscopy. In the present paper DRIFT spectroscopy was used to study methane adsorption on H-mordenite over a broad spectral range.

2. Experimental

HM was obtained by decomposition of NH_4M from Shell with Si/Al $= 5$. Prior to making spectral measurements, the samples were pretreated in vacuum at 673 K for 4 h. Methane adsorption was carried out from a large volume either at room temperature or at 190 K. After the adsorption equilibrium was established, the quartz DRIFT cell containing the methane-loaded zeolite was slowly cooled to 77 K. DRIFT spectra were recorded either at room temperature or at 77 K in the spectral range of 2600–6000 cm^{-1} using a Nicolet "Impact 410" spectrophotometer equipped with a home-built diffuse reflectance attachment. For DRIFT measurements at 77 K the quartz optical cell with the zeolite was immersed into a quartz Dewar flask filled with liquid nitrogen. The observed DRIFT spectra were then transformed into Kubelka–Munk units by a standard program assuming that the reflectability of HM zeolite at 5000 cm^{-1} was equal to 90%, while the background created by the zeolite was subtracted.

3. Results and discussion

A DRIFT spectrum of methane adsorbed on HM zeolite at the pressure 100 Torr and recorded at room temperature in the presence of CH_4 in the gas phase is shown in figure 1. A sharp line at 3016 cm^{-1} belongs to the Q-branch of the vibration-rotational manifold for the ν_3 C–H stretching vibration of gaseous methane. The P and R branches with the well-resolved rotational structure are seen at lower and higher frequencies. In addition, the bands from adsorbed methane with maxima at 3002 cm^{-1} (asymmetric, ν_3, stretching vibration) and 2890 cm^{-1} (symmetric, ν_1, stretching vibration) are clearly visible in the spectrum.

A broad-range DRIFT spectrum of methane adsorbed at 190 K at the equilibrium pressure of 10 Torr and then slowly cooled down and recorded at liquid nitrogen temperature is shown in figure 2. The most intense band in this spectrum with the maximum at 3607 cm^{-1} belongs to the free

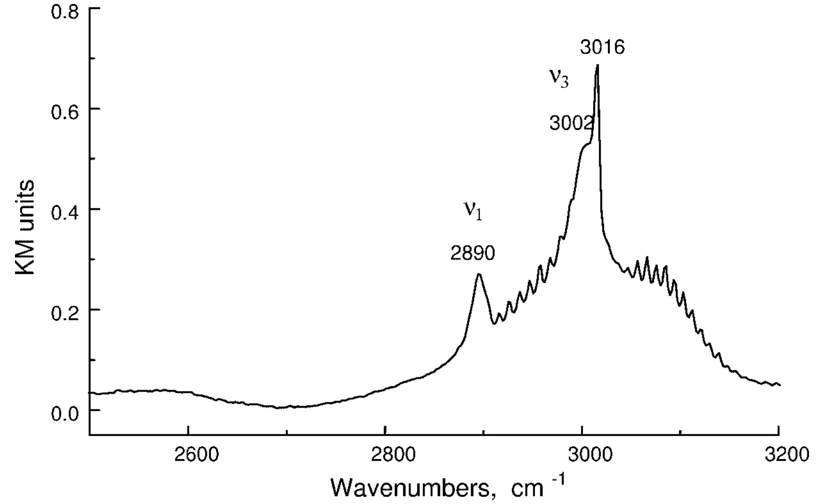


Figure 1. A DRIFT spectrum of methane adsorbed by HM at the pressure of 100 Torr at 298 K. Measurement performed at 298 K in the presence of gaseous methane.

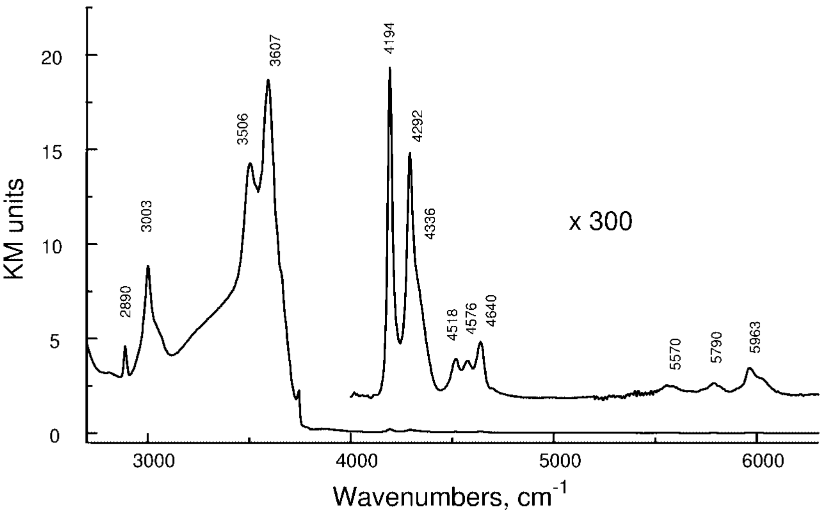


Figure 2. A broad-range DRIFT spectrum of methane adsorbed by HM at the pressure of 10 Torr at 168 K. DRIFT spectrum recorded at 77 K.

bridging OH groups, while the band at 3506 cm^{-1} originates from the OH groups perturbed by the hydrogen bonding with methane. This obviously indicates adsorption of methane on the bridging hydroxyl groups resulting from formation of the weak hydrogen bonds. Similar to figure 1, the bands at 3003 and 2890 cm^{-1} belong to the asymmetric, ν_3, and symmetric, ν_1, stretching frequencies of the adsorbed methane. Due to complete CH_4 adsorption at 77 K, the lines from gaseous methane are absent.

The extremely high sensitivity of DRIFT spectroscopy in the NIR region allows observations of many much weaker bands, which are clearly seen in the spectrum recorded at the three hundred times higher amplification. The bands at 4640 and 4576 cm^{-1} belong to combinations of the unperturbed OH stretching band and to the hydroxyls perturbed by hydrogen bonding with adsorbed methane with the corresponding in-plane OH bending vibrations. The other bands in the NIR region are due to different combinations of bending and stretching vibrations of adsorbed methane, including the combinations of up to three different frequencies.

An expanded DRIFT spectrum covering the range of 2500–3200 cm^{-1} is shown in figure 3. The weak bands from the overtone of the ν_4 bending vibration and from the $\nu_2+\nu_4$ combination of bending vibrations are clearly seen at 2596 and 2820 cm^{-1}, respectively. The wavenumbers for these and other bands of adsorbed methane and their assignments according to Herzberg [8] are collected in table 1.

The near equivalency of the values for $2\nu_4$ frequencies for gaseous methane and for methane adsorbed on HM indicates that CH_4 adsorption does not alter the frequency of the ν_4 bending band. The same is true for the $\nu_2+\nu_4$ combination band. Therefore, perturbation of the ν_2 bending vibration resulting from adsorption is also quite low. Thus, adsorption of methane on hydroxyl groups of H-mordenite has only a minor influence on the ν_2 and ν_4 bending frequencies of C–H bonds.

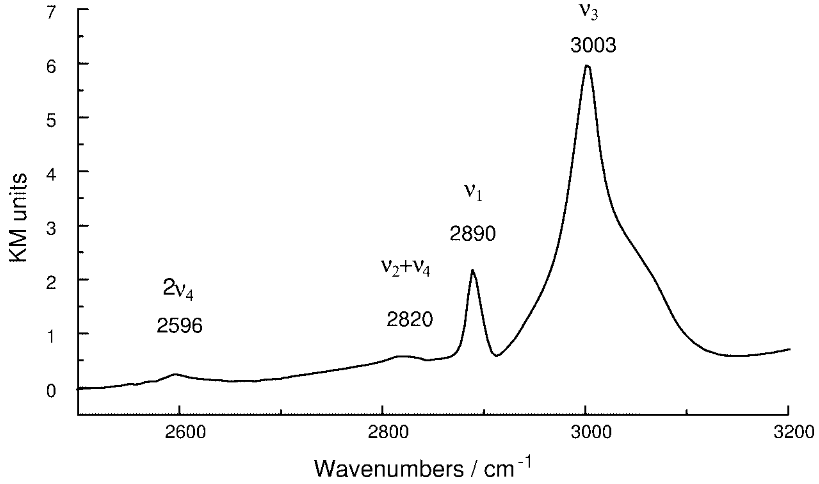


Figure 3. The similar DRIFT spectrum as in figure 2 recorded in a more expanded scale in a sapphire ampoule and Dewar flask to avoid the background created by quartz.

Table 1
Comparison of the wavenumbers of the bands of gaseous methane with those of methane adsorbed on HM zeolite.

Assignment of the bands according to [8]	Wavenumbers of the bands in the gas phase according to [8] (cm^{-1})	Wavenumbers of the bands of methane adsorbed on HM zeolite (cm^{-1})	Red shifts of the bands of adsorbed methane relative to the gas phase (cm^{-1})
ν_4	1306	–	–
ν_2	1526	–	–
$2\nu_4$	2600	2596	−4
$\nu_2 + \nu_4$	2823	2820	−3
ν_1	2914	2890	−24
ν_3	3020	3003	−17
$\nu_1 + \nu_4$	4216	4194	−22
$\nu_3 + \nu_4$	4313	4292	−21
$\boldsymbol{\nu_2 + \nu_3}$	**4546**	**4518**	**−28**
$\nu_3 + 2\nu_4$	5585	5570	−25
$\nu_1 + \nu_2 + \nu_4$	5775	–	–
$\boldsymbol{\nu_2 + \nu_3 + \nu_4}$	**5861**	**5790**	**−71**
$2\nu_3$	6006	5963	−43

The perturbations of the ν_1 and ν_3 fundamental C–H stretching frequencies are considerably stronger. As one can see from table 1, the red shift of the frequency of the ν_1 symmetric vibration relative to that for the gaseous methane is equal to 24 cm^{-1}, while the corresponding shift of the asymmetric, ν_3, vibration to 17 cm^{-1}. These values are close to those reported in the literature for methane adsorption on cationic forms of different zeolites [1–5].

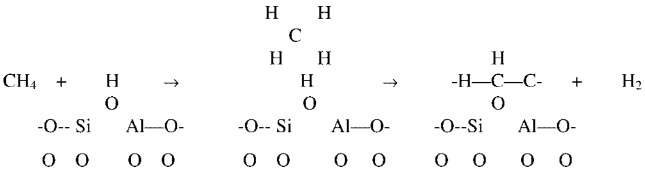
The low-frequency shifts of the $\nu_2 + \nu_3$ and $\nu_2 + \nu_3 + \nu_4$ combinations of bending and asymmetric stretching vibrations are substantially larger (these combinations are indicated in table 1 in bold). For instance, the red shift of the $\nu_2 + \nu_3$ combination frequency relative to the corresponding band for gaseous methane is equal to 28 cm^{-1}. By contrast, the arithmetic sum of the ν_2 and ν_3 frequencies for the gaseous methane coincides with the corresponding frequency in gaseous methane.

The difference of the similar shifts for the triple $\nu_2 + \nu_3 + \nu_4$ combination is even larger (-71 cm^{-1} in comparison with the shift of about -9 cm^{-1} calculated as a sum of the shifts of corresponding fundamental gaseous frequencies). This obviously indicates a high anharmonicity of the multiple combinations resulting from the strong interaction of the bending vibrations with each other or with the asymmetric ν_3 stretching frequency.

In this connection, it is worth noting that according to the modern *ab initio* quantum chemical calculations performed with optimization of geometry of the transition states, the reaction coordinates of catalytic transformations of hydrocarbons on zeolites are rather complicated. In addition to stretching of O–H bonds in acidic hydroxyl groups, they also involve rearrangement of several chemical bonds in the adsorbed molecules [9–20]. Then the energy required for activation of chemical bonds in the initial molecules is partially compensated by formation of the new bonds in the transition states. In this way activation of some chemical bonds is assisted by formation of the others, thus lowering the activation barriers.

For adsorbed molecules the reaction coordinate mainly corresponds to the vibrational activation of chemical bonds. In other words, *it represents a combination of several vibrations with a high anharmonicity of the resulting combination frequency due to interaction of different vibrations with each other*. This interaction results in the lowering of the activation energy. Therefore, a high anharmonicity of the complicated combinations of C–H bending and stretching frequencies in adsorbed methane most likely indicates a strong contribution of these combination frequencies in the reaction coordinate of adsorbed methane activation.

For methane adsorbed on the bridging hydroxyl groups of HM zeolite this conclusion can be illustrated in a following way. It is quite clear that the only possible chemical reaction of adsorbed methane with the acidic hydroxyl groups of mordenite is the protolytic dehydrogenation that results in formation of molecular hydrogen and of the adsorbed methoxy group:



The coordinate for this reaction corresponds in addition to the stretching of the O–H bond also to transformation of the hydrogen-bonded methane into a methoxy group *via* complicated combination of stretching and bending vibrations in the hydrogen-bonded molecule. The stronger perturbation and anharmonicity of this combination vibration in comparison with the free molecule obviously indicates the stronger methane activation.

Thus, based on the results of this paper, it can be suggested that the anharmonic combinations of several vibrations observed in the broad range DRIFT spectra are a better index of activation of adsorbed molecules than the fundamental vibrations generally used for this purpose. Utilization of the combination frequencies as a reaction coordinate certainly is more attractive, since the higher the energy of a combination of vibrations is the more complicated is the combination. Therefore, it is closer to the energy of corresponding transition states than that of the fundamental transitions.

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