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Interaction of methane with surface of alumina studied by FT-IR spectroscopy

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Methane adsorption on alumina was investigated by FT-IR spectroscopy at 173 K. Adsorbed methane gives four distinct IR bands at 3008, 3000, 2900 and 1305 cm^{-1} which are attributed to ν_1 (2900 cm^{-1}), ν_3 (3008, 3000 cm^{-1}), and ν_4 (1305 cm^{-1}) modes of methane respectively. The appearance of the ν_1 mode indicates that the T_d symmetry of methane is distorted by the adsorption. The intensities of these bands increase significantly with outgassing temperatures of alumina, reach their maxima at an outgassing temperature near 773 K, and then decrease with further higher outgassing temperatures. Two hydroxyls with IR bands at 3750 and 3665 cm^{-1} are perturbed evidently by the adsorbed CH_4 thereby resulting in two red-shifted bands at 3707 and 3640 cm^{-1}. Coadsorbed CO slightly affects the adsorbed CH_4 indicating the very weak interaction between CH_4 and surface cations of alumina. It is proposed that the adsorbed CH_4 on alumina is formed mainly via the interaction of CH_4 with both surface hydroxyl and c.u.s. oxygen anion.

Keywords: Methane adsorption; alumina; hydroxyls; FT-IR; coadsorption; CO adsorption

1. Introduction

Adsorption and activation of methane have long been tough subjects in catalysis [1–6]. Over the past decade the studies on methane activation and oxidation on oxide catalysts have attracted much attention [7–9] because of the interests from both academia and industry. However, the methane activation is still far from being understood and one of the possible reasons for the little knowledge of methane activation may be the lack of experimental data of methane interaction with catalyst surfaces. In our previous work, methane adsorbed on cerium oxide [10,11] and magnesium oxide [12] has been studied by FT-IR spectroscopy. It has been found that two types of adsorbed methane are formed on cerium oxide, one interacts with surface active oxygen species similar to O^- and the other interacts

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with the surface lattice oxygen. A severe distortion of the T_d symmetry of methane was evidenced by the appearance and down-shift of the infrared-forbidden vibration (ν_1 mode). For magnesium oxide, adsorbed methane strongly interacts with the Lewis acid–base pair sites on the surface, i.e., $Mg^{2+}_{LC}O^{2-}_{LC}$. It seems that the nature and degree of the interaction of methane with the surface strongly depend on the chemical state of the oxide surface including surface sites such as acid–base centers and surface species like hydroxyls and adsorbed oxygen.

Alumina is a well-known support widely used in catalysts; in particular, its surface hydroxyls and acidic properties are of great importance in catalysis [13,14]. In addition, the surface chemistry of alumina is relatively well characterized. In the present work, the methane adsorption on alumina is studied with an intention to know how methane interacts with the acidic surface, especially which role surface hydroxyls play in the formation of adsorbed methane. Alumina was pre-outgassed at temperatures from 300 to 973 K in order to make differently dehydroxylated surface states. IR spectra of adsorbed methane and hydroxyls on the pretreated alumina were investigated in detail to clarify the perturbation of hydroxyls by the adsorbed methane.

2. Experimental

Commercial γ-alumina (BET surface area, 208 m^2/g) is used in this study. The alumina sample was pressed into a self-supporting wafer for IR study, and the sample wafer was placed in a quartz cell which is connected to a vacuum system and gas reservoirs. The sample in the cell can be treated in various ways at a wide temperature range from 100 to 1000 K. The sample was outgassed in vacuo at given temperatures for 0.5 h and then cooled down to 173 K under vacuum for adsorptions of CH_4 and CO. IR spectra were recorded in situ before gas admission (background) and after the adsorption at 173 K. Coadsorption of CO with CH_4 was performed by introducing CO onto the sample with preadsorbed CH_4, or vice versa, at 173 K.

IR spectra were taken on a Perkin-Elmer 1800 FT-IR spectrometer equipped with a liquid-nitrogen-cooled mercury-calcium-telluride (MCT) detector with 4 cm^{-1} resolution and four scans. All IR spectra of adsorbed species are ratioed against the background spectrum and the band intensity is calculated in integrated absorbance. The purities of CH_4 and CO are better than 99.99% and they were further purified through a liquid-nitrogen trap before the adsorption experiments were performed.

3. Results and discussion

Fig. 1a shows an IR spectrum recorded after exposing the Al_2O_3 (pre-outgassed

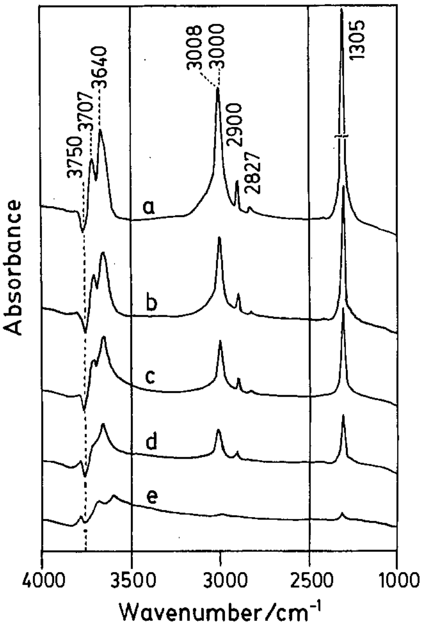

Fig. 1. IR spectra of hydroxyls and adsorbed CH_4 on alumina (outgassed at 773 K), under various pressures of CH_4 at 173 K. (a) 13.0 Torr, (b) 5.0 Torr, (c) 2.5 Torr, (d) 0.8 Torr, and (e) <0.01 Torr.

at 773 K) surface to CH_4 at 173 K. In the 4000–3500 cm^{-1} region there are two distinct bands at 3707 and 3640 cm^{-1} together with two reverse bands at 3750 and 3665 cm^{-1}. These bands originate from the surface hydroxyls, and the appearance of the reverse bands means that the bands of the hydroxyls were reduced somewhat after the methane adsorption. Four strong bands at 3008, 3000, 2900 and 1305 cm^{-1} are observed for adsorbed methane. The bands at 3008 and 3000 cm^{-1} are assigned to the ν_3 mode (deg. stretch), the band at 1305 cm^{-1} is readily ascribed to the ν_4 mode (deg. deform) of the adsorbed methane [11,15]. The band at 2900 cm^{-1} with a shoulder at 2894 cm^{-1} arises from the ν_1 mode (sym. stretch) [11,16] which is an infrared forbidden vibration of the free CH_4 molecule. The break-down of the infrared selection rule indicates that the adsorbed methane interacts with the alumina surface so that its T_d symmetry is distorted to some extent by the surface force. An additional weak band at 2827 cm^{-1} can be attributed to the $\nu_2 + \nu_4$ mode of adsorbed methane [16]. The assignment of the bands due to adsorbed CH_4 and a comparison with that of free CH_4 is summarised in table 1. As seen in figs. 1a–1e, the IR bands due to adsorbed methane are gradually weakened with decreasing CH_4 pressure and finally disappear after a prolonged evacuation. This result reflects that the methane adsorption on the alumina surface is a physical adsorption in nature, accordingly the adsorbed methane can be removed by evacuation.

It is noteworthy that the bands in the hydroxyl region are changed very much

Table 1
Vibrational modes of CH_4 and detected IR bands of adsorbed CH_4 on outgassed Al_2O_3 (in cm^{-1})

Vibrational mode	Gas phase	Adsorbed	Frequency shift
ν_1, sym. stretch	2917 [a]	2900	17
ν_2, deg. deform	1533 [a]	b	b
ν_3, deg. stretch	3019	3008	11
ν_4, deg. deform	1306	1305	1
$\nu_2 + \nu_4$		2827	

[a] Infrared inactive.
[b] Not observed.

by the adsorbed methane. The bands at 3707 and 3640 cm^{-1} appeared after the methane adsorption but attenuated along with the methane desorption (from fig. 1a to 1e), and correspondingly the reverse bands at 3750 and 3665 cm^{-1} were also attenuated with the weakening of the bands at 3707 and 3640 cm^{-1}. The results clearly demonstrate that the adsorbed methane interacts with the surface hydroxyl having OH stretching frequencies near 3750 and 3665 cm^{-1} and accordingly resulting in two reverse bands at 3750 and 3665 cm^{-1}. The perturbed hydroxyls give the red-shifted bands at 3707 and 3640 cm^{-1}. The frequency shifts ($\sim$ 40 and $\sim$ 15 cm^{-1}) of the band due to OH stretching imply a physical interaction between methane and the surface hydroxyls. This suggests that the adsorbed methane is formed partly owing to the weak interaction between methane and surface hydroxyls. Similar red-shifts of OH vibration were observed for CO adsorption on alumina at low temperature [17] where the hydrogen bonding was formed via the oxygen end of CO with the hydrogen atoms of hydroxyls. But the interaction between methane and surface hydroxyls may be more complicated. A tentative interpretation might be that the interaction between methane and hydroxyls is also through a hydrogen-bonding in which the hydrogen atom of methane is bonded to the oxygen atom of surface hydroxyl.

Fig. 2 illustrates the amount of adsorbed methane (measured by integrated absorbance of the band near 3000 cm^{-1}) on alumina pre-outgassed at temperatures from 300 to 973 K. Fig. 3 gives the IR spectra of hydroxyls on alumina pre-outgassed at 373, 573, 773 and 973 K. For alumina outgassed at room temperature, almost no IR bands due to adsorbed methane were detected. With the increasing of outgassing temperatures the IR band intensities of surface hydroxyls are reduced markedly, however the amount of adsorbed methane enhanced greatly. This leads us to draw the conclusion that the adsorbed methane is formed *via* the interactions with both surface isolated hydroxyls and surface coordinatively unsaturated (c.u.s.) oxygen anions which are created through the outgassing at elevated temperatures. Among the surface hydroxyls, those with IR bands at 3750 and 3665 cm^{-1} most possibly contribute to the formation of adsorbed methane. The enhancement of adsorbed methane with outgassing temperature may be explained in term of the increase of surface c.u.s. sites available for methane adsorption.

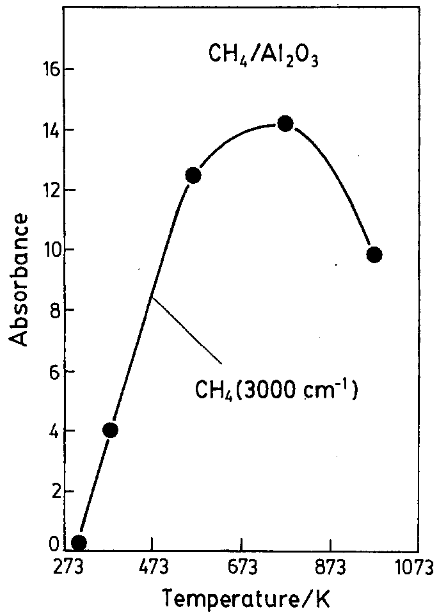

Fig. 2. IR band intensity of 3000 cm^{-1} of adsorbed CH_4 formed at 173 K on Al_2O_3 pre-outgassed at various temperatures.

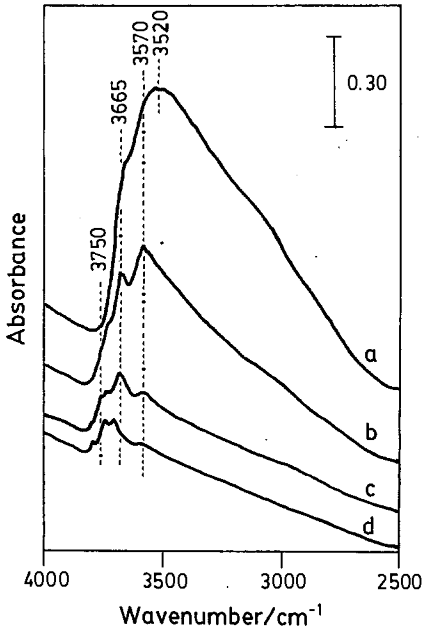

Fig. 3. IR spectra of surface hydroxyls on Al_2O_3 outgassed at (a) 373 K, (b) 573 K, (c) 773 K, and (d) 973 K.

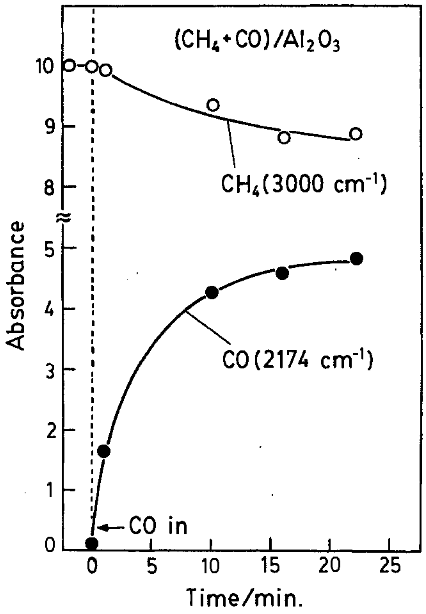

Fig. 4. IR band intensities of coadsorbed CH_4 and CO on Al_2O_3 (outgassed at 773 K) at 173 K with adsorption time.

The decrease of adsorbed methane for alumina pre-outgassed at temperatures higher than 773 K may be due to the severe dehydroxylation which effectively removes the isolated hydroxyls with IR bands near 3750 and 3665 cm^{-1}. IR spectra in figs. 3c–3d evidently show the decrease in band intensities of hydroxyls at 3750 and 3665 cm^{-1} at outgassing temperatures from 773 to 973 K.

The outgassing at high temperatures can produce c.u.s. sites of both surface anions (O^{2-}_{LC}) and cations (Al^{3+}_{LC}). To distinguish which site is mainly responsible for the formation of adsorbed methane, coadsorption of CO and methane was performed for Al_2O_3 (pre-outgassed at 773 K) at 173 K. Firstly an adsorption equilibrium of CH_4 was reached at 173 K, then CO was admitted to the CH_4/Al_2O_3 system through a lone and thin pipe filled with methane atmosphere. CO slowly diffused onto the alumina surface, therefore the band variation can be followed by FT-IR spectroscopy. Adsorbed CO on outgassed Al_2O_3 gives a band centered at 2174 cm^{-1} which is actually composed of two very close bands at 2184 and 2157 cm^{-1}. The band at 2174 cm^{-1} can be assigned to CO adsorbed on surface c.u.s. Al^{3+} site [17–21] derived after an outgassing at high temperatures. It had been found that the band intensity of 2174 cm^{-1} does increase with the elevation of outgassing temperatures. Fig. 4 shows the variations of band intensities due to adsorbed CH_4 (~ 3000 cm^{-1}) and CO (2174 cm^{-1}) with adsorption time. The band intensity of 3000 cm^{-1} is slightly reduced with development of the band at 2174 cm^{-1} of the coadsorbed CO. The adsorbed methane seems to be hardly affected by the coadsorbed CO indicating that the adsorbed methane mainly interacts with surface O^{2-}_{LC} site and surface hydroxyl, while the Al^{3+}_{LC} looks almost like a spectator site for the methane adsorption. The methane adsorption on alumina is quite different from that on magnesium oxide whose c.u.s. cation sites are strongly involved in the formation of adsorbed methane [12].

Based on the above results, it could be concluded that both the surface hydroxyls and c.u.s. oxygen anions contribute to the formation of adsorbed methane on alumina. The residual OH groups having IR bands at 3750 and 3665 cm^{-1} are due to structural hydroxyls that exhibit basicity to some degree [17,21]. There are several distinct IR bands in the 3750–3600 cm^{-1} region (figs. 3c and 3d) similar to those previously observed by Peri [22], but only the hydroxyls with IR bands at 3750 and 3665 cm^{-1} seem most sensitive to the adsorbed methane. It may be speculated that merely the hydroxyl in the vicinity of a surface c.u.s. oxygen anion is the very one available for methane adsorption. The two perturbed bands at 3707 and 3640 cm^{-1} reflect that there are at least two types of adsorbed methane involved in the interaction with the two isolated hydroxyls with IR bands at 3750 and 3665 cm^{-1}. The split bands at 3008 and 3000 cm^{-1}, and 2900 and 3894 cm^{-1} also prove the two types of adsorbed methane formed on alumina.

4. Conclusions

Adsorbed methane can be formed on outgassed alumina at low temperatures. The adsorbed methane mainly interacts with both surface O^{2-}_{LC} site and surface hydroxyl. The fact that the infrared forbidden mode at 2917 cm^{-1} of free methane is induced to an infrared detectable and down-shifted to 2900 cm^{-1} for the adsorbed methane indicates that the T_d symmetry of adsorbed methane is distorted.

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