Direct Observation of Chemisorbed Methane on Cerium(IV) Oxide by FTIR Spectroscopy

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Adsorption of methane on well outgassed CeO_2 at 173–240 K produces IR bands at 3008, 2990, 2875 and 1308 cm^{-1}, which are attributed to chemisorbed methane species formed on the surface coordinatively unsaturated oxygen anions.

The activation of methane is an area of great interest in chemistry, and is receiving considerable academic attention particularly in catalysis science.[1] Because of the abundant resources of natural gas, the use of methane is also attractive to industry. An extensive worldwide effort is now underway to develop catalytic oxidative coupling of methane to form petrochemicals.[2] From the viewpoint of heterogeneous catalysis, the activation of a molecule is achieved through the interaction of the molecule with the surface of a catalyst, namely *via* adsorption. However, direct observation of

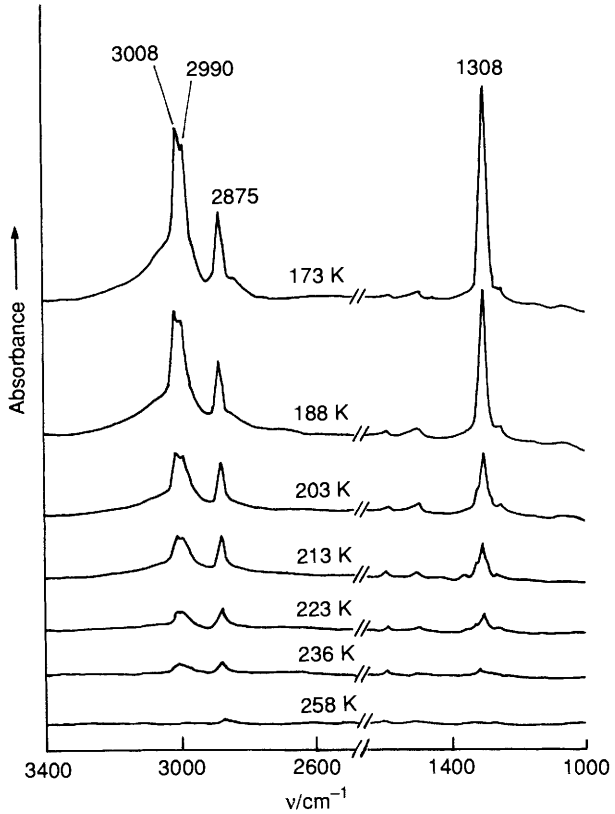

Fig. 1 IR spectra of adsorbed CH_4 on CeO_2 at elevated temperatures, from 173 to 273 K, in the presence of gas-phase CH_4

adsorbed methane is almost absent in the literature mainly owing to the chemical inertness of methane, which means it is difficult to capture on the surface of the catalyst. In the present communication the chemisorbed methane formed on CeO_2 is detected by FTIR (Fourier-transform infrared) spectroscopy over the temperature range of 173–270 K.

CeO_2 was prepared as described previously.[3] The CeO_2 sample was pressed into a self-supporting wafer for IR study using a quartz IR cell in which a sample can be treated *in situ* over a wide temperature range, 100–1000 K. The sample was fully oxidized in O_2 at 873 K and then thoroughly outgassed at 1000 K prior to methane adsorption. The CH_4 (99.99%) used in this study was further purified using a liquid nitrogen trap before the CH_4 entered the IR cell. The IR spectra were recorded at a resolution of 4 cm^{-1} on a Perkin-Elmer 1800 FTIR spectrophotometer equipped with a mercury cadmium telluride detector.

Fig. 1 shows the IR spectra of adsorbed CH_4 obtained at temperatures of 173–273 K under a pressure of 1333 Pa of CH_4. After admission of the CH_4 onto the outgassed CeO_2, at 173 K, five distinct IR bands at 3008, 3000, 2990, 2875 and 1308 cm^{-1} were observed. The intensities of these bands increased slowly and reached their maxima after about 60 min. The band at 3000 cm^{-1} (not indicated in Fig. 1) was submerged by the two neighbouring bands at 3008 and 2990 cm^{-1} with increased time. The band at 2875 cm^{-1} shifted slightly, by 10 cm^{-1}, to higher wavenumbers with the growth of the IR bands. These bands were attenuated apparently at higher temperatures, especially the bands at 3008 and 1308 cm^{-1}, which became significantly weaker with increasing temperatures. All these bands disappeared at temperatures of close to 273 K. These adsorbed species are so unstable on the surface of the catalyst that they cannot be detected at room temperature or higher temperatures. The intensity of the band at 2875 cm^{-1} did not vary in accordance with the bands at 3008 and 1308 cm$-^{1}$. This indicates that there are at least two types of adsorbed species formed on CeO_2 from the adsorption of methane.

Table 1 Vibrational modes of CH_4[4] and observed IR bands of CH_4 adsorbed on CeO_2 at 173 K

Vibrational mode	Gas phase, ν/cm^{-1}	Adsorbed, ν/cm^{-1}	Frequency shift, δν/cm^{-1}
Sym. stretch	2917[a]	2875[a]	42
Degenerate deformation	1533[a]	—[b]	—[b]
Degenerate stretch	3019	3008	11
		3000	19
		2990	29
Degenerate deformation	1306	1308	−2

[a] Infrared inactive; [b] not observed.

Table 1 lists the vibrational modes of free methane[4] and the IR bands observed for methane adsorption on CeO_2. The gas phase CH_4 has four vibrational modes, 2917, 1533, 3019 and 1306 cm^{-1}. Of these frequencies, the modes at 3019 and 1306 cm^{-1} are IR active whereas the other two vibrations at 2917 and 1533 cm^{-1} are IR inactive. The adsorbed CH_4 gives rise to more IR bands than the free CH_4. It is of particular importance that the vibration at 2917 cm^{-1} of free CH_4 not only became IR active but shifted to 2875 cm^{-1} on adsorption onto CeO_2. The band at 3019 cm^{-1} of free CH_4 shifted to 3008, 3000 and 2990 cm^{-1}, respectively, on adsorption onto CeO_2. These results provided strong evidence that chemisorbed methane was formed on CeO_2. The IR inactive mode at 2917 cm^{-1} of CH_4 becomes IR active indicating that the T_d symmetry of CH_4 is seriously distorted by the adsorption. The large frequency shifts displayed in Table 1 also imply that the C–H bond is weakened for the adsorbed CH_4.

According to the variation of the band intensities in Fig. 1, the bands observed could be attributed to two types of adsorbed CH_4 on CeO_2. One has IR bands at 3008 and 1308 cm^{-1} with small frequency shifts corresponding to free CH_4, and the other has IR bands at 2990, 2875 and 1308 cm^{-1}, due to CH_4 interacting strongly with the CeO_2 surface. The former retains the identity of CH_4 and gives two IR bands similar to that of free CH_4 while the latter exhibits larger frequency shifts from the positions due to free CH_4, owing to the stronger chemical interaction with the surface of CeO_2. It is suggested that the chemisorbed CH_4 is most probably formed on the surface lattice oxygen, which is in a coordinatively unsaturated (c.u.s.) state as created by the outgassing at high temperatures,[5] because the formation of the chemisorbed CH_4 largely depends on the pretreatment of CeO_2. The surface c.u.s. oxygen anions polarize the C–H bonds of CH_4 and accordingly induce a change from the IR inactive mode of CH_4 into the IR active mode of adsorbed CH_4. The chemisorbed CH_4, particularly the strongly chemisorbed species, could be assumed to be the precursor of the activated CH_4 on the surface of the oxide.

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