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Generation of methoxide from methane and oxygen under mild conditions over an Sm_2O_3 catalyst investigated by *in situ* IR spectroscopy

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The generation of methoxide over an Sm_2O_3 catalyst was clearly observed under a CH_4–O_2 atmosphere at 323 K by *in situ* Fourier transform IR spectroscopy.

Methane is the simplest and most abundant of saturated hydrocarbons. However, the molecule is stable and difficult to convert to other useful compounds. Therefore, much attention has been paid to how to activate and convert it in order to utilize it effectively. Partial oxidation over suitable catalysts, such as directive oxidation to formaldehyde and oxidative coupling to C_2 hydrocarbons over suitable catalysts, have been widely studied.[1–5] Among them, it was reported that Sm_2O_3 is one of the most effective catalysts for the oxidative coupling of methane.[4,5] The reactions take place at relatively high temperatures (>773 K), so that few investigations have been performed on characterizing the reaction of CH_4 and O_2 over the catalyst surface directly.

We have been investigating the reactivity of C_1 adsorbed species, as intermediates of catalytic reactions, over an Sm_2O_3 catalyst surface by *in situ* Fourier transform IR (FTIR) spectroscopy.[6]

In this work, we studied the reactivity of CH_4 with O_2 over an Sm_2O_3 catalyst by *in situ* FT-IR spectroscopy to clarify the mechanism of the activation of methane. Here we report the surface species produced over the catalyst under a CH_4–O_2 atmosphere at 323 K, *i.e.* under much more mild conditions compared with those required for partial oxidation, in order to clarify the initial stage of the oxidation of methane over the surface.

The Sm_2O_3 catalyst used in this work was prepared by calcination of $Sm(OH)_3$, obtained by hydrolysis of $Sm(NO_3)_3$ (Wako Pure Chemical) with NH_3 (aq), at 773 K. The catalyst was pressed into a self-supporting disk of 20 mm diameter and set in an IR cell connected with a closed gas circulation system. The catalyst was pretreated under H_2 and O_2 repeatedly at 873 K until the bands attributable to carboxylate like species disappeared in the background spectrum of Sm_2O_3, and then evacuated at 1073 K before use. A CH_4 and O_2 mixture, where the content of CH_4 (99.999% purity) or CD_4 (99.9% Matheson ISOTEC Inc) is 10%, was used in this work and prepared just before the experiment. IR spectra were recorded with a FT-IR spectrometer (Jasco FT-IR 7300). All spectra were measured with 100 scans at 4 cm^{-1} resolution and obtained from the ratio of the background spectrum of Sm_2O_3 to that with adsorbed species. The spectra were also subtracted for methane in the gas phase.

Fig. 1 shows the time dependent IR spectra of surface species formed under a CH_4–O_2 atmosphere at 323 K. When the surface was exposed to the mixed gas, the IR bands attributed to the produced surface species are observed at 1580 and 1319 cm^{-1} as shown in Fig. 1(a). With time, the intensities of these bands increase as shown in Fig. 1(b) and (c). Beside these bands, it is also observed in Fig. 1(a)–(c) that bands at 3658, around 2900 and 1050 cm^{-1} are produced the intensities of which also increase with time. The same investigation was carried out using CD_4–O_2 under the same conditions and the spectrum of the surface species is shown in Fig. 1(d). Comparing the spectra in Fig. 1(b) and (d), the bands related to hydrogen shift to lower wavenumbers in Fig. 1(d). Therefore, the band at 3658 (2695) cm^{-1} can be assigned to ν(OH) (ν(OD)) and the bands at around 2900 (2100) cm^{-1} can be assigned to ν(CH) (ν(CD)). These bands indicate surface species with C–H bond(s) are produced accompanied by OH species under CH_4–O_2 at relatively mild conditions over the Sm_2O_3 surface. In order to assign the surface species in more detail, the IR spectra of d_0-methoxide and d_3-methoxide, produced by the adsorption of CH_3OH and CD_3OD, respectively, and surface species produced under a mixture of CO and O_2 over the same surface were examined and the results are shown in Fig. 2.

Methoxide (CH_3O^-) produced from the adsorption of methanol-d_0 gives IR bands at 2921, 2841 2757 and 1049 cm^{-1} as shown in Fig. 2(a), while d_3-methoxide, produced from the adsorption of methanol-d_4, gives IR bands at 2153, 2027, 1135 and 1021 cm^{-1} as shown in Fig. 2(b). When the surface is exposed to the mixed gas of CO and O_2 at 323 K, surface species, which give IR bands at 1591 and 1320 cm^{-1}, are produced as shown in Fig. 2(c). These are attributable to carbonate like adsorbed species produced by the oxidation of CO over the surface.

By comparing the spectra in Figs. 1 and 2, the surface species produced from CH_4–O_2 under the present conditions can be clearly assigned. The bands at 2928, 2841, 2776 and 1050 cm^{-1}, shown in Fig. 1(c), are attributable to d_0-methoxide. Similarly, the bands at 2164, 2022, 1118 and 1010 cm^{-1}, also shown in Fig. 1(d), are attributable to d_3-methoxide. On the

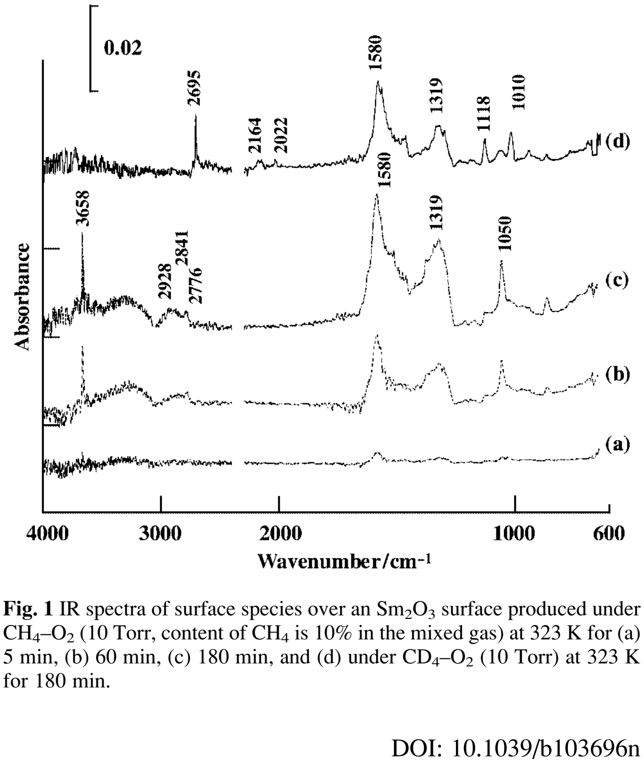

Fig. 1 IR spectra of surface species over an Sm_2O_3 surface produced under CH_4–O_2 (10 Torr, content of CH_4 is 10% in the mixed gas) at 323 K for (a) 5 min, (b) 60 min, (c) 180 min, and (d) under CD_4–O_2 (10 Torr) at 323 K for 180 min.

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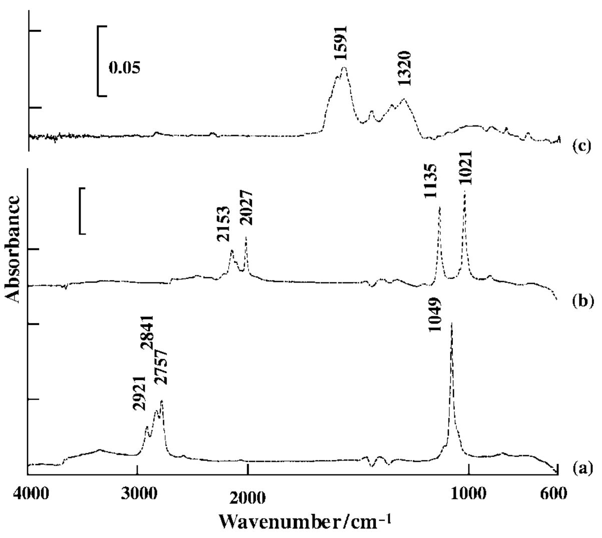

Fig. 2 IR spectra of (a) d_0-methoxide produced from the adsorption of methanol-d_0, (b) d_3-methoxide produced from the adsorption of methanol-d_4 and (c) the surface species produced under CO–O_2 at 323 K over the Sm_2O_3 surface.

other hand, the bands at 1580 and 1319 cm^{-1} shown in Fig. 1 are attributable to adsorbed carbonate like species. Therefore, these results clearly indicate that methoxide is produced directly over the Sm_2O_3 surface under a CH_4–O_2 atmosphere in addition to the production of carbonate at 323 K.

It was confirmed that no IR band attributable to produced surface species was present when the pretreated Sm_2O_3 surface was exposed to CH_4 alone under the same conditions. This suggests that the surface species, attributed to the spectra in Fig. 1, were produced when the surface was exposed to a mixture of CH_4 and O_2.

It was also confirmed that the production rate of methoxide over the surface was strongly dependent on the temperature and the partial pressure of CH_4 in the mixed gas. The production rate of methoxide was relatively slow compared with that of carbonate like species below 300 K and carbonate like species were mainly produced below 273 K. On the other hand, the oxidation of methoxide proceeded further to form formate above 400 K. Furthermore, a relatively low concentration of CH_4 in the mixed gas (as in the present experimental conditions) was favorable for methoxide production. Although further detailed investigations are under way, these results probably reflect the types of oxygen species related to the production of the different types of surface species during oxidation of CH_4 over the surface.

The generation of methyl radicals is widely agreed to occur in the initial stage of the partial oxidation of methane over catalyst surfaces and the formed methyl radicals desorb into the gas phase and dimerize to C_2 hydrocarbons or degrade into CO or CO_2.[7] As a consequence, the reactivity of methyl radicals, produced from methyl radical generators or utilizing stoichiometric reactions, has been widely investigated over various oxide surfaces where partial oxidation of methane effectively proceeds, in order to characterize the partial oxidation of methane.[8–10] However, few reports investigated methane oxidation directly under a CH_4–O_2 atmosphere and clearly confirmed the formation of partially oxidized intermediates, such as methoxide, over the catalyst surfaces. Therefore, the results obtained in this work are notable for clearly confirming the formation of methoxide over Sm_2O_3 from methane and oxygen under relatively mild conditions. The formation of CH_3O–Sm species from CH_4 and O_2 under the present conditions is interesting and important for finding out how to convert methane into other useful compounds under relatively mild conditions as well as clarification of the reaction mechanism of methane oxidation over the catalysts.

Notes and references

1 T. Ito and J. H. Lunsford, *Nature*, 1985, **314**, 721.
2 G. E. Keller and M. M. Bhasin, *J. Catal.*, 1982, **73**, 9.
3 A. Parmaliana and F. Arena, *J. Catal.*, 1997, **167**, 57.
4 K. Otsuka, K. Jinno and A. Morikawa, *Chem. Lett.*, 1985, 499.
5 K. Otsuka, K. Jinno and A. Morikawa, *J. Catal.*, 1986, **100**, 353.
6 Y. Sakata, T. Arimoto, H. Imamura and S. Tsuchiya, *Stud. Surf. Sci. Catal.*, 2000, **130**, 3071 and references therein.
7 J. H. Lunsford, *Langmuir*, 1989, **5**, 12.
8 Y. Tong and J. H. Lunsford, *J. Am. Chem. Soc.*, 1991, **113**, 4741.
9 C. Shi, M. P. Rosynek and J. H. Lunsford, *J. Phys. Chem.*, 1994, **98**, 8371.
10 V. T. Amorebieta and A. J. Colussi, *J. Am. Chem. Soc.*, 1995, **117**, 3856.