In situ Raman Spectroscopic Study of Oxygen Adspecies on a Th-La-O$_x$ Catalyst for Methane Oxidative Coupling Reaction

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The superoxide adspecies O$_2^-$ is identified by in situ Raman spectroscopy on a functioning Th–La–O$_x$ catalyst for methane oxidative coupling reaction at 680–860 °C.

Methane oxidative coupling (MOC) has the potential to form ethane and ethene from natural gas and a large number of catalysts for the reaction have been reported. The oxygen species such as O$_2^-$, O$_2^{2-}$ and O$^-$ involved on catalyst surfaces responsible for the initial methane activation step is of great interest.[1–6] To gain further insight into the nature of the surface oxygen species and their role in the activation of methane, in situ spectroscopic study at the actual reaction conditions is more helpful. Recently, peroxide adspecies O$_2^{2-}$ was reported to be identified in situ on La$_2$O$_3$, Na$^+$-La$_2$O$_3$, Sr^{2+}-La$_2$O$_3$ and Ba^{2+}-MgO catalysts.[7,8] In the present work, in situ laser Raman spectroscopy has been used to characterize the surface oxygen species on a working Th-La-O$_x$ MOC catalyst at 680–860 °C.

The Th-La-O$_x$ (Th:La = 10:1.5, mol ratio) catalyst was prepared by drying (160 °C, 10 h) and calcination (880 °C, 4 h) of a freshly coprecipitated mixture of carbonate and hydroxide. The Th-La-O$_x$ was a very active catalyst for the MOC reaction. Under cofeed reaction conditions of CH$_4$/O$_2$ = 4/1 (mol ratio), GHSV = 6.0×10^4 h^{-1}, atmospheric pressure and 740 °C, a C$_2$-hydrocarbons yield of 14.6% with C$_2$-hydrocarbons selectivity of 55.8% was obtained over the catalyst.

Raman spectra were recorded using a Jobin-Yvon U-1000 Raman spectrometer with argon laser (488.0 nm line, 200 mW) as excitation source; slit width settings corresponded to a resolution of 4 cm^{-1} and 36 scans were accumulated. A high temperature controlled-atmosphere cell[9] was used to obtain in situ spectra on the working Th-La-O$_x$ catalyst; the particle size
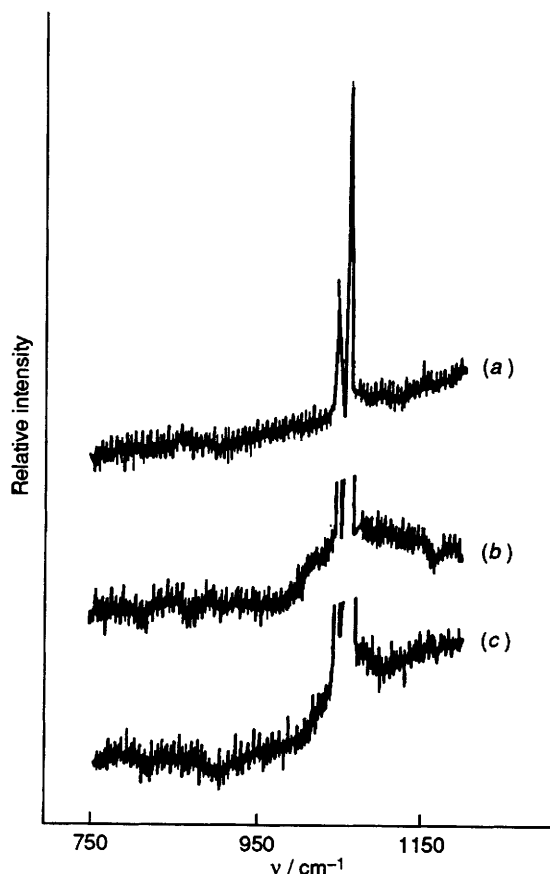

Fig. 1 In situ Raman spectra of the Th-La-O$_x$ catalyst at 740 °C. (a) Spectrum taken 1 h after switching the gas flow from CH$_4$/O$_2$ (4:1, mol ratio) to O$_2$. (b) In a gas flow of CO$_2$. (c) In a gas flow of CO$_2$/H$_2$O(g) (92:8 mol ratio).
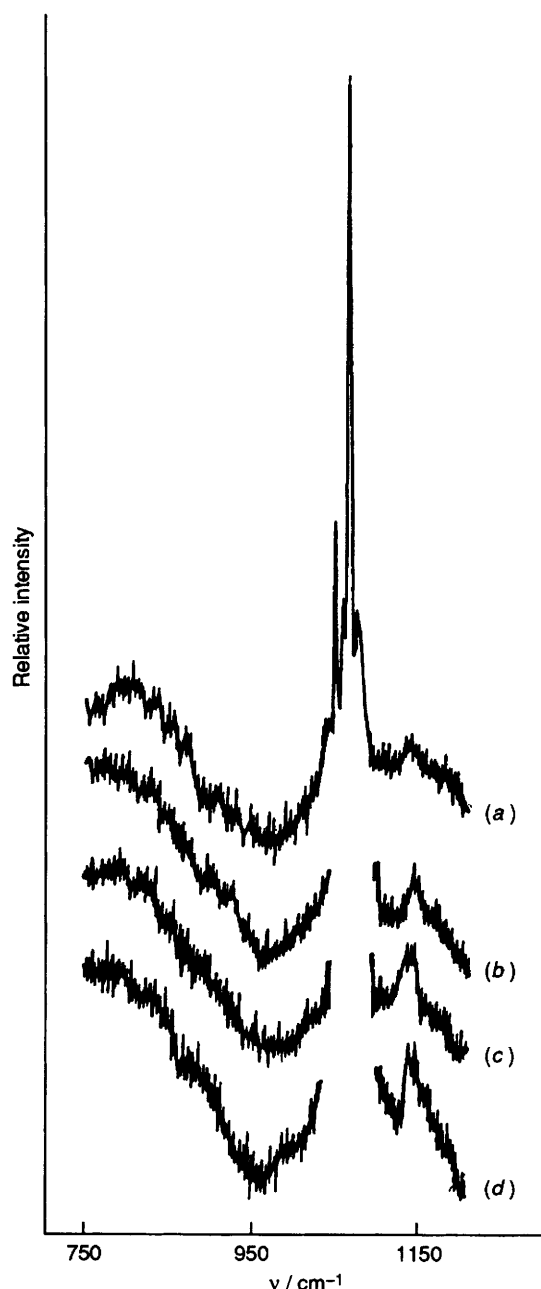

Fig. 2 In situ Raman spectra of the working Th-La-O$_x$ MOC catalyst in a stream of CH$_4$/O$_2$ (4:1, mol ratio) mixture with total gas flow rate of 150 ml min^{-1}, at 1 atm. and the reaction temperature of (a) 860 °C, (b) 800 °C, (c) 740 °C and (d) 680 °C

of the catalyst sample being 50–80 mesh and weight about 1.0 g.

Fig. 1(*a*) shows the *in situ* Raman spectrum of the Th-La-O$_x$ at 740 °C in a flow of O$_2$ taken 1 h after switching the gas flow from CH$_4$/O$_2$ (4/1) mixture. A pair of bands at 1060 and 1046 cm^{-1} were clearly observed. These bands can be assigned to surface carbonate species CO$_3^{2-}$.[10] It is noteworthy that no band assignable to dioxygen adspecies was observed under these conditions.

CO$_2$ and H$_2$O are the products of the MOC reaction. To test whether adsorption of CO$_2$ and H$_2$O on the Th-La-O$_x$ may cause the assignment confused with the Raman band of dioxygen adspecies, a spectrum was recorded when the sample was treated in a flow of CO$_2$ or CO$_2$/H$_2$O(g), respectively. The results show that the adsorption of CO$_2$ or CO$_2$/H$_2$O(g) only cause the increasing band intensity of CO$_3^{2-}$.

Fig. 2 exhibits a series of *in situ* spectra of the working Th-La-O$_x$ catalyst at reaction temperatures of 860, 800, 740 and 680 °C, respectively, under cofeed MOC reaction conditions. Raman bands which can be clearly resolved are those at 1060, 1046 and 1140 cm^{-1}. The very strong bands at 1060 and 1046 cm^{-1} together with a number of shoulders on these bands are attributed to surface carbonate species CO$_3^{2-}$ [shown only in Fig. 2(*a*)]. The band observed at 1140 cm^{-1} can be ascribed to the O–O stretching mode for superoxide species O$_2^-$ on the surface of the Th-La-O$_x$ catalyst. This band position is consistent with those of superoxide adspecies observed on other oxides,[11–13] and with those of the superoxide ligand reported in the matrixes and complexes.[14] It can be clearly observed that the relative intensity of the Raman band at 1140 cm^{-1} increased with decreasing reaction temperature. The intensity of the 1140 cm^{-1} band was also found to enhance with increasing O$_2$ concentration in the feed.

Generally speaking, adsorbed oxygen species transform on the surface of metal oxide catalysts according to eqn. (1).[15,16]

$$O_2 \rightleftharpoons \underline{O_2} \xrightarrow{e} \underline{O_2^-} \xrightarrow{e} \underline{O_2^{2-}} \rightarrow \underline{2O^-} \xrightarrow{2e} 2O^{2-} \text{ (lattice)} \quad (1)$$

(an underlined chemical species signifies a chemisorbed or surface species)

O$_2^-$ adspecies may form from a chemisorbed O$_2$ by acquiring an electron from the metal oxide. The reason that no Raman band of dioxygen adspecies was observed in Fig. 1(*a*) may be that the charged dioxygen adspecies could not be formed easily on the Th-La-O$_x$ surface due to weak electron donation of the surface under this condition—CH$_4$-free flowing O$_2$-stream. This result is consistent with the work of C. Li *et al.* They found that no IR signal corresponding to O$_2^{2-}$ or O$_2^-$ adspecies on cerium oxide could be detected at the temperature of 420 K under the pure O$_2$ atmosphere.[13]. However,

when CH$_4$ was cofed with O$_2$ to pass the catalyst, the catalyst surface may be partially reduced by CH$_4$, then adsorbed O$_2$ can gain an electron easily from the surface and transform into O$_2^-$ adspecies. It has been reported that O$_2^-$ was able to activate methane at the MOC reaction temperature.[4,17] Thus, the O$_2^-$ formed primarily may subsequently take part in methane activation step or transform further to O$_2^{2-}$ adspecies *via* gaining an electron again from the surface. The results of the present work also indicate that, under the reaction temperature between 680 and 880 °C, the steady concentration of O$_2^{2-}$ species, whose Raman signal is usually expected to appear in the region of 750–900 cm^{-1}, on the surface of functioning Th-La-O$_x$ MOC catalyst is below the detectable limit of the Raman spectroscopy.

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