

# In situ FTIR study on the active oxygen species for the conversion of methane to methanol

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In situ FTIR studies showed the generation of a peroxide species by the contact of a H<sub>2</sub>-O<sub>2</sub> gas mixture or of N<sub>2</sub>O with Fe-Al-P-O catalysts at  $\geq 573$  K. This oxygen species oxidized methane into methanol at  $\geq 473$  K, through the formation of methoxide species on the catalysts.

**Keywords:** FT-IR; oxygen species; methane; methanol; iron aluminum phosphate

## 1. Introduction

Direct oxidation of methane into methanol is one of the most challenging subjects in catalysis. It is extremely difficult to obtain methanol by direct oxidation of methane with dioxygen over solid catalysts under atmospheric pressure [1,2]. Recently, we have reported that the selective oxidation of methane to methanol can be achieved by cofeeding hydrogen with oxygen and methane over iron phosphate catalyst [3]. Pulse reaction studies suggested that an active oxygen species was formed in the presence of hydrogen as an activator of O<sub>2</sub> [4]. Hydrogen peroxide and nitrous oxide were effective oxidants for the direct oxidation of methane to methanol over the same catalyst [4–6]. The object of this study is to get further insight into the nature of the oxygen species and its role in the conversion of methane to methanol. So far, the reports concerning the spectroscopic identification of active oxygen species and the reaction intermediate, especially in the partial oxidation of methane into methanol, are very scarce. Recently, superoxide species O<sub>2</sub><sup>-</sup> and peroxide species O<sub>2</sub><sup>2-</sup> were identified on Th-La-O and BaO-MgO catalysts by in situ Raman spectroscopy during the oxidative coupling of methane [7,8]. In this communication, we report an attempt to characterize the active oxygen

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species and the reaction intermediate in the oxidation of methane to methanol by using in situ infrared spectroscopy.

## 2. Experimental

The Fe-Al-P-O sample for this study was prepared by a sol-gel method [9]. According to this method, propylene oxide was added to a mixed aqueous solution of  $\text{FeCl}_3$ ,  $\text{AlCl}_3$  and  $\text{NH}_4\text{H}_2\text{PO}_4$  at 273 K. The mole ratio of Fe : Al : P in the solution was adjusted to be 0.50 : 0.50 : 1.00. The solution was gelled in 2 h and the gel was aged for 20 h at room temperature. The gel was dried at 333 and 393 K for 20 h after having been thoroughly washed with ethanol. The resultant was calcined at 573 K for 20 h and at 823 K for 5 h in air. The BET surface area of the sample thus prepared was  $275 \text{ m}^2 \text{ g}^{-1}$ . X-ray diffraction analysis showed that this sample was amorphous. However, the high specific surface area was proven to be important for gaining a good signal to noise ratio in IR measurements. The catalytic activities were measured under atmospheric pressure using a conventional flow system with a fixed-bed quartz reactor. The details about the reactor design and the experimental procedure have been described elsewhere [4].

For IR-transmission measurement, a Fe-Al-P-O sample was pressed into a self-supporting wafer. The IR experiments were carried out with a Fourier-transform infrared spectrometer (JASCO FT/IR-7000). The quartz-made IR cell equipped with two NaCl windows was connected to a closed-gas-circulation system linked to a vacuum line. The sample in the cell could be heated to 1000 K.

## 3. Results and discussion

The results of the oxidation of methane on the Fe-Al-P-O catalyst with different oxidants are shown in table 1. Similar to the results reported for iron phosphate catalyst [3–6], the cofeeding of  $\text{H}_2$  with  $\text{O}_2$  remarkably increased the conversion of  $\text{CH}_4$  to  $\text{CH}_3\text{OH}$  over Fe-Al-P-O catalyst.  $\text{N}_2\text{O}$  was also a potent oxidant for the

Table 1  
Oxidation of methane by different oxidants on the Fe-Al-P-O catalyst<sup>a</sup>

| Oxidant                   | Temp. (K) | $\text{CH}_4$ conv. (%) | Selectivity (%)        |      |      |               |
|---------------------------|-----------|-------------------------|------------------------|------|------|---------------|
|                           |           |                         | $\text{CH}_3\text{OH}$ | HCHO | CO   | $\text{CO}_2$ |
| $\text{O}_2$              | 723       | 0.16                    | 3.8                    | 25.5 | 58.5 | 12.2          |
| $\text{O}_2 + \text{H}_2$ | 723       | 2.05                    | 23.5                   | 25.6 | 42.4 | 5.5           |
| $\text{N}_2\text{O}$      | 623       | 2.88                    | 32.5                   | 20.5 | 40.0 | 7.0           |

<sup>a</sup> Reaction conditions:  $P(\text{CH}_4) = 33.8 \text{ kPa}$ ,  $P(\text{O}_2) = 8.4 \text{ kPa}$ ,  $P(\text{H}_2) = 50.7 \text{ kPa}$ ,  $P(\text{N}_2\text{O}) = 16.9 \text{ kPa}$ ,  $F = 3.6 \text{ dm}^3 \text{ h}^{-1}$ ,  $W = 0.10 \text{ g}$ .

conversion of  $\text{CH}_4$  to  $\text{CH}_3\text{OH}$  over this catalyst. The space time yield (per gram) increased by about ten times compared with that of the iron phosphate catalyst reported previously [3,4] because of the higher surface area of the catalyst used in this study.

Fig. 1 shows the in situ IR spectra of the Fe-Al-P-O catalyst obtained in  $\text{H}_2$ - $\text{O}_2$  gas mixture at different temperatures. The water produced during the experiments was always condensed using a dry ice-ethanol trap. The absorption of IR by the catalyst itself at each temperature was subtracted. An absorption band at  $895\text{ cm}^{-1}$  appeared as the temperature was increased to 573 K, and its intensity increased further at 623 K. This band did not appear in the presence of  $\text{O}_2$  or  $\text{H}_2$  alone at these temperatures. The bands at 3742 and  $3664\text{ cm}^{-1}$ , which were assigned to the adsorbed OH groups, appeared also in  $\text{H}_2$  without  $\text{O}_2$ . Thus, the OH groups must be formed from the reaction of  $\text{H}_2$  with the catalyst surface. A weak absorption at  $1075\text{ cm}^{-1}$  was observed at 473 K in the presence of  $\text{H}_2$  and  $\text{O}_2$ . However, this absorption disappeared as the temperature was increased to 573 K.

The band at  $895\text{ cm}^{-1}$  shifted to  $849\text{ cm}^{-1}$  when  $^{16}\text{O}_2$  was replaced by  $^{18}\text{O}_2$ . Three absorption bands at 895, 870 and  $849\text{ cm}^{-1}$ , which should be assigned to the stretching modes of  $^{16}\text{O}-^{16}\text{O}$ ,  $^{16}\text{O}-^{18}\text{O}$  and  $^{18}\text{O}-^{18}\text{O}$ , respectively, were observed at  $\geq 573\text{ K}$  when a mixture of  $^{16}\text{O}_2$ ,  $^{16}\text{O}^{18}\text{O}$  and  $^{18}\text{O}_2$  was added in the presence of  $\text{H}_2$ . These observations suggest that a diatomic type of adsorbed oxygen species is generated when  $\text{O}_2$  and  $\text{H}_2$  coexist.

The in situ IR measurement of the Fe-Al-P-O catalyst in the presence of  $\text{N}_2\text{O}$  showed an absorption band at  $890\text{ cm}^{-1}$  besides the bands ( $1286$  and  $2220\text{ cm}^{-1}$ ) ascribed to gas phase  $\text{N}_2\text{O}$  when the temperature was increased above 573 K. The intensity of this band was greatly enhanced when the catalyst was pre-reduced with

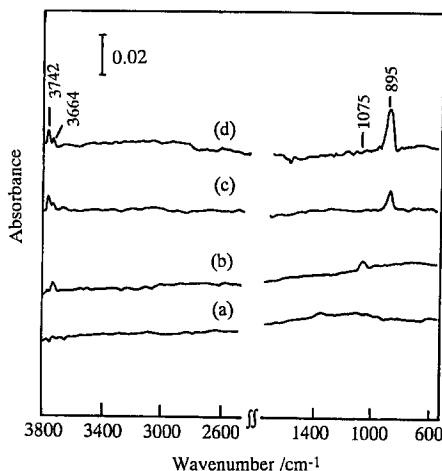
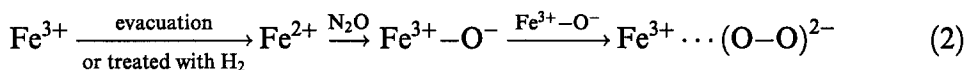
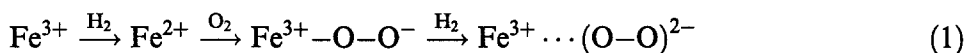


Fig. 1. IR spectra of the Fe-Al-P-O catalyst in  $\text{H}_2$ - $\text{O}_2$  gas mixture ( $P(\text{H}_2) = 13.3\text{ kPa}$ ,  $P(\text{O}_2) = 1.33\text{ kPa}$ ). (a) 298 K; (b) 473 K; (c) 573 K; (d) 623 K. The absorbance due to the catalyst itself at each temperature has been subtracted.

H<sub>2</sub> at 673 K. These results suggest that the same oxygen species giving the absorption band at 890–895 cm<sup>-1</sup> is generated both in the H<sub>2</sub>-O<sub>2</sub> gas mixture and in N<sub>2</sub>O.

Generally, the peroxide species (O<sub>2</sub><sup>2-</sup>) is observed at the absorption region of 800–940 cm<sup>-1</sup> [10]. It has been suggested that the O<sub>2</sub><sup>2-</sup> species adsorbed on Fe<sub>2</sub>O<sub>3</sub> appears at ca. 900 cm<sup>-1</sup> [11]. The O<sub>2</sub><sup>2-</sup> on a reduced CeO<sub>2</sub> was observed at 883 cm<sup>-1</sup> [12]. The O<sub>2</sub><sup>2-</sup> formed from N<sub>2</sub>O on CaO was observed at 880 cm<sup>-1</sup> [13]. Thus, we suggest that the oxygen species observed in this study is an adsorbed O<sub>2</sub><sup>2-</sup> species. In the previous studies, we have suggested that the iron sites on the catalyst surface are the active centers for the conversion of methane to methanol by the H<sub>2</sub> and O<sub>2</sub> gas mixture or by N<sub>2</sub>O [4,6]. Thus, it is reasonable to assume that the O<sub>2</sub><sup>2-</sup> is adsorbed on the surface iron site. The formation of such adsorbed species in the H<sub>2</sub>-O<sub>2</sub> gas mixture and in N<sub>2</sub>O may occur as follows:



The intensity of the band at 890–900 cm<sup>-1</sup> formed in both cases was reduced by evacuation at > 473 K. However, the intensity was nearly unchanged when the evacuation temperature was lower than 473 K. The reactivity of this oxygen species with CH<sub>4</sub> was investigated by introducing CH<sub>4</sub> to the cell. For this experiment, the catalyst had been contacted with N<sub>2</sub>O at 673 K, followed by evacuation at 298 K. The spectrum (a) in fig. 2 was observed after the addition of CH<sub>4</sub> (5.3 kPa) at 298 K. The spectrum was not changed by the addition of CH<sub>4</sub> at 298 K. The results in

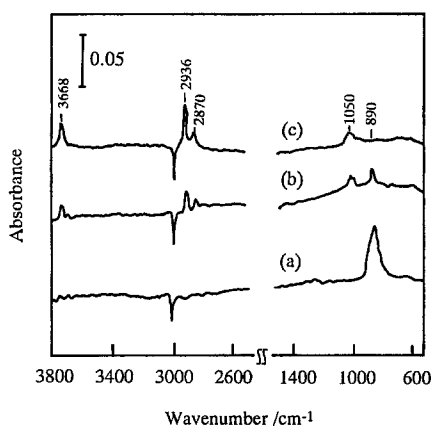


Fig. 2. IR spectra after the reaction of CH<sub>4</sub> with the oxygen species generated from N<sub>2</sub>O at 673 K (*P*(CH<sub>4</sub>) = 5.33 kPa). (a) 298 K; (b) 473 K; (c) 573 K. The spectrum was collected after 30 min at each temperature. The absorbance due to the gaseous CH<sub>4</sub> at each temperature was subtracted. The reverse peak at 3010 cm<sup>-1</sup> arose from the difference in the amounts of gaseous CH<sub>4</sub>.

fig. 2 (b) showed that the intensity of the band at  $890\text{ cm}^{-1}$  decreased significantly when the temperature was raised to 473 K and the bands at 3668, 2936, 2870 and  $1050\text{ cm}^{-1}$  appeared simultaneously. The absorption at  $3668\text{ cm}^{-1}$  must be assigned to the newly formed OH group due to the reaction of  $\text{CH}_4$  with the iron peroxide species. The bands at 2936 and  $2870\text{ cm}^{-1}$  can be assigned to the asymmetric and symmetric stretching vibrations of  $\text{CH}_3$  groups and the bands at  $1050\text{ cm}^{-1}$  to the C–O stretching vibration of methoxide species [14]. The intensities of these bands further increased and that at  $890\text{ cm}^{-1}$  disappeared at 573 K. The reactivity of the oxygen species generated in the  $\text{H}_2\text{--O}_2$  gas mixture with  $\text{CH}_4$  was also studied and similar results to those of fig. 2 were obtained. These observations indicate that the iron peroxide species reacts with  $\text{CH}_4$  at  $\geq 473\text{ K}$ , forming OH and  $\text{CH}_3\text{O}$  groups on the catalyst surface.

In conclusion, the active oxygen species newly formed by cofeeding hydrogen over  $\text{FePO}_4$  and Fe–Al–P–O catalysts is an adsorbed iron peroxide species. We believe that this oxygen species is responsible for the direct conversion of methane to methanol at low temperatures (473–673 K).

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