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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_2–O_2 gas mixture or of N_2O with Fe-Al-P-O catalysts at $\geqslant 573$ K. This oxygen species oxidized methane into methanol at $\geqslant 473$ 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_2 [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 adspecies O_2^- and peroxide species O_2^{2-} 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 $FeCl_3$, $AlCl_3$ and $NH_4H_2PO_4$ 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 $m^2\ g^{-1}$. 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 H_2 with O_2 remarkably increased the conversion of CH_4 to CH_3OH over Fe-Al-P-O catalyst. N_2O was also a potent oxidant for the

Table 1
Oxidation of methane by different oxidants on the Fe-Al-P-O catalyst [a]

Oxidant	Temp. (K)	CH_4 conv. (%)	Selectivity (%)			
			CH_3OH	HCHO	CO	CO_2
O_2	723	0.16	3.8	25.5	58.5	12.2
$O_2 + H_2$	723	2.05	23.5	25.6	42.4	5.5
N_2O	623	2.88	32.5	20.5	40.0	7.0

[a] Reaction conditions: $P(CH_4) = 33.8$ kPa, $P(O_2) = 8.4$ kPa, $P(H_2) = 50.7$ kPa, $P(N_2O) = 16.9$ kPa, $F = 3.6\ dm^3\ h^{-1}$, $W = 0.10$ g.

conversion of CH_4 to CH_3OH 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 H_2–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 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 O_2 or H_2 alone at these temperatures. The bands at 3742 and 3664 cm^{-1}, which were assigned to the adsorbed OH groups, appeared also in H_2 without O_2. Thus, the OH groups must be formed from the reaction of H_2 with the catalyst surface. A weak absorption at 1075 cm^{-1} was observed at 473 K in the presence of H_2 and O_2. However, this absorption disappeared as the temperature was increased to 573 K.

The band at 895 cm^{-1} shifted to 849 cm^{-1} when $^{16}O_2$ was replaced by $^{18}O_2$. Three absorption bands at 895, 870 and 849 cm^{-1}, which should be assigned to the stretching modes of $^{16}O-^{16}O$, $^{16}O-^{18}O$ and $^{18}O-^{18}O$, respectively, were observed at $\geqslant 573$ K when a mixture of $^{16}O_2$, $^{16}O^{18}O$ and $^{18}O_2$ was added in the presence of H_2. These observations suggest that a diatomic type of adsorbed oxygen species is generated when O_2 and H_2 coexist.

The in situ IR measurement of the Fe-Al-P-O catalyst in the presence of N_2O showed an absorption band at 890 cm^{-1} besides the bands (1286 and 2220 cm^{-1}) ascribed to gas phase N_2O when the temperature was increased above 573 K. The intensity of this band was greatly enhanced when the catalyst was pre-reduced with

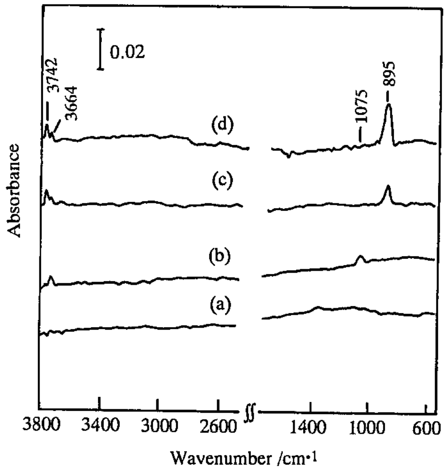

Fig. 1. IR spectra of the Fe-Al-P-O catalyst in H_2–O_2 gas mixture ($P(H_2) = 13.3$ kPa, $P(O_2) = 1.33$ kPa). (a) 298 K; (b) 473 K; (c) 573 K; (d) 623 K. The absorbance due to the catalyst itself at each temperature has been subtracted.

H_2 at 673 K. These results suggest that the same oxygen species giving the absorption band at 890–895 cm^{-1} is generated both in the H_2–O_2 gas mixture and in N_2O.

Generally, the peroxide species (O_2^{2-}) is observed at the absorption region of 800–940 cm^{-1} [10]. It has been suggested that the O_2^{2-} species adsorbed on Fe_2O_3 appears at ca. 900 cm^{-1} [11]. The O_2^{2-} on a reduced CeO_2 was observed at 883 cm^{-1} [12]. The O_2^{2-} formed from N_2O on CaO was observed at 880 cm^{-1} [13]. Thus, we suggest that the oxygen species observed in this study is an adsorbed O_2^{2-} 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_2 and O_2 gas mixture or by N_2O [4,6]. Thus, it is reasonable to assume that the O_2^{2-} is adsorbed on the surface iron site. The formation of such adsorbed species in the H_2–O_2 gas mixture and in N_2O may occur as follows:

$$Fe^{3+} \xrightarrow{H_2} Fe^{2+} \xrightarrow{O_2} Fe^{3+}\text{–O–O}^{-} \xrightarrow{H_2} Fe^{3+}\cdots(\text{O–O})^{2-} \tag{1}$$

$$Fe^{3+} \xrightarrow[\text{or treated with } H_2]{\text{evacuation}} Fe^{2+} \xrightarrow{N_2O} Fe^{3+}\text{–O}^{-} \xrightarrow{Fe^{3+}\text{–O}^{-}} Fe^{3+}\cdots(\text{O–O})^{2-} \tag{2}$$

The intensity of the band at 890–900 cm^{-1} 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_4 was investigated by introducing CH_4 to the cell. For this experiment, the catalyst had been contacted with N_2O at 673 K, followed by evacuation at 298 K. The spectrum (a) in fig. 2 was observed after the addition of CH_4 (5.3 kPa) at 298 K. The spectrum was not changed by the addition of CH_4 at 298 K. The results in

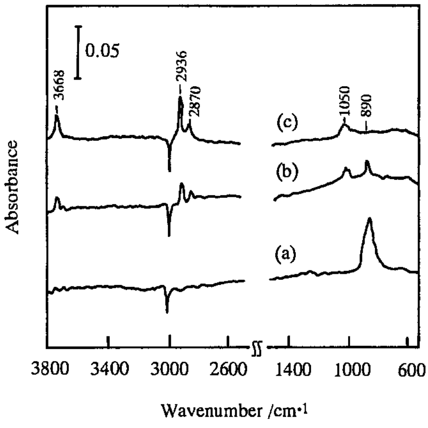

Fig. 2. IR spectra after the reaction of CH_4 with the oxygen species generated from N_2O at 673 K ($P(CH_4) = 5.33$ kPa). (a) 298 K; (b) 473 K; (c) 573 K. The spectrum was collected after 30 min at each temperature. The absorbance due to the gaseous CH_4 at each temperature was subtracted. The reverse peak at 3010 cm^{-1} arose from the difference in the amounts of gaseous CH_4.

fig. 2 (b) showed that the intensity of the band at 890 cm^{-1} decreased significantly when the temperature was raised to 473 K and the bands at 3668, 2936, 2870 and 1050 cm^{-1} appeared simultaneously. The absorption at 3668 cm^{-1} must be assigned to the newly formed OH group due to the reaction of CH_4 with the iron peroxide species. The bands at 2936 and 2870 cm^{-1} can be assigned to the asymmetric and symmetric stretching vibrations of CH_3 groups and the bands at 1050 cm^{-1} to the C–O stretching vibration of methoxide species [14]. The intensities of these bands further increased and that at 890 cm^{-1} disappeared at 573 K. The reactivity of the oxygen species generated in the H_2–O_2 gas mixture with 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 CH_4 at $\geqslant$473 K, forming OH and CH_3O groups on the catalyst surface.

In conclusion, the active oxygen species newly formed by cofeeding hydrogen over $FePO_4$ 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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