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Surface Species Produced by the Reaction between Methane and Oxygen Radical Anion $O^{\bullet -}$ on MgO at 298 K

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The reaction between gaseous CH_4 and surface $O^{\bullet -}$ on MgO was studied at 298 K. The surface $O^{\bullet -}$ was formed through a reaction of N_2O with electrons trapped on MgO and examined with EPR. One mole of surface $O^{\bullet -}$ determined by EPR was found to react with one mole of CH_4 determined by GC. The resultant surface species were observed by an FT-IR and were identified to be methoxide and weakly absorbed methanol. The adsorbed methanol was produced by the reaction of methyl radicals (the initial product) with the surface hydroxy groups. Both products (methoxide and methanol) are found to be decomposed to CO and H_2 at the elevated temperature such as 773 K.

Methane is the main component of natural gas. At present methane is converted to useful chemicals by indirect methods through synthesis gas. Direct methods of methane conversion to methanol (partial oxidation) or ethylene (oxidative coupling of methane) have been recommended from the energy-saving standpoint. However, the product selectivity values reported so far are still too low for practical applications. In order to improve them, establishment of principles of the direct conversion of methane to useful chemicals is important.

In the partial oxidation and oxidative coupling of methane, $O^{\bullet -}$ has been pointed out as an active surface species. Examples are MoO_3/SiO_2 and V_2O_5/SiO_2 catalysts for partial oxidation of methane and Li/MgO catalyst for oxidative coupling of methane.[1—4] In those reactions, active oxygen ion $O^{\bullet -}$ (oxygen radical anion) has been suggested to activate methane.

Methane has been found to react with $O^{\bullet -}$ on MgO at 298 K or even lower temperatures.[5] In this report the reaction between methane and $O^{\bullet -}$ has been suggested to occur in 2 steps. First $O^{\bullet -}$ abstracts one hydrogen atom from methane and produces a methyl radical.

$$CH_4 + O^{\bullet -} \rightarrow CH_3\cdot + OH^- \quad (1)$$

Then the methyl radical reacts with surface oxide anion O^{2-}, and produces a methoxide.

$$CH_3\cdot + O^{2-} \rightarrow OCH_3{}^- + e^- \quad (2)$$

$O^{\bullet -}$ was detected by EPR,[6] but the produced surface species (perhaps methoxide) has not been detected. The concentration of the species was smaller than the detectable level of the IR when those experiments were performed. Thus, the second reaction scheme was a speculation from the reaction between ethane and $O^{\bullet -}$; moreover, the stoichiometry of the first reaction was not clear. So the purpose of this research is to establish the stoichiometry and to detect the surface products (probably methoxide) by recently advanced highly sensitive FT-IR, and to clarify the mechanism of methane–$O^{\bullet -}$ reaction. The mechanism may also help to improve the direct oxidation for example, as methanol synthesis on MoO_3/SiO_2.

Experimental

Ube high surface area MgO powder was used as a precursor. The powder was hydrated to $Mg(OH)_2$ in boiling distilled water for 12 h, extruded into pellets of 1 mm diameter (about 10 mm long) using a hypodermic syringe, and dried in air at 393 K.[6] It was then evacuated at 773 K for 3 h. The $O^{\bullet -}$ radical anion was produced in the same manner as reported previously.[6] Namely, the UV-irradiated MgO was reacted with N_2O and then $O^{\bullet -}$ was produced on MgO. The EPR spectra of $O^{\bullet -}$ were obtained with a JEOL JES-FE-1X spectrometer (X-band) at 77 K. The reactor system is shown in Fig. 1, it has a quartz reactor attached by an EPR tube as a side arm. The g values were evaluated by Mn^{2+} included in Ube MgO (4.0 ppm/mol). The concentration of $O^{\bullet -}$ radical anion was also evaluated on the basis of Mn^{2+} content.

Infrared spectra of surface species on MgO were obtained by FT-IR (Fourier transform Infrared Spectrometer) JASCO 5300 spectrometer. The IR cell was also connected directly to the reaction system (Fig. 1). MgO was degassed at 773 K for 1 h in a cell for FT-IR measurements. The IR cell used here is shown in Fig. 2. Before and after the introduction of 133 Pa of methane on MgO with $O^{\bullet -}$ radical anion, the sample spectra were recorded. In order to identify the adsorbed species, 133 Pa of methanol was introduction on the heat treated (773 K for 1 h) MgO at 298 K (and 373 K).

The amount of methane reacted with $O^{\bullet -}$ was measured by GC (Gas chromatography) M-200 (Aera Japan) with Porapak Q and MS 5A columns. 267 Pa of methane–Ar mixed gas was introduced on $O^{\bullet -}$/MgO. Decrease of methane in the mixed gas was calculated by the change of the methane/Ar ratio. After the reaction between methane and $O^{\bullet -}$ on MgO, catalyst was heated at 773 K for 1

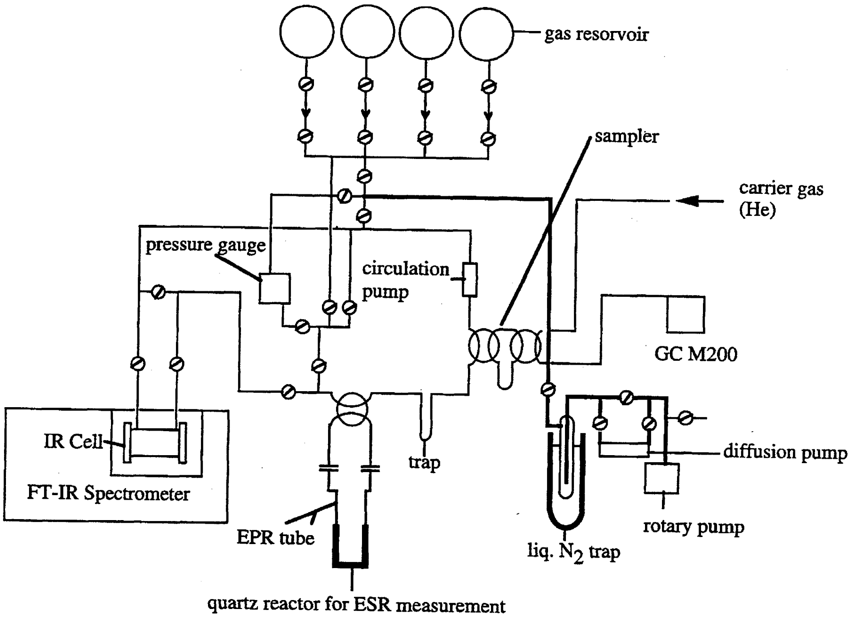

Fig. 1. A schematic diagram of the vacuum systems used in this research.

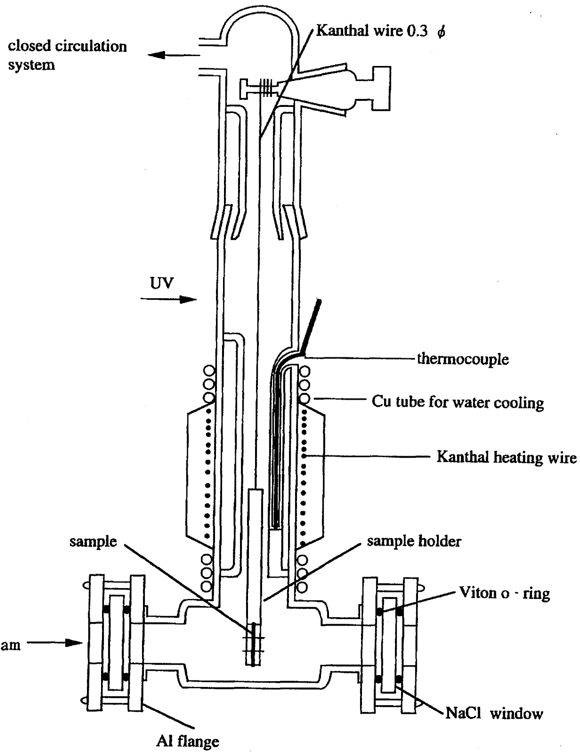

Fig. 2. Infrared cell used in order to detect the surface species produced by the reaction between methane and $O^{\bullet -}$ on MgO at 298 K.

h in the presence of 133 Pa of Ar in order to analyze the surface species by GC M-200. Analysis of desorption products of methanol was also performed as a reference experiment. After methanol was absorbed at 298 K, the catalyst was heated at 773 K for 1 h in the presence of 133 Pa of Ar (Ar was introduced in order to analyze the desorption products of the absorbed methanol). Then the product from absorbed methanol was analyzed by GC M-200.

Results

Reaction between Methane and $O^{\bullet -}$ on MgO at 298 K. The spectrum in Fig. 3 is characterized by $g_{\perp}=2.044$ and $g_{\parallel}=2.003$, which is a typical powder spectrum for an unpaired electron in nearly axial symmetry. This result is in good agreement with the spectrum of $O^{\bullet -}$ reported in Williamson and Lunsford.[7] Upon introduction of 133 Pa of CH_4 to $O^{\bullet -}$ (MgO) at 298 K, the EPR signal of $O^{\bullet -}$ disappeared.

Figure 4 shows the concentration of $O^{\bullet -}$ evaluated by EPR as a function of evacuation temperature of $Mg(OH)_2$. The concentration reached a maximum when the evacuation temperature is 773 K. Thus, the sample was usually evacuated at 773 K. The reaction stoichiometry between methane and $O^{\bullet -}$ was also studied. Concentration of $O^{\bullet -}$ was controlled by UV irradiation time. As is shown in Fig. 5 one mole of $O^{\bullet -}$ was proved to react with one mole of methane.

Surface Species Produced by Methane–$O^{\bullet -}$ Reaction on MgO at 298 K. To detect and identify the surface species, $O^{\bullet -}$ was prepared on MgO wafer. After the introduction of 133 Pa of methane and evacuation, the spectrum was recorded using FT-IR 5300. The spectrum of the resul-

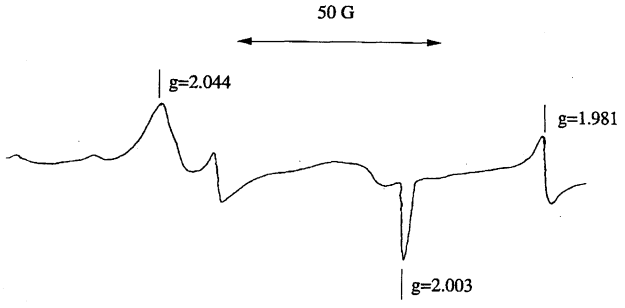

Fig. 3. EPR spectra of $O^{\bullet -}$ measured at 77 K on MgO degassed at 773 K.

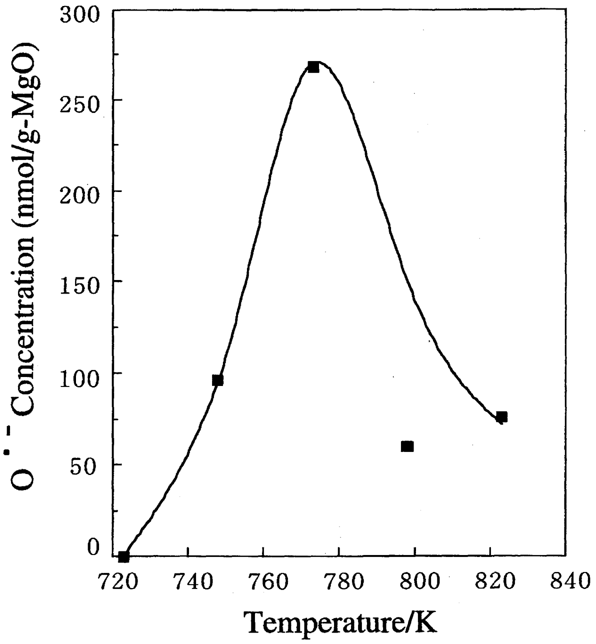

Fig. 4. $O^{\bullet -}$ concentration on MgO (evaluated by EPR) degassed at various temperatures.

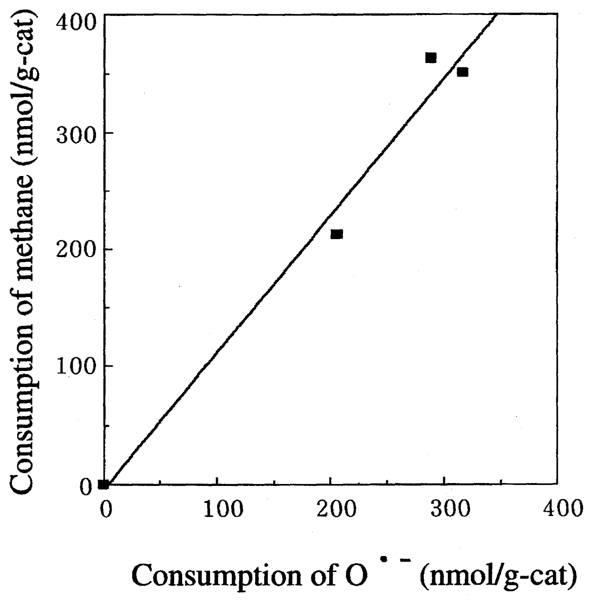

Fig. 5. Variation of methane reacted with $O^{\bullet -}$ on MgO at 298 K as a function of the concentration of $O^{\bullet -}$.

tant species is shown in Fig. 6(a). A band at 1250 cm^{-1} was assigned to N=N=O bond of N_2O. A broad band at 1350—1800 cm^{-1} was assigned to the bending mode of O–H bond of H_2O (this signal could not be subtracted out from the background spectrum completely). Bands at 1053 cm^{-1} and 1107—1092 cm^{-1} were assigned to O–C bonds. These bands must be O–C bonds of either methanol or methoxide. A band of the asymmetric streching mode of C–H bond was observed at 2959 cm^{-1}. In order to identify the surface species observed, the isotope shift by $^{13}CH_4$ was examined in the same manner.

The spectrum of surface species from $^{13}CH_4$ and $O^{\bullet -}$ is shown in Fig. 6(b). A band at 1250 cm^{-1} was unchanged, while a new band was observed at 1027 cm^{-1}. The latter was identified to be the isotopic peak (O–^{13}C bond) of 1053 cm^{-1} band of O–C bond, of which the calculated value was 1030 cm^{-1}. And the isotopic peak (^{13}C–H bond) of 2959 cm^{-1} was observed at 2954 cm^{-1}; its calculated value was 2950 cm^{-1}.

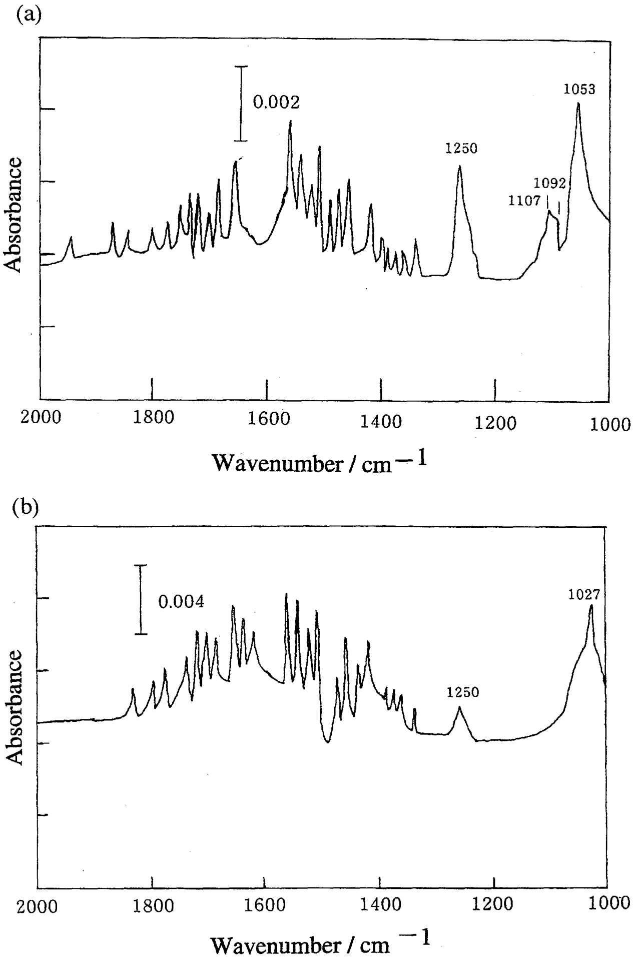

Fig. 6. FT-IR spectra of surface species produced by the methane–$O^{\bullet -}$ reaction (a) and $^{13}CH_4$–$O^{\bullet -}$ (b).

The spectrum of absorbed methanol at 298 K is shown in Fig. 7(a). Bands at 1108 and 1060 cm^{-1} were assigned to absorbances due to O–C bonds. These bands were in good agreement with those that Kagels assigned to methanol weakly absorbed on MgO.[8] So bands at 1108 and 1060 cm^{-1} in Fig. 6 should be the O–C bond of methanol. When methanol was absorbed on MgO at 373 K, a different spectrum was observed. The spectrum of absorbed molecules is shown in Fig. 7(b). A band at 1113—1094 cm^{-1} must also be due to O–C bond. This band was in good agreement with those that Kagels assigned to methoxide.[8] From the results of Fig. 7, a band at 1053 cm^{-1} in Fig. 6(a) was assigned to the O–C bond of weakly adsorbed methanol and a band at 1107—1092 cm^{-1} in Fig. 6(a) was assigned to the O–C bond of methoxide.

Desorption Products of Surface Species Produced by Methane–$O^{\bullet -}$ Reaction on MgO at 298 K. To clarify the

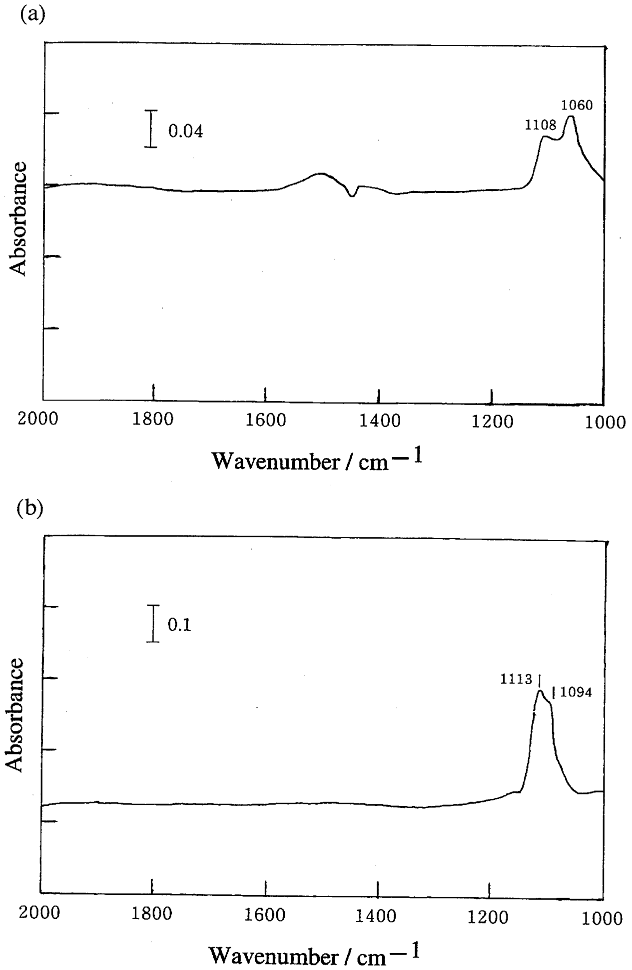

Fig. 7. FT-IR spectra of surface species absorbed on MgO, when methanol was absorbed on MgO at 298 (a) and 373 K (b).

behavior of surface methanol and methoxide produced by the reaction between methane and $O^{\bullet -}$, a desorption experiment was carried out at 773 K after production of surface species on MgO at 298 K. A small amount of CO (31 nmol g^{-1} of MgO) was detected as a main desorption product. So methoxide produced on MgO at 298 K must be decomposed to CO and H_2, as has been suggested by Aika and Lunsford.[5] In order to clarify the behavior of methanol produced on MgO at 298 K, the reference experiment described in the Experimental section was carried out. The main desorption product from absorbed methanol was also CO. Methanol and methoxide produced on MgO at 298 K must be decomposed to CO and H_2, when they were heated at 773 K for 1 h.

Discussion

FT-IR measurements showed that methoxide and methanol were produced by methane–$O^{\bullet -}$ reaction on MgO at 298 K. Methoxide should be produced through a reaction as is shown in Eq. 2. But the reaction steps through which methanol was produced was not clear. We propose that the steps should be Eq. 3 or Eq. 4. Methyl radical reacts with surface OH^- to produce methanol.

$$CH_3\cdot + OH^- \rightarrow CH_3OH + e^- \qquad (3)$$

Methoxide reacts with surface OH^-, to produce methanol.

$$OCH_3^- + OH^- \rightarrow CH_3OH + O^{2-} \qquad (4)$$

But in a reference experiment, the methoxide produced on MgO at 373 K did not react with surface OH^- at 298 K. The methoxide spectrum did not change when measured by FT-IR 1 h after the methoxide was detected by FT-IR. So we suggest the step of methanol production is Eq. 3.

Conclusion

One mole of $O^{\bullet -}$ was proved to react with one mole of methane on MgO at 298 K for the first time. Methanol and methoxide were produced on MgO surface through the methane–$O^{\bullet -}$ reaction on MgO at 298 K. This result suggests that methanol may be produced through the methane–$O^{\bullet -}$ reaction (through the methyl radical–surface OH^- group reaction), if those products can be desorbed without decomposition. But methanol and methoxide produced on MgO at 298 K must be decomposed to CO and H_2, when they were heated (at 773 K for 1 h).

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