

# Partial oxidation of CH<sub>4</sub> over Al/silica catalysts using molecular oxygen

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## Abstract

Partial oxidation of CH<sub>4</sub> using molecular oxygen has been carried out over various commercial silicas and alumina doped silica catalysts using a flow reactor system. Partial oxidation products such as C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, HCHO, CH<sub>3</sub>OH, and CO were formed over these catalysts as well as over a quartz reactor only. The presence of Al ions in silica remarkably enhanced the formation of C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>, HCHO, and CO even at low O<sub>2</sub> concentrations. States of Al ions in silica were studied using MAS NMR of <sup>27</sup>Al. The results indicated that tetrahedrally coordinated Al(4) ions seem to be present and be isolated in silica. The mechanism of CH<sub>4</sub> oxidation is proposed under the heterogeneous participation of O<sub>2</sub> activated on such sites.

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## 1. Introduction

Several reviews concerning the partial oxidation of CH<sub>4</sub> have been reported previously [1–4]. The direct conversion of CH<sub>4</sub> into partial oxidation products has been reported using glass-coated reactors or pyrex and quartz reactors [5–7]. Partial oxidation of CH<sub>4</sub> using O<sub>2</sub> has been reported with supported catalysts such as Fe-silica, [8–12] V-silica, [13–15] Mo-silica [16–18] and various elements-silica [19]. Some workers have also studied CH<sub>4</sub> oxidations over SiO<sub>2</sub> itself [20–22]. In the past, we have also reported the partial oxidation of CH<sub>4</sub> over various commercial silicas, over those prepared from metal Si [23,24] and over ZSM-5(MFI) zeolite [25,26] at low CH<sub>4</sub> pressure of ca. 10 mmHg using a closed circulation system and quartz reactor.

In this work, activities of CH<sub>4</sub> partial oxidation over commercial silicas were compared using a flow reactor system instead of a circulation system. Partial oxidation products were formed such as HCHO, CH<sub>3</sub>OH, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and CO, which were nearly the same as those in homogeneous processes. ADM silica that contains Al impurities exhibited high activities. Then, Al doped silica catalysts were prepared and partial oxidation of

CH<sub>4</sub> was examined over them. The states of doped Al oxide in silica was studied by MAS NMR. Heterogeneous roles of Al ions in the CH<sub>4</sub> oxidation and tentative reaction mechanism were discussed.

## 2. Experimental

### 2.1. Materials

ADM silica catalyst was provided from Shin-Etsu Chemicals (Japan). Silica gel 60 (extra pure, MERCK) and A300 silica (Japan Aerosil) were used. The surface area and impurities in these silicas are shown in Table 1. The Al doped silica catalysts in this work were prepared by an impregnation method using Al(NO<sub>3</sub>)<sub>3</sub> (Wako chemicals, Japan) solution and Silica gel 60 (extra pure, MERCK). The catalysts 0.05, 0.1, 0.5, and 1.0 wt% of Al<sub>2</sub>O<sub>3</sub> in Silica gel 60 were heated at 1000 °C after dryness. Reactant gases were obtained from a cylinder standard gas (CH<sub>4</sub>:N<sub>2</sub> = 1:1 or 2:1, Taiyo-Nissan company, Japan) and air (21% of O<sub>2</sub>, Okaya Sanso, Japan).

### 2.2. Reactors

Partial oxidation of CH<sub>4</sub> was carried out using flow system. The reactor is made of quartz (or pyrex) glass and with a diameter

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Table 1  
Surface area of commercial silicas and their impurities

Silicas	Silica gel 60 (Extra pure, Merck)	ADM silica (Shin-Etsu Chemicals)	A300 (Japan Aerosil)
Surface area (m <sup>2</sup> /g)	ca. 400	12	ca. 300
Impurities (ppm)			
Al <sub>2</sub> O <sub>3</sub>	–	400	<100
Fe <sub>2</sub> O <sub>3</sub>	<2	55	<10
TiO <sub>2</sub>	–	–	<100
CaO	–	275	–

of 18 or 10 mm. About 100 mm of quartz reactor was heated at desired temperatures by furnace. Methane and air were adjusted using mass flow controllers to make the flow speed 28 ml/min at STP. The reaction times were calculated as ca. 18 and 5.5 s at 650 °C. Silica and Al/silica catalysts were placed in the reactor with quartz wool. The reaction temperature was controlled around 550–650 °C by the temperature controller.

### 2.3. Analysis of products

CH<sub>3</sub>OH was analyzed by gas chromatography (GC) using FID detector, PEG 400 column, and He carrier gas. CO and H<sub>2</sub> were analyzed quantitatively using Molecular sieve (MS-5A) column and Ar carrier gas. The remaining methane was evacuated at –196 °C from a sample tube, then the condensed C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and CO<sub>2</sub> were analyzed by Porapack Q column and HCHO by APS-201 (GL science, Japan) column, respectively, using He carrier gas.

### 2.4. Characterization of Al/silica catalysts by MAS NMR spectra

MAS NMR spectra of <sup>27</sup>Al of Al/silica catalysts were obtained using JEOL JNM-LA300 spectrometer (Japan). The spectra were recorded at a frequency of 78.18 MHz, with a pulse length 2 μs, a spinning speed of 5700–6000 Hz and measuring times of 24–48 h. A γ-Al<sub>2</sub>O<sub>3</sub> powder was chosen as a reference sample. The spectra of 0.1–1.0 wt% Al<sub>2</sub>O<sub>3</sub>/silica catalysts were measured. That of 0.05 wt% Al<sub>2</sub>O<sub>3</sub>/silica could not be obtained because its signal was too weak to get a spectrum.

## 3. Results and discussion

### 3.1. Partial oxidation of CH<sub>4</sub> in the presence and absence of silica catalysts

Fig. 1 shows the results of CO formation rates as a function of O<sub>2</sub>/(O<sub>2</sub>+CH<sub>4</sub>). In the presence of ADM silica, CO formation exhibits high activities even at low O<sub>2</sub> concentrations. Little or no formation of CO was observed at low (3–14%) O<sub>2</sub> concentrations in the absence of ADM silica, i.e., only quartz or pyrex reactors. Rates of CO formation increase remarkably above 40–50% of O<sub>2</sub>/(O<sub>2</sub>+CH<sub>4</sub>) and furthermore, the difference of them in the presence and absence of ADM silica becomes smaller. Table 2 shows the results of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub> and H<sub>2</sub> formations. The C<sub>2</sub>H<sub>6</sub> formation is higher at low concentration of

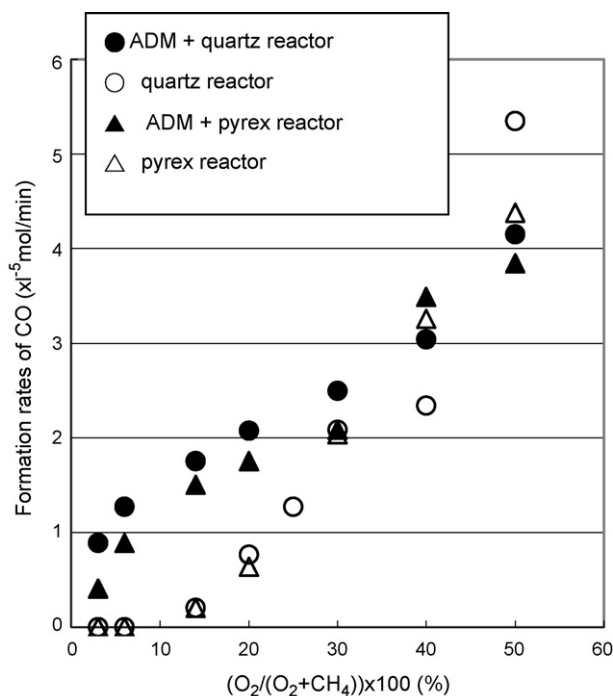


Fig. 1. Rates of CO formation as a function of O<sub>2</sub>/(O<sub>2</sub>+CH<sub>4</sub>) over ADM silica catalyst. Reaction temperature: 650 °C, reaction time: 18 s, ADM silica: 1 g, N<sub>2</sub> contents: 52–73% in the range 3–50% of O<sub>2</sub>/(O<sub>2</sub>+CH<sub>4</sub>).

O<sub>2</sub> (3–14%) in the presence of ADM silica. The C<sub>2</sub>H<sub>4</sub> formation becomes higher at above 30% of O<sub>2</sub>. At around 30% of O<sub>2</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> formations exhibit the same rates. Rates of C<sub>2</sub>H<sub>6</sub> depend on the low O<sub>2</sub> concentrations. The rates of H<sub>2</sub> formation are higher in the range of 3–14% of O<sub>2</sub> than those of C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> (Table 2). Fig. 2 shows the selectivities of CH<sub>3</sub>OH and

Table 2  
Rates of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub> formation as a function of O<sub>2</sub>/(CH<sub>4</sub>+O<sub>2</sub>) over ADM silica catalyst

O <sub>2</sub> /(CH <sub>4</sub> +O <sub>2</sub> ) × 100 (%)	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub> × 10 <sup>-5</sup> mol/min	H <sub>2</sub>
3	0.046 (0) <sup>a</sup>	0.003 (0)	0.14 (0)
14	0.16 (0.05)	0.079 (0)	0.37 (0.08)
30	0.19 (0.24)	0.22 (0.19)	0.41 (0.32)
50	0.13 (0.19)	0.29 (0.36)	0.48 (0.53)

Reaction conditions are the same as those in Fig. 1.

<sup>a</sup> Values in ( ) denotes rates in the case of quartz reactor only, i.e., without ADM silica catalyst.

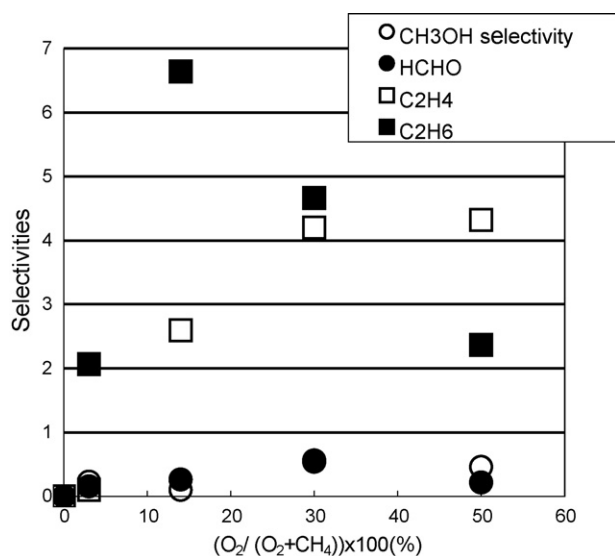


Fig. 2. Selectivities of hydrocarbons produced as a function of  $O_2/(O_2 + CH_4)$  over ADM silica catalyst. Experimental conditions are the same as those in Fig. 1.

HCHO as well as other hydrocarbons. ADM silica exhibits only 1% of selectivity to  $CH_3OH$  and HCHO and several % to  $C_2H_6$  and  $C_2H_4$ . Little difference is observed between  $CO_2$  formation in the presence and absence of ADM silica (Fig. 3). These indicate that  $CO_2$  formation occurs over quartz reactor, i.e., in the absence of the catalysts.

With Silica gel 60 catalyst,  $CH_4$  conversion and  $CO$  formation rates are shown later (Figs. 4 and 5). The  $CO$  formation is smaller than over ADM silica at low concentration of  $O_2$  (3–14%), its activity being nearly the same as quartz reactor

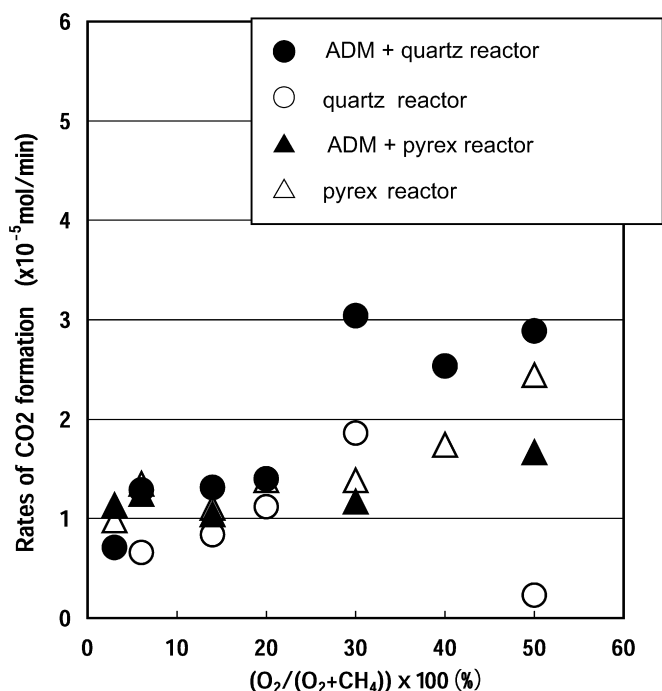


Fig. 3. Rates of  $CO_2$  formation as a function of  $O_2/(O_2 + CH_4)$  over ADM silica catalyst. Experimental conditions are the same as those in Fig. 1.

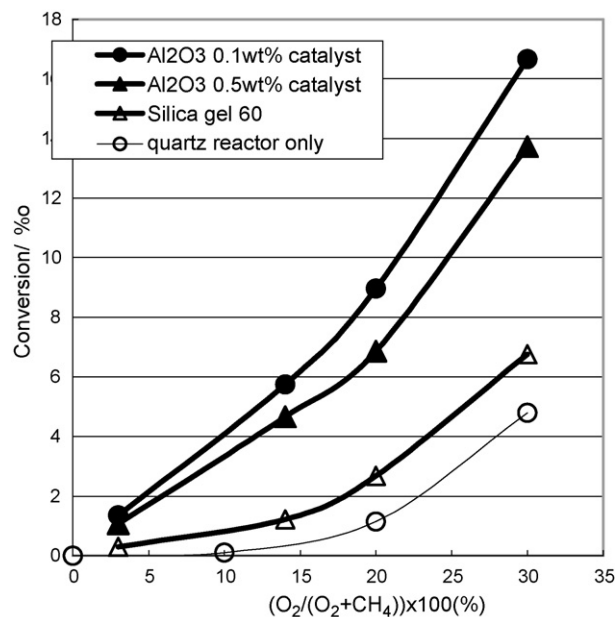


Fig. 4. Conversions of  $CH_4$  over some silica and  $Al_2O_3$  wt%/silica (Silica gel 60) catalysts. Reaction temperature:  $650^\circ C$ , reaction time: 18 s, catalysts: 1 g,  $N_2$  contents: 52–73% in the range 3–50% of  $O_2/(O_2 + CH_4)$ .

only (Figs. 4 and 5). With A300 catalyst,  $CO$ ,  $CO_2$ ,  $H_2$  and  $CH_3OH$  formations were not observed at low  $O_2$  concentrations (3–14%), being the same as those in the absence of catalysts. The A300 catalyst exhibited low activity in the partial oxidation of  $CH_4$  although the figures are not shown.

Table 1 shows that ADM silica contains some impurities of  $Al_2O_3$  and  $CaO$ . On the contrary, Silica gel 60 contains little or no impurities. A300 silica contains some impurities but their amounts are not larger than those in ADM silica. Thus, high activities with ADM silica seem to be originated from the presence of  $Al_2O_3$  or  $CaO$ . It is interesting that the activities are not depending on the surface area of these silicas. Catalysts con-

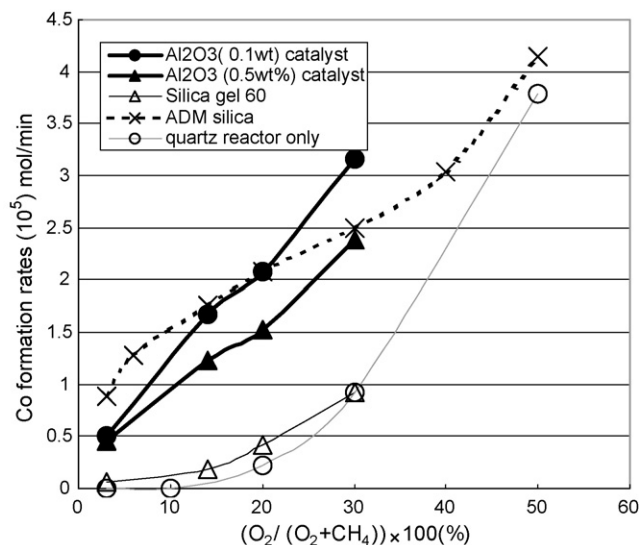


Fig. 5. Rates of  $CO$  formation as a function of  $O_2/(O_2 + CH_4)$  on various catalysts. Experimental conditions are the same as those in Fig. 4.

taining 0.1–0.5 wt% of CaO on Silica gel 60 were prepared and the CH<sub>4</sub> oxidations were examined. These CaO/silicas did not exhibit high activities and their activities were the same as those of Silica gel 60 although the figures are not shown here. Thus, it is concluded that the high activity of ADM silica comes from the presence of Al ions.

### 3.2. Partial oxidation of CH<sub>4</sub> over Al/silica catalysts

It is concluded that impurities of Al oxide in silica play an important role for the partial oxidation of CH<sub>4</sub> as described in Section 3.1. In this section, we attempted oxidation of CH<sub>4</sub> over the prepared Al/silica catalysts that contain 0.05–1.0 wt% of alumina in extra pure Silica gel 60. The 0.1–0.5 wt% catalysts show higher activities than Silica gel 60 and quartz reactor (Fig. 4). The conversions increase with the increase of O<sub>2</sub>%, i.e., O<sub>2</sub>/(O<sub>2</sub> + CH<sub>4</sub>). The catalysts exhibit nearly zero conversion at zero O<sub>2</sub>%. The activities of Al<sub>2</sub>O<sub>3</sub> 1.0 and 0.05 wt% catalysts were lower than those over 0.1–0.5 wt% catalysts though the figures are not shown here. Fig. 5 shows the results of CO formations. The rates increase with O<sub>2</sub> concentrations. The CO formation rates are at the same level as those over ADM silica. The selectivities to CO are ca. 70% at a reaction time of 18 s and ca. 60% at 5.5 s (Fig. 6). The selectivities to CO<sub>2</sub> range from 0% to 20% and they are smaller at a short reaction time of 5.5 s (Fig. 7). Fig. 8 shows that the selectivity to HCHO ranges from 7% to 2% with the increase of O<sub>2</sub>% from 3% to 50% at a reaction time of 5.5 s. Those to CH<sub>3</sub>OH range from 1% to 3.5%, its rate increasing with the increase of O<sub>2</sub>/(O<sub>2</sub> + CH<sub>4</sub>). The selectivity to C<sub>2</sub>H<sub>6</sub> ranges from 15% to 11% at a reaction time 5.5 s (Table 3). These selectivities are the highest among the partial oxidation products. The C<sub>2</sub>H<sub>4</sub> formation shows a reverse tendency of C<sub>2</sub>H<sub>6</sub> formation. The H<sub>2</sub> selectivities are calculated by hydrogen balance and the results are shown in Table 3. The H<sub>2</sub> selectivities are similar to those of C<sub>2</sub>H<sub>6</sub>. Its selectivity decreases

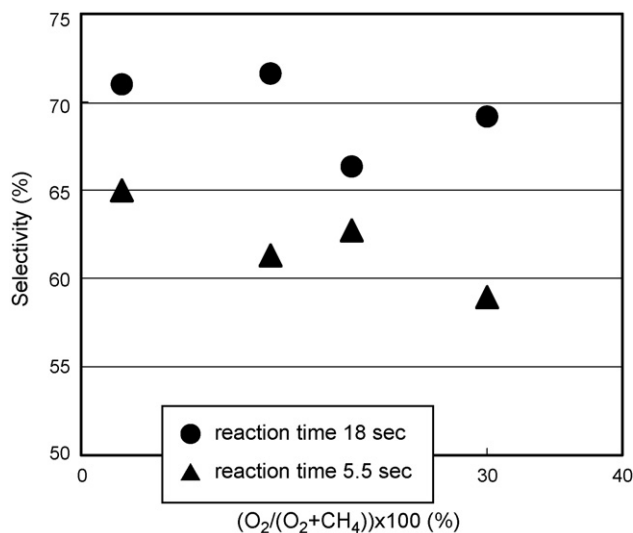


Fig. 6. Selectivities to CO over Al<sub>2</sub>O<sub>3</sub> 0.1 wt%/silica catalyst as a function of O<sub>2</sub>/(O<sub>2</sub> + CH<sub>4</sub>). Reaction time: 18 or 5.5 s. Other conditions are the same as those in Fig. 4.

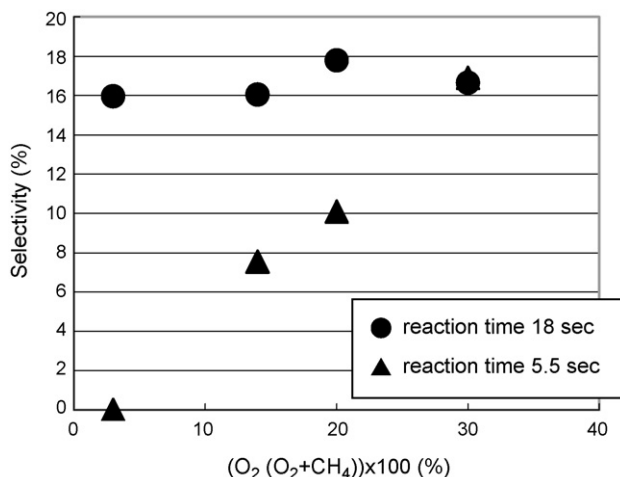


Fig. 7. Selectivities to CO<sub>2</sub> over Al<sub>2</sub>O<sub>3</sub> 0.1 wt%/silica catalyst as a function of O<sub>2</sub>/(O<sub>2</sub> + CH<sub>4</sub>). Reaction conditions are the same as those in Fig. 8.

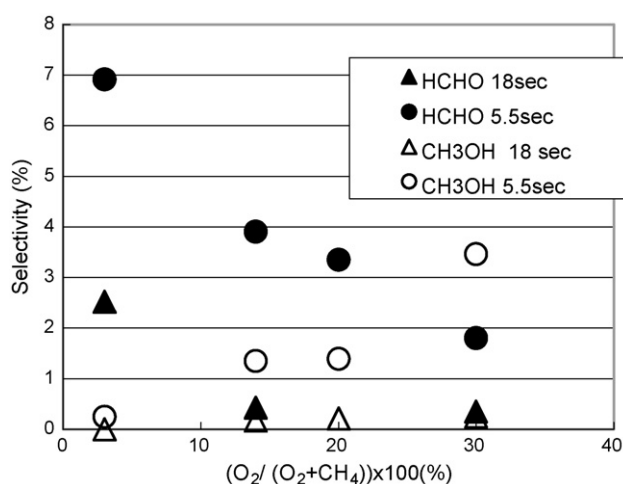


Fig. 8. Selectivities to HCHO and CH<sub>3</sub>OH as a function of O<sub>2</sub>/(O<sub>2</sub> + CH<sub>4</sub>) over Al<sub>2</sub>O<sub>3</sub> 0.1 wt%/silica catalyst. Reaction conditions are the same as those in Fig. 4.

with the increase of O<sub>2</sub>/(O<sub>2</sub> + CH<sub>4</sub>). H<sub>2</sub> seems to be produced with C<sub>2</sub>H<sub>6</sub> formations. H<sub>2</sub> formation may occur on acid sites by cracking CH<sub>4</sub> since the amounts of H<sub>2</sub> are more than those of C<sub>2</sub>H<sub>6</sub>. As described above, 0.1 wt% Al<sub>2</sub>O<sub>3</sub>/silica catalyst prepared from Silica gel 60 exhibited higher selectivities to C<sub>2</sub>H<sub>6</sub>, H<sub>2</sub>, and HCHO at low O<sub>2</sub> concentrations.

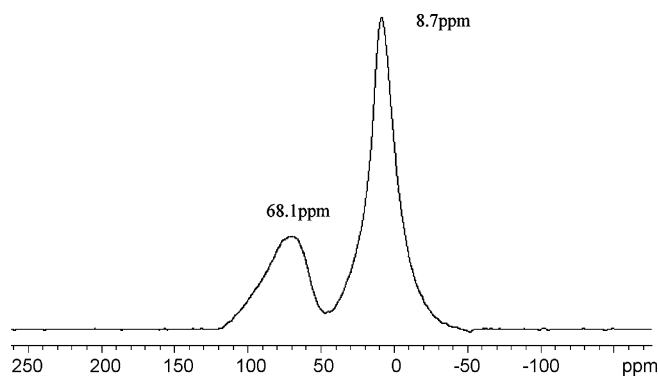
The selectivities over 1.0 wt% Al<sub>2</sub>O<sub>3</sub>/silica were nearly the same over 0.1 wt% Al<sub>2</sub>O<sub>3</sub>/silica catalysts except more CO<sub>2</sub>

Table 3

Rates and selectivities of C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub> formation as a function of O<sub>2</sub>/(CH<sub>4</sub> + O<sub>2</sub>) over Al 0.1 wt%/silica catalyst

O <sub>2</sub> /(CH <sub>4</sub> + O <sub>2</sub> ) × 100 (%)	C <sub>2</sub> H <sub>6</sub>	C <sub>2</sub> H <sub>4</sub> × 10 <sup>-5</sup> mol/min	H <sub>2</sub>
3	0.05 (15%)	0 (0%)	0.23 (16%)
14	0.13 (14%)	0.024 (2.6%)	0.34 (9%)
20	0.16 (15%)	0.053 (4.9%)	0.38 (8.6%)
30	0.18 (11%)	0.10 (6.6%)	0.53 (8.4%)

Reaction time: 5.5 s, and other conditions are the same as those in Fig. 4.

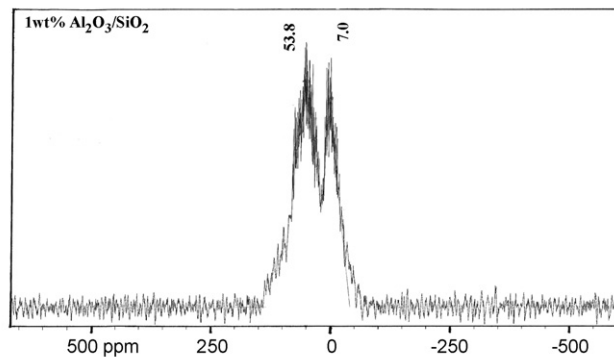
Fig. 9.  $^{27}\text{Al}$  MAS NMR spectra of  $\gamma\text{-Al}_2\text{O}_3$ .

formation. The selectivities over 0.05 wt%  $\text{Al}_2\text{O}_3/\text{silica}$  were also similar to those over 0.1 wt%  $\text{Al}_2\text{O}_3/\text{silica}$  catalyst. But it exhibited little or no formation of  $\text{CO}_2$  and  $\text{C}_2\text{H}_4$  at low oxygen concentrations. Thus, there was a little difference present among 1–0.05 wt%  $\text{Al}_2\text{O}_3/\text{silica}$  catalysts.

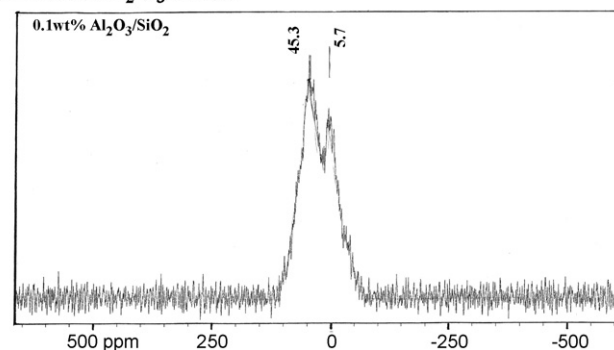
### 3.3. Characterization of Al ions on Silica gel by MAS NMR

According to Kirkpatrick et al., resonance spectra of  $^{27}\text{Al}$  were obtained at +50 to +80 ppm for Al(4) and at –10 to +20 ppm for Al(6) [27]. The  $\gamma\text{-Al}_2\text{O}_3$  exhibits peaks at 68.1 and 8.7 ppm [28], as shown in Fig. 9. Al(4) means tetrahedrally coordinated state and the Al(6) means octahedrally coordinated one. Their area ratio of peak area for  $\gamma\text{-Al}_2\text{O}_3$  is determined as Al(6)/Al(4)=1.9/1 (Table 4), which is the value of imperfect spinel  $\gamma\text{-Al}_2\text{O}_3$  structure. The spectra of  $\alpha\text{-Al}_2\text{O}_3$  was reported one peak of ca. 5 ppm, which is attributed to Al(6) ions although the spectra was not shown [28]. Fig. 10 shows the MAS NMR spectra of 0.1 and 1.0 wt%  $\text{Al}_2\text{O}_3/\text{silica}$  catalysts, respectively. The chemical shifts of Al(4) ions including 0.5 wt%  $\text{Al}_2\text{O}_3/\text{silica}$  catalyst are 54, 50 and 45 ppm (Table 4). They increase to higher magnetic fields with the decrease of Al contents. With Al(4) species, some workers reported that chemical shifts depended on the Al/Si ratio of compounds. The shifts decrease with the decrease of Al ions in Al–Si oxide compounds [28,29]. The change of chemical shifts in this work seems to come from some shielding and from isolation of Al ions. The catalysts containing 0.1–0.5 wt% of  $\text{Al}_2\text{O}_3$  should have both Al(4) and Al(6) ions in silica and the former should have Lewis acid characters due to dehydration at high temperatures such as 650 °C. NMR intensity ratio of Al(6)/Al(4) is larger with 1.0 wt%  $\text{Al}_2\text{O}_3/\text{silica}$  catalyst, which is different from 0.1 wt% catalyst sample. This suggests that 1.0 wt% catalyst contains some Al oxide on silica

### 1 wt% $\text{Al}_2\text{O}_3/\text{silica}$



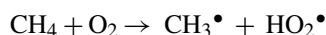
### 0.1 wt% $\text{Al}_2\text{O}_3/\text{silica}$

Fig. 10.  $^{27}\text{Al}$  MAS NMR spectra of  $\text{Al}_2\text{O}_3$  0.1 wt%/Silica gel 60 catalyst and  $\text{Al}_2\text{O}_3$  1.0 wt%/Silica gel 60 catalysts. Shift values are also shown in Table 4.

containing both Al(6) and Al(4) species. Consequently, isolated Al(4) species will be decreased. The amount of Al(4) species with 0.05 wt%  $\text{Al}_2\text{O}_3$  seems to become less than 0.1–0.5 wt% catalysts due to decrease of Al concentrations.

### 3.4. Discussion with the reaction mechanism

It is well known that the process occurs on wall effects in homogeneous processes [2]. Partial oxidation reaction is initiated by methyl radical formation. It is reported that methyl radicals are also formed by  $\text{O}_2$  [2].



In this study, the presence of Al/silica catalyst and  $\text{O}_2$  are needed to facilitate reactions as described in Sections 3.1 and 3.2.

Table 4

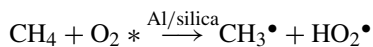
Chemical shifts of Al(4) and Al(6) in MAS NMR spectra of  $^{27}\text{Al}$  and ratio of peak area Al(6)/Al(4)

	$\gamma\text{-Al}_2\text{O}_3$ (Mizusawa)	$\text{Al}_2\text{O}_3$ 1.0 wt%/Silica gel 60	0.5 wt%	0.1 wt%
Al(4) (ppm)	68	54	50	45
Al(6) (ppm)	9	7	4	6
Ratio of peak area Al(6)/Al(4)	1.92	0.67	0.37	0.5

Ratio of peak area was obtained by peak shape analysis.

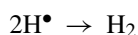
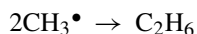


Al/silica

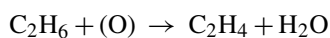
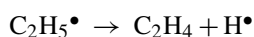
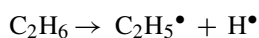


In this work,  $\text{O}_2^*$  seems to be produced on around Al ions, i.e., Lewis acid sites. This may come from the characters of electron donating ( $\text{O}_2$ ) and accepting (Al ions). It is likely to be a kind of adsorption since  $\text{O}_2^*$  will never change to  $\text{O}_2^+$ .  $\text{O}_2^*$  will have the same radical characters as gaseous  $\text{O}_2$ . It will be a heterogeneous step in the homogeneous reactions. Such Lewis acid sites may be present more over 0.1–0.5 wt%  $\text{Al}_2\text{O}_3/\text{silica}$  than over other catalysts as described in Section 3.3.

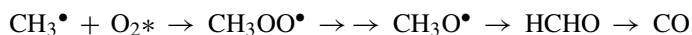
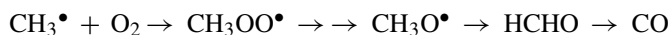
Ethane will be formed in the following steps.  $\text{H}_2$  will be formed at the same time.



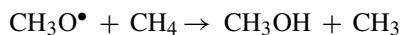
Ethane selectivities decreased with the increase of reaction time, but  $\text{H}_2$  selectivities did not vary so much with the change of reaction time (Table 3). Ethane seems to be dehydrogenated with accompanying  $\text{H}_2$  formation. Ethylene seems to be formed in two ways. The possibility of dehydrogenation by lattice oxygen will not be excluded as described below.



Products CO and HCHO will be produced via  $\text{CH}_3\text{OO}^\bullet$  as described below. The step will also be facilitated by the presence of  $\text{O}_2^*$  as the concentration of the radicals increase on around Al ions. Kobayashi [10] has reported that the selectivity to HCHO in the  $\text{CH}_4$  oxidation is high over low Fe/silica catalyst, i.e., over isolated Fe species. Similar reactions may take place here.



Little amounts of methanol are produced in this study. Methanol will be produced via following steps in the homogeneous process as reported previously [2].



One of  $\text{CH}_3\text{OH}$  processes described above is hydrogen abstraction of  $\text{CH}_3\text{O}^\bullet$  from  $\text{CH}_4$ . Zhang et al. [7] have got high  $\text{CH}_3\text{OH}$  selectivities (–60%) at high pressures and high  $\text{CH}_4$  concentrations using quartz reactor. The process should occur in their cases. However, it will be difficult in this case because of low pressure and low concentration of  $\text{CH}_4$ . Furthermore,

$\text{CH}_3\text{OH}$  should be oxidized to CO and  $\text{CO}_2$  due to long reaction times. The third process described above will become possible if a large amount of  $\text{OH}^\bullet$  are present as well as  $\text{CH}_3^\bullet$ . Details will be a future subject.

#### 4. Conclusions

Partial oxidation of  $\text{CH}_4$  with  $\text{O}_2$  was carried out over a quartz reactor and in the presence of silica and Al doped silica catalysts. The partial oxidation of  $\text{CH}_4$  with molecular oxygen took place over all these conditions. Rates of  $\text{CH}_4$  conversions were enhanced by the presence of 0.1–0.5 wt% alumina/silica even at low  $\text{O}_2$  concentrations. The products such as  $\text{C}_2\text{H}_6$ ,  $\text{C}_2\text{H}_4$ ,  $\text{CH}_3\text{OH}$ , HCHO, CO and  $\text{H}_2$  were formed, which were nearly the same ones in homogeneous reactions. The products such as  $\text{C}_2\text{H}_6$  and HCHO were formed with high selectivities of 15–10%. The states of Al ions by using MAS NMR were determined as tetrahedrally coordinated and isolated Al ions. These seem to facilitate  $\text{O}_2^*$  adsorptions due to Lewis acid characters. This species seem to enhance the partial oxidation products such as  $\text{C}_2\text{H}_6$ , HCHO and CO.

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