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Partial oxidation of CH_4 at low pressure over SiO_2 prepared from Si

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The oxidation of CH_4 with O_2 at low pressure was carried out over SiO_2 prepared from metal Si. The Si showed only total oxidation activity while the Si partly oxidized to SiO_2 showed high selectivities to CH_3OH and HCHO. The results on SiO_2 prepared from Si were compared with those over commercial silicas. The role of SiO_2 in the CH_4 oxidation was discussed.

Keywords: partial oxidation of CH_4; CH_3OH; HCHO; SiO_2 catalyst

1. Introduction

The conversion of CH_4 to CH_3OH and HCHO has been studied by many workers [1–3]. The direct oxidation of CH_4 into CH_3OH at high pressures using glass coated reactors or Pyrex and quartz reactors have been reported by some workers [4,5]. The CH_3OH and HCHO formation from CH_4 has been studied over Mo- or V-oxide/SiO_2 catalysts using N_2O as an oxidant [6–8]. The HCHO formation has been studied over Fe-, V-, and Mo-oxide/SiO_2 [9–11] using O_2 as an oxidant. It is interesting that the selective partial oxidation in these reports occurs over "silica"-based catalysts. Some workers have focused their attention on SiO_2 itself [12–14].

Previously, we also studied [15] the CH_3OH and HCHO formations in the oxidation of CH_4 using O_2 over various commercial SiO_2 catalysts. In this work, we tried to measure the oxidation rates under special conditions over SiO_2 catalyst prepared from metal Si in order to obtain the initial rate of partial oxidation and to understand the role of SiO_2 itself basically. The results were compared with those over various commercial silicas. The effects of oxygen pressures, surface area, and impurities in SiO_2 were examined. The percent of ^{18}O in the products was also examined using $^{18}O_2$ as a reactant. The heterogeneous and homogeneous processes in the partial oxidation were also discussed.

2. Methods

2.1. Materials

SiO_2 was obtained by heating the Si metal (Nakarai Tesque Co., 99.99%) in air at 1173–1373 K. The amount of SiO_2 (mol% in the Si sample) was calculated from the weight increase after heating in the furnace. Commercial silicas such as ADM (Shin-Etutsu Chemicals Co.), Silica gel-60-extra pure (Merck Co.), SIO-4 (JRC, Catalysis Society of Japan), and Aerosil-300 and OX-50 (Nippon Aerosil Co.) were used. CH_4 (> 99%), O_2 (> 99%), and $^{18}O_2$ (98.1at%, Isotec Inc.) were used as reactants.

2.2. Procedures

CH_4 oxidations were carried out using a closed circulation system (ca. 300 cm^3) made of Pyrex glass and a reactor made of quartz (fig. 1). Reactant mixtures of ca. 8 Torr of CH_4 and 0.08–0.24 Torr of O_2 were used for the reaction experiments. The circulation time was regarded as reaction time for 1 or 2 h. Products such as CH_3OH, HCHO, CO_2, and H_2O were caught by a trap at 77 K (fig. 1) during the reaction at 873–973 K. The quartz reactor itself has a slight activity but it was very small, below ca. 5% of the catalytic activity at 873 K. The formation of CO is negligibly small in this case. A

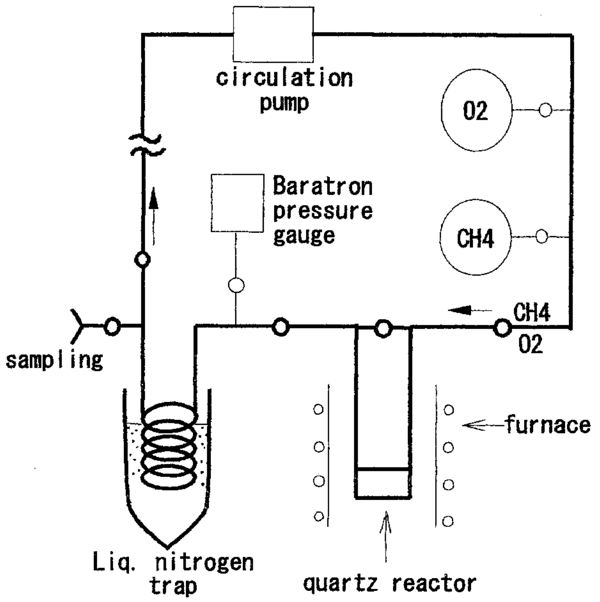

Fig. 1. A closed circulation system for CH_4 partial oxidation.

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short pass was set between the reactor and trap to prevent polymerization of HCHO. After the reaction, the products such as CH_3OH, HCHO, H_2O and CO_2 were kept in the sample tubes at 77 K to prevent HCHO polymerization. Their amounts were determined by gas chromatography using a TSR-1 column. In order to separate water and HCHO well, the pass in front of the column was preheated at ca. 393 K.

In this experiment, an initial rate of CH_4 oxidation is always obtained since only reactants such as CH_4 and O_2 are circulating and their pressures do not decrease so much since the CH_4 and O_2 conversions are below 2–5% and 10–15%, respectively. The CH_4 pressure in this experiment is limited below the saturation pressure at 77 K, i.e., 9.7 Torr.

The ^{18}O% in the products were recorded on a Shimadzu QP-2000A mass spectrometer. The percent of ^{18}O in HCHO and in CO_2 was well determined while that in CH_3OH was not determined owing to disturbation by a small amount of air (32: O_2) in the mass spectrometer. The sample gases were introduced directly to the ion chamber without using a separating column in order to prevent the exchange with ^{16}O water in the column.

3. Results and discussion

3.1. *SiO_2 catalysts prepared from Si*

The oxidation of Si to SiO_2 by air was very low when it was not ground in a mortar while it was oxidized rapidly when it was ground prior to heating. An unoxidized Si and a slightly oxidized Si(5.6%) sample showed the same diffraction patterns of metal Si (cubic system, JPDSC 27-1402) according to X-ray measurements. The FT-IR spectra of metal Si showed no IR absorption. With the 5.6% catalyst, several bands at around 1000–1250 cm^{-1} were observed, which are the same as the results reported for the thin SiO_2 film [16]. These have been attributed to the longitudinal and transversal optical splittings of Si–O vibrations. With the 11–19% catalysts, the intensity of the Si–O band at around 1125 cm^{-1} gets stronger. This suggests that SiO_2 crystal layers become thick for these catalysts. In the case of metal Si, however, it has been reported [17–19] that its surface is generally covered with several layers of protective oxide and that the states of Si^{1+-3+} as well as Si^{4+} seem to be present.

3.2. *Oxidation of CH_4 over SiO_2 prepared from metal Si*

The partial oxidation of CH_4 was carried out over SiO_2 prepared from Si as described above. The results are shown in table 1. In this work, the CO formation was negligibly small. There is no selectivity to CH_3OH and HCHO over the metal Si catalyst though CO_2 formation occurs on it. With the Si5.6 catalyst, the selectivity to HCHO increases remarkably and the activity also increases. With the Si11 and Si19 catalysts, the selectivities to HCHO formation and the activities slightly increase. The selectivities to CH_3OH over these catalysts range around 15%. These results confirm that the selectivities to partial oxidation products such as HCHO and CH_3OH increase by the presence of thick SiO_2 crystal layers on the surface of Si. As described before, the metal Si has nanolayers of SiO_2 [17–19] on the surface. But, these thin layers do not have partial oxidation activity here.

Table 1
The activities of partial oxidation of CH_4 over SiO_2 prepared from metal Si. $p(CH_4) = 8.3$ Torr (1 Torr = 133.3 Pa), concentration of $O_2 = 3\%$, temperature = 873 K, catalyst: 0.5 g [a]

Catalyst SiO_2 (mol%)		CH_4 conversion (% g^{-1} h^{-1})	Product selectivity (%)		
			CH_3OH	HCHO	CO_2
Si		0.2	0	0	100
Si5.6		0.63	13	40	46
Si11		0.88	3	63	33
Si19		0.94	18	64	18
Si*9.6	1	0.08	36	0	64
	2	0.10	8	23	69
Si*19	1	0.19	70	0	30
	2	0.29	37	17	46
	3	0.35	21	39	40

[a] The Si5.6–19 catalysts were prepared after grinding of Si. The Si*9.6–*19 catalysts were prepared without grinding of Si. The numbers of 1, 2, and 3 for Si* catalysts denote the first, second, and third experiments for 1 h each. Oxygen conversions were below 10–15% in 1 h for these reactions.

The activities and selectivities for partial oxidation of CH_4 vary remarkably with the catalyst conditions. For example, the catalysts which were heated and prepared after grinding the metal Si in a mortar had good activities as described above. The catalysts prepared from Si without grinding had low activities for the CH_4 oxidation as shown also in table 1. The Si*9.6 and *19 catalysts show low activity but high selectivity to CH_3OH in the first experiment. When the CH_4 oxidations are repeated for each 1 h, the activities and selectivities gradually change as shown in table 1. The selectivity to CH_3OH decreases and that to HCHO increases. This suggests that the SiO_2 surface changes after the reactions. Fig. 2 shows these selectivities as a function of CH_4 conversion over many SiO_2 catalysts which are prepared from Si as described above. The CH_3OH selectivity is higher at low conversion range below 0.2%. The selectivity to HCHO becomes higher at the conversion range above 1%. The selectivity to CO_2 ranges from 60 to 40%. This suggests that CH_3OH is formed initially at very low conversions below ca. 0.2% and CH_3OH seems to be rapidly dehydrogenated to HCHO. The total oxidation to CO_2 seems to occur independently for partial oxidation. Previous workers [12–

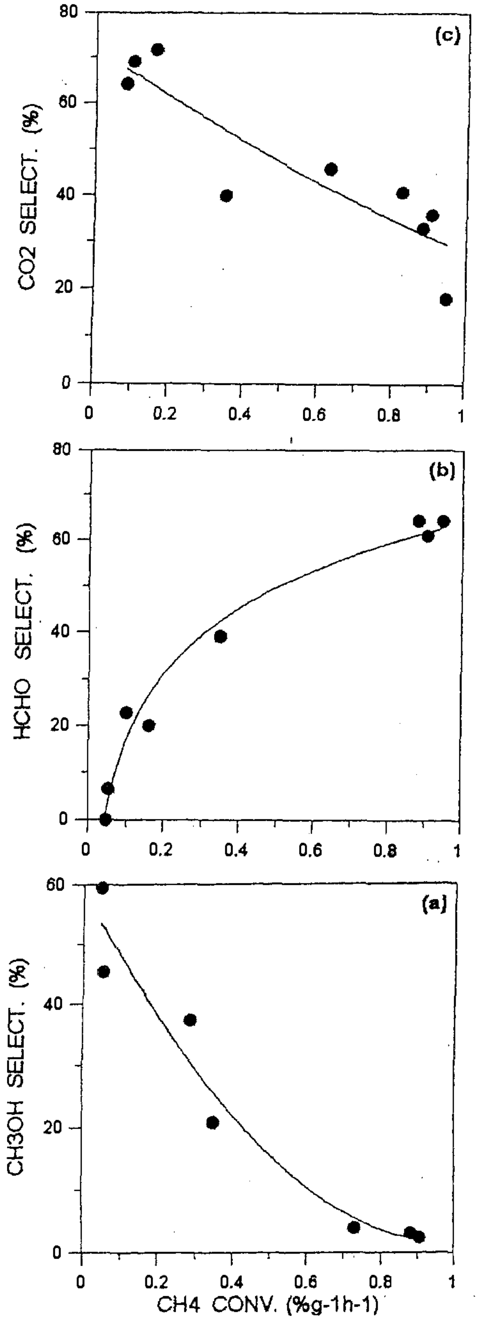

Fig. 2. The CH_3OH (a), HCHO (b), and CO_2 (c) selectivities in the CH_4 oxidation as a function of conversion over SiO_2 prepared from metal Si. $p(CH_4) = 8.3$ Torr, concentration of $O_2 =$ ca. 3%, temperature = 873 K, catalysts: Si5.6–Si29 and Si*5–*19 samples, 0.3–0.5 g were used.

14] have reported the formation of only HCHO in partial oxidation over SiO_2. In this work at low pressure, the CH_3OH formation was confirmed. Only CO_2 formation takes place in spite of low CH_4 conversion over the metal Si catalyst. As described above, its surface is covered with very thin layers of suboxides as well as SiO_2. Such a feature seems to be due to the different activities for hydrogen abstraction and CO_2 formation on suboxides. Details are unclear.

3.3. Dependence on oxygen pressure of CH_4 oxidation

The rate of oxidation of CH_4 was examined at some oxygen pressures (fig. 3). The ADM silica was used as a catalyst since it was prepared by heating of metal Si. The rate of conversion increases with an increase of oxygen pressures. The selectivity to CH_3OH is high below 1% of O_2 concentration, while that to HCHO becomes high above 2–3% of O_2. In the absence of gaseous oxygen, the oxidation reaction does not proceed, in agreement with the results by Parmaliana et al. [13]. These results suggest that gaseous oxygen is needed for the partial oxidation of CH_4.

3.4. Comparison of oxidation activities between Si5.6 and various commercial silicas

The activities and selectivities of the partial oxidation of CH_4 over various silicas are compared to each other. The results are shown in table 2. The rates of conversion range from 0.6 to 1.2% g^{-1} h^{-1}. The selectivities to HCHO range from 40 to 15%. Such differences, however, are not big among these silicas. The surface area of the Si5.6 sample is ca. 0.5 m^2 g^{-1} while those of A300 and SIO-4 are 300–350 m^2 g^{-1}. It is concluded that the size of surface area has essentially little effect on the oxidation rates.

Table 2 includes the impurities in the silicas. The SIO-4 contains very low impurities below several ppm. The OX50 contains 100–800 ppm of Al_2O_3, Fe_2O_3 and TiO_2. Both rates for CH_4 oxidation, however, are nearly the same. The ADM silica contains 400 ppm of Al_2O_3 and 275 ppm of CaO. But there is little rate difference between the Si5.6 and ADM silica catalyst. These suggest that the rates are independent of the impurities as far as their concentrations are concerned as described

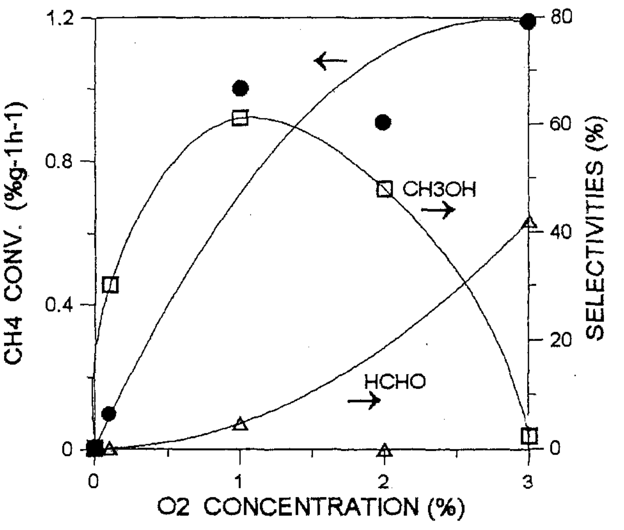

Fig. 3. The CH_4 conversion and product selectivities as a function of O_2 concentration. $p(CH_4) = 8.3$ Torr, temperature = 873 K, catalyst: ADM silica 0.3 g.

Table 2
Comparison of oxidation activities and properties between Si5.6 and various commercial silicas. $p(CH_4) = 8.3$ Torr, concentration of $O_2 = 3\%$, temperature = 873 K, catalyst: 0.3–0.5 g

	Si5.6 (this work)	ADM (Shin-Etsu Chem.)	A300 (Japan Aerosil)	OX50 (Japan Aerosil)	SIO-4 (JRC) [a]	Silicagel 60/E.P. (Merck)
CH_4 conv. ($\% g^{-1} h^{-1}$)	0.63	1.2	0.57	1.0	1.1	0.56
HCHO (%)	40	42	13	17	43	60
CH_3OH (%)	13	4	3	6	8	16
surface area ($m^2 g^{-1}$)	0.5	12	300	50	350	400
impurities (ppm)						
Al_2O_3	< 10	400	< 100	< 800	6.6	–
Fe_2O_3	< 25	55	< 10	< 100	0.5	< 2
TiO_2	< 5	–	< 100	< 300	1.9	–
CaO	< 1	275	–	–	0.3	

[a] See text. The previous results [15] over A300 and ADM silica are somewhat different from those listed here. This is caused by the circulation speed in the circulation system. Oxygen conversions were below 10–20% for these reactions in 1 h.

above. The selectivities to HCHO on A300 and OX50 are a little smaller than those on the SIO-4, ADM, and Si5.6 silicas. This seems to be caused by the presence of TiO_2 in the former silica, i.e., further oxidation to CO_2 and CO.

3.5. The ^{18}O tracer studies over some silica catalysts

The partial oxidation of CH_4 using $^{18}O_2$(98%) was carried out over the Si5.6 and SIO-4 catalysts. With the Si5.6 catalyst, the $^{18}O\%$ in HCHO, H_2O, and CO_2 which were obtained under similar conditions in table 1 (0.3% g^{-1} of CH_4 conversion for 0.5 h) were 3, 0.5, and 50%, respectively. With the SIO-4 catalyst, those of HCHO, H_2O,and CO_2 were 2, 1, and 20%, respectively, under the same conditions in table 2 (2.1% g^{-1} of conversion for 2 h). Only 2–3% of ^{18}O in the HCHO and H_2O are remarkably low in spite of the use of 98% of $^{18}O_2$. These unexpectedly low values seem to be originated from the fast exchange of these products with surface –OH groups at around 873 K after formation. The $^{18}O\%$ values of CO_2 range around 20–50%, which are higher values than those of HCHO and H_2O. However, these values were lower than the 98% of reactant $^{18}O_2$. Similar results were reported by Koranne et al., over V oxide/SiO_2 [20]. Thus, it is difficult to know the source of oxygen in these products by the $^{18}O_2$ tracer studies. However, it is clear that HCHO or CH_3OH interacts rapidly with the surface of SiO_2. The oxygen in CO_2 may come from anions of SiO_2.

3.6. The oxidation of C_2H_6 over silica

In order to know the dehydrogenation activity of silica, the oxidation of C_2H_6 over various silicas was carried out in the presence and absence of oxygen. The results are shown in table 3. The selectivity to C_2H_4 at 873 K is ca. 90%. Thus, the rate of C_2H_4 formation indicates the dehydrogenation activity of SiO_2. The rates over ADM, OX50, and A300 run roughly parallel with the values of surface area in the absence of oxygen. In the presence of gaseous oxygen, the rates increase slightly for A300 and OX50 and ca. 6 times for ADM. There appears no big difference between oxidation reactions in the presence and absence of gaseous oxygen. These data suggest that the C_2H_4 formation takes place via hydrogen abstraction from C_2H_6 by lattice oxygen of SiO_2. In the case of CH_4, the activity of hydrogen abstraction was about 10 times smaller than that of C_2H_6 on SiO_2 at 873 K. Kastanas et al. reported similar results with CH_4 and C_2H_6 [21].

3.7. Summary and tentative mechanism

Our results can be summarized as follows: (1) The results over SiO_2 from metal Si are nearly the same as those over commercial SiO_2 in the partial oxidations of CH_4. The rate of CH_4 partial oxidation does not depend on the SiO_2 area in the range 0.5–400 $m^2 g^{-1}$. (2) The CH_3OH formation was confirmed at very low conversion. (3) Gaseous oxygen is needed for the CH_3OH and HCHO formation over SiO_2 and the rates depend on oxygen pressures. (4) The hydrogen abstraction from

Table 3
Dehydrogenation of C_2H_6 over some silica in the presence and the absence of gaseous oxygen. Reaction time: 5 min, temperature = 873 K, $p(C_2H_6) = 20$ Torr, catalyst: 0.3 g

Silica [a]	Rate of C_2H_4 formation ($\mu mol\ g^{-1}$)	
	without O_2	with 5% of O_2
ADM	0.36	2.2
A300	1.0	1.3
OX50	0.55	0.75

[a] See table 2. This experiment was carried out using a closed circulation system without cooling at 77 K (fig. 1).

C_2H_6 takes place on SiO_2 even in the absence of gaseous oxygen.

Sun et al. [14] have proposed that the HCHO formation did not originate from methyl and methoxy radicals but from methoxy surface complexes under the consideration of activation energy features. Parmaliana et al. [13] have proposed the reaction of surface species of CH_4 and oxygen.

In this work, however, both heterogeneous and homogeneous steps seem to be necessary in the case of CH_3OH formation. The SiO_2 seems to play an important role on the hydrogen abstraction and CH_3 radical formation in the scheme

$$CH_4 \underset{(O)_s}{\rightarrow} CH_3 + (-OH)_s$$

where $(O)_s$ is surface oxygen. A peroxy radical will be formed homogeneously, then methoxy radical will be formed:

$$CH_3 + O_2 \rightarrow CH_3OO \rightarrow CH_3O$$

The CH_3OH and HCHO may be formed homogeneously or heterogeneously on the surface from methoxy radicals. If the steps of peroxy and methoxy radical formations are slow, the rate of CH_3OH or HCHO formation will become slow and the effect of surface area size may disappear. If the reaction proceeds via surface methoxy species or adsorbed species [13,14], the rate should depend on the area of SiO_2 and, furthermore, CH_3OH and HCHO will be produced by the lattice oxygen in the absence of gaseous oxygen. But our results are not in agreement with them. The main role of SiO_2 seem to be in the hydrogen abstraction from CH_4 and from CH_3OH to HCHO without further oxidation in the case of partial oxidation.

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