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Oxidation of methane to formaldehyde over Fe/SiO_2 and Sn–W mixed oxides

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Abstract

In an attempt to develop new catalysts for the formation of formaldehyde from methane, the promotion effect of Fe on SiO_2 and that of Sn on WO_3 have been studied. The formation of formaldehyde on silica can be appreciably enhanced by the impregnation of Fe, as far as iron loadings are kept below 0.1 atom.% (Fe/Si × 100). In the case of Sn–W–Ox catalysts, both the addition of Sn to WO_3 and that of W on SnO_2 were effective to the selective formaldehyde formation. Absorption spectra (UV-Vis) and ESR measurements revealed that tetrahedrally coordinated Fe^{3+} in the silica network plays an important role in the formation of formaldehyde. A thin surface layer consisting of W and Sn oxides can account for the selective formaldehyde formation on the Sn–W–Ox catalysts.

Keywords: Methane oxidation; Formaldehyde formation

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1. Introduction

A great number of attempts and efforts have been made in the last decade to explore heterogeneous catalysts which can produce oxygenates from methane [1,2]. Silica catalysts promoted by MoO_3 or V_2O_5 have been most intensively investigated [3–6], because they can produce formaldehyde from methane and oxygen at low methane conversions. Loadings of the promoters below monolayer coverage is preferable for the high productivity of formaldehyde [4,5]. One of plausible explanations for the role of these promoters is to provide redox centers and accelerate the activation of oxygen [4,6] on silica which exhibits a selective but poor catalytic activity for the formaldehyde formation. Such a phase cooperation in catalysis motivated us to explore new catalysts consisting of two components for the formation of formaldehyde from methane.

In the present study, we have examined the promotion effect of Fe on SiO_2 [7] and that of Sn on WO_3. Tungsten trioxide, as well as silica, exhibits a poor but selective activity for formaldehyde formation. The addition of Fe or Sn on these surfaces is attempted to activate oxygen, since simple oxides of Fe or Sn are relatively active for the complete oxidation of methane. In

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contrast, a suppression of the combustion activity of SnO_2 can be expected by loading WO_3 on it. Active phases responsible for formaldehyde formation are discussed based on the spectroscopic investigation of the related samples.

2. Experimental

Fumed silica (AEROSIL 200V, Degussa; $SiO_2 > 99.9\%$, specific surface area = 200 $m^2 \cdot g^{-1}$) was used as a support and it was impregnated with an aqueous solution of $Fe(NO_3)_3$. Tungsten trioxide (Kanto Chemical Co. Ltd., specific surface area = 3.3 $m^2 \cdot g^{-1}$) and tin dioxide (Kishida Chemical Co. Ltd., specific surface area = 7.5 $m^2 \cdot g^{-1}$) were also used as supports and these were impregnated with a toluene solution of tin octanoate (Nikka Co. Ltd.) and an aqueous solution of ammonium tungstate (Nippon Shin Kinzoku Co. Ltd.), respectively. The impregnated precursors were dried at 100°C and calcined at 700°C in air for 3h. The loadings of promoters on the catalyst supports are expressed as atomic percentages and denoted as $Fe(0.05)/SiO_2$, for example, where numerals in parentheses represent (Fe/Si × 100) in atom.%.

Catalysts of 50 or 100 mg were loaded into a quartz tube reactor (inner diameter: 6mm) where quartz wool was used to hold the catalyst in place. A mixture of methane and oxygen in a ratio of $CH_4{:}O_2 = 95{:}5$ under a pressure of 101 kPa was passed through the reactor at a flow rate of 100 $cm^3 \cdot min^{-1}$. Effluent from the reactor was analyzed by two gas chromatographies. An activated carbon column with a TCD detector was used for the analysis of O_2, CO, CH_4, and CO_2. For the analysis of C_2H_6, HCHO, and CH_3OH, a combined column of Porapak Q and Porapak T fitted with a methanator before a FID detector was used.

Absorption spectra (UV-Vis) of the catalysts were measured with a spectrophotometer equipped with a multi-channel photo detector (MCPD 1000, Otsuka Electric Co.). The optical absorption was expressed simply as log R_0/R_s, where R_0 denotes the diffuse reflectance of pure silica and R_s that of the catalysts. Electron spin resonance (ESR) of the sample was measured in the X-band region by use of a spectrometer (Bruker, ESP-300E) at $T = -196$°C with $P_0 = 5$ mW.

3. Results and discussion

3.1. Fe/SiO_2 catalysts

Table 1 shows some typical results for methane oxidation over Fe/SiO_2 catalysts. The addition of Fe to silica can appreciably promote the formation of formaldehyde [7], as far as Fe loadings are lower than 0.1 atom.%. The productivity of formaldehyde formation on $Fe(0.03)/SiO_2$ is comparable to that reported for V-promoted silica [6]. Iron loadings higher than 1 atom.% caused complete oxidation to

Table 1
Oxidation of methane on Fe/SiO_2 catalysts

Catalyst	Temp., °C	Conv., % CH_4	Productivity, mmol h^{-1} $g_{\text{-cat}}^{-1}$		(Selectivity, %)
			HCHO	CO	CO_2
SiO_2	600	0.002	0.1 (~ 100)	n.d.	n.d.
$Fe(0.03)/SiO_2$	600	0.47	14.5 (60)	6.0 (25)	3.5 (15)
$Fe(1.0)/SiO_2$	600	0.55	4.6 (16)	7.2 (26)	16.0 (58)
$Fe(10)/SiO_2$	600	1.75	1.7 (2)	22.3 (23)	70.1 (75)
α-Fe_2O_3	450	0.21	n.d.	n.d.	10.7 (~ 100)

$P(CH_4) = 96$ kPa, $P(O_2) = 5$ kPa, SV = 120,000 $h^{-1} \cdot ml \cdot g_{\text{-cat}}$-1.
n.d. = not detected.

CO_2. Since α-Fe_2O_3 shows a relatively high activity for the combustion of methane, the deeper oxidation observed for catalysts with high Fe loadings can be ascribed to clusters or small particles of α-Fe_2O_3 dispersed on silica. A different state of Fe can be assumed to exist in the catalysts of low Fe loadings which gave a high selectivity to formaldehyde formation.

The silica catalysts with different Fe loadings were compared in absorption spectra in the UV-Vis region (Fig. 1). A blue-shift, due to a decrease in the particle size, of the band gap absorption (250–600 nm) of α-Fe_2O_3 can be distinctly observed with a decrease in Fe loadings. This blue-shift seems to approach the absorption at a wavelength of 350 nm. Another isolated absorption appears in the spectra of low-Fe catalysts at a wavelength of 260 nm, indicating the existence of iron species different from hematite.

In Fig. 2, an X-band ESR spectrum of the formaldehyde selective Fe(0.03)/SiO_2 and that of the CO_2-selective Fe(10)/SiO_2 were compared. Two main signals were observed at $g = 4.3$ and $g = 2$. The former is assigned to tetrahedrally coordinated Fe^{3+} substituted in the tetrahedral silica network and the latter to octahedrally coordinated ones in cation exchange sites or as cluster of iron oxides [8]. A relative signal ratio of the tetrahedral Fe^{3+} ($g = 4.3$) to the octahedral Fe^{3+} ($g = 2$) was high for the formaldehyde-selective catalysts of low Fe loadings. This fact indicates that tetrahedral Fe^{3+} in the silica network, showing an absorption at $\lambda = 260$ nm, is responsible for the formation of formaldehyde form methane.

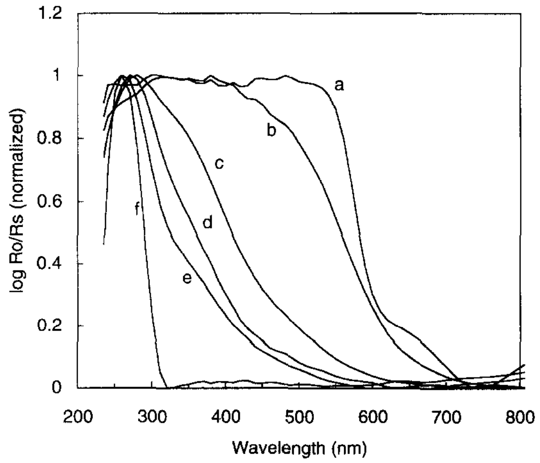

Fig. 1. Absorbance spectra of Fe/SiO_2 catalysts. α-Fe_2O_3 (a), Fe(1)/SiO_2 (b), Fe(0.1)/SiO_2 (c), Fe(0.05)/SiO_2 (d), Fe(0.03)/SiO_2 (e), Fe(0.005)/SiO_2 (f).

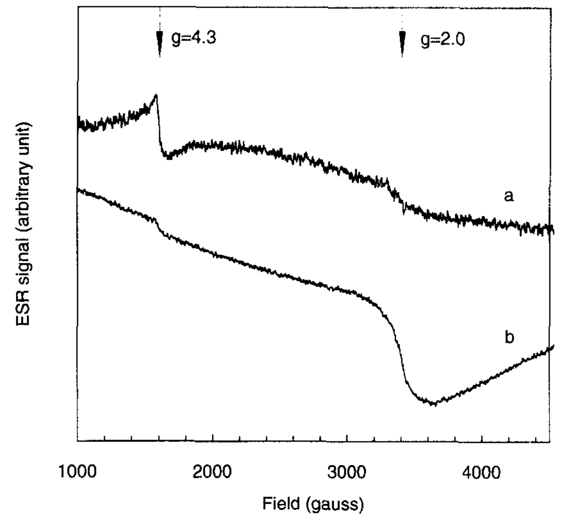

Fig. 2. X-band ESR spectra of Fe/SiO_2 catalysts. Fe(0.03)/SiO_2 (a), Fe(10)/SiO_2 (b). Temperature −196°C.

Tetrahedral Fe^{3+} also exists in the tetrahedral framework of ferrosilicate [8]. It has been reported that such a tetrahedral Fe^{3+} exhibits peculiar catalytic properties different from those of hematite, such as a relatively poor activity in CO oxidation [9], the selective phenol formation from benzene and N_2O [10], and the selective oxidative dehydrogenation of isobutane and propane [11].

3.2. Sn–W–Ox catalysts

Table 2 shows the results of methane oxidation on Sn–W–Ox catalysts. The addition of Sn can enhance the productivity of formaldehyde on WO_3, whereas simple SnO_2 produces mainly CO_2. In contrast to the case of Fe/SiO_2 catalysts, an increase in the loading of Sn on WO_3 did not markedly decrease formaldehyde selec-

Table 2
Oxidation of methane on Sn–W–Ox catalysts

Catalyst	Temp., °C	Conv., %	Productivity, mmol.h^{-1}.g$_{\text{-cat}}$-1		(Selectivity, %)
		CH_4	HCHO	CO	CO_2
WO_3	600	0.006	0.16 (~ 100)	n.d.	n.d.
Sn(1.5)/WO_3	600	0.11	2.5 (93)	0.2 (7)	n.d.
Sn(4.6)/WO_3	600	0.26	4.4 (66)	2.1 (31)	0.2 (3)
SnO_2	600	2.8	0.08 (< 1)	6.3 (9)	64.9 (91)
W(0.7)/SnO_2	600	1.5	1.7 (4)	7.6 (20)	28.6 (76)
W(2)/SnO_2	600	0.3	4.0 (51)	3.6 (46)	0.2 (3)
W(7)/SnO_2	600	0.3	4.0 (51)	3.7 (46)	0.2 (3)

$P(CH_4) = 95$ kPa, $P(O_2) = 5$ kPa, SV = 60,000 h^{-1} · ml · g$_{\text{-cat}}$-1.
n.d. = not detected.

tivity. Furthermore, even SnO_2 catalysts loaded with W (2 and 7 atom.%) show high formaldehyde productivity as observed for WO_3 catalysts loaded with Sn. This indicates that W loadings larger than 2 atom.% can cover the whole surface of SnO_2 and suppress the high combustion activity of original SnO_2. The formation of a new composite phase consisting of Sn and W oxides can be assumed to take place on the surface of both Sn/WO_3 and W/SnO_2 catalysts and to be responsible for the selective oxidation to formaldehyde.

Only WO_3 and SnO_2 were, however, detected as discrete phases by X-ray diffraction and in the UV-Vis spectrum. The formation of a new phase was not observed by XPS. Thus, a catalyst prepared by mechanical mixing of WO_3 and SnO_2 was tested and reaction products were shown in Table 3 with time on stream during reaction. A high selectivity to CO_2 formation was observed at an early stage of the reaction, reflecting the high combustion activity of SnO_2, as expected. With time on stream, methane conversion and carbon oxides formation decreased and in turn formaldehyde formation was enhanced. This change in the catalytic property was markedly accelerated by a successive heat treatment at 700°C in air, resulting in a perfectly formaldehyde-selective catalyst. The sublimation of WO_2 [12] and its deposition onto SnO_2 might lead to the formation of the formaldehyde-selective surface.

4. Summary

The formation of formaldehyde from methane on SiO_2 and WO_3 can be accelerated by the addition of Fe and Sn, respectively. Such a promotion effect is qualitatively explainable as

Table 3
Oxidation of methane on mechanically mixed WO_3 and SnO_2

Time on stream, min	Conv., %	Productivity, mmol · h^{-1} · g$_{\text{-cat}}$-1		(Selectivity, %)
	CH_4	HCHO	CO	CO_2
15	0.4	n.d.	0.8 (9)	8.3 (91)
30	0.2	0.5 (9)	0.3 (6)	4.5 (85)
210 [a]	0.03	0.8 (~ 100)	n.d.	n.d.

Catalyst = mechanically mixed WO_3 and SnO_2 (Sn/W × 100 = 4.6 atom.%), not heat-treated.Reaction temperature = 600°C, $P(CH_4) = 95$ kPa, $P(O_2) = 5$ kPa, SV = 60,000 h^{-1} · ml · g$_{\text{-cat}}$-1, n.d.; not detected.

[a] After successively heat-treated at 700°C in air for 3 hr.

a result of oxygen activation on the oxides which show selective but poor activity for this reaction. Active phases postulated for the formaldehyde formation are, however, different between Fe/SiO_2 catalysts and Sn–W–Ox catalysts. Highly dispersed Fe^{3+}, possibly in tetrahedral coordination, is indispensable for the enhancement of formaldehyde formation on silica. Although new surface layer consisting of W and Sn oxides has not been detected, the experimental data indicate that, at least, the surface of SnO_2 active for combustion is completely modified by WO_3 through a high-temperature treatment.

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