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Selective oxidation of light alkanes to aldehydes over silica catalysts supporting mononuclear active sites — acrolein formation from ethane

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Abstract

The oxidation of light alkanes, particularly ethane, was examined over Cs–M/SiO_2 catalysts (M = Fe, V, Bi). Turn-over-frequency (TOF) and product selectivities were strongly dependent on the loading amounts of M. When the loading amounts of M were less than 0.1 at.% to Si, very high TOF and relatively high selectivities to acetaldehyde and acrolein were observed. The isolated site or mononuclear structure of Fe, V or Bi on the Cs/silica surface is vital for the high aldehyde yields. Cesium was also important for the high reactivity of ethane and the high aldehyde selectivities. The reaction pathways giving acrolein from ethane and the roles of catalytic components are discussed.

Keywords: Selective oxidation; Ethane; Acetaldehyde; Acrolein; Mononuclear; Silica

1. Introduction

Selective oxidation of light alkanes into useful oxygenates is recognized as an important industrial objective in the near future and also as one of the major challenges in catalysis research. In the case of the catalytic ethane oxidation, however, it is not easy to obtain oxygenates with yields higher than 2% [1–3] even if N_2O is used as a selective oxidizing agent [4]. The aldehyde selectivity is much less when oxygen was used as an oxidant, since the produced oxygenates are much more reactive than ethane [5].

We have reported that silica supporting a very small amount of iron (Fe/Si = 0.05 at.%) afforded a selective formaldehyde formation from methane and oxygen at the conversion of methane lower than 1% [6]. Mononuclear, tetrahedrally coordinated Fe^{3+} in the silica network might play an important role in formaldehyde formation [7]. It has been found that the addition of alkali metal elements to the Fe/SiO_2 catalysts can appreciably enhance the formation of acrolein and acetone in the reaction between propane and oxygen [8,9]. More recently, we have demonstrated that acrolein as well as acetaldehyde are obtained with total aldehyde yield higher than 2% when silica catalysts supporting mononuclear active sites (Fe, V, or Bi) are used in the reaction of ethane and oxygen [10–13]. Catalytic role of mononuclear active site in the selective oxidation has also been attracting attention in connection with the enzyme-mimetic catalysts [14,15]. Our recent results [6–13] of the alkane oxidation on the mononuclear active sites are briefly reviewed herein. The aim of this paper is to discuss the distinct catalysis of mononuclear active sites in the selective oxidation of light alkanes as a comparative study on the Cs/Fe/SiO_2, Cs/V/SiO_2 and Cs/Bi/SiO_2 catalysts.

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Table 1
Oxidation of methane on Fe/SiO_2 catalysts[a]

Catalysts	Temperature (K)	CH_4 conversion (%)	Productivity (mmol h^{-1} g^{-1}), selectivity (%)		
			HCHO	CO	CO_2
SiO_2	873	0.002	0.1, ~100	ND	ND
$Fe(0.03)/SiO_2$	873	0.47	14.5, 60	6.0, 25	3.5, 15
$Fe(1.0)/SiO_2$	873	0.55	4.6, 16	7.2, 26	16.0, 58
$Fe(10)/SiO_2$	873	1.75	1.7, 2	22.3, 23	70.1, 75
α-Fe_2O_3	723	0.21	ND[b]	ND	10.7, ~100

[a] $CH_4:O_2 = 95:5$, $SV = 120{,}000\ h^{-1}\ ml\ g^{-1}$.
[b] Not detected.

2. Selective oxidation of methane to formaldehyde over silica-supporting mononuclear Fe

It has been extensively studied that silica can catalyze the oxidative conversion of methane into formaldehyde [16,17]. We have found that the addition of small amounts of 3d-transition metal elements to silica appreciably enhances the formation of formaldehyde [6]. Among the metal elements, Fe afforded the highest promotion effect on the formaldehyde production in the silica-catalyzed oxidation of methane. Table 1 shows the Fe-promoted production of formaldehyde in the oxidation of methane over the silica catalysts [7]. It is clear that the addition of Fe in a very small amount ($Fe/Si = 0.03$ at.%) to silica appreciably enhances the formaldehyde productivity.

Fig. 1 shows the normalized rate of the methane consumption per Fe atom in the Fe/SiO_2-catalyzed oxidation of methane as a function of the surface Fe density. The surface density of Fe was calculated from the loaded amount of Fe and the BET surface area of the catalysts. The lower Fe density ($<0.05\ nm^{-2}$) brings about higher turn-over-rate in a remarkable manner. It is evident that the highly dispersed Fe ($Fe/Si < 0.1$ at.%) on silica plays an important role in the oxidative conversion of methane into formaldehyde.

The silica catalysts with different Fe loadings were compared in absorption spectra of the UV–Vis region (Fig. 2) [7]. A blue-shift, due to the quantum size effect with decreasing the particle size, of the band gap absorption (250–600 nm) of α-Fe_2O_3, hematite, 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. A strong X-band ESR signal observed at $g = 4.3$ revealed that tetrahedrally coordinated Fe^{3+} in the tetrahedral silica network exist mainly in the formaldehyde-selective $Fe(0.03)/SiO_2$ catalyst [7].

As shown in Fig. 3, it is concluded that mononuclear Fe with tetrahedral coordination in the silica matrix is vital for the high productivity of formaldehyde, while polymeric FeO_x cluster brings about the combustion of methane. It is noteworthy that the combination of Fe with silica is essential. Metal oxides,

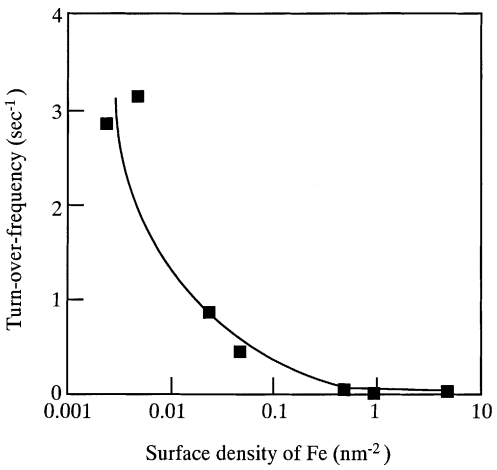

Fig. 1. Normalized rate (turn-over-frequency) of methane consumption in the methane oxidation over the Fe/SiO_2 catalysts as a function of the surface Fe density ($CH_4:O_2 = 95:5$, $SV = 120{,}000\ h^{-1}\ ml\ g^{-1}$, temperature = 873 K).

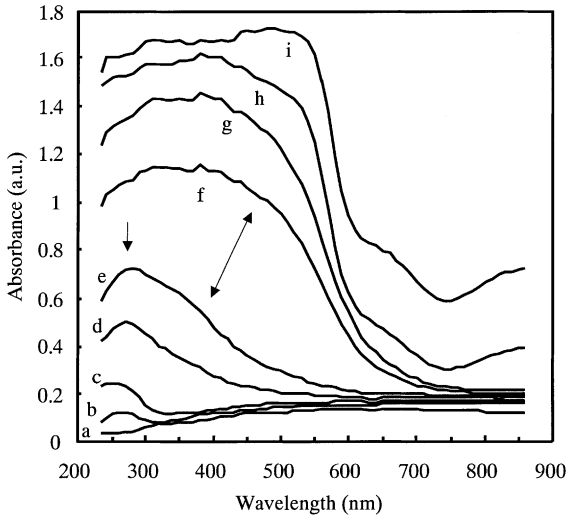

Fig. 2. Absorbance spectra of the Fe/SiO_2 catalysts with different Fe loadings in UV–Vis region: SiO_2 (a); $Fe(0.005)/SiO_2$ (b); $Fe(0.01)/SiO_2$ (c); $Fe(0.05)/SiO_2$ (d); $Fe(0.1)/SiO_2$ (e); $Fe(1)/SiO_2$ (f); $Fe(2)/SiO_2$ (g); $Fe(20)/SiO_2$ (h); α-Fe_2O_3 (i).

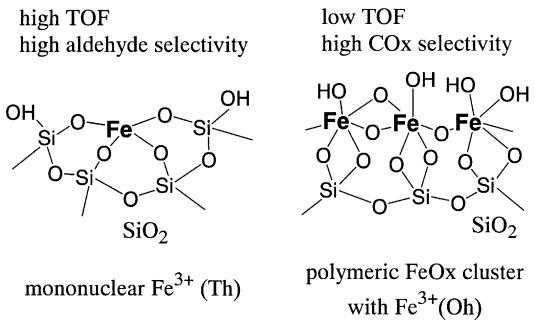

Fig. 3. Schematic illustration of mononuclear Fe^{3+} with tetrahedral coordination and polymeric FeO_x cluster with octahedral coordination in the silica matrix.

such as Al_2O_3, ZrO_2, TiO_2, ZnO, loaded with a small amount of Fe did not give such a high formaldehyde productivity as those observed on the Fe/SiO_2 catalysts.

3. The oxidation of ethane to aldehydes over $Cs–Fe/SiO_2$, $Cs–V/SiO_2$, and $Cs–Bi/SiO_2$

The Fe/SiO_2 catalysts were examined in the oxidation of ethane. As shown in Table 2, $Fe(0.05)/SiO_2$ gives a certain amount of formaldehyde. It was found that an addition of alkali metal elements to the Fe/SiO_2 catalysts with loading amount of 0.5–2 at.% can appreciably enhance the productivity of aldehydes as well as the ethane conversion. Not only the acetaldehyde formation, but a large amount of acrolein was also detected in the products of the ethane oxidation. This fact suggests that the C–C bond formation takes place on the alkali-modified Fe/SiO_2 catalysts. Very low loading amount of Fe is also required for the high aldehyde productivity in this case. The alkali-modified Fe/SiO_2 catalysts with high Fe loadings (>0.1 at.%) show a high activity for combustion. Almost same phenomena have been observed in the propane oxidation [8,9]. In the oxidation of methane, however, only the deep oxidation to CO_x was accelerated by the alkali addition, regardless of the loading amount of Fe.

A combinatorial survey of the $X–M/SiO_2$ catalysts was conducted in the oxidation of ethane, where X denotes alkali metal elements and M denotes other elements including transition metal and some typical elements. Fig. 4 summarizes the results when Cs was chosen as the alkali metal element [13]. The abscissa of this figure denotes temperature required for

Table 2
Oxidation of ethane over the silica catalysts supporting Fe and/or alkali metal elements[a]

Catalysts	CH_4 conversion (%)	Productivity (mmol h^{-1} g^{-1}), selectivity (%)				
		CH_3CHO	C_2H_3CHO	HCHO	C_2H_4	CO_x
SiO_2	0.23	0.04, 18	Trace, 0	0.02, 9	0.05, 23	0.11, 50
$Fe(0.05)/SiO_2$	1.61	0.05, 3	0.08, 5	0.50, 31	0.14, 9	0.80, 50
$Cs(0.6)Fe(0.05)/SiO_2$	6.76	0.36, 5	1.10, 16	0.51, 8	0.35, 5	4.39, 65
$K(0.6)Fe(0.05)/SiO_2$	3.09	0.23, 7	0.45, 15	0.22, 7	0.14, 5	2.05, 66
$Cs(0.6)/SiO_2$	0.16	0.02, 13	0.01, 6	0.03, 19	0.04, 25	0.06, 38

[a] C_2H_6:O_2 = 75:25, SV = 3000 h^{-1} ml g^{-1}, temperature = 748 K.

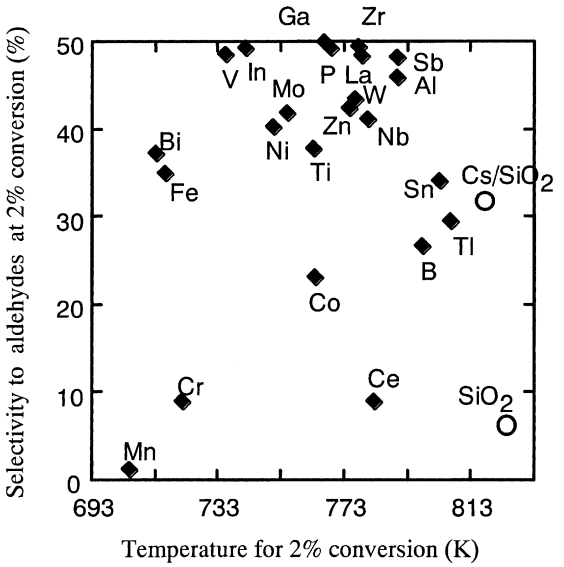

Fig. 4. Comparison of the catalytic performance of Cs–M/SiO_2 (Cs:M:Si = 1:0.1:100, in atomic ratio) in the ethane oxidation. Selectivity was calculated on C_2-basis (C_2H_6:O_2 = 75:25, SV = 3000 h^{-1} ml g^{-1}).

a 2% conversion of ethane on each catalyst. The ordinate shows the selectivity for the sum of acetaldehyde and acrolein at 2% conversion of ethane. The activity of the catalysts as well as the aldehyde selectivity at the same conversion can be compared in this figure.

It is very clear that a lot of additives, M, in the Cs–M/SiO_2 system bring about higher aldehyde selectivity and higher activity for ethane oxidation than those observed on Cs/SiO_2 and additive-free SiO_2. Among them, the catalysts containing Bi and Fe are highly active for ethane oxidation and give aldehydes with relatively good selectivity. Higher aldehyde selectivity is observed on the samples containing V, In, Ga, P, Zr, La, or Sb, which require higher temperatures for 2% conversion than those on the Bi- or Fe-containing catalysts. Among the alkali metal elements, Cs brought about the highest aldehyde productivity and the order was as follows: Cs–Rb > K > Na > Li. This order of alkali metal elements is same in the X–Fe/SiO_2, X–V/SiO_2, and X–Bi/SiO_2 systems [8–13].

Fig. 5 shows the normalized rate of the ethane consumption per V atom and the product selectivity

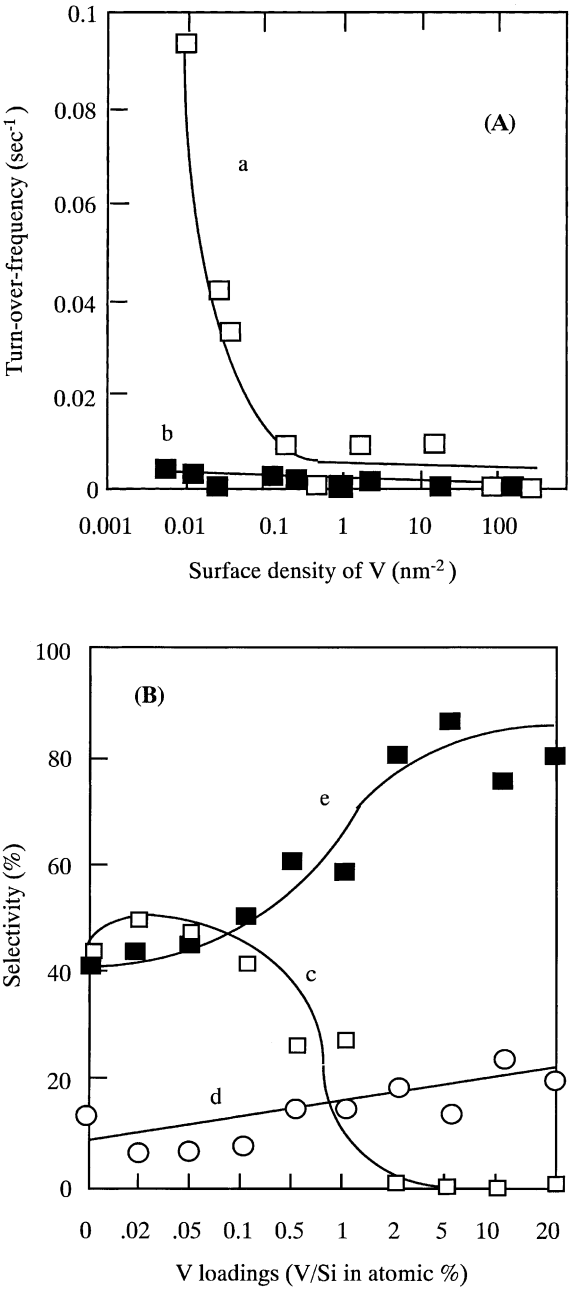

Fig. 5. Normalized rate (turn-over-frequency) of ethane consumption (A) and product selectivity (B) in the ethane oxidation over the Cs–V/SiO_2 catalysts with different V loadings (C_2H_6:O_2 = 75:25, SV = 3000 h^{-1} ml g^{-1}, temperature = 748 K): TOF on Cs–V/SiO_2 (a); TOF on V/SiO_2 (b); total aldehydes on Cs–V/SiO_2 (c); C_2H_4 on Cs–V/SiO_2 (d); CO_x on Cs–V/SiO_2 (e).

in the ethane oxidation over the Cs–V/SiO_2 catalysts as a function of the surface V density [12]. Very high turn-over-frequency (TOF) can be seen on the Cs–V/SiO_2 catalysts with V density lower than 0.1 nm^{-2}. These catalysts correspond to the V loadings of 0.02, 0.05 and 0.1 at.% and afforded high aldehyde yields. In the case of the Cs–Bi/SiO_2 catalysts (Fig. 6), low Bi loadings (Bi = 0.01–0.43 nm^{-2} or 0.02–0.5 at.%) were also advantageous for the aldehyde formation [13]. The blue-shift in the UV–Vis spectra of V and Bi species loaded on SiO_2, similar to Fig. 2, suggested that mononuclear V or mononuclear Bi species plays an important role in aldehyde formation from ethane [12,13]. Polymeric VO_x and BiO_x in the Cs–V/SiO_2 and Cs–Bi/SiO_2 catalysts gave carbon oxides from ethane and oxygen.

4. Reaction pathways giving aldehydes and the role of alkali metal elements

Not only mononuclear Fe, V, or Bi, but also the alkali addition (0.5–2 at.%) and the silica matrix together play an important role in aldehyde formation from ethane and oxygen. In this section, the role of alkali is discussed in connection with the reaction pathways.

Fig. 7 shows the ethane conversion and the product selectivities of the Cs–Bi/SiO_2 catalyst (Bi = 0.02 at.%) as a function of the contact time at 773 K [13]. The ethane conversion increases in proportion to an increase in contact time. A drastic change in the product distribution was observed with contact time. Relatively good selectivity to acetaldehyde observed at a low contact time decreased clearly at higher contact time. The formaldehyde selectivity afforded a similar transformation. In contrast to these transformations, the selectivity to acrolein appreciably increased with contact time, came to a maximum and decreased at a long contact time. Such a relationship, which is commonly observed on Cs–M/SiO_2 (M = Fe, V, Bi), simply suggests that acetaldehyde is the primary product from ethane and is then converted into acrolein and finally into CO_x. Although ethene is more reactive than ethane on the M/SiO_2 catalysts without Cs, a reverse tendency was observed on the Cs-modified M/SiO_2 catalysts (M = Fe, V, Bi). The less reactivity of ethene in these systems indicates that ethene might not be an intermediate from ethane to aldehydes, while alkenes have often been regarded as the intermediates from light alkanes to oxygenates [18].

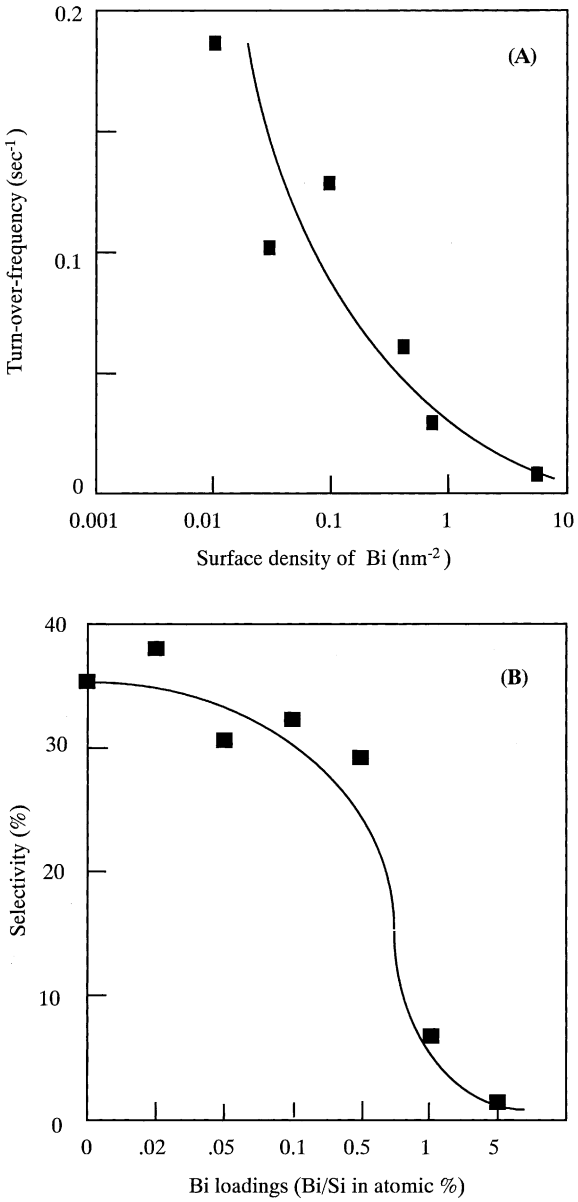

Fig. 6. Normalized rate (turn-over-frequency) of ethane consumption at 748 K (A) and total aldehyde selectivity at 4% ethane conversion (B) in the ethane oxidation over the Cs–Bi/SiO_2 catalysts with different Bi loadings (C_2H_6:O_2 = 75:25, SV = 3000 h^{-1} ml g^{-1}).

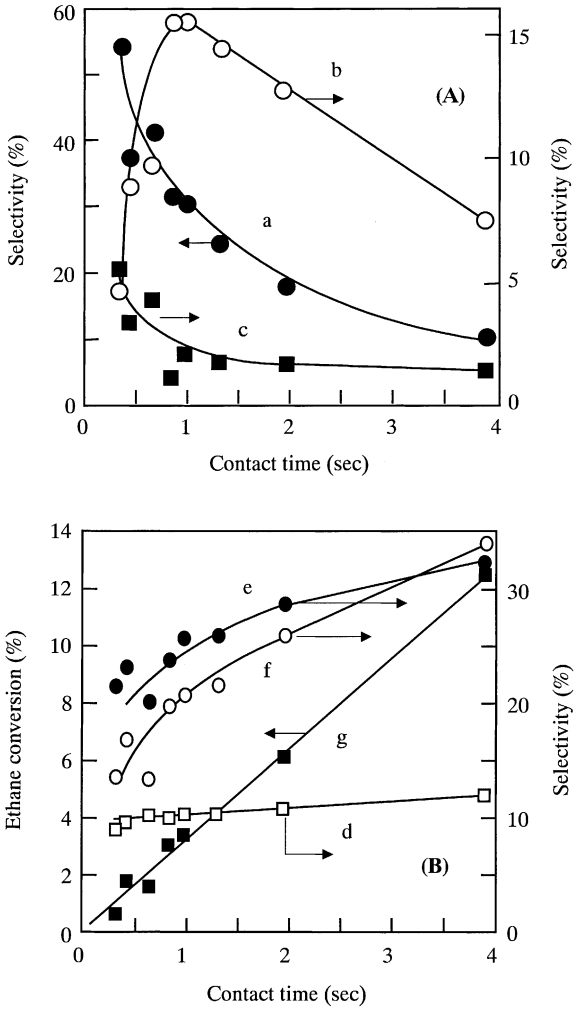

Fig. 7. Effect of contact time on the catalytic performance of Cs–Bi/SiO_2 (Cs:Bi:Si = 1:0.02:100) in ethane oxidation (C_2H_6:O_2 = 75:25, temperature = 773 K). Selectivity to acetaldehyde (a), acrolein (b), formaldehyde (c), ethene (d), CO (e), CO_2 (f), and ethane conversion (g).

The possible route of the acrolein formation is a cross aldol-condensation between acetaldehyde and formaldehyde, catalyzed by alkali [19,20]. We have demonstrated that Cs–SiO_2 as well as Cs–Fe/SiO_2 gives acrolein from acetaldehyde in an oxidic atmosphere [10], where acetaldehyde seems to be reacted with formaldehyde and/or methanol formed in the auto-oxidation of acetaldehyde. Based on the above consideration, we can propose the reaction pathways

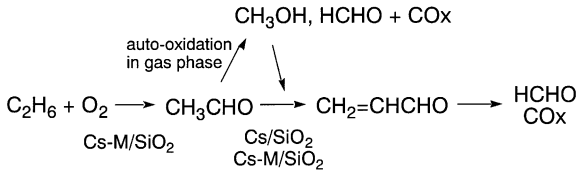

Fig. 8. Proposed reaction pathways for the ethane oxidation over silica catalysts supporting Cs and mononuclear M (M = Fe, V, Bi).

to give acrolein from ethane on Cs–M/SiO_2, as shown in Fig. 8.

The apparent effects of alkali metal elements are summarized as follows: (a) enhancement of the alkane reactivity; (b) reduction of the CO_x selectivity and enhancement of the oxygenate selectivity; (c) shift in carbon number of oxygenates from lower to higher in the distribution of the products. Qualitatively, the same effects of alkali have been observed in the propane oxidation on alkali-modified Fe/SiO_2 [8,9].

It has been reported that the atomic charge of H in the C–H bond of C_2H_6 is slightly positive (+0.002) [21]. The surface basicity in the alkali-modified catalysts might enhance the affinity between ethane and the catalyst surface, and hence the interaction of C–H bond with catalyst. The repulsion between π-electrons in alkene and the basic surface brings about the lower reactivity of ethene. The alkali-promoted selectivity to aldehydes with higher carbon number is explainable from the neutralization of acidic sites and hence the suppression of the C–C bond breaking on acid sites. The C–C bond formation catalyzed by alkali is another reason for this as discussed above.

5. Effect of the active site structure upon the catalytic performance and role of silica

Table 3 summarizes the relationship between the structure of active species M (M = Fe, V, Bi) on silica and their catalysis to give the selective oxidation products. Mononuclear species in the silica matrix often shows the tetrahedral coordination, in which a coordinatively unsaturated bond tend to appear as active site. On the other hand, redox property of active species might be restricted at the highly dispersed state on SiO_2 of the wide band gap oxide, due to the limitation of the electron delocalization.

Table 3
Selective oxidation products from ethane over the M/SiO_2 and $Cs–M/SiO_2$ catalysts supporting mononuclear or polymeric MO_x (M = Fe, V, Bi)

Catalysts (M/SiO_2)	Mononuclear M in the SiO_2 matrix		Polymeric MO_x on the SiO_2 surface	
	Cs-free	With Cs	Cs-free	With Cs
Fe/SiO_2	HCHO	C_2=O, C_3=O (high TOF)	C=C (CO_x)	CO_x
V/SiO_2	Less active	C_2=O, C_3=O (high TOF)	C=C (CO_x)	CO_x
Bi/SiO_2	HCHO, C_2=O, C_3=O	C_2=O, C_3=O (high TOF)	CO_x	CO_x

Indeed, the observed high-energy absorption in the UV–Vis spectra of mononuclear M/SiO_2 indicates the reduction of reactive electrons at around Fermi-level. Although the oxidative dehydrogenation observed on the catalysts with polymeric active sites might proceed with the redox mechanism [18,22–25], it is possible that aldehydes are produced via non-redox mechanism.

Carbon deposition on the catalysts with mononuclear active site, observed under oxygen-lean conditions, may indicate the catalysis for the C–H bond activation of the mononuclear species. Active oxygen can be supplied from silica in which the peroxide species at defect site, such as SSB (strained-siloxane bridge) [26], has been widely accepted [27]. Isolation of active site is favorable for the prevention of successive deep oxidation.

It is noteworthy that Cs-free V/SiO_2 with mononuclear V is less active in the ethane oxidation [12] though Cs-free mononuclear Fe/SiO_2 and Cs-free mononuclear Bi/SiO_2 give certain amount of aldehydes (Table 3). It has been reported that a direct interaction of alkali with the distorted tetrahedral VO_4 species on SiO_2 affects the nature of the V–O bond [28]. This may lead to the enhancement of the aldehyde productivity on the mononuclear V/SiO_2 catalysts modified by alkali metal elements.

6. Concluding remarks

Remarkable catalytic properties of silica with mononuclear active sites have been demonstrated in the selective oxidation of light alkanes into aldehydes. Although some qualitative interpretations for the unique properties, the high TOF and the high aldehyde selectivities, of the mononuclear active sites have been attempted, further detailed analysis at a molecular or an atomic level is required to elucidate more precisely the reaction mechanism on the mononuclear active sites. A comparison with selective oxidation induced by the Fe-containing enzymes, such as MMO (methane mono-oxygenase) and P-450, may help the better understanding of the role of mononuclear catalysis.

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