Acrolein formation in the oxidation of ethane over silica catalysts supporting iron and cesium

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A significant yield of aldehydes was obtained by the partial oxidation of ethane over alkali-modified Fe/SiO_2 catalysts at 475 °C (>2% in the case of $Cs–Fe/SiO_2$). Not only acetaldehyde and formaldehyde but also acrolein were produced in the present system. There are no reports regarding the catalysts for the direct acrolein formation from partial oxidation of ethane. Such significant promoting effect of alkali-modified Fe/SiO_2 catalysts in the partial oxidation of hydrocarbons has never been observed. Aldol-type condensation for formation of acrolein could occur in the partial oxidation of ethane over alkali-modified Fe/SiO_2 catalysts.

Keywords: ethane selective oxidation, acrolein, $Cs–Fe/SiO_2$, aldol condensation

1. Introduction

Direct production of oxygenates from ethane and oxygen is one of the enormous challenges in the catalysis research:

$$C_2H_6 + O_2 \rightarrow CH_3CHO + H_2O \qquad (1)$$

Oyama and Somorjai [1] have reported that a small amount of acetaldehyde is formed as a by-product of the ethene formation in the reaction between ethane and oxygen over silica and silica supporting vanadium oxide. Otsuka et al. [2] have found that BPO_4 could be a better catalyst producing acetaldehyde, which showed a selectivity to acetaldehyde of about 50% at an ethane conversion of 5%. Although pressurized reaction condition from 1 to 2 MPa is favored for the acetic acid formation from ethane and oxygen over $MoVNbO_x$ [3], $VTiO_x$ [4] and $MoVTiO_x$ [5], it seems difficult to obtain the acetic acid yield higher than 1%. Use of N_2O as an oxidant of ethane can bring about a certain progress in the oxygenates yield [6–9]. Such difficulties of the oxygenates formation are mainly due to the smaller stability of the products than that of ethane [10].

Kobayashi et al. [11] have reported that silica supporting a very small amount of iron ($Fe/Si = 0.05\%$ in atomic ratio) afforded a selective formaldehyde formation from methane and oxygen at the conversion of methane lower than 1%. Isolated, tetrahedrally coordinated Fe^{3+} in the silica network might play an important role for the formaldehyde formation [12]. More recently, Teng et al. have found that an addition of alkali metal ions to the Fe/SiO_2 catalysts can appreciably enhance the formation of acrolein and acetone in the reaction between propane and oxygen [13,14].

We have attempted to apply the Fe/SiO_2 catalyst to the oxidation of ethane and found that alkali-modified Fe/SiO_2 provided co-production of acetaldehyde and acrolein from ethane and oxygen. In this paper, reaction pathways and roles of alkali metals have been estimated.

2. Experimental

Catalysts were prepared by impregnating aqueous solutions of $Fe(NO_3)_3 \cdot 9H_2O$ (Kishida Chemicals) and alkali carbonates to silica (Merck extra-pure silica gel, BET surface area $= 400\ m^2\,g^{-1}$, 70–230 mesh). The loadings of promoters on the catalyst supports are expressed as atomic percentages and denoted as $Cs(0.6)–Fe(0.05)/SiO_2$, for example, where numerals in the parentheses represent (Cs/Si, Fe/Si × 100) in at%. Finally, the samples were calcined at 700 °C for 5 h in air. Loading amounts of Fe and alkali metal ions were 0.05 and 0.6 in at% to Si, respectively. After the calcination, the surface areas of the catalysts without alkali metals were almost identical to the initial value of $400\ m^2\,g^{-1}$, but they was about $250\ m^2\,g^{-1}$ for the samples impregnated with alkali metals.

Catalytic activities were measured by use of a flow-type reactor (quartz tube with 6 mm i.d.). Catalysts of 600 mg in weight were placed in the center of the reactor tube with quartz fiber. Space in the reactor (pre- and post-heating zone) was filled with quartz sand (Merck) to reduce the effect of the autoxidation of ethane and products in the gas phase. A reaction gas mixture consisting of 75 vol% C_2H_6 and 25 vol% O_2 was passed through the catalyst bed with a flow rate of $30\ ml\,min^{-1}$ at an atmospheric pressure (space velocity $= 3000\ ml\,h^{-1}$ g-catalyst^{-1}).

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Products were analysed by using two gas chromatographs: a FID-GC (GC-14B, Shimadzu) with a methanizer and a Porapack-Q column, and a TCD-GC (G-1800, Yanagimoto) with a MS-13X column. A FT-IR (FTIR-8200D, Shimadzu) equipped with a gas analytical cell ($l = 130$ mm) and a GC mass spectrometer (HP-G1801A) with a HR-20M column were used for the identification of the products.

The BET surface areas of the catalysts were measured by a flow-type surface area analyzer (Quantasorb Jr.).

3. Results and discussion

Table 1 shows typical results of the ethane oxidation over silica-catalysts-supported iron and alkali metal ions. As reported by Oyama et al. [1], pure silica could catalyze the oxidative dehydrogenation of ethane. Aldehydes in trace amounts were also detected. An addition of iron in a small amount to silica can enhance the catalytic activity. Dehydrogenation, formaldehyde formation and CO_x formation were mainly enhanced by the iron addition. The effect of the Cs addition to silica was small under the present reaction condition.

In contrast to the independent addition of Fe or Cs to silica, coexistence of Cs and Fe on silica can drastically enhance its activity toward the formation of aldehydes. It is noteworthy that an appreciable amount of acrolein was produced. Aldehydes of carbon number more than four (e.g., crotonaldehyde) were not detected. Rubidium seems to play a similar role as Cs for the acrolein formation over the Fe/SiO_2 catalysts. Such a cooperation effect of Fe and alkali was also observed in the propane oxidation into oxygenates [13,14].

As far as the reaction took place below 500 °C, no degradation of the catalytic activity was observed in a few hours at least. Only at a very high conversion of ethane and close to 100% conversion of oxygen, a decrease in the activity and carbon deposition were observed after the reaction.

Figure 1 shows the conversion of ethane and the product yields over the Cs(0.6)–Fe(0.05)/SiO_2 catalyst as a function of the reaction temperature. At lower temperatures, acetaldehyde was the main product among the aldehydes. The yields of acrolein and formaldehyde increased with increasing temperatures. These date were re-plotted as the product selectivities in figure 2. It is clear that the acetaldehyde selectivity decreases with increasing conversion of ethane and, in compensation for this, the acrolein selectivity increased. At higher conversions, increased formations of CO_x and ethene bring about a decrease in the total selectivity to the aldehydes.

Assuming that acetaldehyde is a primary product and that acetaldehyde is successively converted into acrolein with slight CO_x formation, such a behavior shown in figures 1 and 2 can be interpreted without conflict. Ethene might not be the primary product. This is because the ethene selectivity is low at low conversions.

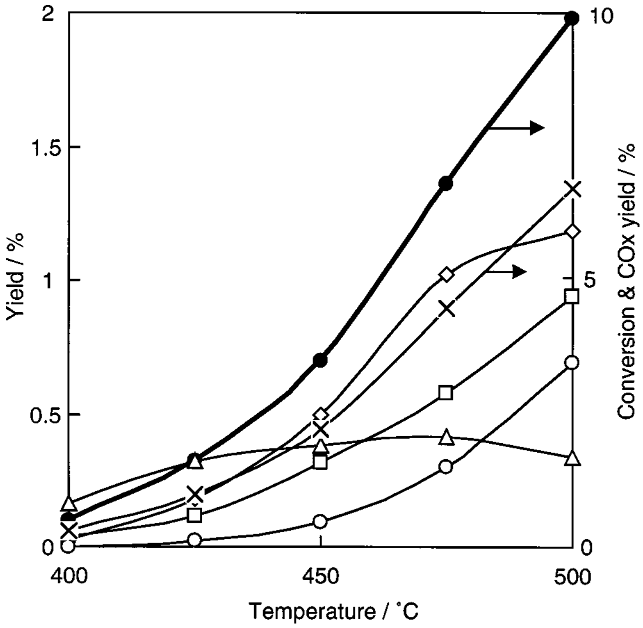


Figure 1. Effect of reaction temperature on the conversion of ethane and product yields over Cs(0.6)–Fe(0.05)/SiO_2 catalyst: (●) C_2H_6 conversion, (□) HCHO yield, (△) CH_3CHO yield, (◇) CH_2CHCHO yield, (○) C_2H_4 yield and (×) CO_x yield. Reactant gas: 75 vol% C_2H_6 + 25 vol% O_2. SV = 3000 ml h^{-1} g-catalyst^{-1}. Yields are calculated upon C_2 basis.

Table 1
Oxidation of ethane over silica supporting Fe and alkali.[a]

Catalyst[b]	C_2H_6 conv. (%)	Yield (%)					
		CH_3CHO	C_2H_3CHO	HCHO	C_2H_4	CO_x	The others
SiO_2	0.23	0.04	trace	0.02	0.05	0.11	–
Fe(0.05)/SiO_2	1.61	0.05	0.08	0.50	0.14	0.80	0.04
Cs(0.6)/SiO_2	0.16	0.02	0.01	0.03	0.04	0.06	–
Cs(0.6)–Fe(0.05)/SiO_2	6.76	0.36	1.10	0.51	0.35	4.39	0.05
Li(0.6)–Fe(0.05)/SiO_2	1.58	0.06	0.13	0.33	0.09	0.97	–
Na(0.6)–Fe(0.05)/SiO_2	2.17	0.13	0.24	0.20	0.09	1.51	–
K(0.6)–Fe(0.05)/SiO_2	3.09	0.23	0.45	0.22	0.14	2.05	–
Rb(0.6)–Fe(0.05)/SiO_2	4.03	0.28	0.55	0.36	0.17	2.67	–

[a] Reaction temperature: 475 °C, SV = 3000 ml h^{-1} g-catalyst^{-1}, yields were calculated upon C_2 basis. Reaction gas = 75 vol% C_2H_6 + 25 vol% O_2.

[b] Numerals in parentheses denote loading amounts of Fe, alkaline to Si in at% (100 M/Si).

In order to investigate the detailed pathway giving acrolein, the oxidation of possible intermediates was tested using pulse reactions. Ethene, ethanol vapor, and acetaldehyde vapor were injected into the reactor with air or nitrogen flow. The product distributions are monitored by FT-IR. Results are summarized in table 2.

Ethene was less reactive than ethane over the Cs–Fe/SiO_2 catalyst. Temperatures higher than 450 °C are needed to examine the ethene oxidation, while the oxidation of ethane is detectable even at 400 °C. Although acetaldehyde and acrolein are produced from ethene, such a lower reactivity of ethene supports the above consideration in which ethene might not be an intermediate giving acrolein.

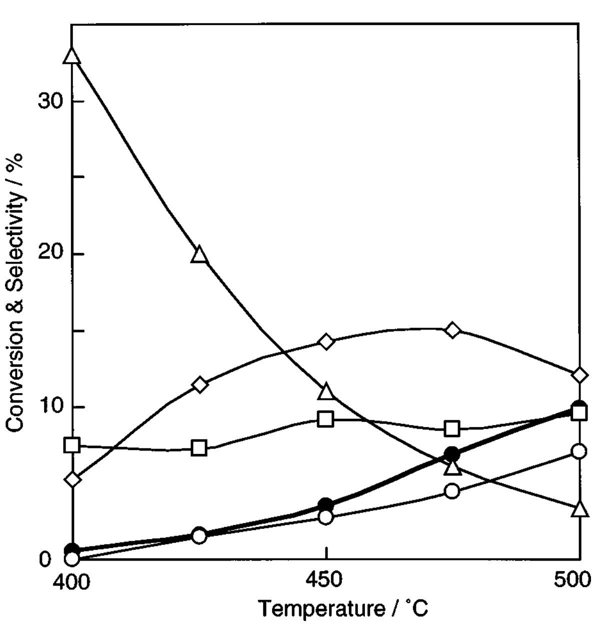


Figure 2. Effect of reaction temperature on the conversion of ethane and product selectivities over Cs(0.6)–Fe(0.05)/SiO_2 catalyst: (●) C_2H_6 conversion, (□) HCHO selectivity, (△) CH_3CHO selectivity, (◇) CH_2CHCHO selectivity and (○) C_2H_4 selectivity. Reactant gas: 75 vol% C_2H_6 + 25 vol% O_2. SV = 3000 ml h^{-1} g-catalyst^{-1}. Selectivities are calculated upon C_2 basis.

As for the low reactivity of ethene, its strong and exclusive adsorption or fast coking from ethene can be considered. Ethene was then added into the reactor, where the oxidation of ethane took place at 450 °C. No retardation of the ethane oxidation by ethene was, however, observed and most of added ethene was detected in the effluent from the reactor. A similar lower reactivity of alkene than alkane has also been observed in the propane oxidation over the alkali-modified Fe/SiO_2 catalysts [13,14]. Repulsion between π-electrons in alkenes and the basic surface of the catalysts might be the reason of the reactivity difference observed.

Although ethanol was not detected in the ethane oxidation, ethanol is one of the plausible intermediates. Indeed, acrolein as well as acetaldehyde can be detected in the ethanol oxidation. At the same time, a large amount of ethene was produced from ethanol. This indicates that dehydration of ethanol takes place easily in this system. In the ethane oxidation over the Cs–Fe/SiO_2 catalysts, however, the ethene formation was not distinct under the conditions for high acrolein selectivity (figure 2).

The reactivity of acetaldehyde was also examined. Even without catalyst, acetaldehyde easily reacts with oxygen. This auto-oxidation gives methanol and a large amount of CO_x. When the catalysts containing Cs (i.e., Cs/SiO_2 and Cs–Fe/SiO_2) were used, an appreciable amount of acrolein was produced. It is noteworthy that no reaction of acetaldehyde was observed over the Cs–Fe/SiO_2 catalyst under N_2 atmosphere. This fact suggests that a simple self-condensation of acetaldehyde does not contribute to the acrolein formation from ethane. In addition to this, acetaldehyde seems to be converted oxidatively into acrolein over the catalysts containing Cs.

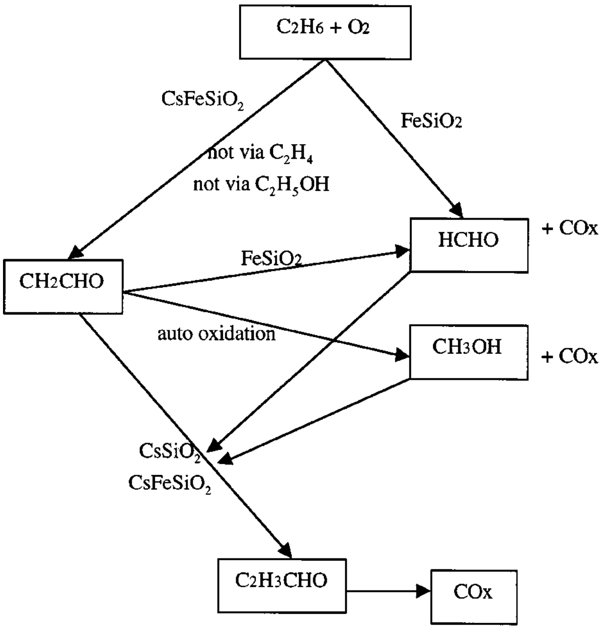
In summary, reaction pathways are proposed in scheme 1. Acetaldehyde is produced on $CsFeSiO_2$ from ethane. Acetaldehyde is then oxidatively converted into acrolein on $CsSiO_2$ and $CsFeSiO_2$. These two catalysts show similar ability to give acrolein from acetaldehyde (table 2), though their oxidation abilities are appreciably different (table 1). In addition to this, acetaldehyde is easily converted into

Table 2

Product distribution in the pulse reaction of C_2 compounds.[a]

Reactant	Catalyst	Temp. (°C)	Product selectivitiy (%)				
			Ac=O	C_3=O	MeOH	$C_2^=$	CO_x
C–C/air	Cs(0.6)–Fe(0.05)/SiO_2	450	10	15		10	65
C=C/air	Cs(0.6)–Fe(0.05)/SiO_2	500	5	15			80
EtOH/air	Cs(0.6)–Fe(0.05)/SiO_2	450	5	5		45	45
Ac=O/air	no	450			25		75
Ac=O/air	Cs(0.6)–Fe(0.05)/SiO_2	450		35		10	55
Ac=O/air	Cs(0.6)/SiO_2	450		40		10	50
Ac=O/air	Fe(0.05)/SiO_2	450		10	5		85
Ac=O/air	SiO_2	450		5	5		60
Ac=O/N_2	Cs(0.6)–Fe(0.05)/SiO_2	450	not reacted				

[a] Carrier gas = 80 vol% N_2 + 20 vol% O_2 or 100 vol% N_2. Amount of reactant added = 1 ml (at gaseous state). SV = 3000 ml h^{-1} g-catalyst^{-1}. Selectivities were calculated upon C_2 basis. Numerals in parentheses denote loading amounts of Fe, alkaline to Si in at% (100 M/Si).



Scheme 1. Proposed reaction pathways from ethane to acrolein.

methanol and CO_x through the auto-oxidation. The direct route of the acrolein formation might be, therefore, the Cs-catalyzed cross-condensation [15,16] of acetaldehyde and formaldehyde or methanol formed in the auto-oxidation of acetaldehyde. Formaldehyde produced on $FeSiO_2$ from ethane also possibly contributes to the cross-condensation.

4. Conclusion

A high yield of acrolein can be obtained by the partial oxidation of ethane in the presence of Cs(0.6)–Fe(0.05)/SiO_2 at 475 °C (ca. 1.1%). Addition of cesium to the Fe/SiO_2 catalysts can enhance both the conversion of ethane and the selectivity to acrolein. Cesium can catalyze an aldol-type condensation between acetaldehyde and formaldehyde to give acrolein. In addition, excess oxidation and/or C–C cracking over the isolated Fe site on silica seems to be spoiled by cesium.

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