

Reaction pathways for the oxygenates formation from propane and oxygen over potassium-modified Fe/SiO₂ catalysts

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The partial oxidation of propane has been compared on Fe/SiO₂ and alkali-modified Fe/SiO₂ catalysts. Addition of K⁺ to the catalyst can appreciably enhance the conversion of propane along with a high selectivity toward oxygenates. Adjacency of Fe and K on the silica surface seems to be important for the high oxygenate yield. Through the study on the reaction pathways, two types of intermediates, one derived from propene and the other from propan-2-ol, were postulated. The former is related to the acrolein formation and the latter to the acetone formation. Contribution of alkali-catalyzed aldol condensation is also discussed for the formation of oxygenates with higher carbon numbers.

Keywords: propane selective oxidation, potassium promoter, Fe/SiO₂, acrolein, acetone, aldol-condensation

1. Introduction

Direct conversion of light alkanes into oxygenates has been attracting interest for the utilization of hydrocarbon resources [1]. Oxygenation of propane has been attempted by using multi-component oxide catalysts [1–6]. Among them, the catalysts containing vanadium and/or molybdenum have been intensively studied in detail to clarify the catalytic active site [7,8].

Kobayashi [9] reported that silica catalysts impregnated with a very small amount of iron (Fe/SiO₂; Fe:Si = 0.05 : 100) can catalyze the oxidative conversion of methane into formaldehyde, and considered that tetrahedrally coordinated Fe³⁺ in the amorphous silica network play an important role [10]. The Fe/SiO₂ catalyst also showed activity in propane selective oxidation to give oxygenates such as acrolein, acetaldehyde, and formaldehyde, however, conversion of propane was low in comparison with the catalysts containing Mo and/or V. Recently, a promotion effect on the oxygenate formation in the propane oxidation has been found by adding K⁺ to the Fe/SiO₂ catalyst (K/Fe/SiO₂) [11]. Over the K⁺-modified Fe/SiO₂ catalyst, selectivity toward oxygenates was kept at 48% when the propane conversion was raised to 10% at 748 K [11].

So far, effects of alkaline promoter on titania or silica catalysts supporting V or Mo have been reported in the alkane selective oxidation [12–15]. Although most of researchers have recognized that alkali metal cations lead to a decrease in surface acidity, different explanations of the promotion effects have been proposed. Actually, because alkali metal ions are considered to be both electronic and structure promoters [13,14,16], it is not particularly surprising that alkali metal ions play different roles when added

in different catalysts. In this study, effect of K⁺ promoter on Fe/SiO₂ in the propane oxidation has been investigated in detail to find the reason why potassium enhanced both propane conversion and selectivity toward oxygenates and to give a possible reaction pathway.

2. Experimental

Silica supporting Fe³⁺ ions was prepared by impregnation of SiO₂ powder (Merck silica gel, extra pure; specific surface area = 400 m² g⁻¹, 70–230 mesh) with aqueous solutions of iron nitrate. Calcination was done at 973 K for 5 h. Silica supporting Fe (0.05 at%) was modified by impregnation with an aqueous solution of potassium carbonate. The loading of Fe³⁺ ions or K⁺ was expressed as the atomic ratio of metal to Si. Potassium-modified Fe/SiO₂ was further calcined at 973 K for 5 h. For comparison, simple mechanical mixtures of Fe/SiO₂ with K₂CO₃ and with K/SiO₂ were also used as catalysts.

The BET surface areas of the catalysts were measured by a flow-type surface area analyzer (Quantasorb Jr.). An X-ray diffraction analysis of the catalysts was carried out by use of a computer-controlled goniometer (Rigaku RINT 2000) with a monochromized Cu K α 1 line.

A fixed bed flow reactor (quartz tube, 6 mm i.d.) was used at atmospheric pressure for catalytic activity measurements. The catalyst sample (300 mg) was fixed in place by quartz wool, and the space of the reactor before and after the catalyst bed was filled with quartz sand. The reactant gas mixture containing 20 vol% of propane, 16 vol% of oxygen, and 64 vol% of nitrogen was passed through the catalyst bed at a flow rate of 50 ml min⁻¹. In the case of the propene oxidation, 20 vol% of propene instead of propane was used under the same reaction conditions.

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Products were analyzed by two gas chromatographs, a FID-GC with Porapack-Q column and a TCD-GC with Molecular Sieve 13X column. The former GC was equipped with a Ni-catalyzed methanizer by which all the oxygenates analyzed were converted into corresponding alkanes just before the FID. Data shown here were obtained after stabilization of the reactions for 1 h.

Oxidation of propanols was also examined to check successive reactions of propanols. Air containing 2.7 vol% propan-1-ol (5 ml) or 5.9 vol% propan-2-ol (5 ml) was injected to the catalyst bed under flowing air with a rate of 50 ml min⁻¹. Products were identified with an FTIR (Shimadzu FTIR-8200 D) having a gas analytical cell (*l* = 130 mm).

3. Results and discussion

Figure 1 shows the conversion and the products distribution of the propane oxidation over K⁺-modified Fe/SiO₂ catalyst as a function of temperature. As already reported in our previous study [11], a variety of oxygenates with carbon numbers from one to four can be seen as the products. Acrolein and acetone account for 67% of the total oxygenates produced at 748 K. With increasing temperature, the propane conversion increases and the selectivity to oxygenates decreases. Deep oxidation of oxygenates into CO_x becomes favorite at higher conversions. Formaldehyde and acetaldehyde seem to be more easily oxidized than C3- and

C4-oxygenates, probably because of the poor stability in C1- and C2-aldehydes [17]. It is worth noting that the acrolein selectivity increases slightly with an increase in temperatures from 673 to 748 K. Besides the high stability of acrolein, a part of acrolein was perhaps produced by a successive reaction of other primary products. The alkene formation is not so remarkable, and a certain amount of propene was detected only at 773 K on K/Fe/SiO₂ and at 798 K on Fe/SiO₂.

Figure 2 shows results of the propane oxidation at 723 K under a varying space velocity (SV). The propane conversion decreases with increasing SV and concomitantly the selectivity to oxygenates, especially C1- and C2-aldehydes, increases. The formation of alkenes and CO_x becomes appreciable under smaller SV or at higher conversions. Among the oxygenate selectivities, only the acrolein selectivity does not depend so much upon the change in the propane conversion. These phenomena as a function of the propane conversion are qualitatively identical to those observed in figure 1.

For comparison with the results shown above, the propane oxidation was examined over K⁺-free Fe/SiO₂ as a function of temperature and of SV. The results are shown in figures 2 and 3. The following points are noticeable in the K⁺-free catalyst:

- (a) the propane conversion is about one third or one fourth of that of K/Fe/SiO₂;

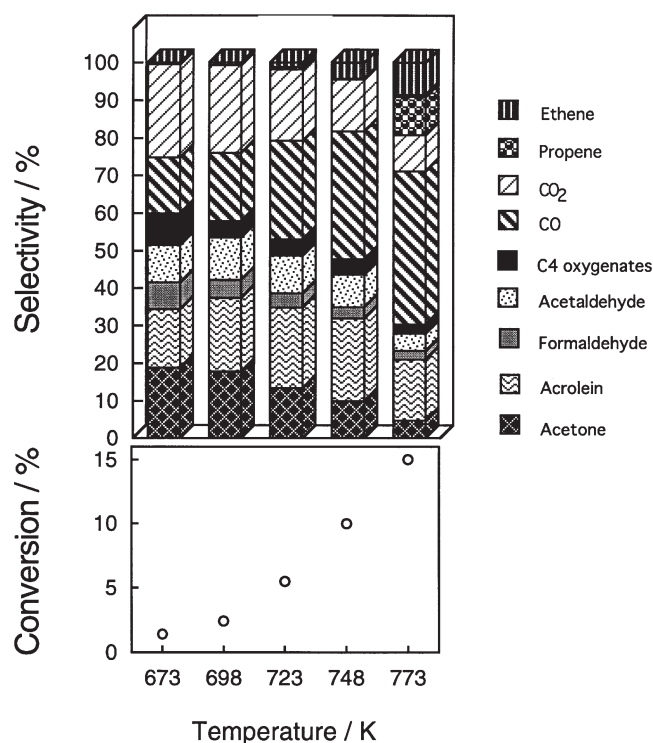


Figure 1. Propane conversion and products distribution over K/Fe/SiO₂ catalyst under different reaction temperature. Reaction gas: 20% C₃H₈ + 16% O₂ + 64% N₂, SV: 10,000 h⁻¹ ml/g_{cat}, atomic ratio of K:Fe:Si = 0.6:0.05:100.

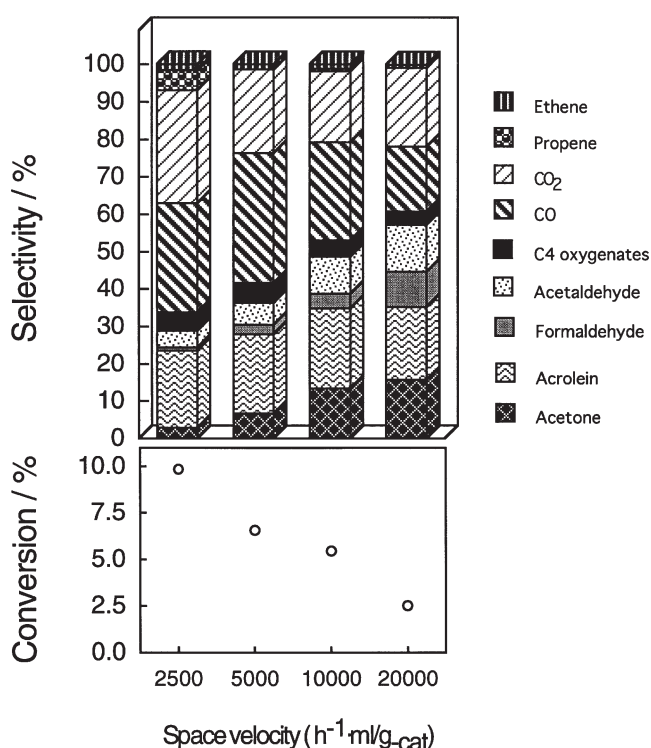


Figure 2. Effect of space velocity on propane conversion and products distribution over K/Fe/SiO₂ catalyst. Reaction gas: 20% C₃H₈ + 16% O₂ + 64% N₂, reaction temperature: 723 K, atomic ratio of K:Fe:Si = 0.6:0.05:100.

- (b) the selectivities to acetone and propene are lower and the selectivities to formaldehyde and acetaldehyde are higher than those of K/Fe/SiO₂;
- (c) C4-oxygenates are not detected in any case.

Table 1 summarizes the results of the propane oxidation over Fe/SiO₂ with a variety of K⁺ loadings, Fe-free K/SiO₂, and a simple mixture of Fe/SiO₂ with K₂CO₃. Almost no effect of the K⁺ addition was observed on Fe/SiO₂ supporting 0.02 at% K⁺, which is much lower than the Fe-loading (0.05 at%) on SiO₂ and probably insufficient

for modification of the isolated Fe site. As for the selectivity to oxygenates, K⁺ loadings higher than 0.35 at% bring about a similar performance upon the Fe/SiO₂ catalysts. The propane conversion, however, was highest upon Fe/SiO₂ supporting 0.6 at% K⁺. Higher K⁺ loadings reduce the specific surface area of the catalysts and probably lead to the lower conversions of propane. This is perhaps due to a partial dissolution of the silica surface during the K⁺ impregnation by use of basic solutions. Optimum concentration of alkali promoter in molybdenum or vanadium catalysts which are used in propene oxidation has been re-

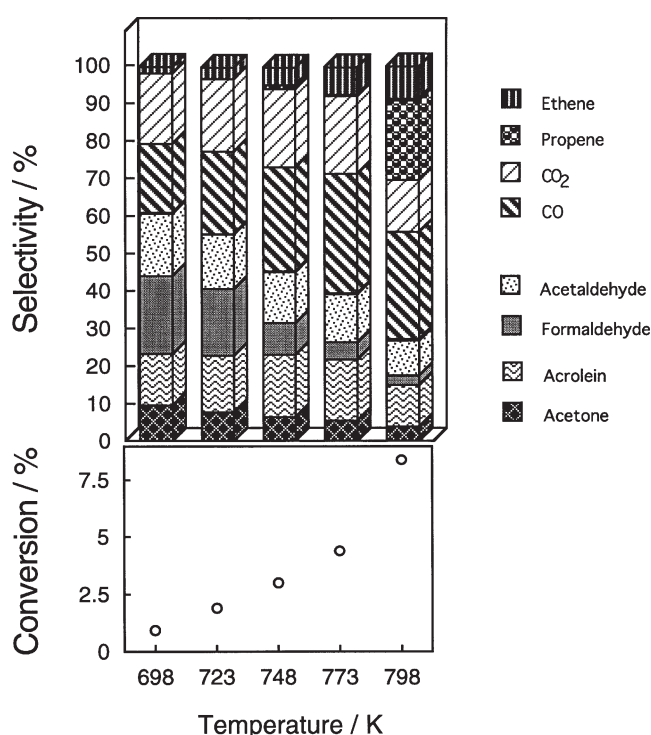


Figure 3. Propane conversion and products distribution over Fe/SiO₂ catalyst under different reaction temperature. Reaction gas: 20% C₃H₈ + 16% O₂ + 64% N₂, SV: 10,000 h⁻¹ ml/g_{cat}, atomic ratio of Fe:Si = 0.05:100.

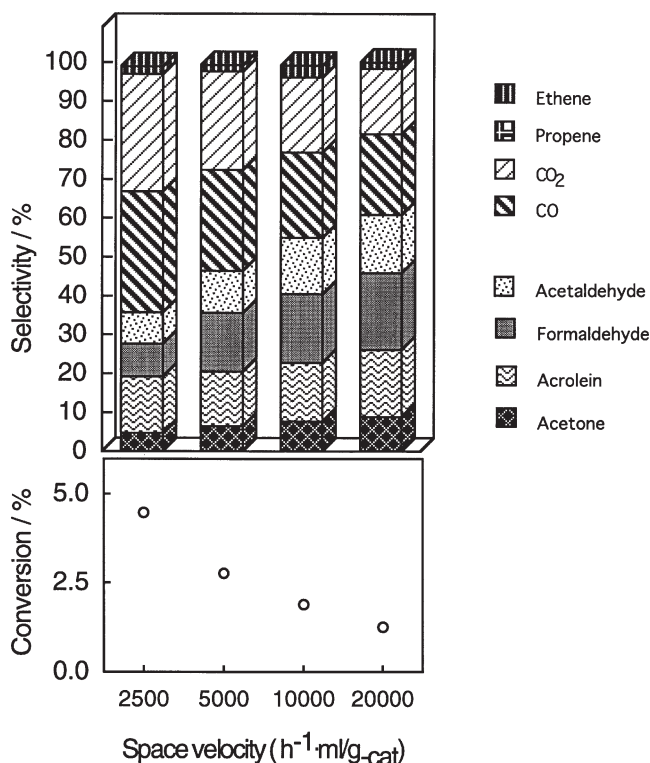


Figure 4. Effect of space velocity on propane conversion and products distribution over Fe/SiO₂ catalyst. Reaction gas: 20% C₃H₈ + 16% O₂ + 64% N₂, reaction temperature: 723 K, atomic ratio of Fe:Si = 0.05:100.

Table 1
Oxidation of propane over the Fe/SiO₂ catalysts at 748 K.^a

Catalyst	Fe/Si or K/Fe/Si (atomic ratio)	Specific surface area (m ² /g)	C ₃ H ₈ conv. (%)	Selectivity (%)							
				Oxygenates ^b						Olefins ^c	CO _x ^d
				Total	C1	C2	C3a	C3b	C4		
Fe/SiO ₂	0.05/100	394.0	3.5	41.5	4.3	11.4	20.6	5.2	0.0	4.3	54.3
K/Fe/SiO ₂	0.02/0.05/100	351.8	3.6	40.9	5.5	10.1	19.2	3.8	2.3	3.7	55.4
	0.35/0.05/100	277.7	7.7	47.7	2.6	9.1	25.2	7.6	3.3	6.1	45.5
	0.6/0.05/100	251.1	10.0	48.0	3.0	9.0	22.0	10.0	4.0	4.0	48.0
	1.0/0.05/100	170.8	7.4	52.9	2.7	9.5	26.2	10.5	4.0	1.9	44.6
	1.5/0.05/100	119.4	4.0	43.5	1.7	7.8	17.1	11.7	5.2	0.9	55.7
K/SiO ₂	0.5/0/100	267.7	0.1	48.5	0.0	5.3	33.5	9.7	0.0	8.2	43.3
K ₂ CO ₃ and Fe/SiO ₂	5/0.05/100	—	3.7	37.4	4.2	5.3	21.9	2.9	3.2	2.6	60.0

^a Reactant gas: 20% C₃H₈ + 16% O₂ + 64% N₂.

^b C1: formaldehyde; C2: acetaldehyde; C3a: acrolein; C3b: acetone; C4: 3-buten-2-one and 2,3-dihydrofuran.

^c Olefins: propene and ethene.

^d CO_x: CO and CO₂.

Table 2
Oxidation of propane or propene over the Fe/SiO₂ catalysts at 723 K.

Reactant	Catalyst	Fe/Si or K/Fe/Si (atomic ratio)	Conv. reactant (%)	Selectivity (%)							CO _x ^c
				Oxygenates ^a						Olefins ^b	
				Total	C1	C2	C3a	C3b	C4		
Propane ^d	Fe/SiO ₂	0.05/100	1.9	55.6	17.8	14.6	15.2	7.7	0.0	3.0	41.4
	K/Fe/SiO ₂	0.6/0.05/100	5.5	53.0	4.0	10.0	21.0	13.0	4.0	2.0	45.0
Propene ^e	Fe/SiO ₂	0.05/100	2.6	62.1	2.9	26.7	28.0	4.4	0.0	3.2	34.2
	K/Fe/SiO ₂	0.6/0.05/100	1.8	52.0	3.8	10.2	30.4	4.6	3.0	0.7	47.3

^a C1: formaldehyde; C2: acetaldehyde; C3a: acrolein; C3b: acetone; C4: 3-buten-2-one and 2,3-dihydrofuran.

^b Olefins: propene and ethene.

^c CO_x: CO and CO₂.

^d Reactant gas: 20%C₃H₈ + 16%O₂ + 64%N₂.

^e Reactant gas: 20%C₃H₆ + 16%O₂ + 64%N₂.

ported [16,18,19]. It was pointed out that a small amount of alkali metal ions acted as the electronic promoters to raise the catalytic activity, but higher concentration of alkali metals in the catalysts produced an inactive phase with transition metals [16]. In the present study, a formation of new phase was not observed by a X-ray diffraction analysis in Fe/SiO₂ with high K⁺ loadings.

Potassium itself seems not to have a ability activating propane, because of the poor activity of K/SiO₂. When a simple mechanical mixture of Fe/SiO₂ with K₂CO₃ (K/Si = 5 at%) was used as a catalyst, a propane conversion almost the same as for Fe/SiO₂ was observed with a higher selectivity to C4-oxygenates and lower selectivities to acetaldehyde and acetone than those for Fe/SiO₂. Qualitatively similar results were obtained if a simple mixture of K/SiO₂ and Fe/SiO₂ (K : Fe : Si = 0.6 : 0.05 : 200) was used as a catalyst. The probability of the adjacency between Fe and K on silica is believed to be much lower in the simple mixture of Fe/SiO₂ with K₂CO₃ or K/SiO₂ than in the K/Fe/SiO₂ catalysts. This strongly suggests that the isolated K⁺ can catalyze the formation of C4 oxygenates but the adjacent Fe–K site is indispensable for the high propane conversion and the high selectivity to acetone.

It can be considered that isomorphous substitution of Si in silica by Fe brings about an advent of acid sites as reported in the case of several zeolites including ferrisilicate [20,21], over which breaking of the C–C bond of propene happened to give C2 and C1 carbonium ions, and then oxygenates with low carbon number [22]. Relatively low selectivities to formaldehyde and acetaldehyde observed on the K⁺-modified catalysts might be due to the neutralization of the acid sites by K⁺ and hence the suppression of the C–C bond scission.

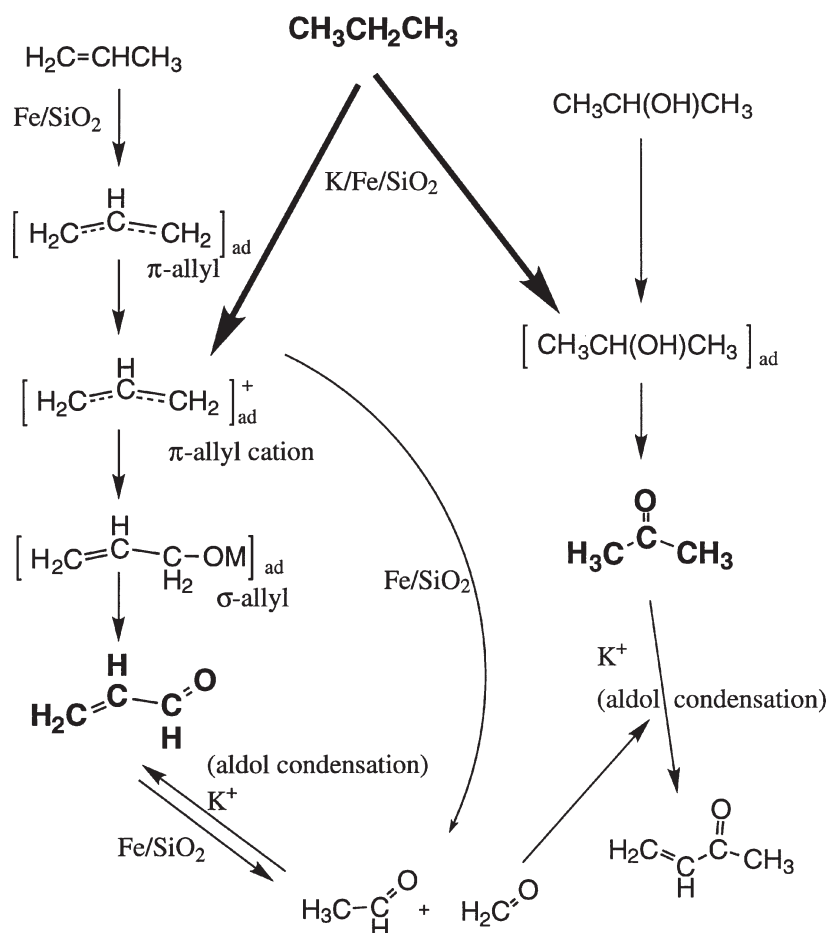
Another explanation of the higher selectivities to the oxygenates with higher carbon numbers is based on alkali-catalyzed aldol-type condensation [23]. It has been reported that alkali elements can catalyze the condensation between acetone and formaldehyde giving 3-buten-2-one [23] which is about 70% of C4-oxygenates produced at 748 K. Acrolein has been also reported to be produced by the aldol-type condensation of formaldehyde with acetaldehyde [24]. Assuming that part of the acrolein is produced this way, the slight

increase in acrolein selectivity with increasing conversion of propane (figures 1 and 2) is explainable.

Gaseous propene has been considered as an intermediate of the propane oxidation to give acrolein over AgBiMoVO catalysts [25]. This mechanism has been accepted by other investigators [26,27]. Therefore, instead of propane, the oxidation of propene was examined at 723 K to check if the propane oxidation over Fe/SiO₂ and K/Fe/SiO₂ proceeds via propene intermediate. The results are shown in table 2. Both the conversion and the acrolein selectivity in the propene oxidation were higher than those in the propane oxidation over K⁺-free Fe/SiO₂. This indicates that propene or propene-derived adsorbate, such as π -allyl [26,28], perhaps is the intermediate in the acrolein formation from propane over K⁺-free Fe/SiO₂. A higher acetaldehyde selectivity from propene supports the deduction of the acetaldehyde formation by the decomposition of propene [29] or acrolein over the K⁺-free catalyst.

On the other hand, the K⁺-modified catalyst showed somewhat lower propene conversion than that of K⁺-free catalyst. The smaller surface area of K/Fe/SiO₂ (see table 1) is one of the reasons for its low propene conversion. However, in addition, the propene conversion over K/Fe/SiO₂ is much smaller than the propane conversion on this catalyst. A rapid coking from propene or an exclusive strong adsorption of alkene on the active site might be excluded from reason of the low propene conversion on K/Fe/SiO₂. This is because no degradation in the activity was observed when about 5 vol% propene was added to the reactant gas mixture for the propane oxidation on K/Fe/SiO₂.

It has been considered that a repulsive interaction between alkenes and basic surfaces of catalysts facilitates the desorption of alkenes from the catalysts [30,31]. This may explain the low reactivity of propene over the alkali-modified surface. If molecular propene was formed on K/Fe/SiO₂, it could be rapidly desorbed from the surface. Actually, the propene formation on K/Fe/SiO₂ is observed at lower temperature than that for Fe/SiO₂. It can be concluded, therefore, that gaseous propene is hard to be assumed as the intermediate leading to the oxygenates in the propane oxidation on K/Fe/SiO₂. Instead, π -allyl cation [32], which might be generated in the propane dehy-



Scheme 1. Proposed reaction pathways for the oxygenates formation.

drogenation and stabilized on the basic surface, is proposed as an intermediate from propane; it would then react with oxygen to give acrolein through σ -allyl species [28,33].

When the propane oxidation on K/Fe/SiO₂ was examined by using catalyst diluted by quartz sand or using a reactor with empty zone above the catalyst bed [25], the catalytic activity was almost not changed. Therefore, radicals in the gas phase [34] probably did not promote the reaction at the present temperature range.

The lower selectivity to acetone from propene both on Fe/SiO₂ and K/Fe/SiO₂ suggests that acetone is not mainly produced via propene or a propene-derived intermediate. Propan-2-ol has been considered as an intermediate for the acetone formation [32,35]. Indeed, addition of alkali brings about an enhancement of the acetone formation in the decomposition of propan-2-ol on V/TiO₂ and Mo/TiO₂ catalysts [14,36]. Therefore, the oxidation of propanols was examined by passing propan-1-ol vapor or propan-2-ol vapor diluted with air through the K/Fe/SiO₂ catalyst at temperatures higher than 573 K. Acetone along with CO_x were detected as the products in the propan-2-ol oxidation, indicating that acetone is probably formed through a propan-2-ol-derived intermediate from propane. Propan-2-ol has been also considered as an intermediate giving propene and acrolein [32,35], but this mechanism cannot be adopted in

the present system. In the case of the propan-1-ol oxidation, only CO_x formation was observed, and this may be due to the instability of propan-1-ol [32].

The reaction pathways proposed on the basis of the above results are given in scheme 1.

Although the peculiar high activity of K/Fe/SiO₂ in the propane oxidation could not be explained sufficiently yet, such an affinity of this catalyst for the alkane oxidation was again observed in the comparison of the ethane oxidation and the ethene oxidation [37]. Activation of oxygen may easily occur on the catalyst surface which has good balance between the acid and basic surface properties and the redox property [1,31,32]. It is plausible that an oxygen species with a high nucleophilicity is formed on the Fe site modified electronically by alkali [16,38] and the repulsive interaction between alkene and the basic surface brings about an apparent affinity of the K/Fe/SiO₂ catalysts toward alkane.

4. Conclusions

The K⁺-modified Fe/SiO₂ catalysts afforded higher conversion and higher selectivity to oxygenates than was observed on the K⁺-free Fe/SiO₂ catalyst in the oxidation of

propane. The role of K^+ for such a high yield of oxygenates was studied and the following factors could be proposed.

(1) Repulsion between alkenes and the basic surface of the K^+ -modified catalysts brings about an apparent or a relative high affinity toward alkanes.

(2) Neutralization of the acid site on Fe/SiO_2 by K^+ suppresses the scission of the C–C bond and hence the formation of the products with lower carbon numbers.

(3) Aldol-type condensation catalyzed by K^+ facilitates the formation of oxygenates with higher carbon numbers.

Electronic influence by K^+ to the isolated Fe site on silica may facilitate the oxygen activation and hence the rate of oxidation. As for the reaction pathway, two different intermediates were postulated. One is a propene-derived intermediate such as π -allyl cation and responsible for the acrolein formation. The other one is related to he acetone formation and is an adsorbate derived from propan-2-ol.

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