

Formation of Oxygenates in the Propane Oxidation over K⁺ Modified Fe/SiO₂ Catalyst

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Oxygenates are formed in the propane oxidation over silica catalysts supporting a very small amount of Fe. Alkali addition to the catalysts can enhance the activity as well as the selectivity to acrolein and acetone.

Direct conversion of light alkanes into oxygenates has been attracting interests for the utilization of hydrocarbon resources. Oxygenation of propane have been attempted by using oxide catalysts most of which include molybdenum, vanadium and/or phosphorous¹⁻⁶. Among them, heteropoly acids³ containing Fe have been reported to give acrylic acid with relatively good selectivity over 20%.

One of the present authors⁷ has reported that silica catalysts impregnated with a very small amount of transition metal ions (M/SiO₂) can catalyze the oxidative conversion of methane into formaldehyde. Tetrahedrally coordinated Fe³⁺ in the amorphous silica network is considered to play an important role⁸. Uddin et al.⁹ reported that ferrisilicate could catalyze the oxidative dehydrogenation of propane. These results motivated us to study the behavior of the Fe/SiO₂ catalyst in the oxidation of propane. In this letter, we report the formation of oxygenates over Fe/SiO₂ and effects of K⁺ addition to the Fe/SiO₂ catalyst on the oxygenate formation.

Silica supporting transition metal ions was prepared by impregnating SiO₂ powder (MERCK silica gel, extra pure; specific surface area = 400 m² g⁻¹, 70–230 mesh) with aqueous solutions of metal nitrates. Calcination was done at 973K for 5 h. In the case of V/SiO₂ and Mo/SiO₂, ammonium salts were used for the impregnation and the samples were calcined at 773K. Silica supporting Fe (0.05 atom % to Si) was then impregnated with an aqueous solution of K₂CO₃, in which the ratio of K to Si was 0.6 atom %, and it was further calcined at 973K for 5h.

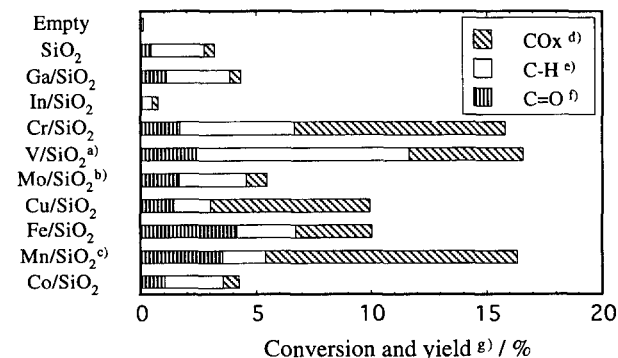


Figure 1. Propane conversion and product distribution in the oxidation of propane over SiO₂ supporting transition metal ions (M/Si=0.05 atom %) at 823K.

P(C₃H₈)=20.2kPa, P(O₂)=16.2kPa, P(N₂)=64.6kPa, SV=10000h⁻¹·ml·g⁻¹.
a): V/Si=0.5 atom %, b): Mo/Si=1.0 atom %, c): at 773K, d): CO and CO₂,
e): C₂H₄, C₃H₆, and CH₄, f): formaldehyde, acetaldehyde, acrolein, and acetone, and g): calculated on C₃ basis.

The specific surface area of the M/SiO₂ catalysts after the calcination was almost equal, within 5% reduction, to that of the fresh SiO₂ support, and the surface area of the K/Fe/SiO₂ catalyst after the calcination was 250 m² g⁻¹.

A fixed bed flow reactor (quartz tube, 6 mm i.d.) was used for activity measurements. The reactant gas mixture containing 20 vol. % propane, 16 vol. % oxygen, and 64 vol. % nitrogen was passed through the catalyst bed (Catal. wt. = 300 mg) at a flow rate of 50 ml min⁻¹ (Space velocity = 1×10⁴ h⁻¹ ml g⁻¹). Products were analyzed by two gas chromatographs, FID-GC with a

Table 1. Oxidation of propane or propene over the Fe/SiO₂ catalysts

Reactant	Catalyst	Fe/Si or K/Fe/Si (atomic ratio)	Temp. (K)	Conv. (%C ₃ H ₈)	Selectivity (%)							
					Total	C1 ^{a)}	Oxygenates C2 ^{b)}	C3a ^{c)}	C3b ^{d)}	C4 ^{e)}	Olefins ^{f)}	CO _x ^{g)}
Propane ^{h)}	Fe/SiO ₂	0.03/100	748	3.5	41.5	4.3	11.4	20.6	5.2	0.0	4.3	54.3
		0.05/100	723	1.9	55.6	17.8	14.6	15.2	7.7	0	3.0	41.4
		0.05/100	748	3.0	45.6	8.6	13.7	16.7	6.4	0	4.7	48.7
		1.0/100	748	1.3	21.1	8.1	1.5	10.7	0.8	0	2.7	76.3
		5.0/100	748	5.4	1.2	0	0.1	1.1	0	0	31.2	67.6
	α-Fe ₂ O ₃	/	748	18.1	0.4	0	0	0	0	0	58.4	41.2
	K/Fe/SiO ₂	0.6/0.05/100	723	5.5	53.0	4.0	10.0	21.0	13.0	4.0	2.0	45.0
		0.6/0.05/100	748	10.0	48.0	3.0	9.0	22.0	10.0	4.0	4.0	48.0
	K/SiO ₂	0.5/0/100	748	0.1	48.5	0.0	5.3	33.5	9.7	0	8.2	43.3
Propene ⁱ⁾	Fe/SiO ₂	0.05/100	723	2.6	62.1	2.9	26.7	28.0	4.4	0	3.2	34.2
	K/Fe/SiO ₂	0.6/0.05/100	723	1.8	52.0	3.8	10.2	30.4	4.6	3.0	0.7	47.3

a) C1: formaldehyde, b) C2: acetaldehyde, c) C3a: acrolein, d) C3b: acetone, e) C4: 3-buten-2-one and 2,3-dihydrofuran,

f) Olefins: propene and ethene, g) CO_x: CO and CO₂, h) reactant gas: 20%C₃H₈+16%O₂+64%N₂, and i) reactant gas: 20%C₃H₆+16%O₂+64%N₂.

Small amount of CH₄ was detected from all the K⁺ free catalysts.

Porapak-Q column and TCD-GC with a Molecular Sieve 13X column.

Figure 1 shows the conversion of propane and the yields of products in the propane oxidation over silica catalysts supporting transition metal ions. Under this reaction condition, non-catalytic auto-oxidation of propane in the empty reactor could be ignored, although remarkable conversion of propane was observed at above 873K giving mainly olefins¹⁰ (olefin selectivity > 90%). As reported by Sokolovskii¹¹ et al., additive-free SiO₂ can catalyze oxidative dehydrogenation of propane. Addition of transition metal ions to SiO₂ enhanced the catalytic activity. Transition metal ions on SiO₂ might provide redox centers which lead to the higher propane conversion. Among the catalysts tested, the highest selectivity to the oxygenates was obtained over Fe/SiO₂ with a relatively high oxygenate yield.

Effect of the loading amount of Fe³⁺ to SiO₂ on the propane oxidation was examined and results were shown in Table 1. As far as the quantity of Fe³⁺ is kept below 0.1 atom % to Si, a pronounced amount of oxygenates are produced where acrolein is a main component among the oxygenates. However, the catalytic property of silica with Fe-loadings exceeding 1 atom % became resemble to that of hematite which gave only olefins and carbon oxides. This indicates that the small quantity of Fe-loading to silica is essential for the oxygenate formation. Highly dispersed Fe³⁺, probably with tetrahedral coordination⁸, on the amorphous silica matrix might play an important role. This distinctly contrasts with the oxidative dehydrogenation of propane over ferrisilicate⁹ which also has the tetrahedral Fe³⁺ in the silicalite network.

Addition of K⁺ to Fe/SiO₂ was found to enhance the catalytic activity and the selectivity to oxygenates. Results are also shown in Table 1. The propane conversion at 723K on K/Fe/SiO₂ is higher than that obtained at 748K on K⁺-free Fe/SiO₂. The selectivity to the oxygenates with high carbon number tends to be high on K/Fe/SiO₂ and concomitantly the less selectivities to olefins and to the oxygenates with low carbon number are observed. Silica supporting only K⁺ (K/SiO₂) is less active to this reaction. Coexistence of K⁺ and Fe³⁺ on silica is, thus, indispensable for the high conversion and the high oxygenate yield in the propane oxidation. It has been proved that other alkali ions such as Cs⁺ and Rb⁺ show similar promotion effect as K⁺ on the oxygenate formation from propane.

Oxidation of propene, instead of propane, has been examined at 723K over Fe/SiO₂ and K/Fe/SiO₂ (Table 1). In the case of Fe/SiO₂, a higher conversion of propene than that of propane was observed with a higher selectivity to acrolein from propene. Although the conversion of propene was lower than

that of propane on K/Fe/SiO₂, a higher acrolein selectivity from propene was also observed. It is worth noting that acetone formation is less in the propene oxidation while the propane oxidation over K/Fe/SiO₂ gave the high acetone yield. When a mixture of 10 vol. % propane and 10 vol. % propene was used as reactants, conversion and selectivities were intermediate values between those obtained in the propane oxidation and in the propene oxidation.

These results might indicate that acrolein is formed via propene or propene-derived adsorbate as an intermediate from propane. It is also suggested that the promotion effect of K⁺ on the propane oxidation might be, at least partly, due to an acceleration of a reaction path related to the acetone formation. It has been reported that an addition of alkali to the catalysts enhances acetone formation and suppresses propene formation in the decomposition of propane-2-ol over V/TiO₂ and Mo/TiO₂ catalysts¹³. Propane-2-ol vapor diluted in air was confirmed to be converted into acetone and COx over the K/Fe/SiO₂ catalyst at 723 K. So, an adsorbate derived from propane-2-ol seems to be one of the possible intermediates for the acetone formation.

Role of alkali metals in the propane oxidation over the Fe/SiO₂ catalysts is still unclear at present. Redox property of Fe might be modified by alkali metals. It is plausible that alkali leads to the suppression of the C-C bond scission on acid site and hence the higher selectivity to C3-oxygenates. Alkali-catalyzed aldol-type condensation¹² between acetone and formaldehyde can give 3-buten-2-one, which constitutes about 70% of C4-oxygenates produced over the K/Fe/SiO₂ catalyst. Detailed reaction mechanism is currently investigated.

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