Formation of Oxygenates in the Propane Oxidation over K^+ Modified Fe/SiO_2 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 phosphorous[1-6]. Among them, heteropoly acids[3] containing Fe have been reported to give acrylic acid with relatively good selectivity over 20%.

One of the present authors[7] has reported that silica catalysts impregnated with a very small amount of transition metal ions (M/SiO_2) can catalyze the oxidative conversion of methane into formaldehyde. Tetrahedrally coordinated Fe^{3+} in the amorphous silica network is considered to play an important role[8]. 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/SiO_2 catalyst in the oxidation of propane. In this letter, we report the formation of oxygenates over Fe/SiO_2 and effects of K^+ addition to the Fe/SiO_2 catalyst on the oxygenate formation.

Silica supporting transition metal ions was prepared by impregnating SiO_2 powder (MERCK silica gel, extra pure; specific surface area = 400 $m^2 g^{-1}$, 70~230 mesh) with aqueous solutions of metal nitrates. Calcination was done at 973K for 5 h. In the case of V/SiO_2 and Mo/SiO_2, 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 K_2CO_3, in which the ratio of K to Si was 0.6 atom %, and it was further calcined at 973K for 5h.

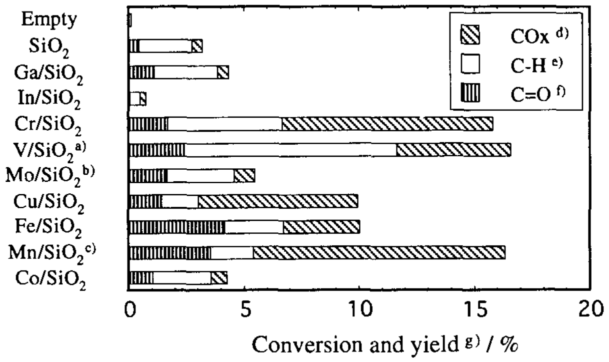

Figure 1. Propane conversion and product distribution in the oxidation of propane over SiO_2 supporting transition metal ions (M/Si=0.05 atom %) at 823K.
$P(C_3H_8)$=20.2kPa, $P(O_2)$=16.2kPa, $P(N_2)$=64.6kPa, SV=10000$h^{-1}\cdot ml\cdot g^{-1}$.
a):V/Si=0.5 atom %, b):Mo/Si=1.0 atom %, c):at 773K, d): CO and CO_2, e): C_2H_4, C_3H_6, and CH_4, f): formaldehyde, acetaldehyde, acrolein, and acetone, and g): calculated on C_3 basis.

The specific surface area of the M/SiO_2 catalysts after the calcination was almost equal, within 5% reduction, to that of the fresh SiO_2 support, and the surface area of the $K/Fe/SiO_2$ catalyst after the calcination was 250 $m^2 g^{-1}$.

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 $ml\cdot min^{-1}$ (Space velocity =1×10^4 $h^{-1}\cdot ml\cdot g^{-1}$). Products were analyzed by two gas chromatographs, FID-GC with a

Table 1. Oxidation of propane or propene over the Fe/SiO_2 catalysts

Reactant	Catalyst	Fe/Si or K/Fe/Si (atomic ratio)	Temp. (K)	Conv. (%C_3H_8)	Selectivity (%)								
					Oxygenates							Olefins[f)]	CO_x[g)]
					Total	C1[a)]	C2[b)]	C3a[c)]	C3b[d)]	C4[e)]			
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_2O_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-dihydrofurane,
f) Olefins: propene and ethene, g) COx: CO and CO_2, h) reactant gas: 20%C_3H_8+16%O_2+64%N_2, and i) reactant gas: 20%C_3H_6+16%O_2+64%N_2.
Small amount of CH_4 was detected from all the K^+ free catalysts.

Porapack-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 olefins[10] (olefin selectivity > 90%). As reported by Sokolovskii[11] et al., additive-free SiO_2 can catalyze oxidative dehydrogenation of propane. Addition of transition metal ions to SiO_2 enhanced the catalytic activity. Transition metal ions on SiO_2 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/SiO_2 with a relatively high oxygenate yield.

Effect of the loading amount of Fe^{3+} to SiO_2 on the propane oxidation was examined and results were shown in Table 1. As far as the quantity of Fe^{3+} 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 Fe^{3+}, probably with tetrahedral coordination[8], on the amorphous silica matrix might play an important role. This distinctly contrasts with the oxidative dehydrogenation of propane over ferrisilicate[9] which also has the tetrahedral Fe^{3+} in the silicalite network.

Addition of K^+ to Fe/SiO_2 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 $K/Fe/SiO_2$ is higher than that obtained at 748K on K^+-free Fe/SiO_2. The selectivity to the oxygenates with high carbon number tends to be high on $K/Fe/SiO_2$ and concomitantly the less selectivities to olefins and to the oxygenates with low carbon number are observed. Silica supporting only K^+ (K/SiO_2) is less active to this reaction. Coexistence of K^+ and Fe^{3+} 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/SiO_2 and $K/Fe/SiO_2$ (Table 1). In the case of Fe/SiO_2, 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 $K/Fe/SiO_2$, 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 $K/Fe/SiO_2$ 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/TiO_2 and Mo/TiO_2 catalysts[13]. Propane-2-ol vapor diluted in air was confirmed to be converted into acetone and COx over the $K/Fe/SiO_2$ 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/SiO_2 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 condensation[12] between acetone and formaldehyde can give 3-buten-2-one, which constitutes about 70% of C4-oxygenates produced over the $K/Fe/SiO_2$ catalyst. Detailed reaction mechanism is currently investigated.

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