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Selective Partial Oxidation of Propane over Metal Phosphate Catalysts

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Catalytic oxidation of propane was studied over metal phosphates using propane rich feed. Oxidation reached measurable rate at 620-700 K over the catalysts. Over $Cu_2P_2O_7$, $Ni_2P_2O_7$, and $LaPO_4$, propene, acetaldehyde, and methanol were principal products and the sum of these selectivities reached 70-80 mol%. Maximum selectivity of acrolein, 11.5 mol%, was observed over $Mn_2P_2O_7$. Selectivity of propene reached 50.7 mol% over $Co_2P_2O_7$. Deep oxidation was dominant over $Cr_4(P_2O_7)_3$,$(ZrO)_2P_2O_7$, and $CePO_4$.

Propane is one of the major components of natural gas and is produced in the catalytic cracking of naphtha. It has been mainly used as a fuel because no catalysts effective for selective conversions have been found. It is of interest to transform propane into intermediate feedstocks by catalytic processes. The catalytic partial oxidation of propane has been studied using metal oxide catalysts and it has been known that two types of reaction take place. One is the synthesis of acrolein and acryllic acid, and another is the formation of acetaldehyde and methanol accompanying C-C bond fission of propane molecules. The former reaction was observed over MoO_3-V_2O_5, SnO_2-Sb_2O_5, V_2O_5-P_2O_5, and TeO_2-P_2O_5-V_2O_5 catalysts[1,2] although the yields of the products were fairly low. The latter reaction took place over $Ca_{2-x}Bi_{2+2x/3}O_6$,[3] which has lattice oxygen defects. However, the reaction was accompanied by the deep oxidation to CO and CO_2 in relatively higher selectivity.

Recently, two noteworthy reports were appeared. Moro-oka et al.[4] found out the catalysts effective for the former reaction. An Ag-doped bismuth vanadomolybdate performed the acrolein selectivity more than 60% at 13% conversion of propane. Otsuka et al.[5] reported that B-P mixed oxide catalysts were effective for partial oxidation of propane, and the selectivity and the yield of the partial oxidation products (propionaldehyde, acetone, acrolein, acryllic acid, acetaldehyde, and propene) over the B-P-O (B/P=1) catalyst were 50 and 27%, respectively, at 806 K and at W/F=0.67 g h dm^{-3}. We have found out the catalytic selective conversion of propane to propene and oxygen containing compounds such as methanol, acetaldehyde, and acrolein over metal phosphates. Catalysts were prepared as following procedure. Precipitate obtained by pouring an aqueous solution of metal chloride into an aqueous solution of $Na_4P_2O_7$ was washed thoroughly with ion-exchanged water and the filtrate was dried at 400 K overnight. The powder formed was pressed into pellets, then calcined in N_2 stream at 773 K for 2 h. Reactions were achieved using a conventional flow type reaction system using a 18-mm-i.d. Pyrex glass tube reactor with a fixed catalyst bed inside. 5.4 g of the catalyst granules (20-32 mesh) was used for the reaction without addition of diluents. The effluent gas, from the reactor was cooled to ambient temperature. Condensed liquid, and feed and effluent gases were analyzed by GC. A blunk test was carried out using no catalysts and it was confirmed that no reactions took place at the temperatures up to 700 K.

The results of the propane oxidation over various metal phosphates are shown in Table 1. As can be seen from Table 1, all the oxygen fed were practically consumed completely at 620-700 K over most of the catalysts regardless of the reaction conditions. Propene formation by oxidative dehydrogenation, cracking into methane and ethene, oxygen containing compounds (OCC) formation such as aldehydes, alcohols, and carboxylic acids, and deep oxidation proceeded over every catalyst. After the reaction, a small amount of carbon deposition was observed over some catalysts, however, more than 95% of the carbons reacted was recovered in all the experimental runs.

High propene selectivities of 43-50% were observed over $(VO)_2P_2O_7$ and $Co_2P_2O_7$, while these reached 20-30% over the other catalysts. Ethene was a principal product of the cracking and a small amount of methane was also formed over every catalyst.

The cracking products showed 7-15% selectivity over all catalysts except for

Table 1. Oxidation of propane over metal phosphate catalysts

Catalyst	RC[a]	Temp	Conv./%		Selectivity/mol%							
					Hydrocarbon		Oxygen containing compound					CO+
		K	C_3H_8	O_2	C_3H_6	others[b]	CH_3CHO	CH_2CHCHO	CH_3OH	Acids[c]	others[d]	CO_2
$(VO)_2P_2O_7$	B	673	6.3	97.7	3.35	10.0	4.7	4.3	25.2	9.9	3.5	21.8
$VOPO_4$	B	673	8.3	95.4	3.37	7.8	3.8	4.4	32.6	22.8[e]	1.4	28.0
$Cu_2P_2O_7$	B	623	8.6	87.8	25.3	9.5	20.2	1.9	20.2	0.6	4.7	17.6
	B	648	9.5	92.4	28.7	15.8	16.2	1.7	7.8	0.5	4.4	19.8
$Ni_2P_2O_7$	A	633	22.6	99.5	22.3	7.3	12.3	2.0	18.8	0.4	7.4	29.5
	B	623	7.9	99.6	29.1	9.9	21.1	1.9	15.7	0.4	5.3	16.6
$Mn_2P_2O_7$	A	643	21.2	94.5	26.5	6.3	5.4	11.5	19.9	0.5	4.0	25.6
$LaPO_4$	A	623	21.5	99.3	23.6	8.1	14.2	0.4	15.6	0.7	3.8	33.6
$Co_2P_2O_7$	A	673	2.9	16.0	50.7	2.9	8.5	8.1	-	0.4	10.4[f]	19.0
$Cr_4(P_2O_7)_3$	A	653	7.4	80.3	27.4	7.1	0.8	0.7	-	0.4	7.7	56.1
$(ZrO)_2P_2O_7$	A	673	3.5	32.7	31.2	2.1	3.6	+	1.3	+	2.9	58.9
$CePO_4$	A	633	1.2	9.5	65.7	1.1						33.2
	A	723	10.9	92.3	37.6	3.4	0.1	0.1	-	+	+	58.8

a)Reaction conditions,A:feed(mol%) C_3H_8 40,O_2 20,N_2 10,H_2O 30, W/F=5.4 g s cm^{-3} B:C_3H_8 62.5,O_2 10,N_2 10,H_2O 17.5, W/F=8.5 g s cm^{-3}. b)C_2H_4,CH_4. c)CH_3COOH,C_2H_5COOH. d)CH_3COCH_3,C_2H_5CHO. e)CH_3COOH. f)CH_3COCH_3.

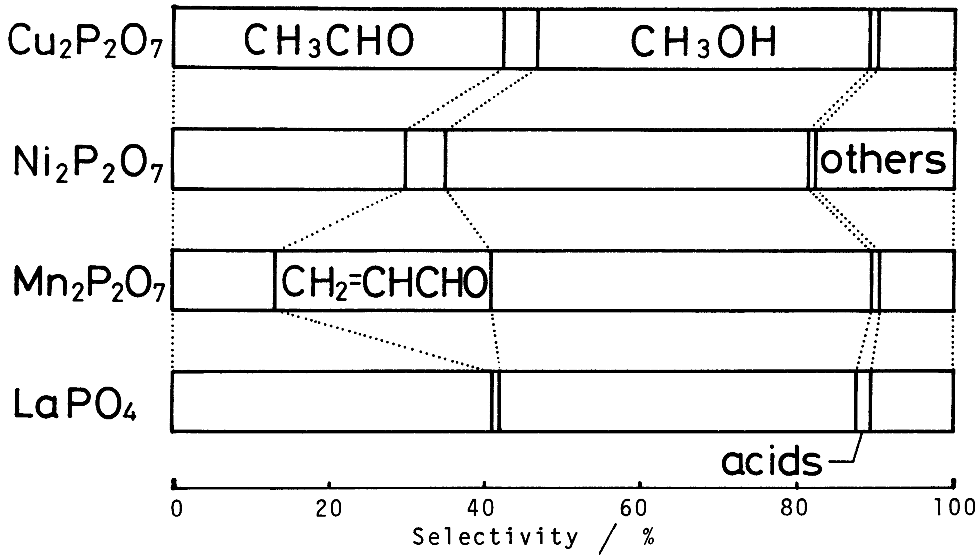


Fig.1. Product distribution in oxygen containing compounds.

$Co_2P_2O_7$, $(ZrO)_2P_2O_7$, and $CePO_4$.

The yield of OCC was much dependent on the catalysts. The OCC yields went up to over 40% in the cases of $Cu_2P_2O_7$, $Ni_2P_2O_7$, and $Mn_2P_2O_7$. The product distributions of OCC over the catalysts were shown in Fig 1. Methanol, acetaldehyde, and acrolein were principal products and the sum of these occupied about 90% of OCC.

Reaction temperature slightly affected the product distribution. The formations of acetaldehyde and methanol were reduced with increasing the reaction temperature while the cracking was favored.

$(VO)_2P_2O_7$ and $VOPO_4$ are composed of V(IV) and V(V),respectively. Comparing the results of both catalysts, it can be seen that the formation of carboxylic acid was much favored over $VOPO_4$. It has been known that carbon-carbon bonds in propene molecule are oxidatively cleaved to give acetic acid over oxide catalysts containing V(V). The marked formation of acetic acid over $VOPO_4$ suggests that the reaction pathway may be composed of oxidative dehydrogenation to propene and succesive acetic acid formation due to the catalysis by V(V).

A small amount of acrolein was formed on all catalysts. Among the catalysts

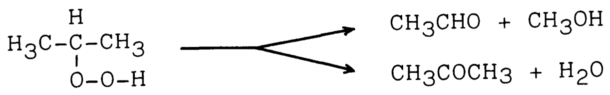
Table 2. Oxidation of propane over Mn-P-O catalysts prepared by different methods

Catalyst[a)]	Temp / K	Conv./% C_3H_8	Conv./% O_2	Selectivity/mol% Hydrocarbon C_3H_6	Hydrocarbon others[b)]	Oxygen containing compound CH_3CHO	CH_2=CHCHO	CH_3OH	acids[c)]	others[d)]	CO+ CO_2
$Mn_2P_2O_7$ (1)	643	21.1	94.5	26.5	6.3	5.4	11.5	19.9	0.5	4.0	25.6
Mn-P-O (2)	633	16.8	69.1	36.4	7.1	10.0	2.7	10.6	0.6	2.0	30.5
Mn-P-O (3)	593	26.6	96.0	23.3	7.7	10.1	3.8	17.5	0.4	9.4	27.8
Mn-P-O (4)	693	5.8	59.3	26.7	2.3	0.1	0.6	-	-	tr	70.3

a)Preparation (1)$Na_4P_2O_7 \rightarrow MnCl_2$, (2)$Mn(NO_3)_2 \rightarrow H_3PO_4$, (3)$H_3PO_4$(0.2 M),$MnCl_2$(0.2 M)→ 3rd vessel, (4)$H_3PO_4$+NaOH,$MnCl_2$(0.2 M)→3rd vessel. b)$C_2H_4$,$CH_4$. c)$CH_3COOH$,$C_2H_5COOH$.

tested, maximum selectivity, 11.5%, was observed on the $Mn_2P_2O_7$ catalyst. This selectivity corresponds to 28% of OCC.

Acetone was formed over $Co_2P_2O_7$ specifically. The conversion of propane increased at very narrow range of temperature over most of catalysts and oxygen was then consumed almost completely. This feature strongly suggests that chain reaction takes place. Acetone formation has been reported in liquid-phase oxidation of propane using both heteropoly acid and one of ruthenium and iridium chloride complexes. Acetaldehyde, methanol and acetone were thought to be formed from an identical intermediate over metal phosphate catalysts as following reaction pathways.



Anyhow, it was proved that propane was converted into hydrocarbons and OCC at about 80% selectivity over some metal phosphate catalysts.

The results of propane oxidation over the $Mn_2P_2O_7$ catalysts prepared from different methods are shown in Table 2. Catalysts (1) and (2) were prepared by pouring of an aqueous solution of $Na_4P_2O_7$ into an aqueous solution of $MnCl_2$ or $Mn(NO_3)_2$. Catalysts (3) and (4) were prepared by the same method that consisted in pouring of solutions of H_3PO_4 and $MnCl_2$ into a separate vessel, except for pH of a $MnCl_2$ solution. The solution was pre-adjusted to pH= 5.2 using a NaOH solution for catalysts (4). Analysis of the catalysts by XRD revealed that catalyst (1) was composed of $Mn_2P_2O_7$ and the other catalysts were amorphous. As can be seen from Table 2, activities of the catalysts and product distributions were significantly affected by the preparation methods and starting materials of the catalysts.

Catalyst (4) was less active and non selective. Catalysts (2) and (3) gave relatively similar product distributions, suggesting that the method of precipitate formation is not principal factor to govern selectivity. The selectivity of acrolein of catalysts (2)-(4) did not exceed that of catalyst (1). The catalyst prepared using pyrophosphate, $Na_4P_2O_7$, seems to be favorable to produce oxygen-containing compounds.

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