

Novel Catalysts for Oxidative Dehydrogenation of Iso-Butane to Iso-Butene

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Oxidation of iso-butane was studied using metal pyrophosphate catalysts and it was found that iso-butene was formed with 82% selectivity over $\text{Ni}_2\text{P}_2\text{O}_7$ at 550 °C. $\text{Zn}_2\text{P}_2\text{O}_7$, $\text{Cr}_4(\text{P}_2\text{O}_7)_3$, and $\text{Mg}_2\text{P}_2\text{O}_7$ showed 60-70% iso-butene selectivity, and 9-22% selectivity to CO and CO_2 . Deep oxidation into CO and CO_2 was promoted over $\text{Cu}_2\text{P}_2\text{O}_7$ and $\text{Sn}_2\text{P}_2\text{O}_7$. Only small amounts of oxygenated products such as alcohols, aldehydes, ketones, and carboxylic acids were formed over every catalyst.

MTBE (Methyl-tert-butyl ether) which is formed from iso-butene and methanol, has been utilized in many countries as a gasoline additive to improve octane number and to reduce the evolution of oxidant in auto exhaust. Thus, it is estimated that the demand of iso-butene will increase. While, propane and butanes, which are major components of petroleum gas, are mainly used for fuel. The production of iso-butene from its corresponding alkane, iso-butane, will be much more important in the near future.

A great many studies on the catalytic dehydrogenation of iso-butane have been carried out and some commercial plants are now working, however many problems still remain such as carbon deposition on the catalyst, short catalyst life, and thermodynamic limitation of the conversion.

On the other hand, the catalytic oxidative dehydrogenation of iso-butane has no equilibrium limitation, however, in general, complete oxidation tends to proceed in alkane oxidation and it is quite difficult to stop the oxidation at intermediate stages such as corresponding olefin, alcohol, aldehyde, carboxylic acid, or ketone formation.

We have been studied the partial oxidation of lower alkanes^{1,2)} and have currently found that various metal pyrophosphates are effective for the oxidative dehydrogenation of iso-butane into iso-butene. In this paper, we report novel catalysts for the selective oxidative dehydrogena-

tion of iso-butane.

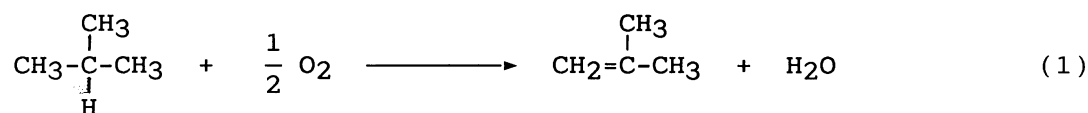
Metal pyrophosphates were prepared according to the following procedure. An aqueous solution of sodium pyrophosphate was added into an aqueous solution of metal nitrates or chlorides and the precipitates formed were separated by filtration. The precipitates were washed and then dried at 130 °C overnight. Catalytic reaction was carried out using an ordinary flow type reaction system with a fixed catalyst bed. The reactant gas mixture of 75 vol% iso-butane, 5% oxygen, and 20% nitrogen as an internal standard was fed into the reactor. The reactant gas and effluent gas were analyzed by gas chromatography.

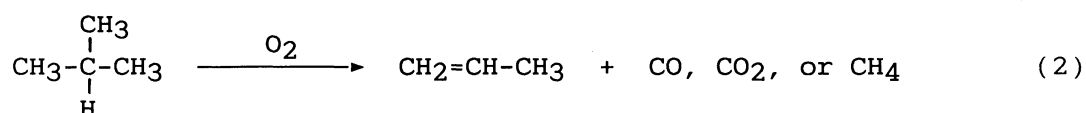
Table 1. Oxidation of iso-butane over $\text{Ni}_2\text{P}_2\text{O}_7^{\text{a)}$

Temp / °C	450		500		550	
Conv. / %						
i-C ₄ H ₁₀	0.64		7.44		10.8	
O ₂	3.8		95.1		98.8	
	Rate	Select.	Rate	Select.	Rate	Select.
1/4 CH ₄			0.24	0.4	1.09	1.1
1/2 C ₂ H ₆					0.03	trace
1/2 C ₂ H ₄			0.05	0.1	0.11	0.1
3/4 C ₃ H ₆			3.13	4.7	6.92	7.0
i-C ₄ H ₈	1.29	21.7	53.1	79.3	82.4	82.8
1/4 CO			4.17	6.2	4.41	4.4
1/4 CO ₂	0.06	1.0	2.01	3.0	1.80	1.8
1/2 CH ₃ CHO	0.37	6.2	0.28	0.4	0.26	0.3
(CH ₃) ₂ CHCHO	0.11	1.8	0.15	0.2	0.49	0.5
3/4 CH ₃ COCH ₃	1.13	19.0	0.64	1.0	0.47	0.5
3/4 CH ₂ =CHCHO	0.21	3.5	0.20	0.3	0.09	0.1
CH ₂ =C(CH ₃)CHO	2.23	37.5	1.99	3.0	1.26	1.3
1/4 CH ₃ OH	0.55	9.2	0.40	0.6	0.20	0.2
1/2 CH ₃ COOH			0.01	trace	0.02	trace

a) Feed gas composition (mol%) : iso-butane 75.0, O₂ 5.0, N₂ 20.0; Catalyst 5.5 cm³ (5.26 g), Feed rate : 30 cm³ min⁻¹. rate = μmol min⁻¹, select. = selectivity %

The results of the catalytic reaction over $\text{Ni}_2\text{P}_2\text{O}_7$ are shown in Table 1. Very small amounts of iso-butane were reacted to produce methacrolein, acetone, and iso-butene at 450 °C. At 500 °C, most of the oxygen was consumed and iso-butene was formed selectively. Other major products were CO, CO₂, propylene, and methacrolein. The selectivity to iso-butene reached 82.8% at 550 °C. The sum of the selectivities to methane, CO, and CO₂ was nearly equivalent to the selectivity to propylene. This suggests that the following two reactions proceeded selectively on the catalyst.





It is clear from Table 1 that about 90% of the consumed iso-butane was converted to iso-butene and propylene which is also an important raw material in petrochemistry.

Table 2 shows the results over $\text{Zn}_2\text{P}_2\text{O}_7$. The conversion of oxygen reached 67.8% even at 450 °C and the formation rate of iso-butene was $19.8 \mu\text{mol min}^{-1}$ which is considerably larger than that over $\text{Ni}_2\text{P}_2\text{O}_7$. The higher selectivity to propylene (about 16%) and oxygenated compounds (about 13%) characterizes this catalyst. The formation rate of iso-butene increased moderately with increasing reaction temperature. The selectivity to iso-butene also increased with temperature, however it has not exceeded 70% at temperatures up to 550 °C.

Table 2. Oxidation of iso-butane over $\text{Zn}_2\text{P}_2\text{O}_7^{\text{a)}$

Temp / °C	450		500		550	
Conv. / %						
i-C ₄ H ₁₀	3.87		5.56		8.06	
O ₂	67.8		94.1		97.6	
	Rate	Select.	Rate	Select.	Rate	Select.
1/4 CH ₄	0.53	1.4	0.98	1.9	2.25	2.8
1/2 C ₂ H ₆			0.02	trace	0.07	0.1
1/2 C ₂ H ₄	0.19	0.5	0.23	0.4	0.25	0.3
3/4 C ₃ H ₆	6.17	16.1	8.52	16.2	12.59	15.9
i-C ₄ H ₈	19.8	51.8	32.0	60.9	55.4	69.9
1/4 CO	2.92	7.6	4.28	8.2	4.69	5.9
1/4 CO ₂	3.63	9.5	2.87	5.5	2.60	3.3
1/2 CH ₃ CHO	0.45	1.2	0.40	0.8		
3/4 CH ₃ CH ₂ CHO	0.15	0.4	0.10	0.2		
(CH ₃) ₂ CHCHO	0.47	1.2				
3/4 CH ₃ COCH ₃	1.58	4.1	1.01	1.9	0.49	0.6
3/4 CH ₂ =CHCHO	0.12	0.3	0.09	0.2		
CH ₂ =C(CH ₃)CHO	1.92	5.0	1.80	3.4	0.87	1.1
1/4 CH ₃ OH	0.33	0.9	0.17	0.3		
1/2 CH ₃ COOH	0.02	0.1	0.04	0.1	0.02	trace

a) Feed gas composition (mol%) : iso-butane 75.0, O₂ 5.0, N₂ 20.0;
Catalyst 5.5 cm³ (4.95 g), Feed rate : 30 cm³ min⁻¹.
rate = $\mu\text{mol min}^{-1}$, select. = selectivity %

The results over various pyrophosphate catalysts are summarized in Table 3. $\text{Ni}_2\text{P}_2\text{O}_7$ showed the highest catalytic activity, followed by $\text{Zn}_2\text{P}_2\text{O}_7$ and $\text{Mg}_2\text{P}_2\text{O}_7$.

These catalysts, however, differ from one another in their

Table 3. Oxidation of iso-butane over various metal pyrophosphates^{a)}

Catalysts	Specific surface area/m ² g ⁻¹	Conv./%	Yield/% C'4	Select./%			
				C'4	C'4+C'3	oxy.	CO _x
Ni ₂ P ₂ O ₇	12.0	10.8	8.94	82.8	89.8	2.78	6.2
Zn ₂ P ₂ O ₇	4.0	8.06	5.63	69.9	85.8	1.74	9.2
Mg ₂ P ₂ O ₇	5.7	6.38	3.80	59.6	80.8	0.31	11.4
Cr ₄ (P ₂ O ₇) ₃	8.0	3.85	2.53	65.7	70.6	5.2	22.4
Co ₂ P ₂ O ₇	4.0	4.81	2.38	49.5	80.7	9.58	2.85
Mn ₂ P ₂ O ₇	14.2	4.30	1.90	44.2	65.6	3.34	26.5
Sn ₂ P ₂ O ₇	3.5	2.37	1.04	43.8	50.5	7.22	40.5
Cu ₂ P ₂ O ₇	6.2	3.34	0.96	28.7	29.7	1.82	60.7

a) C'4=iso-C₄H₈, C'3=C₃H₆, oxy.=oxygenated compounds (at 550°C).

selectivities to iso-butene. The selectivity to iso-butene is much higher over Ni₂P₂O₇. The selectivity to propylene is relatively high over Mg₂P₂O₇. Co₂P₂O₇, Mn₂P₂O₇, and Cr₄(P₂O₇)₃ showed moderate activity and the selectivity to iso-butene laid at 45-65%. It can be said that the low conversion over Cu₂P₂O₇ and Sn₂P₂O₇ not always means the low activity in catalytic oxidation. Because deep oxidation into CO and CO₂ requires much more molecular oxygen than oxidative dehydrogenation, complete consumption of oxygen would limit the conversion.

About 10 μmol min⁻¹ of iso-butane converted into hydrocarbons such as iso-butene, propylene, and methane at 550 °C in a blank experiment using silicon carbide granules, suggesting that iso-butene was formed catalytically over the pyrophosphates.

It was confirmed by TPD measurements that metal pyrophosphates possess no adsorbed oxygen on their surfaces. Iso-butane molecule has a tert-carbon atom which tends to form tert-carbenium ion, so that the acidic character and the reactivity of lattice oxygen governs the catalytic activity. This is now under investigation.

In conclusion, Ni₂P₂O₇ and Zn₂P₂O₇ are the catalysts that yield the best results for selective iso-butene formation from iso-butane.

References

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