The Oxyhydration of Olefin over Transition Metal Oxide Catalysts

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(Received October 9, 1970)

A number of catalytic oxidations of olefin have been developed on the transition metal oxide catalysts. Though the mechanisms of these oxidations have been extensively studied by the tracer technique with regard to the behavior of olefin,[1] little work has been done on the behavior of active oxygen. In this communication, we wish to report evidence which demonstrates that the oxygen atom is introduced into the oxidized product of olefin in two different ways, depending on the type of product. One is the case where the oxygen atom is introduced from molecular oxygen, and another is where the atom is introduced from the water molecule:

$$A + \frac{1}{2}O_2 \longrightarrow AO \qquad (1)$$

$$A + \frac{1}{2}O_2 + H_2O^* \longrightarrow AO^* + H_2O \qquad (2)$$

where A is the olefin to be oxidized.

Table 1. $H_2{}^{18}O$ tracer in the oxidation of propylene to acrolein over MoO_3–Bi_2O_3 catalyst

Run	Reaction temp. (°C)	C_3' conv. (%)	Selectivity to acrolein (%)	^{18}O content (%) H_2O[a)]	^{18}O content (%) CH_2=CHCHO
1	360	2.50	73.0	3.92	0.26±0.2
2	385	4.35	65.5	3.84	0.00±0.2
3	433	9.45	55.0	3.73	0.16±0.2
4	460	14.80	51.0	3.40	0.18±0.2

a) Average of the values for input (4.00) and output gas.
GHSV: 600 m*l*-STP/m*l*-cat·hr
Gas composition; C_3H_6 20 vol%, O_2 30%, H_2O 30%, N_2 20%.

A typical example of Eq. (1) is the oxidation of propylene to acrolein over the MoO_3-Bi_2O_3 catalyst. The oxidation of propylene was done in the presence of the water vapor, 4% of which was $H_2{}^{18}O$. As can be seen in Table 1, the concentrations of ^{18}O in acrolein are far lower than those in water in the reactant gas. It can be concluded that the oxygen atom in acrolein comes from molecular oxygen, not from the water molecule, although it is well known that the presence of water vapor in the reactant gas mixture increases the selectivity to acrolein.

An example of Eq. (2) is the oxidation of propylene to acetone, which was previously reported by the present authors.[2] Propylene was oxidized to acetone in the presence of $H_2{}^{18}O$ vapor on the SnO_2-MnO_3 catalyst at two different temperatures. The experimental results are summarized in Table 2. As is shown in Table 2, the concentrations of ^{18}O in acetone are almost equal to those in water in the reactant gas. The exchange reaction of the oxygen atom between molecular oxygen and water:

$$^{16}O_2 + H_2{}^{18}O \rightleftarrows {}^{16}O^{18}O + H_2{}^{16}O \qquad (3)$$

did not occur under the reaction conditions adopted in this experiment. These results clearly show that the oxygen atom in acetone comes from water, not from molecular oxygen. It has been suggested, regarding the mechanism of this oxidation, that acetone is formed *via* the hydration of propylene to form an alcoholic intermediate, followed by oxydehydrogenation.[3] The results obtained in this work present strong evidence for this proposed mechanism of acetone formation.

It has been proved that there are two different ways of oxygen introduction in the heterogeneous oxidations of olefin over metal oxide catalysts. It seems interesting that these two paths of the introduction of oxygen atoms to oxidized products correspond to two typical enzymatic oxidations, *i. e.*, oxidations by oxygenase[4] and oxidase.

Table 2. $H_2{}^{18}O$ tracer in the oxidation of propylene to acetone over SnO_2–MoO_3 catalyst

Run	Reaction temp. (°C)	GHSV (m*l*-STP/ m*l*-cat·hr)	C_3' conv. (%)	Selectivity to acetone (%)	^{18}O content (%) H_2O (input)	^{18}O content (%) H_2O (output)	^{18}O content (%) CH_3COCH_3
1	125	600	3.99	93.7	5.48	4.62	5.35
2	125	600	3.99	93.7	5.48	4.91	5.26
3	225	2000	1.67	68.1	8.60	—	8.39

Gas composition is same with Table 1.

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[1] H. H. Voge and C. R. Adams, *Advan. Catal.*, **17**, 151 (1967).

[2] Y. Moro-oka, S. Tan, Y. Takita, and A. Ozaki, This Bulletin, **41**, 2820 (1970).

[3] S. Tan, Y. Moro-oka, and A. Ozaki, *J. Catal.*, **17**, 132 (1970).

[4] O. Hayaishi, Proc. 6th Intern. Congr. Biochem., New York 1964.