BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 681—682 (1973)

^{18}O Tracer Studies of Catalytic Oxidations of Olefin over Transition Metal or Metal Oxide Catalysts. II. Oxidation of Propylene to Acrolein over Pd-Carbon Catalyst

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(Received June 27, 1972)

In the first paper of this series, we reported a new type oxygen incorporation where oxygen atom in water molecule is incorporated into the oxidized products, *i.e.*,

$$\text{A(olefin)} + 1/2\text{O}_2 + \text{H}_2\text{O}^* \rightarrow \text{AO}^* + \text{H}_2\text{O} \qquad (1)$$

We demonstrated by use of $H_2{}^{18}O$ tracer that the oxidation of propylene to acetone over SnO_2-MoO_3 catalyst follows Eq. (1) and called it oxyhydration.[1,2] Further study has been carried out to find new oxyhydrations. The route of oxygen incorporation was examined using $H_2{}^{18}O$ tracer in the catalytic oxidation of propylene to acrolein over Pd-carbon catalyst which was independently found by Fujimoto *et al.*[3] and by Seiyama *et al.*[4].

Experimental

Pd-carbon catalyst was prepared from activated charcoal and palladium chloride.[3] 10—20 mesh activated charcoal was boiled for 5 hr in dilute nitric acid solution and then washed with water until pH of the filtrate become higher than 4. This was impregnated with palladium chloride dissolved in 0.5 N HCl solution and allowed to stand for 24 hr. Palladium chloride supported on the activated charcoal (5 wt% $PdCl_2$) was reduced to metallic palladium by hydrogen gas at 250°C for 5 hr and activated by air at 230°C for 12 hr.

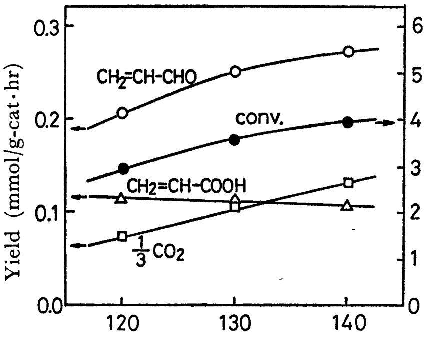

Fig. 1. One pass conversion of propylene and yields of oxidized products in the oxidation of propylene over Pd-carbon catalyst.

All the runs were carried out using a conventional flow system at atmospheric pressure. The reactor was a Pyrex tube of 8 mm diameter. The exit gases were cooled by water to separate gaseous and liquid phases, and analyzed by gas chromatography and mass spectrometry.

The ^{18}O content of the oxidized products was determined by mass spectrometry after separation and purification by gas chromatography. The mass spectra obtained at 80 V of ionization voltage were corrected for natural abundances, no isotope effect being assumed for the ionization efficiency. The ^{18}O content of acrolein was calculated from the peak height ratio, h_{58}/h_{56}, in the corrected mass spectra. The ^{18}O content of the unreacted oxygen was determined by mass spectrometry after it was converted into carbon dioxide by the reaction with the stoichiometric amount of carbon monoxide using a closed circulating reaction system and Pt-asbestos catalyst.

Results and Discussion

Propylene was oxidized at 120—140°C over Pd-carbon catalyst. 1.9 g of the catalyst was used in the fixed catalyst bed. The flow rates of each reactant gas were 10.0, 8.0, and 27.6 ml-STP/min for propylene, oxygen and water, respectively, GHSV being 530 ml-STP/ml-cat hr.

The activity of Pd-carbon catalyst and selectivity for each product changed gradually during the first few hours. They became constant after 10 hr and did not change any more in the subsequent runs. The main products were acrolein, acrylic acid, and carbon dioxide.[3] Although small amounts of acetone and acetaldehyde were produced, their total yield did not exceed 10% of the converted propylene. The values of one pass conversion of propylene and the yields of the main products at three different temperatures are shown in Fig. 1. The selectivity to acrolein was 50—55% of the converted propylene.

Tracer experiment was carried out at 130°C. Propylene was oxidized over Pd-carbon catalyst under the same conditions as mentioned above except that water in the reactant gas was replaced by water enriched with $H_2{}^{18}O$. The results are summarized in Table 1.

The values in the third column of Table 1 give ^{18}O content of the acrolein produced in the presence of 5.48% $H_2{}^{18}O$. In every run, ^{18}O tracer is found in acrolein with reasonably high concentrations. Thus, it is clear that the oxygen atom comes mostly from the water molecule. This suggests that acrolein is produced by an interaction between propylene and some active species derived from water on Pd-carbon cata-

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[1] Y. Moro-oka, Y. Takita, and A. Ozaki, *J. Catal.*, **27**, 177 (1972).

[2] Y. Moro-oka, Y. Takita, and A. Ozaki, This Bulletin, **24**, 293 (1971).

[3] K. Fujimoto, H. Yoshino, and T. Kunugi, 4th Oxidation Symposium (Tokyo), p. 111, (1970).

[4] T. Seiyama, M. Aramaki, N. Takeyama, and N. Yamazoe, *Kogyo Kagaku Zasshi*, **74**, 672 (1971); T. Seiyama, N. Yamazoe, J. Hojo, and M. Hayakawa, *J. Catal.*, **24**, 173 (1972).

lyst. However, another possibility should be examined, *i.e.*, the incorporation of ^{18}O into the oxidized product results from the following exchange reactions.

$$^{16}O_2 + H_2{}^{18}O \rightleftarrows {}^{16}O^{18}O + H_2{}^{16}O \tag{2}$$

$$CH_2\text{=}CH\text{-}CH^{16}O + H_2{}^{18}O \rightleftarrows CH_2\text{=}CH\text{-}CH^{18}O + H_2{}^{16}O \tag{3}$$

These oxygen exchange reactions were also examined using $H_2{}^{18}O$ tracer. The ^{18}O contents of the unreacted oxygen are listed in the last column of Table 1. They suggest that a slight oxygen exchange reaction takes place between molecular oxygen and water under the conditions adopted in the runs. However, the values are too low to explain the ^{18}O contents found in the acrolein produced. Thus, the possibility that ^{18}O in the acrolein was incorporated from the $^{16}O^{18}O$ molecule formed by the exchange reaction as expressed in Eq. (2) can be rejected.

TABLE 1. ^{18}O CONTENT OF THE PRODUCT IN THE OXIDATION OF PROPYLENE TO ACROLEIN OVER Pd-CARBON CATALYST[a)]

Reaction	^{18}O content (atomic %) CH_2=CH-CHO	 O_2 (unreacted)
Oxidation	3.62	0.20
	4.36	0.22
	3.41	0.14
Exchange[b)]	0.75	—
	1.13	—

a) ^{18}O content of the reactant water is 5.48%.
b) Oxygen exchange reaction between acrolein and water.

Another oxygen exchange reaction between acrolein and water was examined using $H_2{}^{18}O$ tracer. The reaction conditions were the same as adopted in the oxidation runs, except that propylene in the reactant gas was replaced by nitrogen. The contact time of acrolein and its concentration in the reactant gas were adjusted to those produced in the oxidation runs. The results are shown in Table 1. Although some exchange reaction was observed under the conditions, the rate of exchange reaction was smaller than that of oxidation. The ^{18}O contents found in the produced acrolein are not attributable to the exchange reaction as given by Eq. (3). It seems reasonable that acrolein is produced by direct interaction between some active species of propylene and water, and that the oxidation of propylene on Pd-carbon catalyst is at least partly an oxyhydration.

Although the incorporation of ^{18}O into acrolein seems to be due to some direct interaction between the active species of propylene and water, ^{18}O content found in the acrolein was somewhat lower than that of water in the reaction system. The ^{18}O content of the issuing water was not determined because of inaccuracy of the mass spectrometry of water. However, since the conversion of propylene was lower than 4%, the ^{18}O content of the issuing water calculated on the mass balance of ^{18}O is higher than 5.30%. This indicates that the incorporation of oxygen into the acrolein also involves some active species originating from molecular oxygen as well as water. One possible explanation is that the oxidation to form acrolein involves a hydroxyl group which is formed by a reaction between atomic oxygen and propylene or some intermediate derived from propylene. If this is the case, the hydroxyl group formed on the catalyst surface would be indistinguishable from the active species of water, and the oxidation to form acrolein might be a sort of chain reaction.

A number of transition metal oxide catalysts have been developed for the oxidation of propylene to acrolein. Keulks[5)] and Wragg *et al.*[6)] have proved by using ^{18}O tracer that the oxygen ion in the oxide catalyst is incorporated into the oxidized acrolein over MoO_3-Bi_2O_3 catalyst. Our results demonstrate that the mechanism of the oxidation of propylene to acrolein over Pd-carbon catalyst differs from that of the oxidation of propylene to acrolein over the transition metal oxide catalyst such as MoO_3-Bi_2O_3 and strongly supports the mechanism proposed by Fujimoto *et al.*[3)] and Seiyama *et al.*[4)] They found that the rate of oxidation of propylene to form acrolein depends on the partial pressure of water,[3)] and estimated the following mechanism for this oxidation.

$$CH_2\text{=}CH\text{-}CH_3 \xrightarrow[-H]{} CH_2\text{=}CH\text{=}CH_2 \tag{4}$$

$$CH_2\text{=}C\text{=}HCH_2 \xrightarrow[+OH]{} CH_2\text{=}CH\text{-}CH_2OH \tag{5}$$

$$CH_2\text{=}CH\text{-}CH_2OH \xrightarrow[-2H]{} CH_2\text{=}CH\text{-}CHO \tag{6}$$

A hydrogen atom in methyl group of propylene is abstracted on the catalyst surface to form an allylic intermediate. Some active species of water such as hydroxyl group attacks one of the terminal carbon atoms of this intermediate to form allyl alcohol which is easily oxidized to acrolein.

The authors wish to thank Dr. K. Fujimoto and members of Prof. Kunugi's laboratory of the University of Tokyo for many useful suggestions.

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5) G. W. Keulks, *J. Catal.*, **17**, 232 (1970).

6) R. D. Wragg, P. G. Ashmore, and J. A. Hockey, *ibid.*, **22**, 49 (1971).