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(Note)

ETHYLENE OXIDATION OVER SILVER CATALYST TRACED BY OXYGEN-18

By

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HERZOG[1] has reported recently ethylene oxidation over silver catalyst at 320°C with gaseous oxygen and nitrous oxide ; the latter is known to form oxygen adatoms on catalyst surface. Rate of ethylene oxidation with O_2 gas was remarkably larger than that with N_2O, and in excess of ethylene a ratio of ethylene oxide to CO_2, *i.e.*, selectivity of partial oxidation, was by seven times higher with O_2 than that with N_2O, while it was *ca.* 2.5 if the oxidizer was excess. He has attributed the increase of selectivity with N_2O to molecular oxygen formed by combination of oxygen adatoms and concluded that ethylene oxide may be formed by adsorbed molecular oxygen, while adsorbed oxgen adatoms oxidize ethylene completely into CO_2.

In the present work we follow HERZOG's experiments by using oxygen–18 to elucidate the mechanism. A conventional closed circulation apparatus made of Pyrex glass with an U-tube reactor, in which granular silver was mounted, was used and the reactor was protected from contamination by using dry ice-methanol traps. Analysis was made by supplying a known amount of reacting gas to a gaschro-mass spectrometer with helium carrier. A typical time course of oxidation with O_2 at 280°C is shown in Fig. 1 (a), where the activity markedly decreased in early 30 minutes and after that ethylene oxide decreased by further oxidation, while ethylene oxide was not detected in oxidation with N_2O as shown in Fig. 1 (b). Without coexistence of ethylene, N_2O was not appreciably decomposed at 280°C over silver catalyst, accordingly, N_2O is consumed by reaction with ethylene. The following stoichiometric reaction was established in the latter case of oxidation, by taking account of amount ratio of the products, CO_2 and N_2.

$$C_2H_4 + 6N_2O = 2CO_2 + 2H_2O + 6N_2 .$$

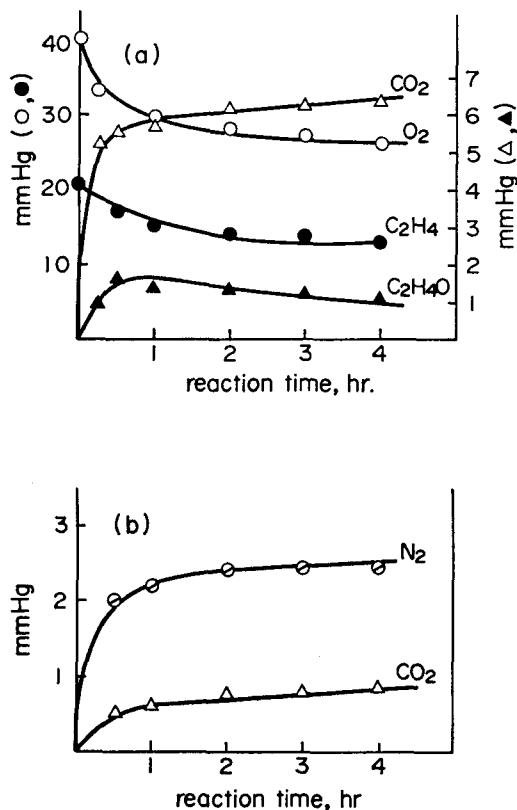*) Research Institute for Catalysis, Hokkaido University, Sapporo 060.

Fig. 1. Time course of ethylene oxidation with O_2 gas (a) on Ag catalyst at 280°C, and oxidation with N_2O (b), where initial pressures of C_2H_4 and N_2O were 20 and 80 mmHg and the plots for O_2, C_2H_4 and C_2H_4O are omitted.

Similar results were obtained at 240°C.

A typical time course of a reaction with a mixture of N_2O, $^{18}O_2$ and C_2H_4 are shown in Fig. 2, and distribution of ^{18}O in reacting gases are given in Table 1. The results may be briefly summerized;

i) ^{18}O-concentration in oxygen gas does not change throughout the oxidation,

ii) ^{18}O atoms in carbon dioxide is distributed randomly and gradually diluted by ^{16}O atoms from N_2O,

iii) N_2O does not exchange oxygen with $^{18}O_2$.

The results of i) and iii) show that oxygen gas and N_2O are consumed irreversibly, accompanying none of oxygen exchange between them. Dilution of carbon dioxide by ^{16}O atoms indicates that contribution of N_2O to ethylene oxidation predominates in a later stage of the reaction, suggesting some change
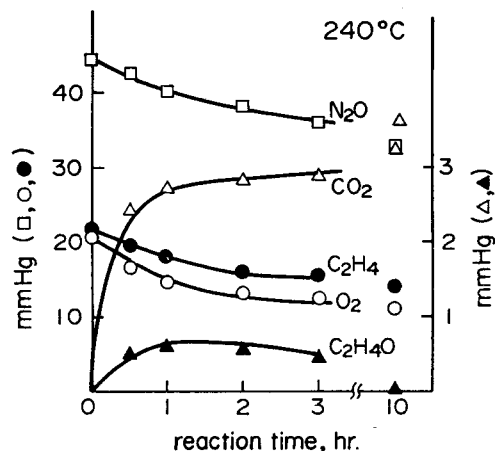
Fig. 2. Time course of ethylene oxidation on Ag catalyst at 240°C. Initial pressures of C_2H_4 and N_2O were 20 and 80 mmHg, respectively.

TABLE 1. The [18]O atom distribution in gaseous O_2, N_2O and CO_2 in the reaction given in Fig. 2. (Mole %)

Reaction time, hr	$^{18}O_2$	$^{18}O^{16}O$	$^{16}O_2$	$C^{18}O_2$	$C^{18}O^{16}O$	$C^{16}O_2$	$N_2^{18}O$	$N_2^{16}O$
0.5	85.2	13.0	1.8	—	—	—	0	100
1.0	84.7	12.4	2.9	81.5	16.0	2.5	0	100
2.0	85.5	11.5	3.0	76.6	21.4	2.0	0	100
3.0	85.6	12.6	1.7	71.2	25.5	3.3	0	100
10.0	86.3	11.9	1.8	48.2	42.2	9.6	0	100

of the catalyst surface. This inference was further assured by oxidation of ethylene with a mixture of 20 mmHg oxygen of 0.93 ^{18}O–atomic fraction, 40 mmHg N_2O and 20 mmHg ethylene on a freshly prepared catalyst at 240°C. The reaction gave in early 40 minutes 2.0 mmHg carbon dioxide with 0.86 ^{18}O–atomic fraction and 0.2 mmHg of ethylene oxide with 0.88 ^{18}O–atomic fraction, while 3.5 mmHg carbon dioxide of 0.65 ^{18}O–atomic fraction and a trace of ethylene oxide with nearly unchanged ^{18}O–atomic fraction were found after 7 hours. These results infer that formation of ethylene oxide in early stage was caused mainly by oxygen gas and after that ethylene oxide, at least, is oxidized into CO_2 mainly by N_2O and probably ethylene, too.

Rapid oxygen isotopic mixing of gaseous carbon dioxide mentioned in ii) was examined by adding 1.6 mmHg of CO_2 with isotopically unequilibrated

oxygen gas of *ca.* 20% ^{18}O–content at the initial time. About 1.6 mmHg of carbon dioxide was formed additionally in early 30 minutes, that is, about a half of the total carbon dioxide. Values listed on the line *calc.* in Table 1 were obtained by assuming carbon dioxide formed by oxidation has the same [18]O content as that of oxygen gas and isotopic equilibration between formed carbon dioxide and added CO_2 is rapid as suggested by the results of Table 1. These values are in good agreement with the observed values given in the line *obs.* of

TABLE 2. The [18]O atom distribution in gaseous CO_2 at 30 minutes
of the reaction given in Fig. 2 with initially added 1.6
mmHg $C^{16}O_2$. (Mole %).

Sample of CO_2	Pressure, mmHg		$C^{18}O_2$	$C^{18}O^{16}O$	$C^{16}O_2$
Initially added	1.6		0	0	100
formed by oxidation	1.6		3.9	32.2	63.9
Whole of carbon dioxide presenting in gas phase	3.2	*calc.*	1.0	18.0	81.0
		obs.	1.4	20.6	78.0

the Table, and proves again the conclusion that oxidation of ethylene is caused practically by O_2 gas but not N_2O in an early stage of the oxidation and rapid oxygen isotopic mixing in carbon dioxide in gas phase.

By summerizing the above results we propose two kinds of oxygen intermediates, X and Y, where X is species effective for ethylene oxide formation and Y is for carbon dioxide formation. A reaction scheme of ethylene oxidation over silver catalyst may be given qalitatively as
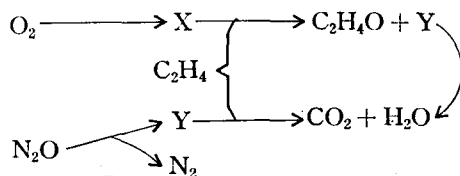

where steps of adsorption of O_2, N_2O and C_2H_4 and of desorption of C_2H_4O, CO_2 and H_2O are not expressed clearly so far as the present results concern. Intermediate X as well as Y is mainly supplied from O_2 in early stage of reaction over a freshly prepared silver catalyst, but in later stage, catalyst surface changes to be active for decomposition of N_2O to give Y and inactive for X formation from O_2, resulting in progress of consecutive oxidation of formed ethylene oxide. Such a change of catalyst surface may relate to the practical neccessity of addition of some promoters to silver to obtain a high and

steady selectivity for ethylene oxide formation.

Rapid randomization of oxygen isotopes in carbon dioxide may be caused by some reversible steps, involving the intermediate Y, *e.g.*,

$$CO_2 + Y \rightleftharpoons CO_3(a) \quad \text{and/or} \quad CO_2 \rightleftharpoons CO(a) + Y,$$
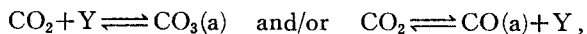
where (a) denotes absorbed state of the species.

SACHTLER *et al.*[2] have proposed on the basis of their results of IR spectrometiric studies that X and Y are adsorbed molecular and atomic oxygen, respectively, and X and Y are in equilibrium at temperatures above 110°C Such a critical temperature for mixing of X and Y, however, should be investigated further especially on reference to a catalyst being fresh or not and the sort of catalyst carrier.

Acknowledgement

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