Reduction Process of Silver(I) Oxide By Ethylene in the Presence of Oxygen

Toshiro YAMASHINA and Masahiro SEO

Faculty of Engineering, Hokkaido University, Sapporo

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It has been postulated by several workers[1-3] that the some particular species of surface oxygen on silver catalyst may be reactive for the partial oxidation of ethylene. In order to reveal the property of the species, it is of interest to study the reaction process of silver oxide with ethylene. In the present report, the reaction velocity was found to be considerably accerelated by the presence of oxygen in ethylene, an optimum pressure of oxygen being found to give the maximum velocity.

The CP grade Ag_2O powder was used as the sample of silver oxide in the experiment. Gravimetric analysis by hydrogen reduction showed that the sample contains the nonstoichiometric excess oxygen of 7.8%, *i. e.*, $Ag_2O_{1.078}$. The reaction gases were prepared by redistillating the cylinder grade ethylene (99.8%) and oxygen (99.9%) at liquid nitrogen temperature. The reaction velocities were measured in all glass, closed system (1800 m*l*) of a Gulbransen type microbalance with a sensitivity of 6.34×10^{-7} g/div. (1 div.=0.01 mm).

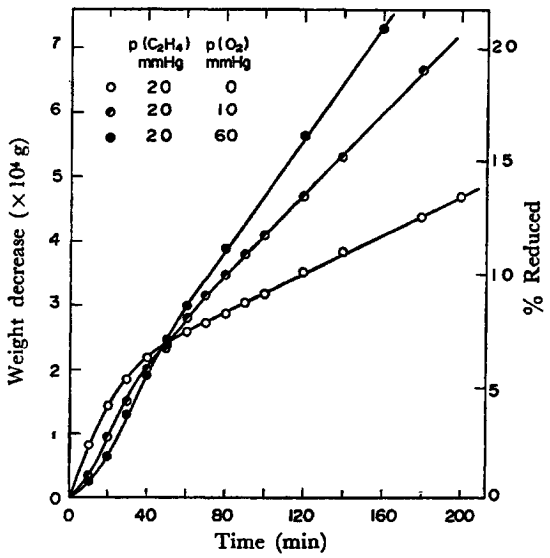

Fig. 1. Typical reaction curves of silver(I) oxide with ethylene and oxygen (170°C).

The reaction experiments were performed in duplicate and were found to be quite reproducible. Figure 1 shows typical results for the reaction of silver oxide (100 mg) with ethylene of 20 mmHg at 170°C in the presence of oxygen. The progress of the reaction with the time was followed by a complicated form in the initial 50 min. It was found that after about 8% reduction of silver oxide sample, the reaction became to proceed linearly with time in any case. The reaction rate constants are shown in Fig. 2 as a function of the oxygen

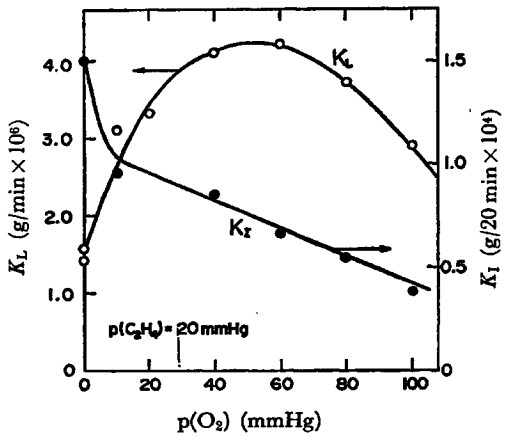

Fig. 2. Reaction velocities as a function of oxygen pressure under a constant pressure of ethylene (170°C).

pressure, where K_I is the reduced amount with the reaction during initial 20 min while K_L is the reaction velocity estimated from the slope of the linear part subsequent to the initial process of 50 min. It is noted that K_I and K_L values changed in much different ways with the oyxgen pressure, K_I being decreased with the pressure while in the curve for K_L the maximum reaction rate being observed in about 50 mmHg of oxygen pressure. No changes in weight of the silver oxide sample were found in pure oxygen (50 mmHg) at 170°C. It is of particular interest that the reaction of silver oxide with ethylene could be accelerated by the coexisting oxygen in the certain partial pressure. It would appear that a coupled reaction of oxidation-reduction on the surface occurred to accelerate the reaction of silver oxide with ethylene.

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3) S. Kagawa, E. Tokunaga, K. Kono and T. Seiyama, *Shokubai (Catalyst)*, **9**, (No. 4) 10 (1967).