Partial Oxidation of Propene by Active Oxygen generated Electrochemically on Gold through Yttria-stabilized Zirconia

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Propene was partially oxidized to acrylaldehyde by oxygen species generated electrochemically on an inert gold film via yttria-stabilized zirconia at 450 °C.

Yttria-stabilized zirconia (YSZ) is a well known solid electrolyte that can transport oxide ions through its lattice via anion vacancies. A cell system using YSZ as solid electrolyte, e.g. $P(O_2)$, M/YSZ/M', $P(O_2)'$ (M and M'; electrodes) can serve as an 'oxygen pump,'¹ by which the oxygen flux transferred across the YSZ can be controlled by the electric potential externally applied between the two electrodes. The application of electrochemical cells using YSZ for such catalytic oxidations as ethylene oxidation,² ethylbenzene oxidative dehydrogenation,³ and methane oxidative coupling⁴ on metal or metal oxide catalysts has been demonstrated. However, the characteristics of the surface oxygen generated electrochemically through the YSZ have not been well established, since all the cell systems previously studied have been equipped with metal or metal oxide catalysts that can activate oxygen and therefore catalyse the oxidation by themselves. In the present work, we report the partial oxidation of propene by oxygen species electrochemically generated on Au film via YSZ. It is generally accepted that an Au film alone cannot catalyse oxidation by the surface oxygen supplied directly from the gas phase.⁵

An electrochemical reactor was constructed from an 8 mol% yttria-stabilized zirconia disc 32 mm in diameter and 1



Figure 1. The rate of acrylaldehyde production on Au anode as a function of oxygen flux through YSZ.

mm in thickness. Thin compact films of Ag (2 μ m thick) and Au (1 μ m thick) were prepared as the cathode and the anode, respectively, on each face of the disc by vacuum evaporation. The two electrodes were connected with gold wire to an electrical circuit for controlling the oxygen transfer flux¹ from the Ag cathode to the Au anode across the YSZ. An oxygen pressure of 101.3 kPa was maintained on the cathode of the cell. A gaseous mixture of propene, nitrogen, and helium was passed over the anode side for testing the activity of oxygen species generated on the Au anode film. The products in the effluent gas were determined by gas chromatography using a thermal-conductivity detector and nitrogen as an internal standard.

In a blank test where nitrogen gas alone flowed across on the Au anode instead of the reaction gas mixture at 450 °C, it was confirmed that the oxygen pumping was well controlled by the electric potential, *i.e.*, the amount of oxygen gas evolved coincided well with the value calculated from the electric current across the YSZ. When the propene-nitrogen-helium mixture (5:5:90) was passed at a rate of 1.4 l/h across the Au anode at 450 °C, no oxidation of propene occurred under open circuit conditions when no oxygen was pumped through the YSZ. The oxidation took place when oxygen was pumped under closed-circuit conditions, and an increase in the current by oxygen pumping resulted in an increase in the rate of propene oxidation. No evolution of dioxygen was observed in this case. Acrylaldehyde (selectivity based on converted propene, S 60%), carbon dioxide (S 30%), and carbon monoxide (S 10%) were detected as products at a conversion of about 1%. The rate of acrylaldehyde formation is plotted in Figure 1 as a function of the oxygen flux. The rate of acrylaldehyde production increased with increasing oxygen flux (circular symbols). The applied potential was varied from zero to 2.4 V in these experiments. The addition of oxygen (60 ml/h) to the mixed-gas flow at the anode side did not affect the rate of acrylaldehyde production even when the applied

potential was varied (square symbols). In the latter case, there was no detectable acrylaldehyde produced under open circuit conditions.

The results obtained above clearly indicate that there is no activity at an Au surface for the oxidation of propene to acrylaldehyde by surface oxygen supplied directly from the gas phase and, furthermore, that there is substantially no influence of applied potential on the acrylaldehyde-production activity of the surface oxygen from the gas phase. Acrylaldehyde production from propene appeared to be performed only by the 'active oxygen species' generated electrochemically on the Au anode surface through the YSZ.

It seems reasonable to expect that electrochemical cells using YSZ can have certain advantages when applied to the catalytic oxidation of hydrocarbons, because of the 'unique' oxygen species generated electrochemically through YSZ.^{2–4} The potential advantages here led us to seek to clarify the uniqueness of the oxygen species; specifically, we asked could an inert metal be endowed with catalytic-oxidation activity by supplying such oxygen species to its surface? We have now answered this question affirmatively by revealing the 'unique activity' of the oxygen species generated on an inert Au metal surface by the electrochemical reactor. Attempts to establish a more complete view of the oxygen species are underway.

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