Partial Oxidation of Ethane into Acetaldehyde by Active Oxygen generated Electrochemically on Gold through Yttria-stabilized Zirconia

T. Hayakawa,[a] K. Sato,[b] T. Tsunoda,[c] K. Suzuki,[a] M. Shimizu[a] and K. Takehira*[a]

[a] *Department of Surface Chemistry, National Institute of Materials and Chemical Research, Tsukuba Research Center, AIST, 1-1, Higashi, Tsukuba, Ibaraki 305, Japan*

[b] *Institute of Materials Science, University of Tsukuba, Tennodai, Tsukuba, Ibaraki 305, Japan*

[c] *Department of Inorganic Chemistry, National Institute of Materials and Chemical Research, Tsukuba Research Center, AIST, 1-1, Higashi, Tsukuba, Ibaraki 305, Japan*

Ethane is partially oxidized to acetaldehyde by oxygen species generated electrochemically on an inert gold film *via* yttria-stabilized zirconia at 475 °C.

A cell system using yttria-stabilized zirconia (YSZ) as a 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 the oxidations of ethylene,[2] ethylbenzene[3] and methane[4] 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, except in our previous study.[5] We found that propene was partially oxidized into acrylaldehyde over an inert Au anode film under the oxygen pumping: this suggests that the oxygen species transported through YSZ onto the Au surface was active for the selective oxidation of propene into acrylaldehyde.[5] In this paper, we report the selective oxidation of ethane into acetaldehyde by the same oxygen species.

An electrochemical reactor was constructed from an YSZ disk 32 mm in diameter and of thickness 1 mm. Thin compact films of Ag (1.7 μm thick) and Au (1.0 μm thick) were prepared as the cathode and the anode, respectively, on each face of the disk by vacuum evaporation. The two electrodes were connected with gold wire to an electrical circuit for controlling the oxygen transfer flux from the Ag cathode to the Au anode across the YSZ by changing the applied voltage. An oxygen pressure of 101.3 kPa was maintained on the cathode of the cell. A gaseous mixture of ethane, 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 GC using a thermal-conductivity detector with nitrogen as an internal standard.

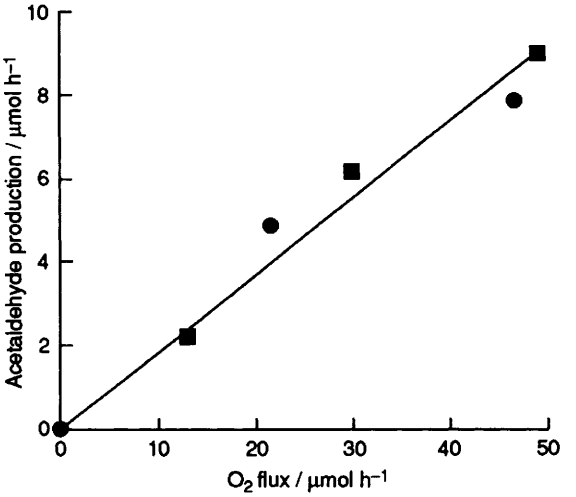

Fig. 1 The rate of acetaldehyde production on Au anode as a function of oxygen flux through YSZ

Electric current was measured to estimate the transport rate of oxide ions *via* four electrons reduction–oxidation steps across the YSZ. The amount of oxygen gas evolved in the anode compartment coincided well with the value calculated from the electric current across the YSZ. When the ethane–nitrogen–helium mixture (5 : 5 : 90) was passed at a rate of 1.2 $dm^3\ h^{-1}$ over the Au anode at 475 °C, no oxidation of ethane 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 increasing oxygen pumping resulted in an increase in the rate of ethane oxidation. No evolution of dioxygen was observed in this case. The rate of acetaldehyde production is plotted in Fig. 1 as a function of the oxygen flux. The rate of acetaldehyde production increased with increasing oxygen flux (■). The applied potentials varied from zero to 1.0 V in these experiments. At the O_2 flux of 49.4 $\mu mol\ h^{-1}$, the production rate of acetaldehyde and CO_2 was 8.9 and 21.9 $\mu mol\ h^{-1}$, respectively, and the O_2 consumption rate of 47.2 $\mu mol\ h^{-1}$ was calculated by assuming water as another oxidation product. Mass balance calculated between oxygen evolution and consumption was good and no other product was observed except a trace amount of ethene. Selectivities of acetaldehyde and CO_2 were 45 and 55%, respectively, based on converted ethane (0.75%). The conversion can be increased by lowering the rate of ethane flow. The addition of oxygen (60 ml h^{-1}) to the mixed-gas flow at the anode side did not affect the rate of acetaldehyde production even when applied potential was varied (●). There was no detectable acetaldehyde produced under open circuit conditons in spite of the presence of O_2 on the Au anode. When ethene (in place of ethane)–nitrogen–helium mixture (5 : 5 : 90) was passed at the same conditons, CO was substantially produced together with acetaldehyde and CO_2 and the rate of production of each again increased with increasing oxygen flux.

The results obtained above clearly indicate no activity of an Au surface for the oxidation of ethane to acetaldehyde by surface oxygen supplied directly from the gas phase and, furthermore, no influence of applied potential on the acetaldehyde-production activity of the surface oxygen from the gas phase. It is likely that acetaldehyde production from ethane is achieved only by the 'active oxygen species' generated electrochemically on the Au anode surface through the YSZ.

It has been reported that ethane was oxidized to ethene and acetaldehyde over Mo, V, B, P and Nb oxide catalysts, where N_2O was used as the oxidant[6] because O_2 afforded low selectivity of oxygenated products.[7] In the N_2O oxidation of ethane over the Mo/SiO_2 catalyst, O^- ions, derived from N_2O, react with ethane by hydrogen-atom abstraction. The resulting ethyl radical reacts with surface Mo=O to produce a surface ethoxide, which may either decompose to ethene or react further with the surface OH^- to form acetaldehyde.[6b] It is likely that O^- ions can be formed over the present Au anode surface during the four-electron oxidation of O^{2-} to O_2 at the boundary between Au and ZrO_2 (YSZ) and oxidatively dehydrogenate ethane. The ethyl radical thus formed can react with the surface oxygen to produce a surface ethoxide, which may react with the surface OH^- of ZrO_2 to form acetaldehyde. The surface oxygen over the Au anode is rather weakly bound to the anode surface compared to the Mo=O, and the ethoxide therefore may be more stable and react in preference with the surface OH^- to form selectively acetaldehyde.

Received, 15th April 1994; Com. 4/02257B

References

1 E. C. Subbarao, *Solid Electrolytes and Their Applications*, Plenum, New York, 1980.

2 M. Stoukides and C. G. Vayenas, *J. Catal.*, 1981,**70**, 137.

3 J. N. Michaelis and C. G. Vayenas, *J. Catal.*, 1984, **85**, 477.

4 D. Eng and M. Stoukides, *Catal. Rev. Sci. Eng.*, 1991, **33**, 375.

5 T. Hayakawa, T. Tsunoda, H. Orita, T. Kameyama, H. Takahashi, K. Takehira and K. Fukuda, *J. Chem. Soc., Chem. Commun.*, 1986, 961.

6 (*a*) M. Iwamoto, T. Taga and S. Kagawa, *Chem. Lett.*, 1982, 1469; E. Iwamatsu, K.-I. Aika and T. Onishi, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 1665; K.-I. Aika, M. Isobe, K. Kido, T. Moriyama and T. Onishi, *J. Chem. Soc., Faraday Trans. 1*, 1987, **83**, 3139; A. Erdohelyi and F. Solymosi, *Appl. Catal.*, 1988, **39**, L11; A. Erdohelyi and F. Solymosi, *J. Catal.*, 1990, **123**, 31; A. Erdohelyi and F. Solymosi, *J. Catal.*, 1991, **129**, 497; A. Erdohelyi, F. Mate and F. Solymosi, *J. Catal.*, 1992, **135**, 563. (*b*) L. Mendelovici and J. H. Lunsford, *J. Catal.*, 1985, **94**, 37.

7 E. M. Thorsteinson, T. P. Wilson, F. G. Young and P. H. Kasai, *J. Catal.*, 1978, **52**, 116; A. Argent and P. G. Harrison, *J. Chem. Soc., Chem. Commun.*, 1986, 1058; Y. Murakami, K. Ohtsuka, Y. Wada and A. Morikawa, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 340; S. T. Oyama, A. M. Middlebrook and G. A. Somorjai, *J. Phys. Chem.*, 1990, **94**, 5029; O. Desponds, R. L. Keiski and G. A. Somorjai, *Catal. Lett.*, 1993, **19**, 17.