

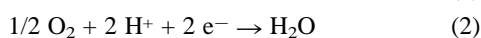
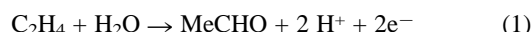
Selective synthesis of MeCHO by C₂H₄–(O₂+NO) cell system

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The formation rate of MeCHO and current for the C₂H₄ | Pd | H₃PO₄ | graphite | O₂ + NO (NO₂) cell are ten times higher than those for the C₂H₄ | Pd | H₃PO₄ | Pt | O₂ cell.

The selective synthesis of MeCHO has been demonstrated by a C₂H₄–O₂ cell system that was assembled as [C₂H₄, H₂O(g) | Pd-black/graphite/PTFE anode | aq. H₃PO₄ in silica wool | Pt-black/graphite/PTFE cathode | O₂].¹ Oxidation of C₂H₄ to MeCHO at the anode [eqn. (1)] and reduction of O₂ to H₂O at the cathode [eqn. (2)] proceeded respectively.



The cell system has several advantages compared with the current Wacker process using a mixture of C₂H₄ and O₂ catalysed by PdCl₂ and CuCl₂ in HCl solution.² For example, (i) the cell system is chloride free, and (ii) no separation processes for products and catalysts are required. Recent attractive heterogeneous catalytic systems have the same advantages.^{3,4} The cell system has additional advantages, (iii) the reaction rate and the current are easily controlled by variable resistance, and (iv) the danger of explosion is reduced because C₂H₄ and O₂ are separated by the membrane.^{1,5–7} However, the rate of MeCHO formation attained in this C₂H₄–O₂ cell system (1–2 TON per Pd atom in 1 h)¹ has to be improved dramatically. The TON obtained in the current Wacker process is greater than 10.² Therefore, the purpose of this work is to demonstrate the enhancement of the formation rate of MeCHO by one order of magnitude for the C₂H₄–O₂ cell system.

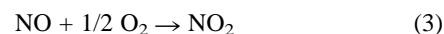
First, the potentials at the anode and the cathode for the C₂H₄–O₂ cell were measured at 353 K. The details of electrochemical measurement have been described elsewhere.⁸ The potentials at the anode and the cathode were +0.26 V (vs. Ag | AgCl) and +0.86 V respectively under open circuit conditions: the electromotive force (EMF) was 0.60 V. The potentials were changed to +0.65 and +0.67 V under short circuit conditions. The difference in the anode and the cathode potentials under short circuit conditions is due to an Ohm resistance. Thus, the over-potential at the anode was larger than that at the cathode. However, it should be noted that a considerable over-potential existed at the cathode, 32% of the EMF, for the electrochemical reduction of O₂.

If the over-potential at the cathode could be decreased by some means, an additional electrochemical potential could be applied at the anode which should increase the formation rate of MeCHO and the current. On the basis of this concept, many trials were performed for improving the rate of MeCHO formation. In conclusion, it is found that the addition of nitric oxide in a stream of O₂ dramatically enhances the current and the formation rate of MeCHO.

Fig. 1 shows a time profile for the formations of MeCHO and CO₂ [Fig. 1(a)] and for the current [Fig. 1(b)] with and without addition of NO into an O₂ stream. The apparent surface areas of the electrodes were 2 cm². The content of Pd in the anode was 120 μmol. When the circuit was shorted, a current of 3 mA cm⁻² flowed and MeCHO was selectively produced (>97%). When NO was added to the stream of O₂, a drastic increase in the current (35 mA cm⁻²) and the formation rate of MeCHO

were observed. When the NO addition was stopped, the current and the formation rate of MeCHO immediately decreased. Then, the current and the formation rate of MeCHO increased again with the addition of NO. It is clear that the addition of NO to the O₂ stream reversibly accelerates both the current and the formation rate of MeCHO. Although the formation rate of CO₂ was also increased by the addition of NO, the selectivity to MeCHO was still quite high (>95%).

The cathode and anode potentials for the C₂H₄–(O₂+NO) cell system were measured. The cathode potential under open circuit conditions is 1.0 V, which was considerably higher than the value (0.86 V) for the C₂H₄–O₂ cell. A separate experiment showed that the cathode potential for the C₂H₄–NO cell was 0.85 V. When NO was added to the O₂ stream in the cathode compartment, formation of a dark brown gas was observed, indicating the formation of NO₂ [eqn. (3)]. The increase in the cathode potential by the addition of NO and O₂ must be due to the formation of NO₂, which could be a stronger oxidant than O₂ or NO.



The anode potential under open circuit conditions is 0.26 V. The EMF for the C₂H₄–(O₂+NO) cell is 0.74 V, which is larger than the value (0.60 V) for the C₂H₄–O₂ cell. When the circuit was shorted, the potentials of the anode and the cathode were changing to 0.88 and 0.93 V, respectively. The over-potentials at the anode and cathode were 0.62 and 0.07 V. The over-potential of 0.07 V at the cathode was smaller than that of 0.19 V for the C₂H₄–O₂ cell, although the current was one order of

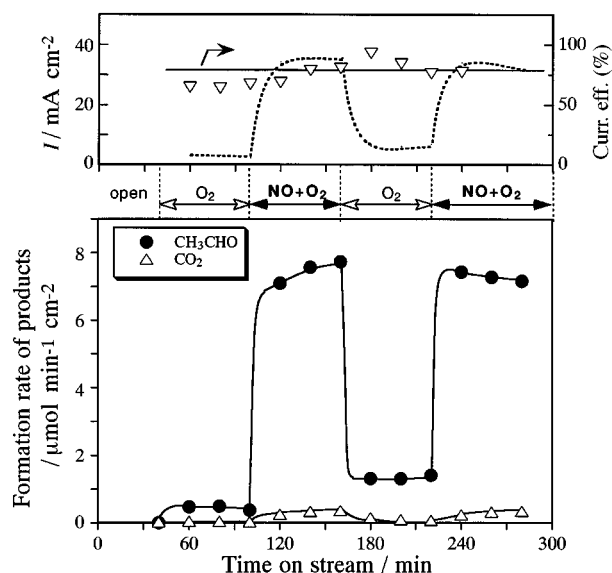


Fig. 1 Effects of NO addition into the O₂ stream at the cathode on the formation of MeCHO with the C₂H₄–O₂ cell: (●) MeCHO and (△) CO₂. C₂H₄ (39 kPa), H₂O (13 kPa), anode | aq. H₃PO₄ in silica wool | cathode, O₂ (51 kPa), He (50 kPa) or NO (50 kPa). *T* = 353 K. Anode: Pd-black/CF/PTFE, total flow rate = 32 ml min⁻¹. Cathode: Pt-black/graphite/PTFE, total flow rate = 32 ml min⁻¹.

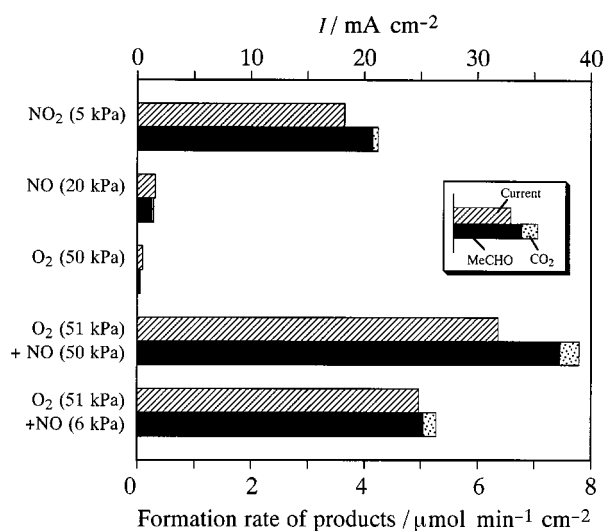


Fig. 2 Effects of some oxidants of the C₂H₄-oxidant cell with graphite/PTFE cathode on the Wacker oxidation. C₂H₄ (39 kPa), H₂O (13 kPa), anode | aq. H₃PO₄ in silica wool | cathode, oxidants. Oxidants: NO₂ (5 kPa), NO (20 kPa), O₂ (50 kPa), NO (50 kPa) + O₂ (51 kPa), and NO (6 kPa) + O₂ (51 kPa). *T* = 353 K.

magnitude larger than that for the C₂H₄-O₂ cell. This fact suggests that the electrochemical reduction of NO₂ is very easy compared with that of O₂.

The cathode used so far in this work was Pt-black/graphite/PTFE. If the reduction of NO₂ occurs quite easily, we may exclude Pt-black from the cathode. In fact, a cathode without Pt-black (graphite/PTFE cathode) showed very good electrocatalytic performance; a high current of 40 mA cm⁻² and selective MeCHO formation (3% yield and 8 TON in 1 h). The optimum reaction conditions were studied for the C₂H₄-(O₂+NO) cell using the graphite/PTFE cathode. Then, a maximum yield of 15% and 31 TON in 1 h were obtained, which is fairly good productivity for MeCHO formation.

The results for the oxidation of C₂H₄ using different oxidants are compared in Fig. 2. The cathode in these experiments was graphite/PTFE. A current of 18.5 mA cm⁻² flowed and MeCHO was selectively produced with the C₂H₄-NO₂ cell, although the pressure of NO₂ was only 5 kPa. A mixture of O₂

and NO was an excellent oxidant but O₂ or NO alone were not effective oxidant at the graphite cathode. When *P*_{NO} was reduced from 50 to 6 kPa for the C₂H₄-(O₂+NO) cell, the formation rate of MeCHO and the current were slightly decreased. The influences of *P*_{NO} on the formation rate and the current were small. When NO₂ (5 kPa) was introduced into the anode compartment, catalytic oxidation of C₂H₄ to CO₂ (1.2 μmol min⁻¹ cm⁻²) and MeCHO (0.4 μmol min⁻¹ cm⁻²) proceeded under open circuit conditions. The selective synthesis of MeCHO from C₂H₄ with NO₂ catalysed by the Pd anode does not proceed. No enhancing effects due to the addition of NO₂ into the anode compartment on the formation of MeCHO and the current were observed under short circuit conditions. These facts confirm that NO₂ produced from a mixture of O₂ and NO works as a strong oxidant at the cathode.

The products for the reduction of NO₂ and NO at the cathode were trace formation of N₂ and N₂O in the gas phase and a small amount of NH₂OH or NH₃ (< 4% current efficiency) in the diaphragm. There are no other products containing nitrogen. These observations suggest that NO₂ is being reduced to NO and H₂O [eqn. (4)].



The NO produced here would regenerate NO₂ according to [eqn. (3)]. Thus, NO works as a mediator (or catalyst) for the electrochemical reduction of O₂.

Notes and References

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