

Catalysts for Butane Reforming in Zirconia Fuel Cells

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The ability of fuel cells to use hydrocarbon fuels efficiently is important if they are to compete with battery power. Solid oxide fuel cells, particularly zirconia fuel cell devices, are generally well suited to utilise a variety of fuels. They are commercially attractive, especially in remote locations where battery supply and maintenance costs are prohibitive but where fuel, particularly butane, is readily available. Butane can be safely stored at high energy density and is thus a useful fuel for zirconia fuel cells in remote areas. Partial oxidation would be the preferred route to reform butane, but this requires a suitable catalyst. Ruthenium is an excellent partial oxidation catalyst, giving nearly total reformation of butane and producing high levels of hydrogen. However, problems such as carbon deposition and catalyst optimisation need to be addressed. Here, work with a zirconia fuel cell successfully fuelled by butane and using a ruthenium catalyst under controlled reaction conditions is discussed.

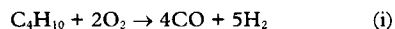
Zirconia fuel cell devices can be small-scale and portable. They can generally use a variety of fuels, including hydrocarbons, since they are not susceptible to carbon monoxide poisoning. They do not require external reformation of the fuel.

Butane is a particularly attractive fuel because it is cheap, easily stored and is available at remote sites, where battery power is expensive. The main problem with butane, when fed directly into zirconia devices, is its tendency to deposit carbon on the fuel cell anodes. A possible solution to eliminate this is by reforming the butane through the addition of steam (1), carbon dioxide (2), or air to bring about partial oxidation (3). For the fuel cell device described here partial oxidation of butane by air has been used, as this provides the simplest device construction. The system in Figure 1 shows the position of the partial oxidation catalyst upstream of the fuel cell electrodes on the zirconia tubes (4).

Catalytic Reactions

Partial catalytic oxidation is widely used for the reformation of butane (5) and other paraffins (6, 7) to higher value chemical feedstocks,

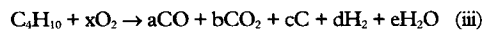
such as formaldehyde or butadiene (8, 9). Such products are not suitable as feeds for fuel cells. Therefore, new catalysts must be found to convert the butane to synthesis gas – the preferred form of butane reaction product for fuel cell use (10):



while preventing the total oxidation of the butane to water and carbon dioxide:



This reaction requires more than simple restriction of the availability of oxygen (11), as carbon tends to be deposited on the anode during the reaction:



where the numbers x, a, b, c, d and e vary according to the conditions.

A number of catalysts are known to convert methane to synthesis gas (12–16) on a variety of catalyst supports (17–21), but methane reacts in a much simpler way than butane since it has no C–C bonds to give the intermediate hydrocarbon products formed by butane. Even so,

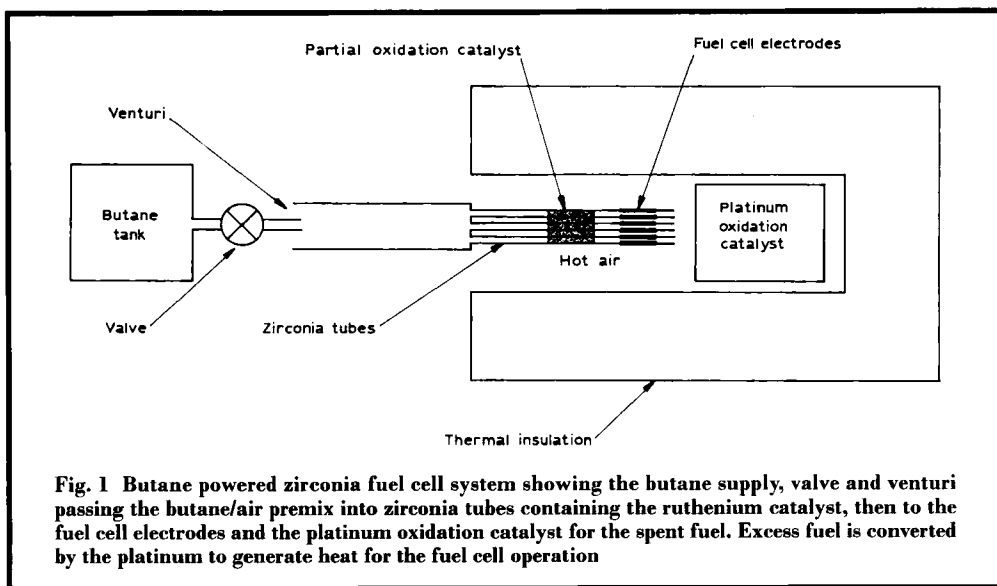


Fig. 1 Butane powered zirconia fuel cell system showing the butane supply, valve and venturi passing the butane/air premix into zirconia tubes containing the ruthenium catalyst, then to the fuel cell electrodes and the platinum oxidation catalyst for the spent fuel. Excess fuel is converted by the platinum to generate heat for the fuel cell operation

there are ten principal reactions of methane (22), and correspondingly more with butane.

The purpose of this work, therefore, was to find a catalyst formulation capable of favouring the production of synthesis gas from butane.

Catalyst Materials

Various catalyst materials were tested in the rig shown in Figure 2. By separating the catalyst from the fuel cell, better control of the experimental conditions was possible than in Figure 1. Product gas from the catalyst could be analysed by gas chromatography, with thermal conductivity detection, using both nitrogen

and helium carrier gas to measure the concentrations of hydrogen, carbon monoxide, carbon dioxide and C1 to C4 hydrocarbons, before the gas entered the fuel cell section.

The catalysts investigated were those already known to produce synthesis gas from methane, that is: nickel, ceria, platinum and ruthenium (23), supported on δ -alumina fibres (Saffil, ICI) mounted in a nickel support within a stainless steel reactor tube. The reactor temperature was controlled between 600 and 850°C.

Three conditions were found to be necessary for the successful partial oxidation of butane to synthesis gas:

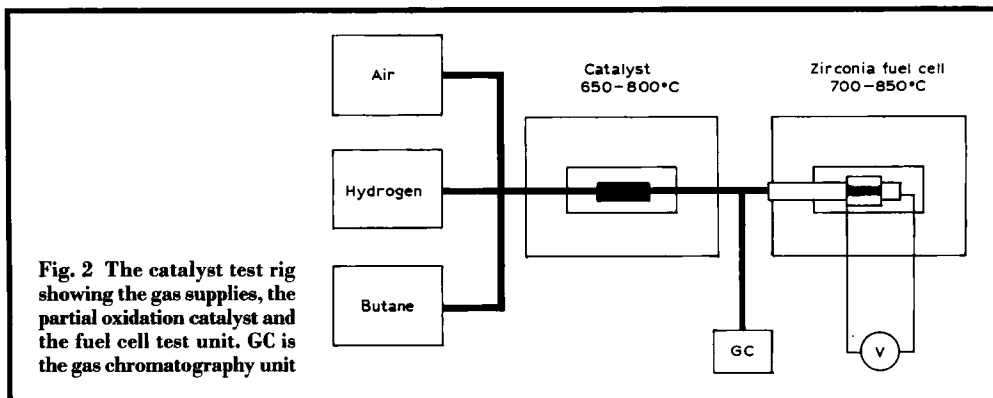


Fig. 2 The catalyst test rig showing the gas supplies, the partial oxidation catalyst and the fuel cell test unit. GC is the gas chromatography unit

- the correct catalyst
- the correct temperature and
- the correct butane:air ratio.

The amount of butane conversion and hydrogen generation for the four catalysts tested at 700°C is shown in Figure 3. It can be seen that ceria and nickel catalysts were not much more efficient than the reactor tube without catalyst: only about 40 per cent of the fuel was converted and hydrogen production was less than 55 per cent of its potential. Significant quantities of butane and intermediate hydrocarbons remained in the product gas, causing severe coking problems.

Platinum yielded the highest butane conversion rate but tended to push the reaction through to total oxidation, giving predominantly carbon dioxide and water, and much coking. Ruthenium was the best catalyst, giving a high butane conversion, and generating 80 per cent of the possible hydrogen. Optimum performance conditions for the ruthenium system were therefore investigated more fully.

Optimisation of the Ruthenium Catalyst Performance

The temperature of operation of the ruthenium on alumina catalyst was tested over the range 600 to 850°C with various butane:air mixtures. The optimum temperature range was found to be 750 to 800°C at a butane:air ratio of 1:10, see Figure 4. Under these conditions,

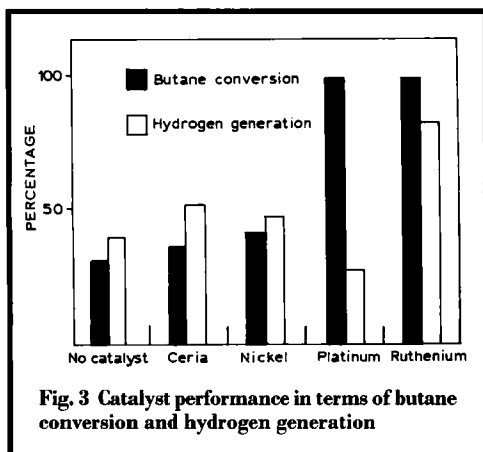


Fig. 3 Catalyst performance in terms of butane conversion and hydrogen generation

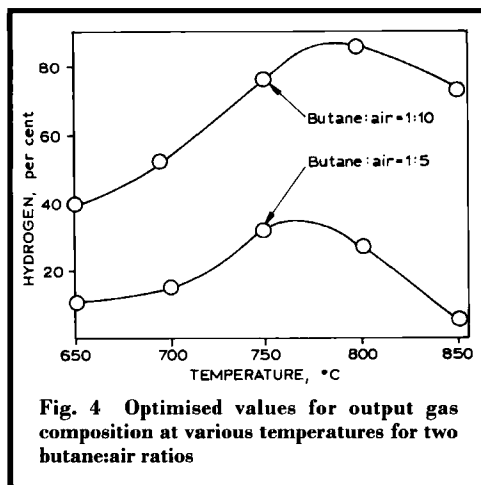


Fig. 4 Optimised values for output gas composition at various temperatures for two butane:air ratios

negligible coking was observed and the output gas had a high hydrogen content and sufficient carbon dioxide to assist in reforming any residual hydrocarbons, downstream on the fuel cell anode.

Reformed output produced under optimised conditions was fed to a zirconia fuel cell tube which had a nickel cermet anode and a lanthanum strontium manganite cathode, maintained at 850°C. Electrical power could be drawn from this cell at 0.7 volts, which compared favorably over short term tests with results obtained using pure hydrogen fuel. Although there were some current fluctuations, the power output was maintained over a period of several hours. By contrast, non-optimised conditions resulted in erratic and rapidly diminishing performance with time, as the cell then coked up almost immediately.

The effect of using a ruthenium catalyst was demonstrated dramatically in Figure 5. Here, using the apparatus of Figure 2, the catalyst in the partial oxidation unit was varied. When alumina fibre was used as a reference with hydrogen as the fuel gas, a good fuel cell output was observed, as expected, over many hours, shown by the horizontal line in Figure 5. However, when hydrogen was replaced by a mixture of butane:air in a 1:10 ratio and passed over the alumina fibre support, the fuel cell failed within 5 hours, as is shown in Figure 5.

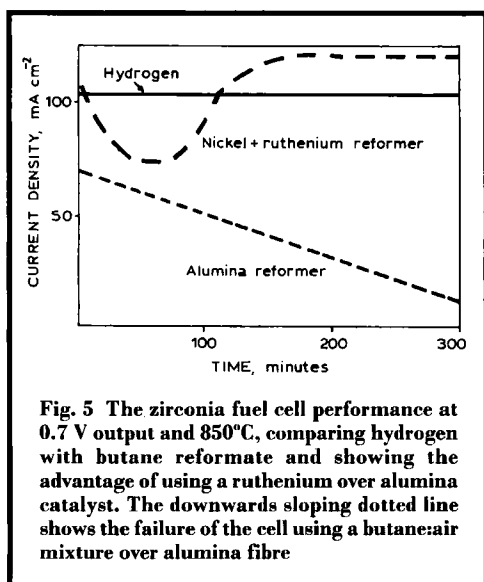


Fig. 5 The zirconia fuel cell performance at 0.7 V output and 850°C, comparing hydrogen with butane reformat and showing the advantage of using a ruthenium over alumina catalyst. The downwards sloping dotted line shows the failure of the cell using a butane:air mixture over alumina fibre

After coating the alumina fibre catalyst support with 10 weight per cent ruthenium, and repeating the procedure, the fuel cell initially gave a slight drop in performance on switching from hydrogen to the butane:air mixture. However, after a short time the power output

increased to a higher value than with hydrogen. The ruthenium catalyst was thus seen to promote the partial oxidation of butane.

Conclusions

Butane can be successfully converted by a ruthenium catalyst for use in zirconia fuel cells. The optimum conditions are to employ partial oxidation of the butane above 750°C at a 1:10 butane:air ratio with the ruthenium supported on alumina. The fuel cell performance is then comparable to the output obtained when using hydrogen, and the deposition of carbon on the catalyst and the cell is eliminated.

As it is known that methane conversion to synthesis gas by ruthenium is aided by using titania as the support material (17), the effects of other support materials, including zeolites and lanthanides (24), are going to be tested and the influence of the catalyst support on the product characteristics will be examined in long term evaluation of the system.

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