Mass-Spectrometric Observations of Plasma-assisted Catalysis

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Abstract:

Plasma discharges are known to facilitate the catalysis of reactive gas mixtures [Ref: 1, 2, 3 & 4]. A variety of plasmas, including surface barrier discharges, have been demonstrated to enhance the efficiency of the catalysts such as nickel/alumina or silver/alumina, used in conventional thermally activated reactors. The observed improvements have included a lowering of the onset temperature at which the catalyst becomes effective, and an increase in the over-all efficiency of the process. A number of diagnostic methods have been employed to study the synergistic behaviour of plasmas and heated catalysts, the technique adopted often being specific to the monitoring of a particular reaction product. The work described here is aimed at demonstrating the versatility of mass-spectrometric methods in following the behaviour of typical plasma-assisted catalytic processes.

QGA Gas Analyser

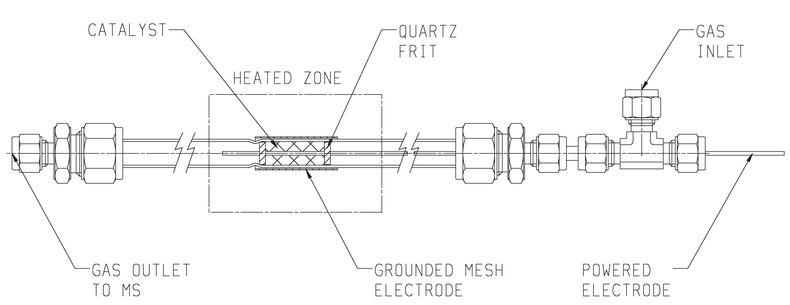


Figure 1.

Instrumentation:

The reactor consists of a quartz tube with a tungsten electrode running through it. Quartz frit discs were used to centralise the electrode and confine the catalyst. A number of excitation methods were available for generating a plasma in the reactor. For the measurements described here the central electrode was powered using a 0 to 3 Watt, 20 kHz supply and generated a plasma between the electrode and a grounded electrode surrounding a section of the reactor tube which included the volume occupied by the powdered catalyst (refer to Figure 1). The experiments included ones with nickel/alumina and palladium/alumina catalysts. The gases of interest were introduced using a mass-flow control system with helium as the carrier gas. It is intended to use other carrier gases such as nitrogen in future work. The effluent gases from the reactor were sampled using the capillary sampling connection to the Hiden QGA Gas Analyser. The capillary connection provided the pressure reduction required to give a pressure of at or below 10^{-6} Torr in the ionisation source of the mass spectrometer.

Experimental results:

Oxidation of carbon monoxide.

Figure 2a shows a typical mass scan for the gas sampled from the reactor when the input gas flow consisted of helium containing 0.2% of CO and 0.4% of O_2. Figure 2b shows the result of subtracting a scan taken when the plasma was off from one taken when the plasma was operating (both scans being taken at room temperature). The formation of carbon dioxide at the expense of the carbon monoxide and oxygen is clearly seen.

When the catalyst was heated, with or without the plasma being on, the conversion to carbon dioxide during heating cycles was as shown in figure 3.

In the first cycle, from time 00 to 20mins, the plasma was off, whereas in the second cycle, from 25mins to 50mins, the plasma was on from 26mins until 38mins and again from 43.5mins to 47min. The heating cycle from 28 to 41mins was at the same rate of input power to the heater as in the first cycle. While the catalyst was significantly above its onset activation temperature, the plasma had no observable effect (no reduction in the CO_2 signal at 38mins when the plasma was turned off) but at lower temperatures, such as the period between 43.5 and 47mins when the heating power was off and the catalyst cooling, the plasma was clearly effective.

The onset activation temperature (at around 32/33mins) was also lower when the plasma was on.

Examination of the time histories of all masses from m/e=10 to 50 showed the only mass other than 28, 32 and 44 to show significant variation with temperature or plasma on/off was m/e=16, presumably O+. This is likely to have been produced in the mass spectrometer's source from the carbon dioxide. There is likely to have been CO+ produced in the same way, so that the time variation of the m/e=28 signal has 2 components, one directly from the CO in the gas stream and one from the product carbon dioxide. These could be distinguished in a more detailed study using threshold ionisation methods as we have described elsewhere [Davies et al., Ref 5].

Figure 2a.

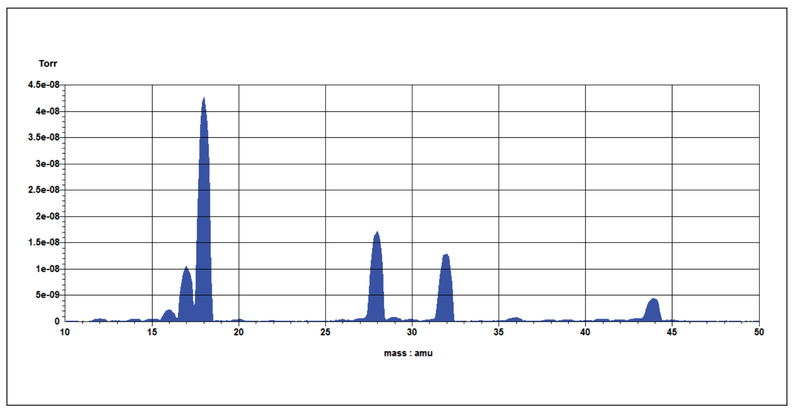
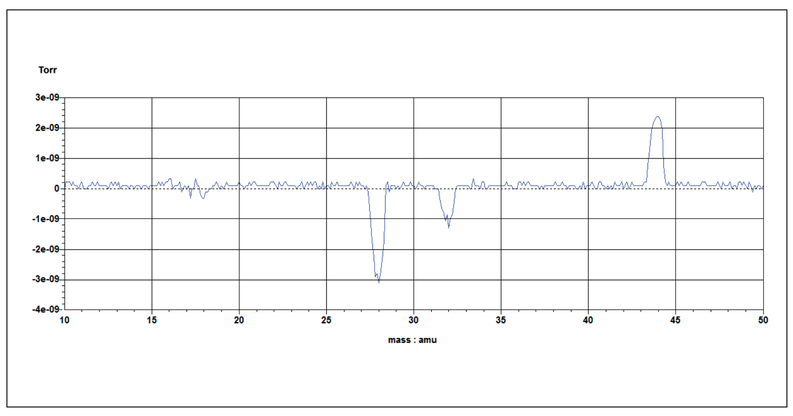


Figure 2b.



Dry Reformation of Methane.

For the methane reformation experiments, the first tests were made using palladium/alumina catalyst and a 3:1 mixture of methane and carbon dioxide in a helium carrier gas. The principal reaction as discussed by Silverwood et al. [Ref 3] is:

$$CH_4 + CO_2 = 2CO + 2H_2.$$

Figure 4 shows two heating/cooling cycles. In the first cycle the plasma was off and the activation temperature of the catalyst was reached at t=13mins, the production of hydrogen and carbon monoxide continuing to increase as the temperature increased until 27mins when the heating was stopped. The hydrogen and CO intensities then decreased as the reactor cooled and the m=16 CH_4^+ signal recovered. At t=44mins the plasma was turned on and the methane conversion restarted, the reactor then being well below the catalyst's activation temperature. When the heating of the reactor was resumed the production of hydrogen and CO for a given temperature was approximately 20% higher than it had been in the absence of a plasma. The figure also shows the behaviour of the H_2O^+ signal which is produced as the result of the reaction $H_2 + CO_2 = CO + H_2O$. This reaction did not appear to be influenced by the plasma.

Figure 5 shows the effect of three 'plasma on' phases during a period after the reactor had reached its maximum temperature. Note that the reactor temperature was essentially constant during the period from 15 to 30 mins and then cooled back to below threshold activation by 40mins. The final 'plasma on' period shows the effects of conversion with no catalytic contribution.

Similar experiments were carried out using a Nickel/Magnesium oxide catalyst. Figure 6 shows one heating cycle. The plasma was only operated for four short periods at times of 1:34, 2:19, 2:33 and 2:48. The effects were clear but not dramatic. The marked variations in the relative abundances from 2:10 onwards are unexplained since the temperature of the reactor was relatively stable from then until 2:40, but indicate a deterioration in the catalyst's effectiveness.

Figure 3.

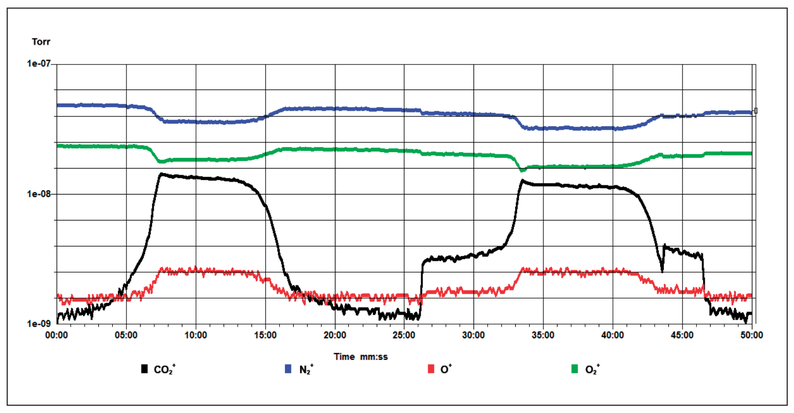
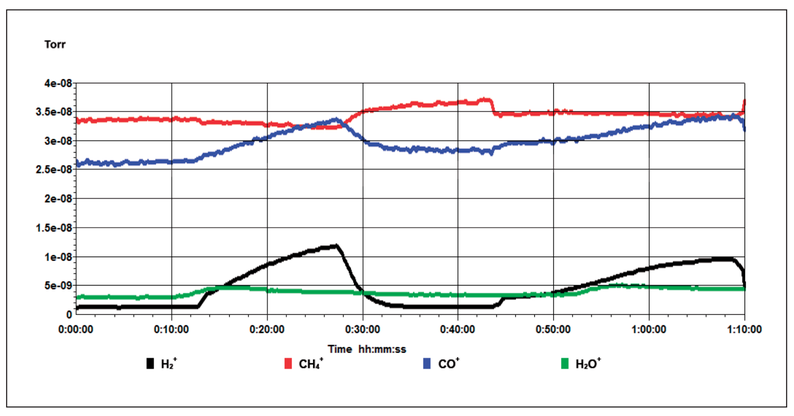


Figure 4.



Conclusions

The measurements illustrate the ability of the instrument to monitor the behaviour of plasma-enhanced catalysis processes. The Gas Analyser responds rapidly to any time-dependant variation of the products of the processes. The relative positions of the catalyst and plasma regions of the reactor may be readily altered. Future experiments will include studies of the role of the carrier gas in determining the plasma's contribution to the reaction processes.

References

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[2] C. E. Stere et al., ACS Catal. (2014) 4 (2) 666-673

[3] I. P. Silverwood et al., Catalysis Today (2010) 155, 319-325

[4] H. J. Gallon et al., (2010) 7th ICRP & 63rd GEC PR3-004

[5] S. Davies et al, Vacuum (2013) 101, 416-422

Figure 5.

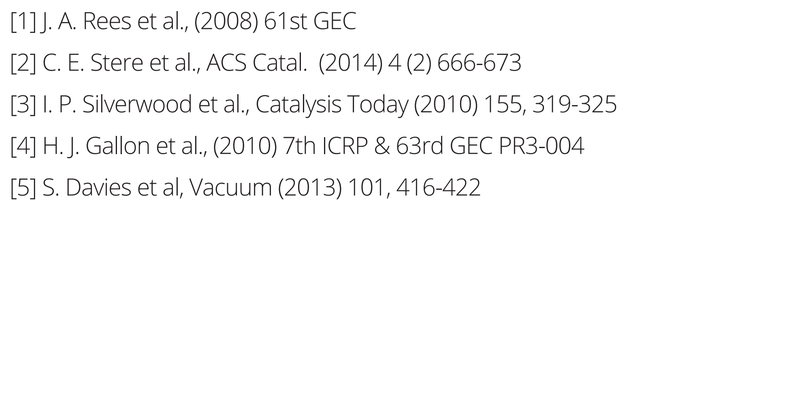
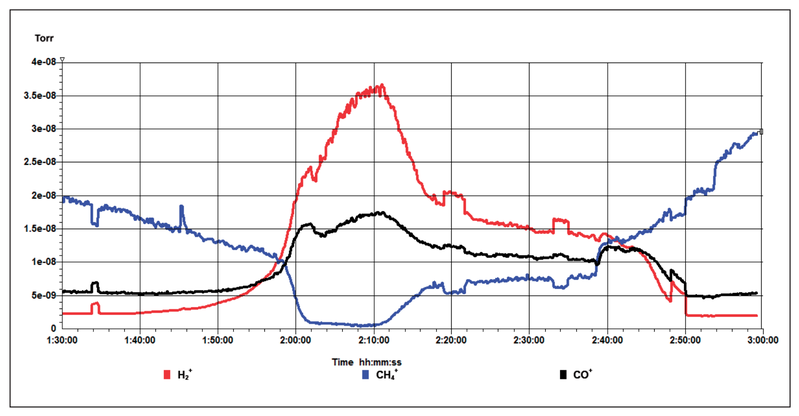


Figure 6.



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