Plasma Modification of Catalysts Using a Dielectric Barrier Discharge

D.T Lundie[a], J.A. Rees[b]

[a]Catalysis Division, [b]Plasma and Surface Analysis Division,

Hiden Analytical Ltd, 420 Europa Boulevard, Warrington, WA5 7UN, UK Tel: +44 (0)1925 445 225

INTRODUCTION:

The combination of plasmas and catalysis under moderate temperatures is an emerging area [1].

The techniques are commonly combined in one of two ways. In the first of these the catalyst is introduced into the plasma, in plasma catalysis (IPC) while in the second, the catalyst is placed down-stream of the discharge zone, post plasma catalysis (PPC). The introduction of a plasma to a catalysis system may produce a change in the distribution or type of reactive species available for reaction or a change of catalyst properties, such as an increase in dispersion or a change in catalyst structure.

In the present work, a micro-reactor has been constructed that allows the study of catalysis using traditional temperature-programmed techniques. The reactor also allows a dielectric barrier discharge (DBD) to be generated over the whole length of the catalyst region or to precede it. The DBD produces a cool plasma at atmospheric pressure and generates surface modifications of the catalyst and is a source of ions and radicals for reaction processes. Test reactions have been studied to show differences in reaction product distributions and activation temperatures when compared with the catalyst alone.

The reactor has also allowed catalysts to be held in the plasma in order to attempt to modify the catayst surface before testing them in a more conventional microreactor system.

[1] J.Van Durme, J. Dewulf, C. Leys, H. Van Langenhove, Appl. Catal. B Environ. 78 (2008) 324-333.

ATMOSPHERIC-PRESSURE PLASMA REACTORS

A variety of electrical plasmas may be operated at atmospheric pressure and the range of applications of plasmas in areas such as waste gas treatment, surface modification, and chemical synthesis is expanding rapidly.

Plasma sources designed around discharges generated over the surface of a dielectric covering one of the discharge electrodes, ("dielectric surface barrier discharges"), are versatile examples. The plasma is typically obtained using a high frequency source to generate a discharge in a flow of helium to which two or more reactant gases are added. The plasma consists of electrons with energies up to 25ev and near-thermal, excited and ionised gas species, near-thermal, excited and ionised gas species.

EXPERIMENTAL

A microreactor based on the Hiden CATLAB was constructed to allow a catalyst to be heated under controllable temperature and gas flow conditions. The microreactor was connected to the Hiden QIC-20 capillary inlet mass spectrometer system. In addition to the standard furnace arrangement a dielectric barrier discharge (DBD) could also be generated over the length of the catalyst or in an area before the catalyst. The DBD consisted of an inner coaxial tungsten wire electrode of 1.0 mm diameter and an outer cylindrical metallic electrode wrapped around a quartz tube and connected to ground. The tungsten electrode is connected to the open-circuit end of the secondary winding of a high voltage transformer operated at 50 kHz.

Initial reactions were performed using 1% Pd/Al_2O_3 catalyst. The test reaction used was the oxidation of CO to form CO_2. Plasma modified catalysts were also investigated using a test catalyst of Ni/MgO. The Ni/MgO was held in the plasma reactor under a flow of He for 1 hr. Subsequently the Ni sample was characterised using TPR/TPD measurements using the Hiden CATLAB microreactor system. A schematic of the plasma reactor setup is shown in Figure 1.

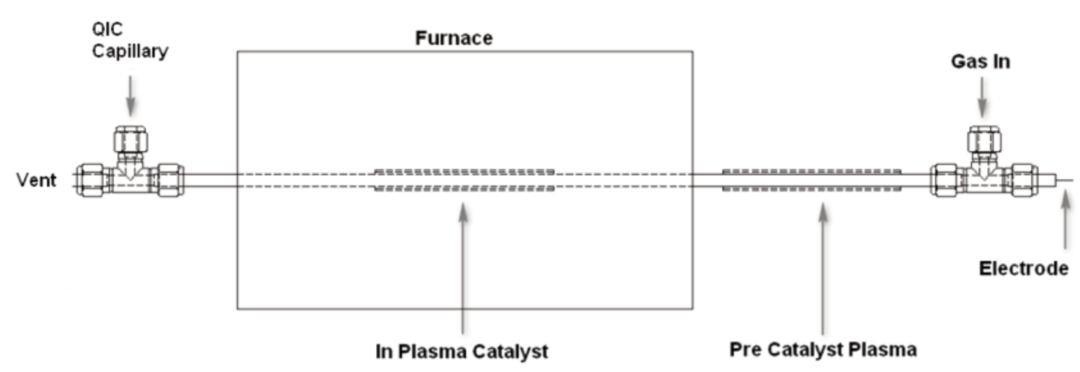

Figure 1: Schematic of Plasma Reactor

RESULTS – PLASMA REACTION TESTING

Blank experiments (no catalyst, no plasma, not shown) were performed and showed that no reaction occurs below 500˚C.

Figure 2 shows the results of using the plasma only to oxidise the CO. The figure shows that some conversion of CO to CO_2 occurred instantly when the plasma was switched on.

Figure 3 shows the results of using the catalyst only. The sample was ramped at 15˚C/min to 600˚C. The figure shows that complete conversion of CO to CO_2 occurred at around 250˚C.

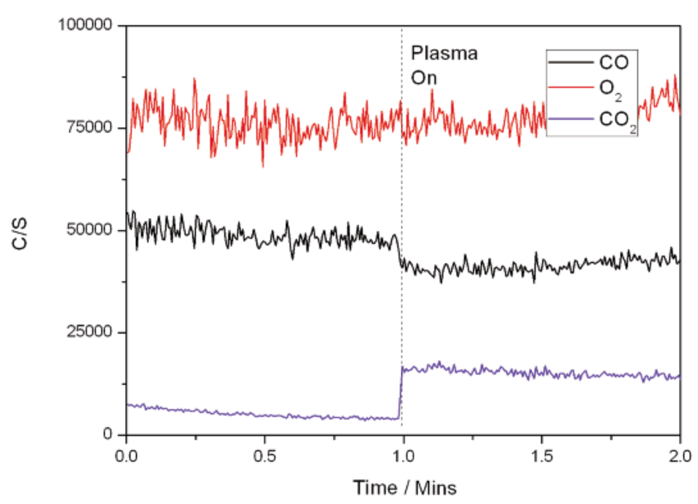

Figure 2 Plasma Only Reaction

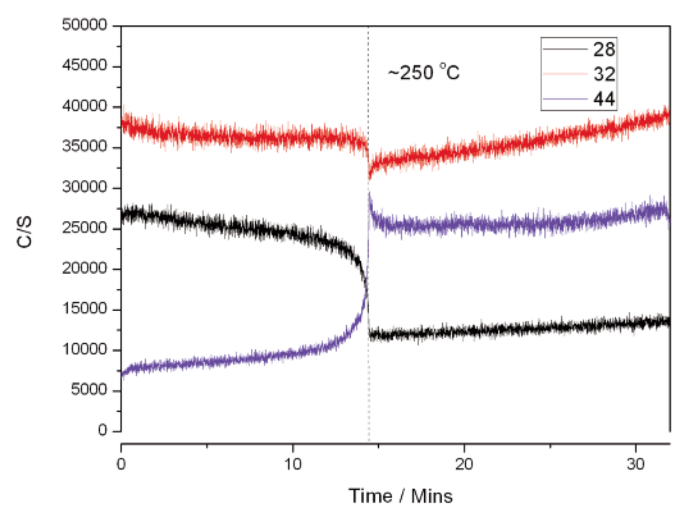

Figure 3 Catalyst Only Reaction

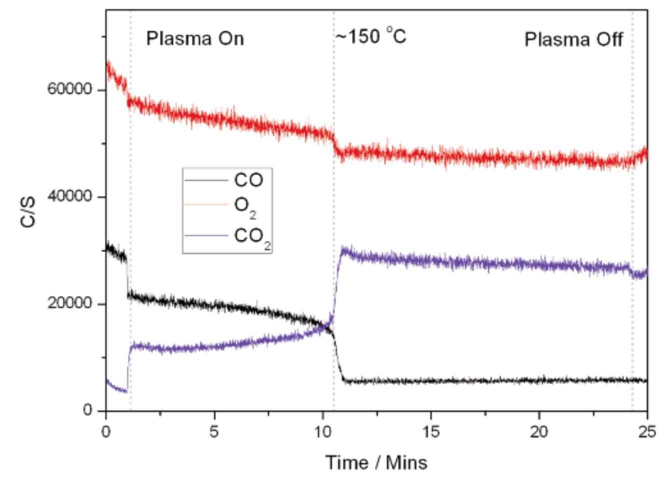

Figure 4 Plasma + Catalyst Reaction

The plot shown in Figure 4 is the result of a combined plasma and heating experiment. Here the plasma was generated over the length of the catalyst (IPC). Before heating commenced the plasma was switched on. An initial increase in CO_2 production is seen at this point. Upon heating it can be seen that complete conversion of CO to CO_2 occurs at 150˚C, 100˚C below the temperature at which reaction occurs with the catalyst and temperature alone.

In a separate experiment the plasma was generated pre the catalyst bed (PPC). Switching on of the plasma showed similar initial increase in CO_2 production. Upon heating it was seen that there is complete conversion of CO to CO2 at 150˚C. This is identical to the results seen with the plasma generated over the length of the catalyst. This suggests that the decrease in reaction temperature is due to the ionised gas species created in the plasma being more reactive over the catalyst and not due to any modification to the catalyst surface by the plasma being responsible for the decrease in reaction temperature.

RESULTS – PLASMA MODIFIED CATALYSTS

Characterisation of the Ni catalysts was performed using TPR/TPD experiments. Figure 5 shows TPR experiments of the modified and unmodified catalysts. Figure 5 shows clear differences in the TPR profiles with the modified catalyst having a significant low temperature reduction peak not seen in the unmodified sample. This difference in the reduction profile suggests some modification of the Ni particles has occurred using the plasma system

The H_2 TPD profiles shown in Figure 6 also show significant differences between the modified and unmodified samples. The unmodified samples shows at least 3 H_2 desorption peaks. The modified sample shows a similar number of peaks however one of the peaks T_{max} 190˚C is of significantly higher intensity. This indicates that the plasma modified Ni sample has a different morphology of Ni particles compared with the unmodified sample. The differing intensities would also suggest an increase in Ni dispersion has occurred.

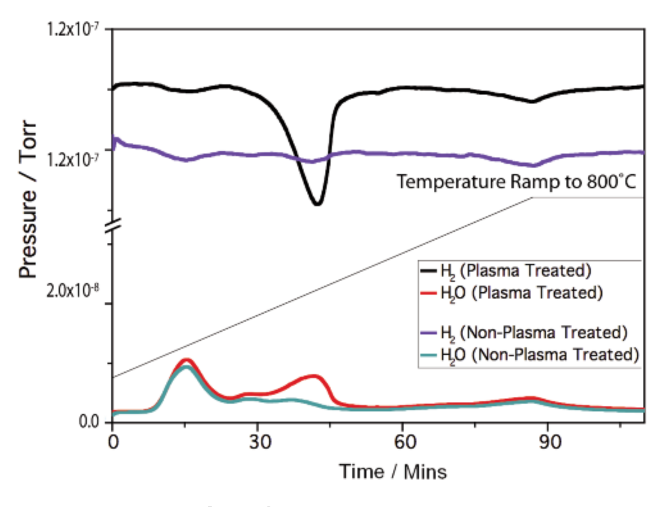

Figure 5 Ni/MgO TPR

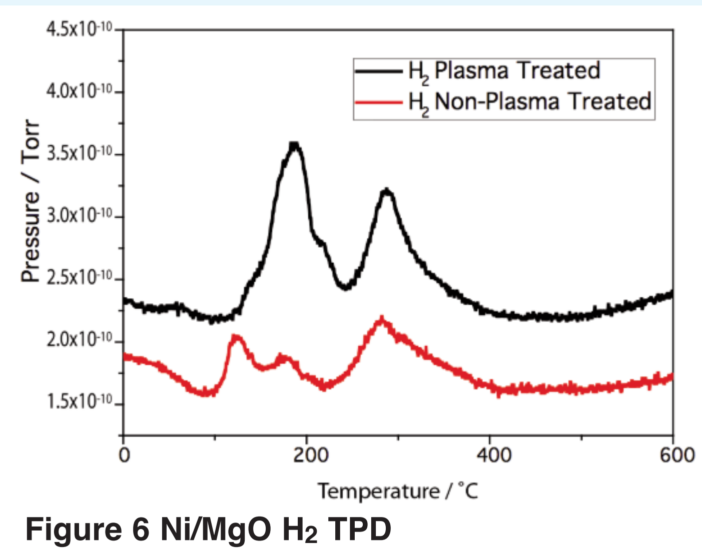

Figure 6 Ni/MgO H_2 TPD

Conclusions:

In the present model reactor, carbon monoxide and oxygen are used as the reactant gases. The reactive species produced in the plasma include atomic oxygen and ions such as CO^+, O^+, O_2^+, CO_2^+, O^-, O_2^- and CO_3^-. These species interact to give carbon dioxide as the major reactor product. The conversion of CO into CO_2 using a combination of plasma and catalysis is of obvious interest, as are potential improvements in the efficiency of the process through control of the plasma conditions. It is possible to greatly increase the overall efficiency of the conversion by exploiting the synergy between plasmas and catalysts.

The TPR/TPD results show the potential for modifying Ni catalysts using a dielectric barrier discharge plasma. Further work is required to investigate changes in reactivity of the modified plasmas.