Reaction Studies of a Combined Plasma Catalyst Reactor

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Abstract

The combination of plasmas and catalysis under moderate temperatures is an emerging area [1]. The techniques are commonly combined in one of two ways. The first is the introduction of a catalyst in the plasma discharge (in plasma catalysis, IPC), the second by placing the catalyst after the discharge zone (post plasma catalysis, PPC). The introduction of a plasma to a catalytic system may have several effects such as 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.

A microreactor has been constructed that allows the study of catalysis using traditional temperature programmed techniques. However, the reactor also allows a dielectric barrier discharge (DBD) to be generated over the whole length of the catalyst region (IPC). DBD produces a cool atmospheric plasma and is an established technique for generating surface modifications and as a source of ions and radicals for reaction processes. A number of test reactions have been studied to show difference in reaction product distributions and activation temperatures when compared with the catalyst alone. Reaction product distributions were measured using a conventional capillary inlet mass spectrometer. A molecular beam inlet mass spectrometer (MBMS) was also used to sample the reactive gas species generated inside the plasma/catalyst system. Combining these two techniques gives a unique insight into plasma catalysis process.

[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 application of such plasmas in areas such as waste gas treatment, surface modification, and chemical synthesis is expanding rapidly.

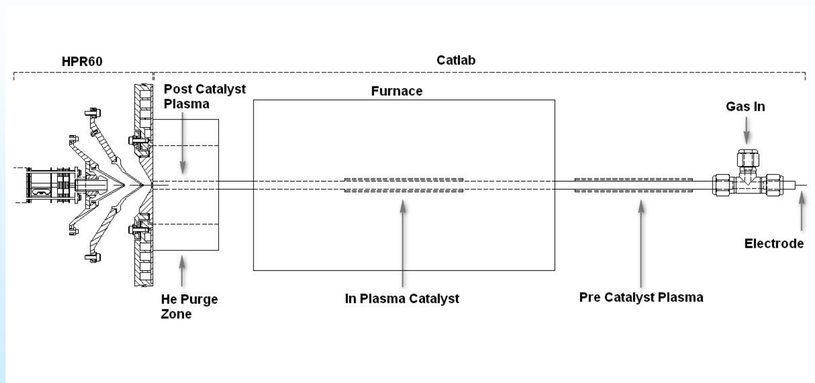
Plasma sources designed around discharges generated over the surface of a dielectric covering one of the discharge electrodes, (“dielectric surface barrier discharges”), are versatile examples. The plasma is typically obtained using a high frequency source to generate a discharge in a flow of helium to which two or more reactant gasses are added. The plasma consists of electrons with energies up to 25ev and 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 HPR-60 molecular beam mass spectrometer system (MBMS). The MBMS allows analysis of both the gaseous species and the ions and radicals produced in the plasma. In addition to the standard furnace arrangement a dielectric barrier discharge (DBD) could also be generated over the length catalyst or either before or after 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 the 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 50kHz [4].

Reactions were performed using 1% Pd/Al_2O_3 catalyst. The test reaction used was the oxidation of CO to form CO_2. In all experiments the concentration of O_2 was in excess of that required to completely convert CO.

A schematic of the reaction setup is shown below in Figure 1



Results

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.

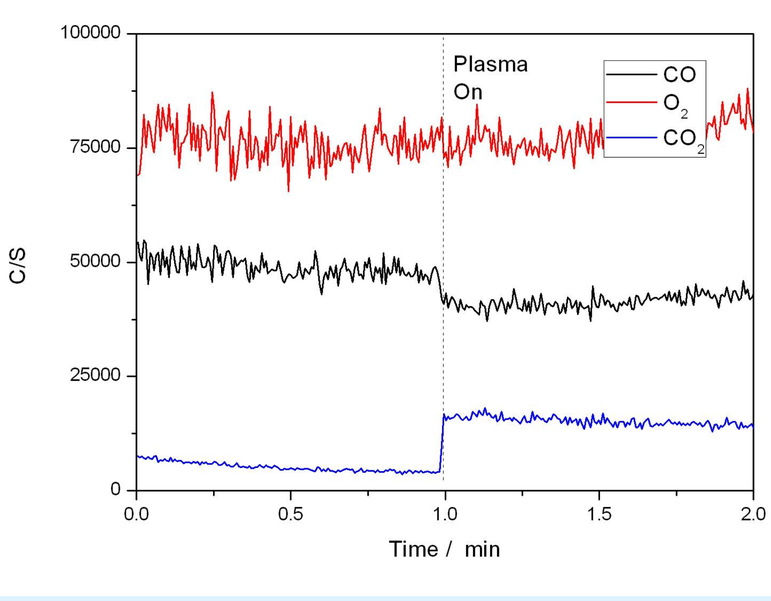
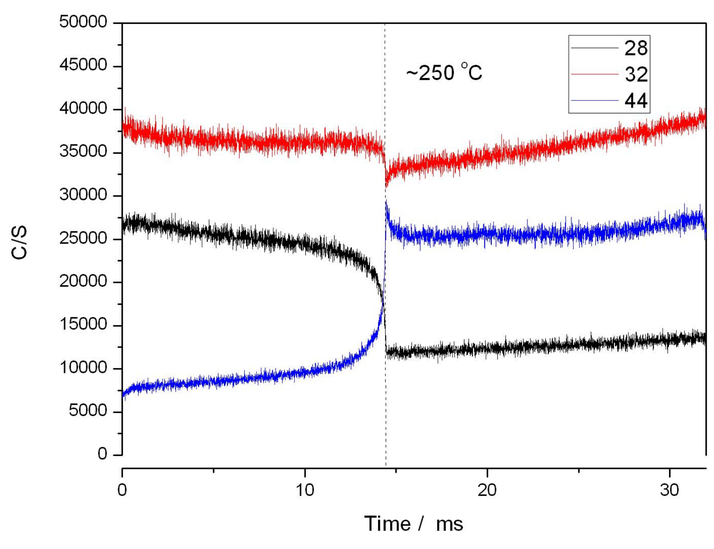


Figure 3 shows the results of using the catalyst only. The sample was ramped at 15 °C/min to 600 °C. The figure shows that complete conversion of CO to CO_2 occurred at around 250 °C.



The plot shown in Figure 4 is the result of the combined plasma and heating experiment. In this case the plasma was generated over the length of the catalyst. 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.

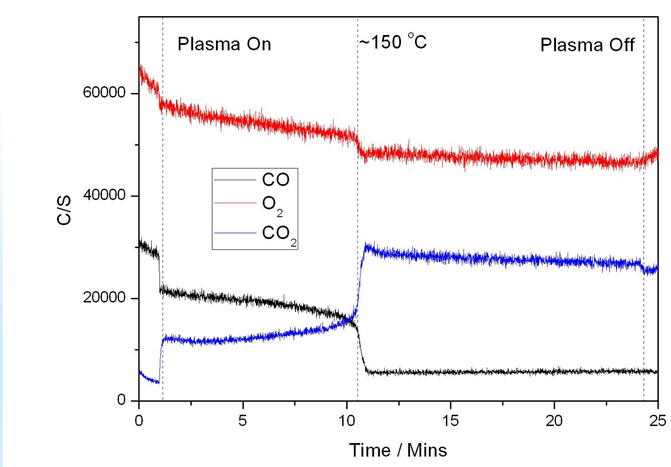
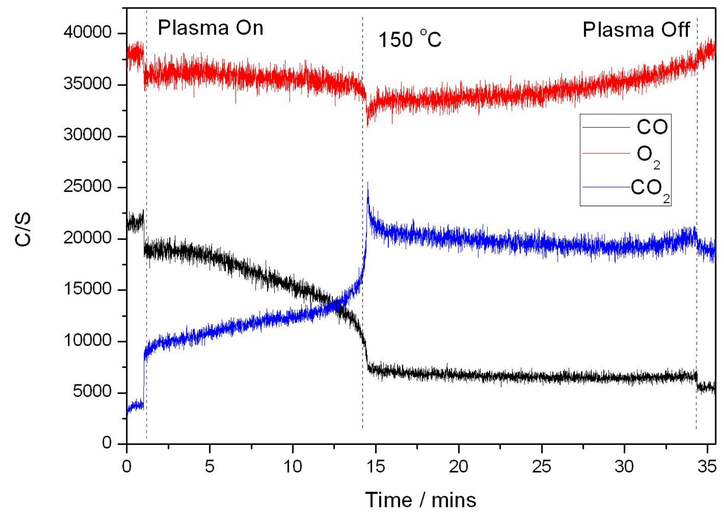


Figure 5 is the result of a different combined plasma and catalyst heating experiment. In this case the plasma was generated in a region before the catalyst bed. Before heating the plasma was switched on and showed the same initial increase in CO_2 production as before. Upon heating it can be seen that there is complete conversion of CO to CO_2 at 150 °C. This is identical to the result of the experiment with the plasma generated over the length of the catalyst. This suggests that the decrease in temperature seen in the reaction going to completion 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.



Conclusions

In the present model reactor, carbon monoxide and oxygen are used as the reactant gasses. 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 IPC 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.