MASS SPECTROMETRIC DIAGNOSTICS AND MODELLING OF SELECTED SPECIES IN CH_4/H_2 AND C_2H_2/H_2 PLASMAS

C. G. Schwärzler, O. Schnabl, J. Laimer and H. Störi

Institut für Allgemeine Physik, Technische Universität Wien
Wiedner Hauptstraße 8-10, A-1040, Austria

ABSTRACT

The chemistry of hydrocarbon-hydrogen mixtures in an r.f. plasma reactor with external heating was investigated by means of time resolved mass spectrometry and modelling. Residence time in the reactor and other process parameters was similar to those of diamond growing PACVD processes. Mass spectrometry was calibrated for the four stable species CH_4, C_2H_2, C_2H_4 and C_2H_6. Modelling and experiment show quantitative agreement with respect to concentrations as well as time dependencies. Atomic hydrogen fraction is calculated to be 6-8‰ for an r.f. power of 200 W and 1% for 400 W. Three-body efficiency of H_2 relative to Ar for the reaction C_2H_6 (+M) $\Leftrightarrow$ 2 CH_3 (+M) is suggested to be 5.7.

INTRODUCTION

Getting insights into the chemical processes of hydrogen-rich hydrogen-hydrocarbon mixtures is important for a better understanding of low pressure diamond synthesis. As direct measurement of instable species in the gas phase is difficult kinetic modelling of the gas phase reactions is widely in use. Yet, experimental proof of model results is necessary. This article concentrates upon the combination of modelling the chemical processes in the gas phase of a hydrogen r.f. plasma with time resolved mass spectrometry of selected stable species.

EXPERIMENT AND MODEL

The experimental set-up has been described in detail elsewhere /1/ , /2/. In principle it consists of an electrodeless, capacitively coupled, r.f. discharge (13.56 MHz) inside a quartz tube with an inner diameter of 2.5 cm. The discharge over a length of 24 cm was operated from a solid-state generator with a peak power output of 1.1 kW through an automatic matching network. Before this set-up was slightly modified it was used for diamond deposition on Silicon Carbide substrates /3/.

Over the length of 80 cm the quartz tube is positioned inside an electric furnace to gain a homogeneous temperature changeable from room temperature up to 1200 °C. Over the central 40 cm that includes the plasma zone the temperature is accurate within ±5 K. This was verified with a Chromel-Alumel thermocouple and confirmed by two-wavelength pyrometry. The initial gas composition consisting of H_2 (99.999% purity) with small admixtures of either CH_4 (99.995%) or C_2H_2 (99.2%) was supplied to the upstream end of the tubular reactor via mass flow controllers. Methane and acetylene fractions relative to hydrogen were 0.5%. The pressure inside the tube was adjusted by a throttle valve.

The gas composition at the downstream end of the tubular reactor was analysed by a quadrupole mass spectrometer. A specially designed helium flushed probe system was inserted into the quartz tube in a way so that the tip of the probe with a 0.3 mm diameter hole reached right into the plasma zone. Fig. 1 shows the probe system.

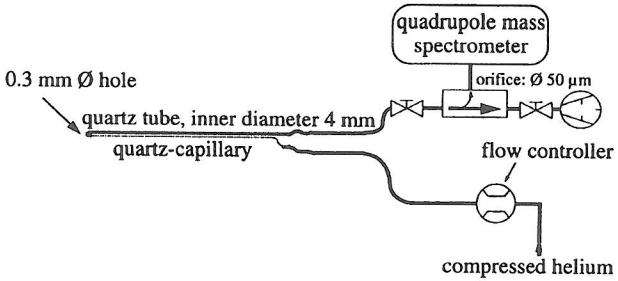

Fig. 1 Probe system for time resolved mass spectrometry

Through that hole in the tip of the probe the gas mixture from the plasma zone was extracted. High purity helium (99.9999%) was used to flush the probe in order to transport the gas sample quickly to a platinum orifice of 50 µm diameter that was located directly beneath the ion source of the mass spectrometer. The probe system was pumped with a 9 m^3h^{-1} pump. The helium flow was adjusted to extract about 10% of the gas inside the reactor. With respect to time resolution the most limiting factor is the time constant resulting from the volume of the spectrometer system together with the limited pumping speed of the turbomolecular pump of the mass spectrometer. We found the related time constant to be 24.5 ms and independent from reactor pressure /4/. We can now directly compare the results of modelling with mass spectrometric data by convoluting the kinetic modelling results with the instrumental response function.

The system was calibrated for the four most prominent stable hydrocarbon species namely methane CH_4, acetylene C_2H_2, ethene C_2H_4 and ethane C_2H_6. This was done by measuring the signals gained for known mixtures of those species and hydrogen without plasma. From these measurements calibration coefficients relative to hydrogen were calculated and afterwards used to gain the mole fractions of those four stable species. In the sampled gas there are also instable species and it is necessary to consider their reactions inside the probe system as well. Modelling shows that CH_3 and C_2H_3 are the instable species with mole fractions worthwhile to be taken into account. The conditions inside the probe system were modelled. As atomic hydrogen recombines fast due to diffusion to the nearby quartz surface of the probe system the lack of atomic hydrogen characterises the situation. The recombination efficiency on quartz is large, especially at the high temperatures of the probe tip inside the plasma and furnace /5/. We calculated species conversion rates for the transformation of the instable species into the various stable ones. Methyl is mostly lost making C_2H_6 as reported earlier by Harris et al /6/ but also, to an much larger extent forms methane. C_2H_3 is transformed mostly into C_2H_4, but to a few percent also to C_2H_2. We took these transformations into consideration when comparing results from modelling with mass spectrometric data.

The computer model is based on the Chemkin Computer Code from Sandia National Laboratories /7/. The effect of the plasma on the gas phase chemistry was included by adding a unidirectional production rate for atomic hydrogen $H_2 \rightarrow 2H$. This

rate is an arbitrary parameter of the model. It leads to the super-saturation of atomic H necessary for driving the gas phase during the non-equilibrium state. A direct and absolute determination of the H concentration in the experiments is in progress /8/. The model includes 15 hydrocarbon species as well as atomic and molecular hydrogen. It is based upon a model already published /9/. With respect to the evidence of C_2 shown in emission spectrometric data /10/ C_2 was now included in the model. Table 1 shows the kinetic data added to the model to take care of C_2.

reaction	A	β	E_a
$C_2 \Leftrightarrow C + C$	3.72E+14	0	580.5
$C_2H + H \Leftrightarrow C_2 + H_2$	3.61E+13	0	118.3
$C_2H + C_2H \Leftrightarrow C_2H_2 + C_2$	1.81E+12	0	0

Table 1 Kinetic data for C_2 reactions. Units are kJ-mol-cm-s.

The experiments have been performed at pressures of 20 or 50 mbar and r.f. powers of 200 or 400 W. For measuring the time dependence of the species concentrations the plasma was pulsed with a pulse repetition rate of 0.3 Hz. The duty cycle lasted 33% of that time.

RESULTS AND DISCUSSION

Under the given experimental conditions methane and acetylene were the most prominent stable species observed regardless of the type of hydrocarbon added to hydrogen to make up the initial gas mixture. Smaller concentrations of ethene and ethane were also found. When comparing the results of modelling with mass spectrometric data, the fractions of methane and acetylene and their time dependency are found to agree very well. The fraction of ethene is predicted by to model only to a factor of about 2 to 3. The comparison of the measurements of ethane C_2H_6 with its model predictions turned out to be within the right order of magnitude, but has to be treated very carefully because of the influence of the probe system on methyl. As the amount of methyl in the gas phase is some orders of magnitude larger than the amount of ethane, the detected ethane is influenced in a non predictable way.

Fig. 2 shows the comparison between mass spectrometric data and model calculation. Furnace temperature for this experiment was 600 °C and plasma power was 200 W. Initial gas composition was 0.5% acetylene in hydrogen. Pressure was 20 mbar.

The time scale for the experimental data starts at the time when plasma was switched on and was corrected for the delay which is caused by the limited transportation speed inside the probe system. The convolution process is the reason for the time evolution of the acetylene starting at zero mole fraction. Species which are not present in the feed gas but are formed during the plasma pulse are not affected.

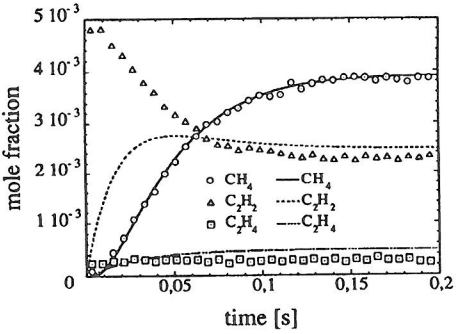

Fig. 2 Model (lines) and experiment (dots)

The comparison between model calculation and experiment for a feed stock consisting of 0.5% methane in hydrogen is shown in Fig. 3. Again furnace temperature was 600 °C and reactor pressure was 20 mbar. Plasma power was 400 W.

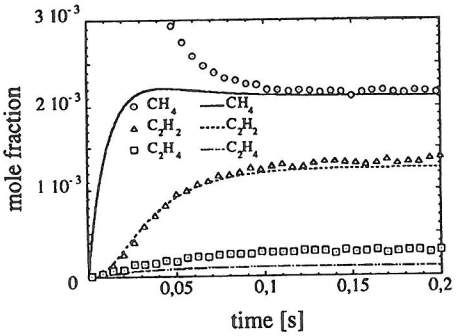

Fig. 3 Comparison between model and experiment for a feed stock consisting of 0.5% methane in hydrogen

The model calculations suggest atomic hydrogen concentrations of 6 to 8‰ for a r.f. power of 200 W and 1% for 400 W. Furthermore the three-body efficiency of H_2 relative to Ar for the pressure dependent reaction C_2H_6 (+M) ⇔ 2 CH_3 (+M) seems to be 5.7.

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