Study of Ar/CF_4/H_2 inductively coupled plasma: Effect of hydrogenated and/or oxygenated atmosphere. Comparison to Ar/CH_4 system.

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ABSTRACT

The decomposition process of carbon tetrafluoride by Ar/H_2 plasma was investigated by thermodynamic calculations and by experiments using a simple flow RF induction coupled plasma. On-line optical emission spectroscopy in plasma discharge and off-line gas chromatography of effluent gases were used for diagnostic. Results were compared to those obtained for Ar/CH_4 system.

INTRODUCTION

The design of a depollution process for the destruction of halogenated organic substances has to consider simultaneously the destruction efficiency and the nature of effluent products. Previous theoretical and experimental works [1,2] were conducted in our laboratory to study the application of thermal plasma technique in the field of depollution.

Using CF_4 as a model molecule, it had been concluded that the association of a double flow inductively coupled plasma torch to a fluidized spouted bed reactor of limestone particles seems to be promising [1]. Indeed, thermal plasma is suitable for stable molecules decomposition (like CF_4) since it provides high temperature and high flow of radicals. The use of limestone spouted bed in plasma post discharge provides an efficient thermal quenching of hot gases and permits the trapping of toxic halogens (HF, F_2, HCl,..) by heterogeneous reactions and the formation of inert solid products ($CaCl_2$, CaF_2, ..).

The objective of this work is to compare the decomposition of CF_4/H_2 mixture to CH_4 one using simple flow RF plasma torch. This is in order to better understand the decomposition of halogenated molecules at high temperatures and to point out the effect of heterogeneous reactions initiated by fluorine with solid oxides on the formation of carbon oxides as main products. On-line optical emission spectroscopy in the plasma discharge is used to observe emitting intermediary species. Off line chromatography (GC/TCD) permits the determination of decomposition yields and main products distributions.

THERMODYNAMIC CALCULATIONS

Detailed thermodynamic calculations for different systems of C-F-H-O had been already carried out [3]. It consisted on the use of the minimisation of Gibbs free energy method and it permitted to predict gas composition at equilibrium in function of temperature, pressure, and element ratios. Results showed that CF_4 starts to decompose at 2500 K to give fluorinated radicals (CF_x), atomic fluorine and carbons. Hydrogen addition produces exclusively HF which is stable up to 4000 K. The addition of oxygen to the system leads to the formation of carbon oxides and the toxic COF_x molecules.

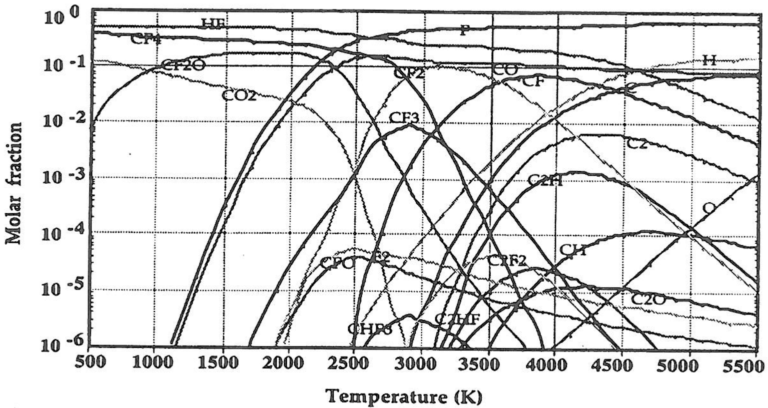

Fig. 1: Complex chemical equilibrium of CF_4 - 1/2 H_2O mixture; pressure= 1 atm.

These calculations (fig. 1) allow to conclude that simultaneous addition of hydrogen and oxygen are favourable for the decomposition of halogenated compounds. Optimal temperature intervals and optimal element ratios were estimated in order to minimise the formation of stable toxic gases such as COF_2. Main products will be carbon oxides and halogen acids (HF,..) which can be trapped and eliminated from effluents easily [3,4].

EXPERIMENTAL

The experimental set-up is shown in fig 2. An ICP RF (64MHz-3kW) plasma torch (13.5 cm long, 3 cm i.d.) works in atmospheric pressure with argon as the plasma gas with a flow rate of 13 Sl/mn. CF_4, H_2 or CH_4 were injected in the centre of the plasma with molar fractions ranging between 0 and 0.7%.

The plasma torch is surrounded by an alumina tube (8.5 cm long, 6 cm i.d.) in order to avoid the contamination with air. A capillary quartz tube of 4mm diameter is placed downstream the plasma jet at a distance of 8 cm from the RF coil. It permits gas sampling for off-line chromatography analysis. For this purpose, a Delsi GC/TCD 121 ML apparatus equipped with a carboxen-1000, 26 m long, 6.5 mm i.d., packed column was used to determine the decomposition yield of CF_4 or CH_4 and to quantify major carbon containing products [5].

On-line optical emission spectroscopy of the plasma discharge is carried out by using an optical fiber connected to two Jobin Yvon HR1000 spectrometers offering the possibility to observe the (2250-4500 A° with 3600 line/mm) and (3000-8000 A° with 2400 line/mm) wave-length regions respectively. The two apparatus were equipped with a Hamamatsu photomultiplier and a chart recorder.

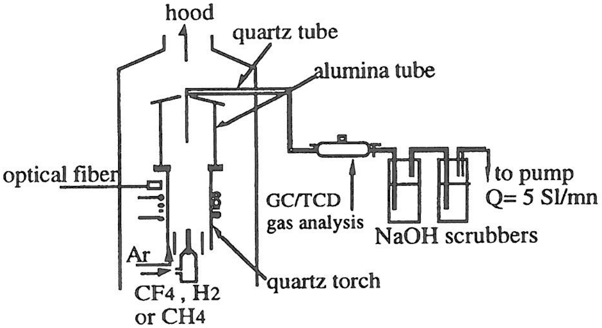

Fig. 2: Flow sheet of the experimental set-up

RESULTS AND DISCUSSION

Case of the Ar/CF_4 system

A first series of experiments consisted on the injection of CF_4 in the Ar plasma torch with different molar fractions ranging between 1‰ and 6.5‰. The applied electrical power was fixed at 2 kW.

The analysis of the effluent gases by GC/TCD showed that the decomposition rate of CF_4 was 44% and carbon containing products were CO and CO_2 with a CO_2 selectivity of 41%. Fluorine was trapped in NaOH solution scrubbers to be quantified by Capillary electrophoresis ionic analysis but the nature of effluent fluorinated molecules could not be identified by this method.

Results showed also that decomposition rate and products distribution were independent of the initial molar fraction of CF_4. This allows to conclude that the global decomposition is a first order reaction. On the other hand, the formation of oxides using a free oxygen gas mixture in an isolated system could only be explained by the existence of a corrosion phenomenon of the quartz tube by highly reactive fluorine radicals liberating oxygen in the gas mixture:

$$4\,F^\circ + SiO_2\,(s) \longrightarrow SiF_4\,(g) + O_2\,(g) \qquad \text{(global reaction)}$$
$$O_2\,(g) \Longleftrightarrow 2\,O^\circ$$
$$O_2\,(\text{or } O^\circ) + CF_x \longrightarrow (CO, CO_2) + xF$$

Optical emission spectroscopy confirmed the existence of heterogeneous reactions with the tube walls by the observation of atomic Si emissions (between 2400 and 2550 A°). Emitting carbon containing species was also observed. Molecular emissions of C_2 (Swan system) served to calculate a vibrational temperature of about 5000 K for Ar-2‰CF_4 mixture. The intensity of CI atomic emission (2478 A°) was followed in function of the CF_4 molar fraction (fig. 6). Details on emission spectroscopy are reported in reference [6].

Case of Ar/CF_4/H_2 system

This series of experiments had been done with a fixed molar fraction of CF_4 (1.8‰) and a fixed applied power (2kW). Concerning chromatography analysis, it was found that the addition of hydrogen increased the decomposition rate and implied the decrease of carbon oxides to the benefit of the deposition of carbon black on the quartz tube. On the other hand, the selectivity of CO_2 in effluent gases decreases whereas that of CO increases (fig. 3).

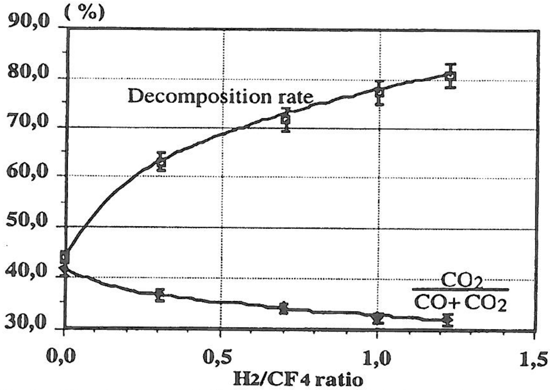

Fig. 3: Effect of hydrogen addition on CF_4 (1.8‰ mol.) decomposition. Applied power: 2 kW; Ar flow: 13 Sl/min.

Concerning results obtained with emission spectroscopy, it had been pointed out that the absolute intensity of Si I (2507A°) decreased with H_2 addition whereas that of carbonic excited species (C and C_2) increased (figs. 4, 5).

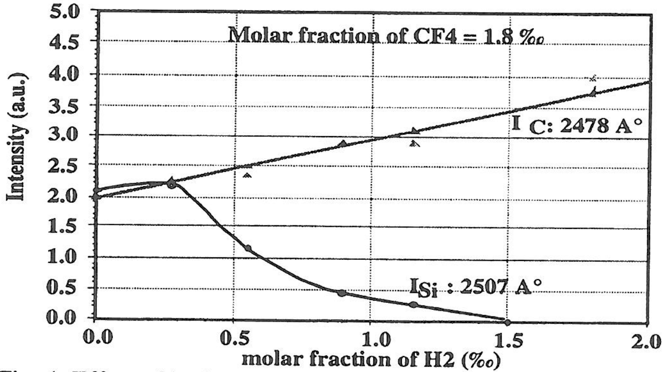

Fig. 4: Effect of hydrogen addition on Si (I) and C (I) emissions. Applied power: 2 kW; Ar flow: 13 Sl/min.

Spectra of C_2 emissions permitted also the calculation of vibrational and rotational temperatures which were estimated at about 6000 K [6].

The comparison of H_α line emission at 6562.8A° for mixtures containing CF_4 or not (fig. 5) showed that hydrogen emission decreased drastically when CF_4 was added.

These observations can be explained by the following points:

-When hydrogen is added to an Ar/CF_4 mixture it reacts especially with fluorine to form HF acid which is still stable at high temperatures (fig. 1) and it is less corrosive than fluorine radicals. So, hydrogen addition tends to decrease heterogeneous reactions producing oxygen.

-The diminution of oxygen in the gas mixture will decrease carbon oxides production especially CO_2 one with the formation of carbon black.

These observations are also confirmed by the thermodynamic predictions concerning the role of hydrogen on the decrease of carbon oxides production [4].

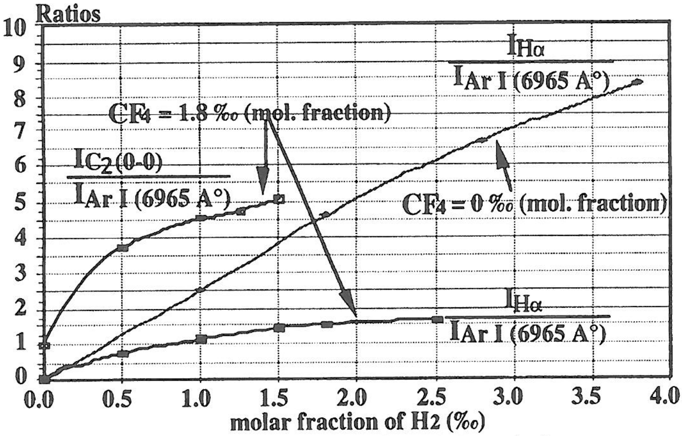

Fig. 5: Variations of H_α and C_2(0-0) emissions (normalised with ArI (6965A°) intensity) in function of H_2 addition.

comparison to the Ar/CH_4

A detailed study of Ar/CH_4 (1‰) R.F. plasma has been already reported [7]. Carbon atoms and CH_x radicals present in the plasma post-discharge were quantified by the monitoring of chemiluminescent reactions with N atoms which forms CN radicals. Also the gas temperature was determined from CN rotational spectrum to be around 4000K in the plasma discharge.

The purpose of the present work was to determine of the main stable products of the decomposition of methane. Thus, it has been found that the major products were C_2H_2 in the gas phase and carbon black in the solid one. The selectivity of acetylene was independent of the injected quantity of CH_4 and it was about 30%. The decomposition yield was also invariable and greater than 99%. The absence of carbon oxides confirm the hypothesis that the system doesn't contain oxygen impurities.

On the other part, spectroscopy measurements permitted to follow CI (2478A°), Swan system of C_2, H_α and H_β emissions. The $A^2\Delta$-$X^2\Pi$ of CH molecular bands at 4300A° haven't been detected. These results are compared to those obtained with CF_4 mixtures.

In order to avoid the effect of carbon soots deposition on the emission transmission factor which is important in the case of methane systems, emission intensities were divided on a reference Ar emission line. The Ar I (3949A°) has been chosen as reference for UV emissions and the Ar I (6965A°) for emissions in the visible wave-length region (see also fig. 5). This method was also used to compare the methane system to the carbon tetrafluoride one under the same luminosity emission conditions.

Results concerning atomic carbon emissions (fig: 6) show that Ar/CH_4 and Ar/CF_4 mixtures have the same emission intensities for the same molar fractions.

Furthermore, these emissions vary linearly in function of the molar fraction. This can be explained by the fact that temperatures in the plasma discharge are high enough to decompose all injected CF_4 or CH_4. Also, excited state densities of produced atomic carbon will only depend on the injected quantity and not on the nature of the carbonic species.

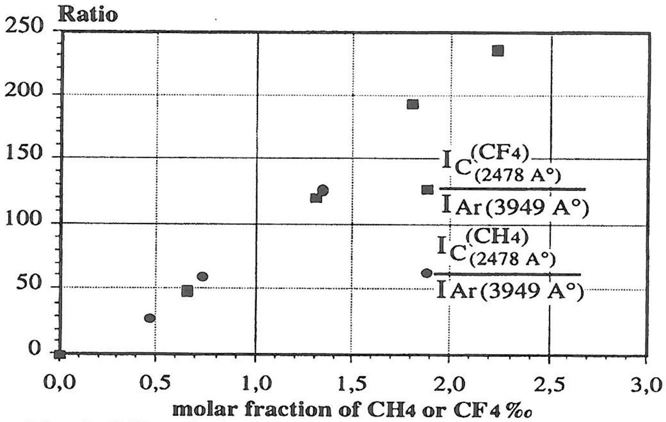

Fig. 6: C (I) emissions from Ar/CH_4 and Ar/CF_4 mixtures.

CONCLUSION

Preliminary results concerning the thermal decomposition mechanism of CF_4/H_2 mixture in Ar RF plasma torch have been obtained by optical emission spectroscopy and gas chromatography analysis. It has been concluded that heterogeneous reactions between fluorine and the quartz tube walls of the torch are responsible for the formation of oxygen in the gas phase. The comparison to Ar CH_4 system confirmed this and permitted also to resume that CF_4 is totally decomposed in the plasma discharge. The fact that the final decomposition rate is less than 50% shows that heterogeneous reactions are largely more slow than recombination reactions. These results are in good agreement with thermodynamic and kinetic predictions.

ACKNOWLEDGEMENTS

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