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Increased recombination of CH_3 radicals on stainless steel

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Abstract

By using a so-called 'stream technique', which consists of flowing gas in laminar regime along a quartz tube, we determine that CH_3 radicals are completely removed from the pumped mixture ($CH_4/C_XH_Y/H_2/H/CH_3$) after several hundred collisions with the inner surface of a stainless steel insert ($T = 380–470$ K). The methyl sticking coefficient decreased to $\sim 10^{-6}$ and the recombination coefficient increased up to ~ 0.01 at impingement with the metal surface. After passing through the heated zone no hydrocarbon deposition occurred at 300 K. However, unsaturated hydrocarbons, which formed in discharge zone and appeared as a result of interaction of radicals with stainless steel, condensed in a liquid phase at a temperature of ~130 K and partial pressure of 0.01–0.1 Pa. Liquid films underwent partial polymerization and formed island deposits, which were stable at 300 K.

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Keywords: Erosion and deposition; Impurity transport; Neutrals; Recombination

1. Introduction

Adsorption/deposition of hydrocarbon radicals and excited molecules is considered to be one of the most likely potential mechanisms leading to tritium accumulation in the plasma-shaded areas of the ITER divertor, liner and pump duct, which connects the divertor with cryogenically-cooled sorption pumps [1,2]. Therefore, suppression or control of hydrocarbon deposition in these areas are important issues, which require investigations of possible reactions of long-lived hydrocarbon radicals (methyl (CH_3) and ethyl (C_2H_5)) with the surface of structural materials [3].

In principle, the separation of hydrocarbon radicals and molecules from typical D/T/He mixtures of the exhaust can be carried out in two ways: (1) by maximum hydrocarbon hydrogenation and their transformation in methane on a catalyst surface; (2) by enhancing and controlling hydrocarbon deposition in a certain place of the pump duct with subsequent recovery of hydrocarbon deposit outside the working setup.

The possibility of hydrocarbon hydrogenation (e.g., methyl) in the pumping gas mixture in ITER is investigated here by experiments using the stream technique.

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2. Experiment

To study the processes of CH_3 radical transport, deposition and recombination a cylindrical quartz tube was used (1 cm in radius, 100 cm in length). As a source of radicals, a radio-frequency (RF) inductive discharge was used in flows of methane or methane/hydrogen mixtures (CH_4 pressure ~30 Pa at gas flow of 6.9 sccm, hydrogen flow changed from 0 to 70 sccm) at the tube inlet. The discharge was limited by a stainless steel (SS) grid [4,5]. In the downstream region behind the grid (afterglow zone, Fig. 1) a tube section (approximately 10–15 cm length) could be heated by a movable cylindrical furnace up to 1200 K or cooled down to 77 K by a movable cryostat with liquid nitrogen (LN trap).

Polymer-like carbon films were deposited on the tube wall at 300 K. The 'stream technique' allows to measure the transport length L and diffusion coefficient D and to calculate the surface loss probability β of deposited species if the carbon deposition rate decreases along the tube as exp $(-x/L)$ [4]. To do this, Si samples ($10 \times 5 \times 0.3$ mm) were located along the whole tube length. After exposure in the discharge and afterglow zones, the Si samples were removed from the tube and the carbon areal density was measured by electron probe microanalysis (EPMA). The carbon deposition rates along the tube (open diamonds) are shown in Fig. 2.

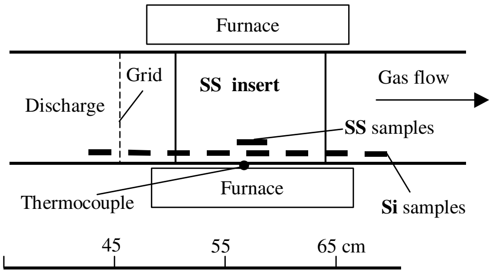

Fig. 1. Schematic of the experimental reactor with cylindrical SS insert.

Transport parameters for this case are presented in Table 1 [6]. The magnitudes of D and β are typical for the deposition of a-C:H films from CH_3 radicals [3,7]. We assume that CH_3 radicals are precursors for film deposition. The flow (~8×10^{15} CH_3/s) and concentration (~2×10^{13} cm^{-3}) of CH_3 radicals near the grid were determined in carbon deposition experiments at a wall temperature of 200 K. We assume that at this temperature most of the radicals are deposited as a-C:H film [8]. We further assume that the integral from the deposition curve at 200 K is equal to the total flow of radicals emanating from the RF discharge. In most experiments the radicals and atomic hydrogen flows emerging from the discharge were kept constant and the average flow velocity was 120 cm/s. From the known radical flow in radial direction and the carbon deposition rate, we determine the sticking (s) and recombination ($\gamma = \beta - s$) coefficients (Table 1). The value s is typical of the formation of a-C:H films from methyl [7,9]. Notice also that $\gamma > s$. Under the test conditions every radical moving along the tube underwent about 50–100 collisions with the surface per 1 cm of tube length.

The H atom concentration (~5×10^{11} cm^{-3}) near the grid was determined in CH_4 discharge erosion experiments with hard a-C:H films (W. Jacob, Garching, Germany) located at different distances from the grid at 650 K [4]. We assume that the erosion coefficient of such films is equal to 0.02 at.C/at.H [10].

In a hydrogen/methane RF discharge, hydrocarbons of type C_2H_Y, (where $Y = 2, 4, 6$) and C_3H_Z ($Z = 6, 8$) were also present besides radicals, methyl, and atomic hydrogen. The content of these gases in the mixture was determined by means of a gas freezing technique. At 77 K the initial gases, methane and hydrogen, do not condense on the tube wall, but other reaction

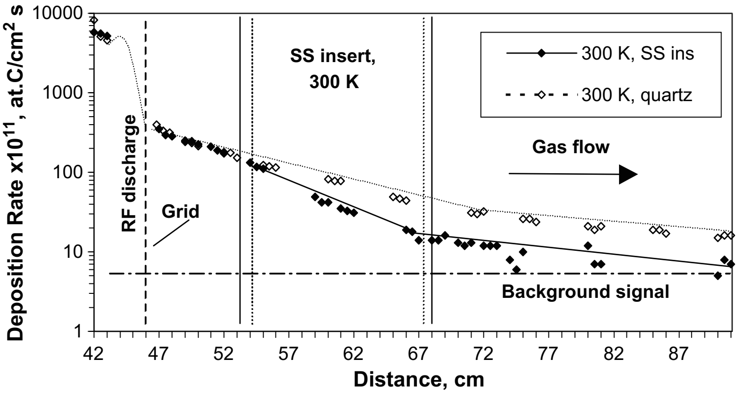

Fig. 2. Variation of the carbon deposition rate from $CH_4/C_XH_Y/H_2/H/CH_3$ mixture along the tube without (open diamonds) and with (filled squares) SS insert at 300 K. Exposure time was 4 h.

Table 1
Transport parameters for CH_3 radicals in gas-carrier (CH_4) and tube wall covered with the soft a-C:H film ($T = 300$ K, $P(CH_4) = 30$ Pa, gas flow = 6.9 sccm) [6]

Transport lengths, L, cm, in the range Δx	Diffusion coefficient, D, (cm^2/s)	Surface loss probability, β	Sticking coefficient, s	Recombination coefficient, γ
$L_1 = 10.5 \pm 0.5$ $\Delta x\{45–70$ cm$\}$	500 ± 100	0.0004	0.0001	0.0003
$L_2 = 27.6 \pm 2$ $\Delta x\{72–92$ cm$\}$	500 ± 100	0.0001	0.0001	<0.00005

products, like C_2H_Y and C_3H_Z, condense. When the temperature of the cooled region is increased, these hydrocarbons evaporate. The simultaneous monitoring of the total pressure and temperature of the selected tube section permitted us to obtain the evaporation spectra. Finally, by knowing the functional dependence between the pressure and the gas flow we were able to determine the gas content in every thermal peak. In a separate experiment a gas sampling and mass spectrometry analysis of CH_4 RF discharge products were performed. Above described hydrocarbons and hydrogen were detected in these mass spectra. As a result of these experiments, we can estimate the composition of the gas mixture produced in the CH_4 RF discharge, ($\times 10^{15}$ particles/cm^3): CH_4-7; C_2H_Y-0.2; C_3H_Z-0.1. We estimate that the CH_4 conversion factor [11] in our experiments is about 10%.

Due to very low sticking coefficients the hydrocarbon molecules of type C_2H_Y and C_3H_Z do not condense in the temperature range 300–800 K [12]. In our setup hydrocarbon radicals with sticking coefficients $s = 0.05–1$ [7] (if they would flow out of the discharge) would contribute to deposition only near the SS grid (Figs. 1 and 2).

A hollow cylinder SS insert (14 cm in length) was introduced in the tube section to study the catalytic activity. Prior to the experiment the SS cylinder was cleaned in hydrogen plasma of RF discharge directly in the quartz tube at 650 K. The residual carbon was removed from the SS surface under the discharge conditions. Most of the eroded hydrocarbons deposited again on Si samples placed downstream at 350–300 K. It was assumed that the SS surface is 'carbon-free' because carbon film deposition rate on the Si samples did not exceed 8×10^{11} at.C/cm^2 s. The indicated deposition rates were reached after 5 h exposure of SS in pure hydrogen plasma.

3. Results and discussion

Fig. 2 shows the deposition rates along the tube axis both for cases with and without an insert at 300 K. For the case with the insert, at first the methyl radicals interacted with SS surface. It can be seen that the slope of the deposition curve changes in the zone within the insert. In stream technique [4] this means that the radical surface loss probability β increased 3 times up to $\beta = 1.3 \times 10^{-3}$ (see Table 1). In the subsequent experiments the β coefficient decreased with the increase of the thickness of the carbon deposits inside the insert. After 12 h exposure it approached the typical value of $\beta = 4 \times 10^{-4}$ (Table 1).

In all presented experiments, in addition to Si samples, one or two SS ($10 \times 5 \times 0.6$ mm) samples were placed inside the insert. Areal densities of deposited carbon films on Si and SS samples in each certain tube section were close to each other (300 K). In the temperature range 380–420 K the carbon deposits on the Si and SS samples were not observed.

The pattern of carbon deposition changed substantially when the temperature of the insert was increased to 380 K (Fig. 3). A sharp drop of deposition occurred at the SS insert inlet and basically no deposition occurred inside the insert. A slight increase of deposition was seen at the outlet of the insert. EPMA measurements showed that the sticking coefficient s decreased by an order of magnitude for a SS surface held at 330–340 K and decreased by an order of magnitude ($s < 10^{-6}$) at 380 K. At the same time the β coefficient (and therefore, the 'effective' recombination coefficient γ) increased up to $(5 \pm 1) \times 10^{-3}$. The word 'effective' means the transformation of methyl not only into methane but also into other light hydrocarbons.

In the experiment shown in Fig. 3 the CH_3 radical yield was higher than in a majority of the experiments. However, the influence of the SS insert (380 K) on carbon deposition profile revealed with clearness.

The tendency of s to drop and of γ to increase is seen as a positive feature for the selection of a catalyst for methyl/methane transformation. However, part of radicals passed through the insert. It is also possible that new species (e.g., CH_2 or C_2H_x) arose at the insert outlet. The presence of oscillations of the deposition rate at the tube section with coordinates 67–81 cm provides evidence that this might be the case.

When the temperature at the center of the insert was maintained at 420 K, the methyl sticking coefficient inside the insert did not exceed 10^{-6} (Fig. 4). In this case, hydrocarbon deposition practically did not occur in the tube part (300 K) behind the insert. This points to the fact that the γ value increases in the region at high

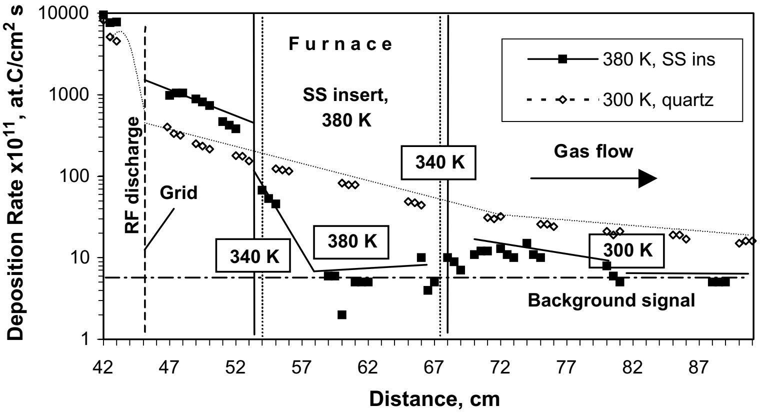

Fig. 3. Variation of the carbon deposition rate from $CH_4/C_XH_Y/H_2/H/CH_3$ mixture along the tube without (open diamonds) and with (filled squares) SS insert. Temperature of insert center was 380 K. Exposure time was 4 h.

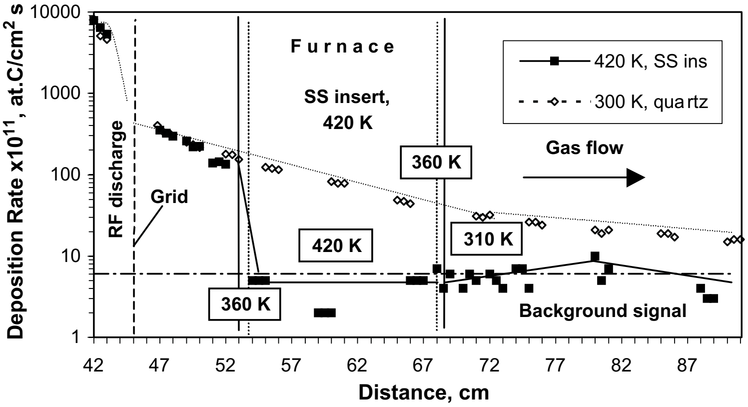

Fig. 4. Variation of the carbon deposition rate from $CH_4/C_XH_Y/H_2/H/CH_3$ mixture along the tube without (open diamonds) and with (filled squares) SS insert. Temperature of insert center was 420 K. Exposure time was 4 h.

temperature. This positive trend towards lower values of s and higher values of γ continues up to an insert temperature of 470 K.

For estimating the surface loss probability on SS at 420 K additional experiments were performed using shorter inserts. Traces of carbon deposits on Si samples (350–300 K) located downstream behind the insert appeared at insert length of 3.5 cm. For such insert length the radicals underwent about 300–400 collisions with the surface. Based on the results of these experiments, we conclude that the surface loss probability of radicals is in the range of $(0.5\text{–}1) \times 10^{-2}$.

At first glance, one could say that the results of these investigations yield to well defined conditions for an effective catalyst to suppress carbon deposition as well as transformation of radicals in volatile hydrocarbons (CH_4, C_2H_2, C_2H_4, and others). However, unsaturated hydrocarbons formed in the discharge zone and inside the SS insert did not adsorb on the surface at 300 K, but they could only adsorb and condense onto surfaces maintained at 77–130 K.

Actually, hydrocarbons condensed and liquid films formed in LN trap zone located behind the heated insert. When the temperature rose up to 300 K, the largest part (>90 %) of the condensate evaporated and another part was retained on Si samples as polymer-like island films. Sublimation of these polymer films started only at 400 K. Low-temperature polymerization may hinder the operation of sorption pumps. In our experiments, unsaturated hydrocarbons were separated from the exhausted gas mixture by the cold (77 K) trap, 4 cm in length, placed downstream behind the SS insert.

Based on our estimates, we conclude that the formation of carbon films may be substantially suppressed in heated pumping system ($T \approx 420$ K). The deposition rate of carbon films does not exceed 10^{11} at.C/cm^{2}s or 10^{-5} nm/s at CH_3 radicals and H_2 molecules partial pressures of 10^{-2} and 10 Pa, respectively.

Polymerization in cryopanels can be suppressed by a cold trap (80 K) placed in front of them.

4. Conclusions

Analysing the processes of carbon deposition from the products of an RF CH_4 discharge at 300 K allowed to conclude that the methyl radical is the dominant precursor of a-C:H film formation in the downstream region of our setup. During interaction of discharge products with a heated (380–470 K) SS wall the carbon deposition rate dropped sharply. The sticking coefficient of methyl radical decreased to $\sim 10^{-6}$ and recombination coefficient increased up to 0.01. After passing through the heated zone (3.5–4 cm length) no hydrocarbon deposition occurred at 300 K.

However, unsaturated hydrocarbons, which formed in the discharge zone and appeared as a result of interaction of radicals with stainless steel, condensed in a liquid phase in the temperature range of 77–130 K and partial pressure of 0.01–0.1 Pa. Liquid films underwent partial polymerization and formed island deposits, which were stable at 300 K.

Based on these preliminary results one can conclude that deposition of carbon films may be substantially suppressed in a heated pump duct (380–470 K). If this is true, and further experiments are planned to confirm this, deposition rate of carbon films in the ITER pump duct might not exceed 10^{-5} nm/s at CH_3 radicals and H_2 molecules partial pressures of 10^{-2} and 10 Pa, respectively. Polymerization on cryopanels can be suppressed by a cold trap (80 K) placed in front of them.

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