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Spatially Resolved Laser-Induced Fluorescence Imaging of OH Produced in the Oxidation of Hydrogen on Platinum

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The laser-induced fluorescence technique has been used to study OH radicals desorbed from a polycrystalline Pt foil in the $H_2 + O_2$ reaction. The experiments were performed under steady-state reaction conditions in the pressure range 10–100 mTorr at a catalyst temperature of 1300 K. Concentration profiles of OH radicals as a function of the distance from the catalyst were measured by imaging the fluorescence light with a diode array detector. The measurements in this pressure range support our earlier conclusion that the detected OH radicals are produced by catalytic reactions on the surface (S. Ljungström *et al.*, *Surf. Sci.* **216**, 63 (1989)). No evidence was found for the catalytic promotion of gas-phase reactions, as has been observed in studies of similar reactions with catalytically stabilized thermal burners at higher pressures. Analysis of the measured concentration profiles shows that the desorbed OH radicals can best be described by a cos θ distribution. The effects of gas-phase collisional processes have been investigated by evaluation of the local rotational distribution of the desorbed OH radicals.

1. INTRODUCTION

Free radicals, such as OH, CH, O, and H appear often as intermediate species in chemical reactions and are generally of great importance in increasing the reaction rate by initiating chain reactions in combustion processes (*1*, *2*). These intermediate radicals are, however, very short-lived and are quickly consumed in chain reactions which lead to the formation of the final reaction products. Identification and measurements of the concentrations of such radicals as well as internal energies of radicals are therefore of fundamental interest in the mapping of reaction paths. The inherent reactivity of these radicals makes them difficult to investigate in a nonintrusive way. However, optical techniques offer great advantages in this respect. Of the optical techniques available for flame detection, various laser techniques seem most suitable, since they can also give high temporal and spatial resolution. Laser-induced fluorescence (LIF) has for many years been very powerful in the diagnostics of combustion processes (*3*), has also been used for multiple species detection (*4*), and, perhaps most important, it has been developed for multiple point detection using multielement detectors (*5*).

The importance of free radicals has also been addressed during recent years in studies of the combustion of hydrocarbons in catalytically stabilized thermal burners (CST) (*6*). Combustion is, in this case, obtained by mass-transfer-limited surface oxidation processes which maintain the surface walls at a sufficiently high temperature to initiate and sustain gas-phase reactions. Combustion in a catalytic burner therefore represents an interplay between catalytic and gas-phase reactions where the wall effects are very important. An understanding of this kind of interplay requires measurements of the concentration of free radicals close to the catalyst as a function of the mixture of the reactants, and the composition and temperature of the wall (catalytic) material. Cattolica and Schefer (*7*) and, more recently, Pfefferle *et al.* (*8*) used the

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LIF technique to image the spatial distribution of OH radicals in the boundary layer close to a heated catalytic plate of platinum and a noncatalytic one of quartz. The catalytic ignition of hydrogen, ethane, and methane showed a maximum in concentration outside the burner wall, for certain gas mixtures, indicating gas-phase reactions.

OH radicals desorbed from polycrystalline Pt foils and single crystals during the $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ reaction have been studied by Lin and co-workers (*9, 10*) and by our group (*11–14*) in the vicinity of the catalyst using the LIF technique. These measurements were performed in the pressure range 10^{-5}–1 Torr (1 Torr = 133.3 $N\,m^{-2}$) and in the catalyst temperature interval 900–1300 K, which is well above the ignition temperature for the $H_2 + O_2$ reaction at atmospheric pressure. The influence of possible gas-phase reactions was therefore analyzed in several ways by Ljungström *et al.* (*13*), for example by replacing the Pt sample with a noncatalytic Au foil, which might be expected to induce gas-phase reactions by thermal stimulation, where no indication of water production was found. Further, the optimal mixing ratio for water production, which was found to occur around 20% H_2, to be compared with the stoichiometric ratio (67% H_2), did not change by the addition of a buffer-gas. It was thus concluded that the detected OH radicals were dominantly produced as intermediate species in the catalytic surface reaction.

In this work, we have investigated the desorption of OH by imaging onto a diode array detector the spatial distribution of the laser-induced fluorescence radiation from OH radicals outside a polycrystalline platinum catalyst at low pressure. This imaging technique was also used to measure the angular distribution of desorbing molecules and the rotational population of desorbed OH radicals at different total pressures.

2. EXPERIMENTAL

The details of the experimental setup have been thoroughly described elsewhere (*13*), but are summarized here with special attention given to the features which are unique for the imaging experiments. Briefly, the setup consists of a simple, turbo- or Roots-pumped, stainless-steel, high-vacuum chamber. A quadrupole mass spectrometer is used for partial pressure measurements. The sample, in the form of a polycrystalline foil, 3.3 mm × 20 mm × 0.025 mm, purity 99.95%, is mounted in the main chamber on a simple manipulator which allows the sample to be moved vertically. The catalyst is resistively heated and the temperature is controlled by a four-point arrangement and kept constant (at 1300 K in the experiments reported here) by microcomputer control. The concentration of OH radicals in the region outside the foil is measured with the LIF technique. As an excitation source we used the light from a frequency-doubled, pulsed, excimer-pumped dye laser (Lambda Physik EMG 102 E and FL 2002 E) in the wavelength region 306.3–307.5 nm, covering an absorption band of OH ($A^2\Sigma(v = 0) \leftarrow X^2\Pi(v = 0)$ (*15*)). The UV laser beam is focused with a quartz lens (f = 1000 mm) to the probed region outside the catalyst.

In the imaging experiments reported in this work, the concentration profiles of OH molecules were measured at several points along the laser beam at a fixed distance below the surface, as shown schematically in Fig. 1. The concentration of OH radicals as a function of the distance from the catalyst was studied by moving the sample vertically. The LIF emission was collected by a quartz lens (Nikon UV quartz 4.5, f = 105 mm) and focused onto a gateable intensified diode array (PAR OMA III, gated at 100 ns). The signal was averaged over several shots and the background, with the laser tuned off the resonance, was subtracted.

To increase the signal-to-noise ratio in the probing of a certain transition during a limited measuring time, the laser was tuned to the specific wavelength to find the maximum of the signal. Data were then collected by averaging over a large number of pulses. This procedure may lead to uncertainties

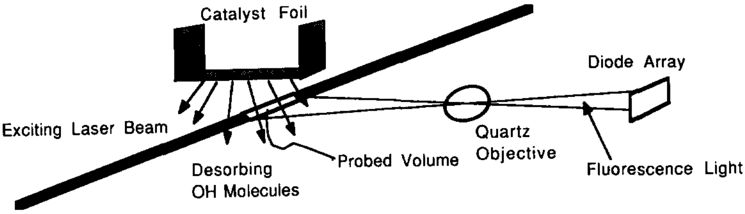

FIG. 1. Schematic overview of the probed volume, exciting laser light, and fluorescence detection with the OMA system.

when different transitions (i.e., different peaks) are compared (as discussed in connection with Fig. 5). However, by not scanning the laser, the influence on the OH concentration of a certain parameter, e.g., pressure, catalyst temperature, and varying distance between the surface and the detection zone, can be correctly investigated.

3. RESULTS AND DISCUSSION

3.1 OH Measurements

At sufficiently high temperatures the intermediate OH molecules produced in the surface reactions desorb from the surface before reacting to form the final product, H_2O. An example of a recording of a LIF measurement, when the laser wavelength is scanned over a rotational band of the OH molecule, is shown in Fig. 2. Assignments of the peaks as R_1 (N), $R_2(N)$, and $R_{21}(N)$ were made according to the work of Dieke and Crosswhite (*15*), where N is the rotational quantum number. Measuring the height of each peak and normalizing to the corresponding transition probability give the population in the initial state. Applying this procedure to all peaks in the scan will give the internal rotational distribution or the "rotational temperature" of the recorded OH radicals (*9, 14*), as discussed in detail below. In order to determine the total yield of desorbing OH, different rotational levels in the $^2\Pi$ state were probed and it was found that for the experimental conditions used here the $R_1(5)$ transition represents an almost constant fraction of the total OH yield. Thus, this transition was used to monitor the spatial distribution of the total yield of OH, while varying different experimental parameters.

3.2 Imaging of the OH Concentration

Figure 3 shows the fluorescence intensity, I_{OH}, of the $R_1(5)$ transition along the catalytic foil at a total pressure of 10 mTorr and relative hydrogen concentration α $(= p_{H_2}/p_{tot})$ = 0.08 (where the maximum in OH desorption was found in earlier work (*13*)). The laser beam was focused and passed 0.4 mm below the catalytic foil, for which the horizontal extension is indicated in the figure. The average diameter of the focused laser beam outside the catalyst was calculated to be ~160 μm with a variation of less than 1% over the probed volume. Optical transitions used for the measurements of the concentration of OH radicals are therefore uniformly saturated in this volume, resulting in uniform concentration profiles. There may be some uncertainty in the vertical distance z between the foil and the laser beam resulting from a small curvature of the foil or if the foil and the laser beam are not exactly parallel.

To investigate the fluorescence intensity, I_{OH}, at different distances from the sample a series of experiments was performed at a pressure of 100 mTorr, a surface temperature of 1300 K, and α = 0.08 at distances from z = 0.2 to 3.5 mm. An overview of the fluorescence intensities from these measurements is presented in Fig. 4a. Note how the fluorescence intensity decreases with increasing distance between the laser beam

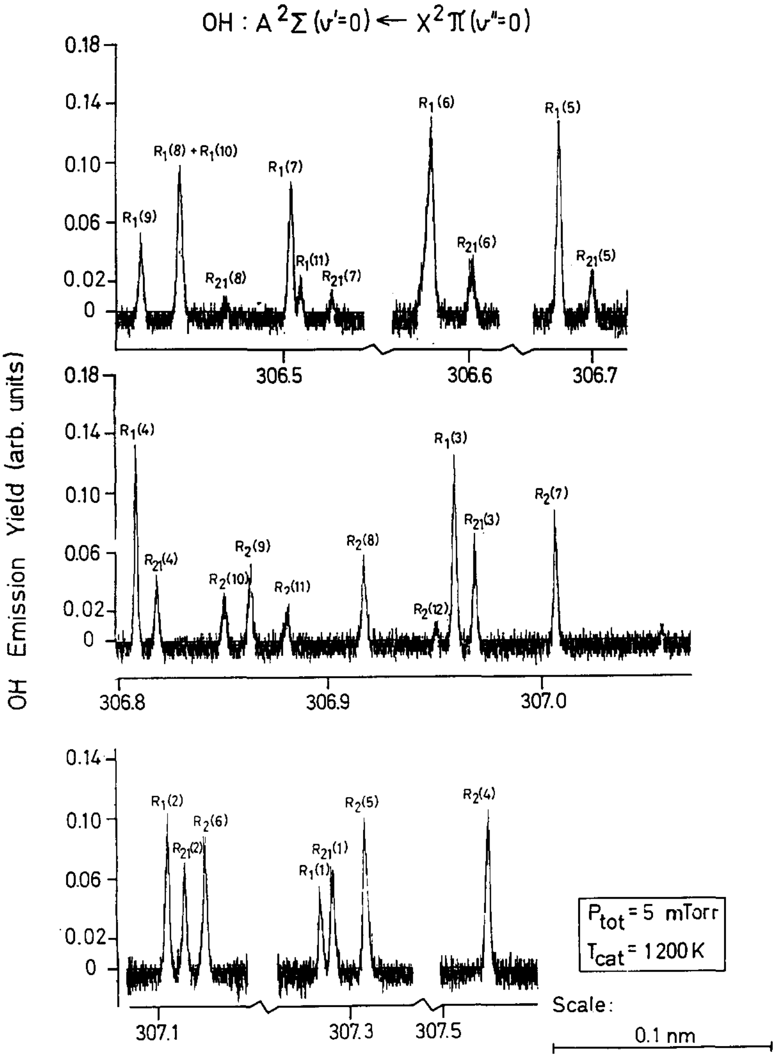

FIG. 2. Fluorescence intensity collected from OH after laser excitation. The different branches observed here are $R_1(N)$, $R_2(N)$, and $R_{21}(N)$, where N is the rotational quantum number.

and the foil. Summation of I_{OH} at different points along the catalyst for various distances, z, illustrates how the total OH yield varies with the distance from the surface. This is shown in Fig. 4b. The decrease in the number of OH molecules with z shows that the OH radicals are produced at the surface and not by gas-phase reactions in this pressure regime. This is in contradiction to what was found by Pfefferle *et al.* (*8*), where the concentration of OH exhibited a maximum at a distance of a few millimeters from the catalytic foil. Radicals that are produced on the catalyzed thermal burner will be desorbed, and then initiate and sustain gas-phase reactions. Measurements with a noncatalytic heated quartz plate showed, on the other hand, a decrease in OH concentration as a function of the distance from the surface. Their experiments, which were performed at atmospheric pressure, therefore give a clear indication of surface-initiated

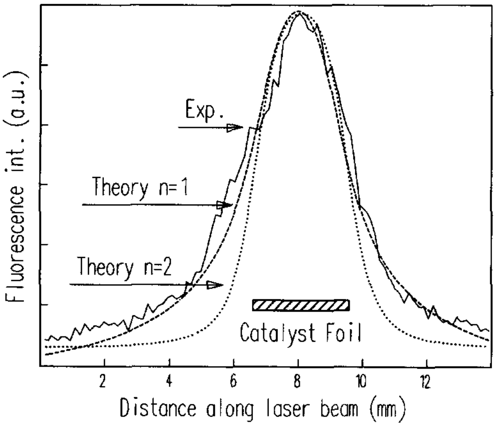

FIG. 3. The variation of the fluorescence intensity from the $R_1(5)$ transition along the laser beam at 10 mTorr total pressure and a catalyst temperature of 1300 K. The distance between the foil (indicated in the figure) and the detection zone, z, was 0.4 mm. The expected results from $\cos^n\theta$ distributions for desorption with $n = 1$ (dashed line) and $n = 2$ (dotted line) are also shown.

gas-phase reactions. Our experiments, which were performed in the pressure regime 2–200 mTorr, show that at least the dominant part of the probed OH radicals originate from surface reactions.

3.3 Desorption Process

Measurements of the angular distribution of desorbing molecules from a surface is normally performed by moving a detector, with or without mass selection, outside the surface (*16*). The recorded data are then often fitted to one, or a sum of $\cos^n\theta$ distributions. $n = 1$ corresponds to the Knudsen law (*17*), which is expected for a case where the sticking coefficient is independent of angle. In this type of experiment the distance between the surface and the detection zone is normally large compared with the diameter of the sample area from which the desorbing molecules originate. However, this method is not suitable for studies of radicals, especially for OH in the presence of water vapor.

The imaging technique applied in this work can however be used to obtain information about the angular dependence of the desorption process. Assuming a $\cos^n\theta$ distribution of the desorbed OH radicals in the LIF measurements, the concentration of OH has been evaluated by integrating the contribution from every point on the surface in the direction along the laser beam. Such theoretical distributions normalized to the maximum of the experimental data are shown for $n = 1$ and $n = 2$ in Fig. 3. The best fit is obtained for $n = 1$ indicating a $\cos\theta$ distribution of the desorbed OH species.

3.4 Gas-Phase Cooling

Recently, we employed the LIF technique to study the rotational state population of the desorbed OH radicals in a probed volume at a distance of 2 mm from the catalyst in the pressure range 2–200 mTorr at a catalyst temperature of $T = 1200$ K. In this type of measurement, LIF scans of the type shown in Fig. 2 are recorded for different pressures. The relative intensities of the different peaks are then normalized with the corresponding transition probabilities as described in detail in Ref. (*14*), resulting in populations of the probed rotational states. The distribution between the rotational levels is then normally described by assuming that the population is given by a Boltzmann distribution of a certain temperature.

Increasing the pressure, the rotational distributions of the desorbed OH molecules showed a strong pressure dependence due to gas-phase collisional processes. A least-squares fit of the Boltzmann plots of the rotational populations gave reasonably straight lines at low (2 mTorr) and high (200 mTorr) pressures, while slightly curved lines were observed in the intermediate pressure regime. These rotational distributions were characterized by an effective rotational temperature of "T_{rot}" = 1000 K at low pressures and $T_{\mathrm{rot}} = 500$ K at high pressures. The measurements were made at a surface temperature of 1200 K. The fall-off of T_{rot} with increasing pressure illustrates the rotational cooling of the OH molecules caused by collisions when they travel away

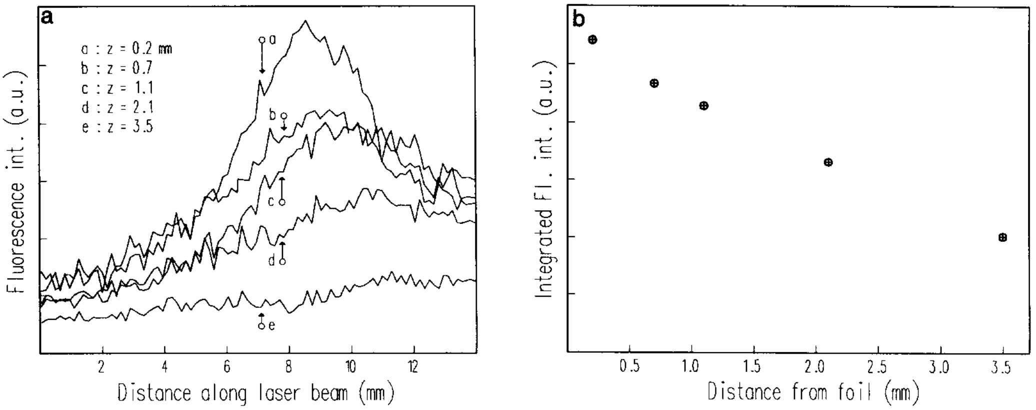

FIG. 4. (a) The fluorescence from OH at five different distances from the surface (z = 0.2, 0.7, 1.1, 2.1, and 3.5 mm, respectively) at 100 mTorr and 1300 K. (b) The total OH concentration at different distances from the catalytic surface.

from the surface before they are excited by the laser light. In the limit $p \rightarrow 0$, Boltzmann type distributions were found with a rotational temperature T_{rot}/T = 0.81 ± 0.03, demonstrating a rotational cooling upon desorption. This change in rotational temperature was found to be compatible with the desorption of thermally equilibrated molecules on the surface which lost one rotational quantum number on desorption. In these measurements the rotational temperature represents the *average rotational distribution* in the probed volume (11 mm × 1 mm^2). Use of the imaging technique, however, opens the possibility to measure the *local rotational distribution*.

This cooling process has been illustrated by imaging the intensity of different rotational transitions of the desorbed OH radicals outside the catalyst. The resulting curves for $R_1(1)$–$R_1(7)$ and $R_1(9)$ transitions are shown in Fig. 5 at a total pressure of 100 mTorr and a catalyst temperature of 1300 K. Measurements of the intensity of each peak at a certain distance along the laser beam followed by normalization to the transition probability, as described above, give *local rotational distributions* of the desorbed OH radicals. Further analysis of these distributions in a Boltzmann plot gives the *local rotational temperature* of the OH radicals outside the catalyst. Analysis of this type for various distances along the laser beam gave the rotational temperatures shown at the top of Fig. 5a. A significant rotational cooling takes place with increasing distance from the catalyst. This cooling effect can be illustrated in a more pronounced way by autoscaling the different peaks at a certain distance along the laser beam, as illustrated in Fig. 5b. Note how levels with high rotational quantum numbers, e.g., N = 9, 7, 6, are less populated the further away from the sample they are probed, while levels with low N become more populated. Knowledge of rotational redistributions of this kind may be of great help in the understanding of the catalytic promotion of gas phase reactions.

4. CONCLUSIONS

The measurements presented in this work provide an example of how the spatially resolved LIF imaging technique can be used for studies of desorbed intermediate OH radicals produced in the oxidation of hydrogen on platinum. The LIF imaging technique provides a unique possibility to study the angular distribution of desorbed OH radicals and their spatial concentration as a function of distance along the catalyst, as well as distance from the catalyst. The spa-

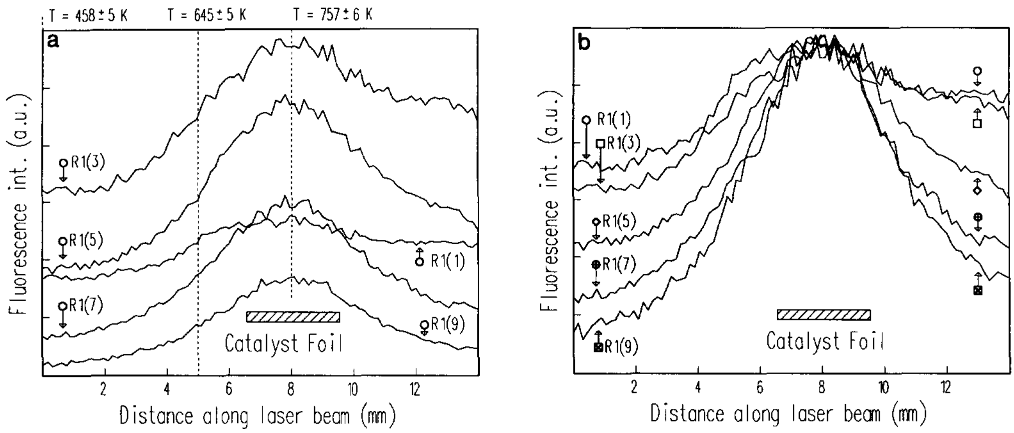

FIG. 5. (a) The fluorescence intensity from different transitions in OH, at $T = 1300$ K and $p = 100$ mTorr. The rotational temperatures determined in Boltzmann plots at different distances along the laser beam are indicated at the top. (b) The same curves as in Fig. 5a normalized over the catalyst.

tial distribution is found to be well described by a cos θ dependence for desorption. The total number of OH radicals was found to decrease with increasing distance from the surface, indicating that these radicals originate from the surface. Further analysis of the rotational distribution of the desorbed OH radicals gives the *local rotational distributions* and has shown that the OH radicals are rotationally cooled as a result of interactions with the reactant gases.

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