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Matrix isolation and laser diagnostic studies of catalytic oxidation of H_2 and D_2 on platinum

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The reaction of hydrogen (or deuterium) and oxygen on pure polycrystalline platinum surfaces has been investigated in the 10^{-5} to 10^{-6} Torr range using the matrix isolation and laser-induced fluorescence techniques. Water, formed with a 1.1 ± 0.2 kcal/mole activation energy, was the only product detected by infrared spectroscopy at catalyst temperatures between 150 and 700 °C. Laser-induced fluorescence experiments were used to observe the production of HO radicals both in argon matrices and in the gas phase. HO production was found to have an activation energy of 31 ± 1 kcal/mole and could only be detected escaping from the surface at catalyst temperatures above 500 °C. The dependence of H_2O and HO radical production on the partial pressures of H_2 and O_2 has been made. Reaction mechanisms are discussed in relation to other studies of the oxidation of hydrogen on single crystal and polycrystalline platinum surfaces.

I. INTRODUCTION

The adsorption chemistry of hydrogen and oxygen on single crystal and polycrystalline platinum surfaces has been the subject of many recent investigations,[1] particularly in relation to the mechanisms of isotopic exchange and $H_2 + O_2$ reactions. The H_2-D_2 exchange reaction has been extensively studied in the past, and the results of recent work indicate that the reaction is favored at step or corner sites on otherwise flat, low-index crystal planes.[2] The kinetics and mechanisms of the exchange reaction, which involves at least one dissociatively adsorbed reactant, depend strongly upon the structure and nature of the surfaces and experimental techniques employed. The adsorption of oxygen on platinum has also been shown to be favored at steps and defects and to occur dissociatively according to the thermal desorption study of Collins and Spicer.[3] This result was nicely confirmed by the oxygen 16–18 isotope exchange reaction observed on highly oriented Pt(100) ribbons at temperatures above 300 °K.[4]

The reaction of H_2 with O_2 on Pt has been studied under a variety of conditions. Recently, Smith and Palmer[5] investigated the oxidation of D_2 by O_2 on a Pt(111) surface using a modulated molecular beam technique. They measured the rate of D_2O production as a function of the catalyst and D_2 beam temperatures, as well as isotropic D_2 and O_2 pressures. The D_2O production rate

$$r_{D_2O} \propto P_{D_2}^{2.0} P_{O_2}^{0.8} \exp(-3600/kT_{D_2}) \exp(-12\,000/kT_{Pt})$$

was concluded to be consistent with the mechanism

$$4D^* + O_2^* \rightarrow 2D_2O + 5^* ,$$

where "*" denotes an active site of the Pt catalyst.

Contrary to the results obtained by Smith and Palmer mentioned above, the reaction of H_2 and O_2 on Pt surfaces with more steps and defects involves primarily dissociatively adsorbed H and O atoms.[6,7] Netzer and Kneringer[6] studied the reaction on the Pt(100) surface by FDMS (flash desorption mass spectrometry). They showed that the production of H_2O on this surface has little or no activation energy for H_2-rich ($H_2/O_2 \gtrsim 1$) mixtures above 200 °C. Additionally, they found evidence for a strongly bound H_2O on Pt, which was estimated to be of the order of 5% of a monolayer, based on their flash desorption data. This latter observation was noted to be in sharp contrast to the results of Norton[7] who found, in an XPS study, that H_2O desorbed completely from a polycrystalline Pt foil at 170 °K. On the other hand, Norton's experiment also indicated a shift in the characteristic O1s line from 530.2 ± 0.2 to 533 ± 0.5 eV upon addition of H_2 to an O_2-covered Pt surface.[7] This result had also been observed in an earlier LEED study by Tucker.[8] This new, strongly adsorbed "H_2O" species may actually be the adsorbed HO radical. The O1s binding energy of this new species falls within the range of that observed for $K_2Pt(OH)_6$ (533 ± 1.5 eV).[7]

The existence of discrete Pt–OH species had been observed by infrared spectroscopy earlier by Morrow and Ramamurthy[9,10] using a silica-supported Pt catalyst. On the basis of observed infrared absorption spectra, including those of ^{18}O- and D-labeled results, two distinct Pt–OH species were believed to be present when O_2 was added to an H_2 and H_2O-covered Pt surface.[9,10] Most recently, Sexton[11] has reported the observation of a Pt–OH group on Pt(111) surfaces which were pretreated with O_2 prior to the deposition of H_2O at ~150 °K. Sexton employed the technique of electron energy loss spectroscopy. At this low temperature, O_2 was found to be indispensable for the appearance of the Pt–OH absorption peak, presumably due to the surface reaction $O^* + H_2O^* \rightarrow 2HO^*$.

Recently, we have applied the technique of matrix isolation (MI) to characterize products of catalytic reactions on heated polycrystalline Pt surfaces under low pressure (10^{-6} to 10^{-5} Torr reactant partial pressure) conditions.[12–15] This technique is ideally suited to mechanistic studies since we have shown that not only stable products but also free radical species can be readily trapped in inert solid matrices and identified by

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[a] NRC/NRL Postdoctoral Research Associate.

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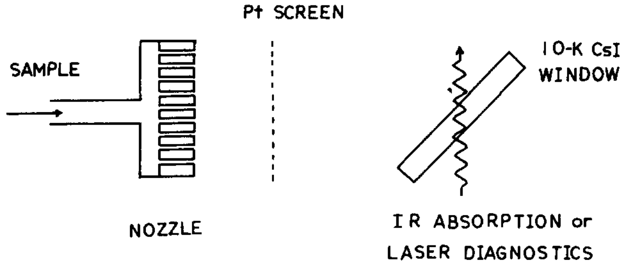

FIG. 1. Schematic diagram for the matrix isolation experiments.

conventional infrared and laser diagnostic techniques.[12-15] The present investigation was performed in order to study the kinetics of H_2O production from the $H_2 + O_2$ reaction on Pt as well as to observe whether any free radical products were present in the reaction. Shalya *et al.*[16] have previously reported the detection of ESR-active species in the oxidation of H_2 on Pt under high pressure conditions. Although we failed to detect free radicals (such as HO and HO_2) by infrared absorption spectroscopy, the application of the very sensitive laser-induced fluorescence (LIF) technique[17] did reveal the presence of the HO radical trapped in the 10 °K argon matrix.[14] We have further confirmed the presence of this radical product in the gas phase using a more sophisticated data processing system.[15] In this article, we report the energetics for H_2O and HO production from a "clean" polycrystalline Pt wire employing both the MI and LIF techniques. The mechanisms for the formation of both products are discussed in detail.

II. EXPERIMENTAL

A. Matrix isolation experiments

The matrix isolation apparatus which was used for investigation of catalytic reactions has been described in detail elsewhere.[12,13] The basic principle of the present matrix isolation experiment is shown schematically in Fig. 1.

Argon (Matheson, prepurified), hydrogen (Matheson, ultrahigh purity), deuterium (Matheson, C. P.), oxygen (Matheson, extra dry), and $^{18}O_2$ (Miles Laboratories, Inc., 99 at. % ^{18}O) gases were used without further purification. The Pt catalyst was cleaned before each run by heating it to 800 °C in a 5 Torr oxygen atmosphere for 1 h. Then the current was turned off and the catalyst was allowed to cool while the optical window was cooled to 10 °K and the system evacuated. The refrigerator required 45 min to cool the window. After cooling down, the catalyst was heated to 900 °C for 5 min to remove any traces of adsorbed gases under the highest vacuum conditions presently attainable ($\lesssim 10^{-5}$ Torr). $Ar:H_2(D_2)$ and $Ar:O_2$ samples were prepared in separate 1500 cc stainless steel vessels stored on a single stainless steel vacuum manifold, using standard procedures. Deposition was performed by simultaneously opening both containers to the manifold behind the leak valve so that the gases could mix before being passed through the catalyst. It was shown that no reaction to form H_2O occurred under these conditions in the absence of the Pt catalyst.

Infrared absorption experiments were performed by condensing $Ar:D_2:{}^{18}O_2$ samples at a rate of ~2 mmole/h for 4 to 6 h at catalyst temperatures between 150 and 700 °C onto a CsI window positioned at 45° to both the direction of deposition and the infrared analysis beam so that spectra could be measured during deposition without moving the sample (see Fig. 1).[12,13] Relative $D_2{}^{18}O$ concentrations were measured by the optical density of its principal ν_2 absorption at 1187 cm^{-1}.[18] Spectra were recorded on Perkin-Elmer 457 and Beckman IR-12 infrared spectrophotometers.

In a separate experiment,[14] the laser-induced fluorescence technique was applied by condensing 4.3 mmole of $Ar:H_2:O_2$ (198:1:1) samples onto a highly polished copper plate in a 30 min period. After completion of the deposition, the shroud was rotated by 90° for the detection of HO radicals. The HO ($A\,^2\Sigma \rightarrow X\,^2\pi$) emission was induced by a frequency-doubled Chromatix CMX-4 laser operated with a Rhodamine 6G/water–soap solution. The laser fundamental was blocked with a Corning 7-54 filter prior to sample excitation, and scattered laser light was removed with a Hoya-34 filter in front of the spectrometer entrance slit. Fluorescence from the matrix was collected and focused onto the entrance slit of a Jarrel-Ash 0.25 m monochromator. An RCA 7265 photomultiplier tube was used to detect the fluorescence, and the signal was monitored on a Tektronix 7633 oscilloscope. This experiment showed for the first time the production of the HO radical from the Pt-catalyzed $H_2 + O_2$ reaction at relatively low temperatures.

The presence of HO radicals was further confirmed by the result of an experiment in which an $Ar:H_2:O_2$ (198:1:1) sample was microwave discharged in the gas phase prior to deposition. The resulting fluorescence spectrum was in good agreement with the spectrum of Goodman and Brus for the HO radical isolated in a solid argon matrix[19] and with that observed in the present $H_2 + O_2$ catalytic reaction.

B. Laser-induced fluorescence for HO detection in the gas phase

The sources of H_2, O_2, and Ar were the same as for the MI–LIF experiments described above. Mixtures of H_2 in argon and O_2 in argon were prepared separately.

The experimental apparatus used to detect the production of HO in the gas phase is shown schematically in Fig. 2. The reaction cell consisted of a black-anodized cylinder equipped with the following: a stainless steel reactant-gas mixing nozzle in the top and a vacuum port in the bottom for continuous pumping; sidearms with light baffles and Brewster-angle windows for passage of the excitation laser pulses; a large-aperture window for collection of fluorescence at 90° to the laser propagation axis and to the gas flow direction.

A Pt (99.999% purity, 0.5 mm diameter) wire was coiled to form a grid which was suspended in the horizontal plane just below the gas-mixing nozzle. Typically, before each run, the catalyst wire was heated at 800 °C for 30 min in a static O_2 atmosphere at 5 Torr pressure, followed by pumping at 850 °C for 10 min.

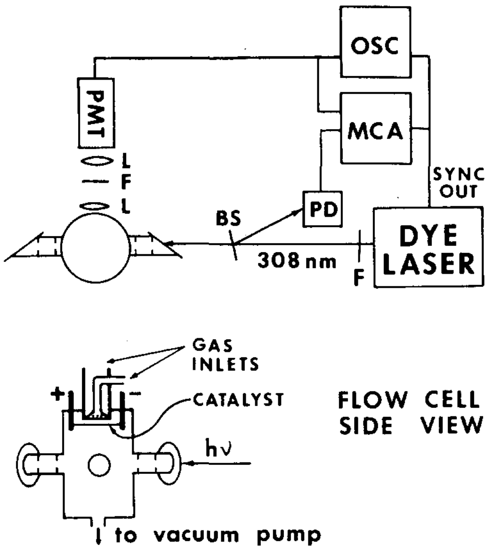

FIG. 2. Experimental layout of the fast flow system using the laser-induced fluorescence technique to detect HO radicals in the gas phase produced from the catalytic oxidation of H_2 by O_2 on platinum.

The catalyst wire was heated resistively, and the wire temperature was determined as before. Gas pressures were measured *in situ* with an MKS model 145 Baratron capacitance manometer.

The Chromatix CMX-4 dye laser was used to excite the $A\,^2\Sigma \leftarrow X\,^2\pi$ transition of HO in the gas phase, as was done in the MI experiment described above. The wavelength of the second harmonic laser output was tuned to 307.8 nm, corresponding to the Q_1 rotational bandhead frequency of the (0–0) vibronic transition of HO. The HO resonance fluorescence was detected with an RCA 7265 or an EMI G 13D 411 photomultiplier tube. A dielectric interference filter with transmission maximum at 309 nm was used in the collection optics to discriminate against stray light at other wavelengths. The signal from the photomultiplier tube was sent to an oscilloscope for real-time display and to a signal averager (Nicolet model 1072) for intensity accumulation.

The laser intensity at 307.8 nm was monitored with a diode whose output was also accumulated on the signal averager. The accumulated photomultiplier signal was normalized to the accumulated laser intensity signal for several hundred shots, typically.

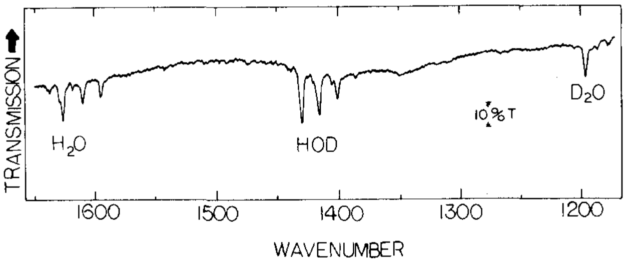

FIG. 3. Infrared absorption spectrum of H_2O, HDO, and D_2O in solid argon in the 1200 to 1650 cm^{-1} spectral region following the reaction of H_2, D_2, and O_2 with excess argon on a 500 °C Pt wire.

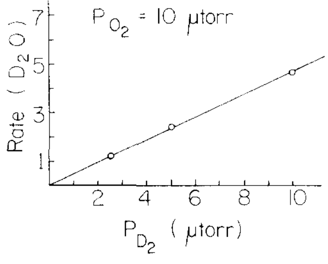

FIG. 4. Dependence of $D_2{}^{18}O$ production rate on the partial pressure of D_2. Catalyst temperature and $^{18}O_2$ partial pressure were held constant in each experiment. D_2 partial pressure was varied between 2.5 and 10 μTorr.

It was observed that changing experimental variables such as catalyst temperature and reactant gas pressures resulted in a change in HO fluorescence intensity which required only a few seconds for the signal equilibration to be effected. Data obtained at different Pt catalyst temperatures was collected randomly to assure that the stability of the system was being maintained. The signal at each temperature was corrected for background noise as determined in separate runs.

III. RESULTS

When an $Ar:D_2:O_2$ (198:1:1) mixture was deposited in the matrix isolation system without a catalyst, no evidence for any reaction was observed by infrared spectroscopy. When identical gas samples were passed through a heated platinum grid,[13] the only reaction product observed by IR absorption was D_2O. Figure 3 shows a typical IR absorption spectrum in the H_2O and D_2O bending region obtained from an experiment in which an $Ar:H_2:O_2$ mixture was mixed with an $Ar:D_2$ mixture in the low pressure (~200 mTorr) region of the deposition line prior to the reaction chamber. This spectrum shows an apparent statistical mixing of hydrogen isotopes among the three reaction products H_2O, HDO, and D_2O. The observed vibrational frequencies of these molecules are in good agreement with the known spectra of H_2O, HDO, and D_2O isolated in solid argon.[20-23] The result of this experiment clearly shows that dissociatively adsorbed H and D atoms are involved in the production of water. A more detailed discussion of the reaction mechanism will be given later.

Figures 4 and 5 show the dependence of the $D_2{}^{18}O$

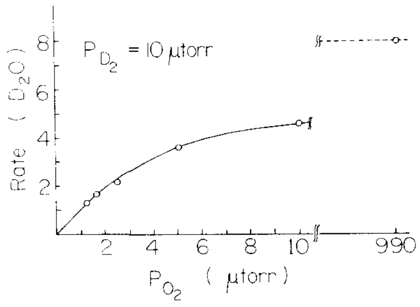

FIG. 5. Dependence of $D_2{}^{18}O$ production rate on the partial pressure of $^{18}O_2$. Catalyst temperature and D_2 partial pressure held constant in each experiment. $^{18}O_2$ partial pressure was varied between 1 and 10 μTorr. The point at the upper right shows the D_2O production rate when an $^{16}O_2:D_2 = 99:1$ sample was deposited.

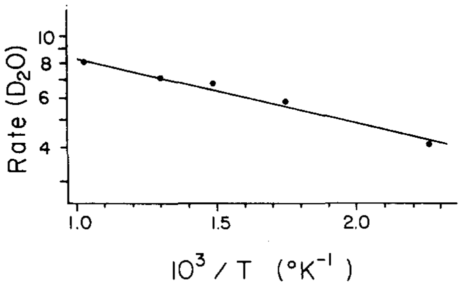

FIG. 6. Arrhenius plot for the rate of $D_2{}^{18}O$ production at catalyst temperatures between 150 and 700 °C using $Ar : D_2 : {}^{18}O_2 = 198 : 1 : 1$ samples.

production rate on the partial pressure of D_2 and ${}^{18}O_2$, respectively. We used D_2 and ${}^{18}O_2$ to eliminate any interferences from atmospheric impurities. In these two separate series of experiments, the partial pressure of D_2 or ${}^{18}O_2$ was systematically varied, while the partial pressure of the other reactant (typically 200:1 $Ar:{}^{18}O_2$ or D_2) was kept constant. The result presented in Fig. 4 shows a linear increase in the rate of $D_2{}^{18}O$ production with D_2 pressure. The result in Fig. 5, however, indicates a clear early leveling off in $D_2{}^{18}O$ production rate as the pressure of ${}^{18}O_2$ is increased. This is most dramatically demonstrated by the result of an experiment in which pure ${}^{16}O_2$ instead of Ar was used as the matrix. Here the rate of $D_2{}^{16}O$ formation was found to increase by less than a factor of 2, while the pressure of O_2 was increased by as much as two orders of magnitude. The interpretation of this inhibition or "blocking" effect by O_2 will be given later.

We have also investigated the effect of the catalyst temperature on water production. Figure 6 shows the results of five separate runs for which the initial rate of $D_2{}^{18}O$ appearance was measured as a function of temperature. Samples of the 198:1:1 $Ar:D_2:{}^{18}O_2$ mixture were passed through the catalyst between 150 and 700 °C. In each experiment, the rate of $D_2{}^{18}O$ appearance was observed to have a short induction time, after which the rate became essentially steady and constant. The result, shown in Fig. 6, leads to an activation energy (or temperature coefficient) of 1.1 ± 0.2 kcal/mole. This value is considerably lower than that for HO production, to be discussed below.

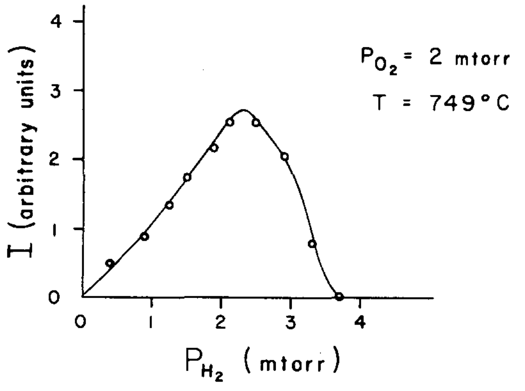

FIG. 7. Intensity of HO LIF signals as a function of H_2 pressure at $T_{Pt} = 749$ °C and $P_{O_2} = 2$ mTorr.

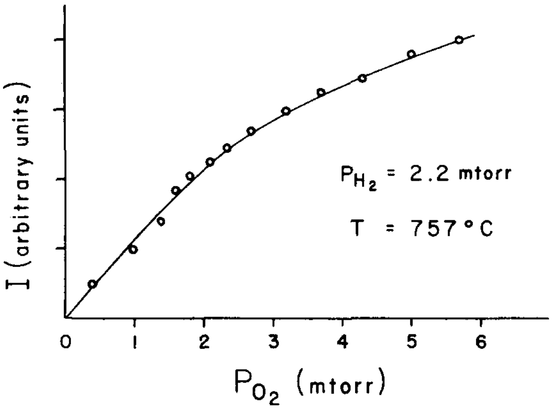

FIG. 8. Intensity of HO LIF signals as a function of O_2 pressure at $T_{Pt} = 757$ °C and $P_{H_2} = 2.2$ mTorr.

The infrared spectra of HO[24] and HO_2[25–27] in solid argon have been reported before, but neither was observed in the present work, presumably due to their low concentrations. The more sensitive technique of LIF was first used for the detection of HO in Ar matrices at catalyst temperatures above 600 °C.[14] The spectral characteristics of the HO produced in the catalytic reactions have been shown to be in excellent agreement with those reported by Goodman and Brus[19] and with our own spectrum produced by discharging a mixture of Ar, H_2, and O_2 during condensation as mentioned earlier. The electronic excitation was made in the (0–0) band of the HO ($A\,{}^2\Sigma \leftarrow X\,{}^2\pi$) transition near 310 nm, and the induced fluorescence from the matrix was observed to peak at 340 ± 2 nm with a broad width of 24 nm at half-maximum.

After the initial success of the above MI and LIF study, a new experimental apparatus was constructed for HO detection in the gas phase as shown in Fig. 2. Additionally, signal averaging was employed for both induced fluorescence and excitation laser intensity to minimize shot-to-shot fluctuations. The data obtained from this system were considerably more reproducible and were free from the large, background fluorescence problem which was encountered in the MI experiments.

Figures 7 and 8 show the intensities of HO LIF signals as functions of H_2 and O_2 partial pressures. These data were taken from experiments by keeping the partial pressure of either gas constant and varying the other to the desired values. Argon-diluted 1.0% H_2 and O_2 were used in these runs. The data presented in Fig. 7 indicate a rapid change in the effect of increased H_2 pressure on the steady-state concentration of the HO radical with a drastic change in slope from positive to negative at ~1:1 $H_2:O_2$ ratios. The addition of O_2, as shown in Fig. 8, however, results in a monotonic increase in the HO production rate. Interestingly, these observations are consistent with the effects of H_2 and O_2 addition on the decomposition of H_2O using the same Pt catalyst.[28]

Figure 9 presents the data gathered from experiments in which the temperature of the Pt catalyst was varied from 590 to 760 °C. In these experiments, the total pressure of the $Ar:H_2:O_2$ (2230:1:12) mixture was kept

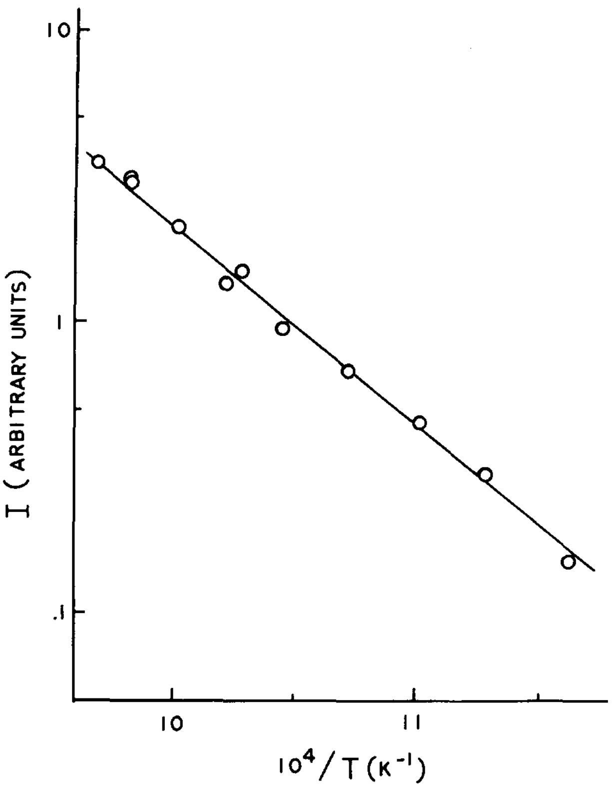

FIG. 9. Arrhenius plot for HO production at different temperatures. $P_{H_2} = 0.35$ mTorr and $P_{O_2} = 4.3$ mTorr, diluted with Ar to a total pressure of 780 mTorr.

constant at 780 mTorr. From the slope of this Arrhenius plot, the activation energy for the production of the HO radical was calculated to be 31 ± 1 kcal/mole. A similar but slightly less extensive set of runs carried out with 270 mTorr of the Ar:H_2:O_2 (198:1:1) mixture gave rise to a value of 32 ± 3 kcal/mole, which is in good accord with the above value.

IV. DISCUSSION

The results of previous studies on the H_2–D_2 and $^{16}O_2$–$^{18}O_2$ isotopic exchange reactions mentioned in the Introduction and the observations made in the present work for the oxidation of H_2 (D_2) by O_2 on polycrystalline Pt surfaces are consistent with the following mechanism involving dissociatively adsorbed H (D) and O atoms:

$$H_2 + 2^* \rightarrow 2H^* , \qquad (1)$$

$$O_2 + 2^* \rightarrow 2O^* , \qquad (2)$$

$$H^* + O^* \rightarrow HO^* + ^* , \qquad (3)$$

$$H^* + HO^* \rightarrow H_2O + 2^* , \qquad (4)$$

$$HO^* \rightarrow HO + ^* . \qquad (5)$$

Similar mechanisms are believed to be valid also for the decomposition of H_2O[28] [which is initiated by the reverse of Reaction (4)], and the oxidation of H_2 by N_2O[29] on the same Pt catalyst from which the production of the HO radical was found to have similar activation energies.

Reactions (4) and (5) are competitive processes that involve adsorbed HO species. Introduction of an excess amount of hydrogen is expected to enhance Reaction (4) at the expense of Reaction (5), and thus results in an increase in H_2O production rate and a decrease in the steady state concentration of HO leaving the Pt surface, as shown by the results in Figs. 4 and 7, respectively. Addition of more oxygen, however, was found to promote the production of both H_2O and HO simultaneously, with the latter being enhanced to a larger extent. This can also be understood in terms of the above mechanism, as the increased concentration of adsorbed O atoms does not remove but promotes HO* formation which favors both Reactions (4) and (5). However, the increased production of HO*, although favoring Reaction (4) to some extent, also diminishes the availability of H* for H_2O formation. This may explain in part the blocking effect of excess O_2 on H_2O production reported previously[6] and also demonstrated by the results presented in Fig. 5. The counterpart of Reaction (4) involving adsorbed O atoms

$$O^* + HO^* \rightarrow HO_2 + 2^* \qquad (6)$$

is probably unimportant under our experimental conditions because of the instability of the HO_2 radical. Reaction (6) may directly form $H^* + O_2^*$ (or $O_2 + ^*$) instead. Unfortunately, the HO_2 radical cannot be readily detected by means of LIF.

The production of HO_2 at low temperatures and high pressures, however, could account for the observed ESR signal in trapped oxidation products (at 77 °K) from the $H_2 + O_2$ reaction (≳10 Torr, 1:4 O_2:H_2 using Pt wires maintained at 330 °K).[16] In view of the large activation energy required for the HO to desorb from the Pt surface, it is quite unlikely to have any appreciable amounts of HO radicals present for ESR detection in these low temperature experiments. The detectivity of the HO radical with a typical dye laser is of the order of 10^9 particles/cm^3 which is about the concentration level of the HO produced at our low temperature limit (820 °K).

The low activation energy (1 kcal/mole) observed for H_2O production in this work agrees fully with the result reported by Netzer and Kneringer.[6] This considerably lower activation energy, in comparison with that for HO desorption, of 31 kcal/mole measured under similar experimental conditions results from the fact that the energy barrier required for H_2O desorption from Pt surfaces is negligible and also that the vast amount of energy released from Reaction (4) due to the formation of the new H–OH bond (118 kcal/mole) could be partly used for the desorption process.

Since the activation energies observed for HO production in the oxidation of H_2 by N_2O[29] and in the decomposition of H_2O,[28] both carried out with the same Pt catalyst, lie in the vicinity of 30 kcal/mole, it is quite likely that the value of 31 kcal/mole represents closely the energy required to break the average Pt–OH bond from Pt surfaces. This value is lower than that measured earlier in the matrix isolation experiment (41 ± 4 kcal/mole).[14] This difference is believed to have resulted from the uncertainty in the latter experiment because of the presence of large laser-induced background emissions as well as the fluctuation in laser intensity, which was not properly eliminated by means of signal averaging. Additionally, in the matrix isolation experiment, we measured integrated HO concentrations after a period of time (typically 30 min) rather than differential steady-state HO concentrations as was done in the present work.

V. CONCLUDING REMARKS

In this study, we have investigated the kinetics and mechanism of the oxidation of H_2 and D_2 by O_2 on polycrystalline Pt surfaces. The rates of water and hydroxyl radical production have been studied as functions of temperature and reactant pressures.

Water production was measured by matrix isolation infrared absorption spectroscopy and the hydroxyl radical by the laser-induced fluorescence technique employing a tunable dye laser, frequency-doubled to near 300 nm to excite the (0–0) band of the HO ($A\,^2\Sigma^+ \leftarrow X\,^2\pi$) transition in the gas phase. The formation of water was found to vary very little with temperature ($E_a = 1$ kcal/mole), whereas the production of hydroxyl radicals was found to have an activation energy of 31 kcal/mole, which is believed to be associated with the direct desorption process $HO^* \rightarrow HO\cdot + ^*$.

The production of both water and the hydroxyl radical was observed to be enhanced by an increase in the partial pressure of O_2. Water production, however, exhibited a rapid leveling off in its rate as the O_2 pressure was further increased. This blocking effect was partly attributed to the increase in the steady state concentration of HO^* at the expense of H^* (by $H^* + O^* \rightarrow HO^*$). The increase in hydrogen pressure was found to promote linearly the rate of water production at the great detriment of HO^*, an effect attributable to the enhanced removal rate of the adsorbed HO species via $H^* + HO^* \rightarrow H_2O + 2^*$, as the partial pressure of H_2 is increased.

The results of this work have demonstrated again the usefulness of the MI and LIF techniques for studying the kinetics and mechanisms of heterogeneous catalytic reactions under relatively low pressure (10^{-6}–10^{-5} Torr) conditions. The great sensitivity of LIF and other techniques with the laser (such as surface-enhanced Raman spectroscopy) is expected to broaden considerably the diagnostic capability for the characterization of adsorbed species on surfaces and products of surface reactions.

In the present work, the MI and LIF techniques were employed separately in different experiments. We plan to integrate both diagnostic methods using a single flow system. The employment of such improved techniques as FTIR (Fourier transform infrared) absorption and emission spectroscopy, computer-automated data processing, and a more powerful laser is expected to increase product detectivity by at least an order of magnitude.

The present work will be extended in the near future in the following three areas:

(1) the characterization of the internal states of the HO radical formed in the recombination reaction $H^* + O^* \rightarrow HO(v,j) + 2^*$ on platinum to examine the extent of energy equilibration between the surface and the product;

(2) the kinetics of the $H + MO \rightarrow HO + M$ reactions, where MO is a metal oxide molecule on such metal surfaces as Pt, Ni, Pb, Cu, etc.; and

(3) the production of other free radicals such as NH, NH_2, CN, CHO, etc., from heterogeneous catalytic reactions.

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