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Chemisorption of Xenon and Fluorine on Nickel and Palladium

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A radiotracer technique was used to study the adsorption of xenon in the presence of fluorine on nickel and palladium foils. Isotherms measured at temperatures of 243-373°K showed that xenon was adsorbed. Examination of the surfaces by electron microscopy showed that the presence of xenon markedly influences the attack of fluorine on the metal. It is suggested that xenon is chemically bound to fluorine in the absorbed state, and that this constitutes the intermediate in the catalyic formation of xenon difluoride.

INTRODUCTION

The reaction of xenon with fluorine to form xenon difluoride has occurred readily on heated filaments of palladium and nickel (*1*). The surfaces of these metals under reaction conditions are covered by a layer of the difluoride. Zero-order kinetics were observed for the xenon pressure, a result which could be explained if a large concentration of chemically bound xenon is present on the catalyst surface.

The chemisorption of xenon has not been reported previously but appeared to be possible under the conditions of the catalytic reaction. The experiments described here were designed to measure the uptake of radioactive ^{133}Xe in the presence of fluorine on the catalyst surfaces.

EXPERIMENTAL METHODS

The apparatus (Fig. 1) consisted of an adsorption vessel, pressure gauges, xenon and fluorine reservoirs, a mixing bulb and an ampoule of radioactive ^{133}Xe. The materials of construction were inert to attack by dry fluorine at room temperature. The line and bulbs were of Pyrex glass with greaseless Teflon vacuum taps (Fisher and Porter). Stainless steel and Monel were used for the mounting of the adsorption vessel. Two pressure gauges were used: a Bourdon gauge with a sensitivity of ca. 1 torr and a diaphragm capacitance manometer with a sensitivity of 10^{-2} torr.

Adsorption Vessel and Counter

Details of the adsorption vessel are shown in Fig. 2 and consist of a counter C mounted above a specimen holder. The construction of the counter which contained a thin Pyrex glass window W has been described previously (*2*). For safety reasons krypton was used as a counter filling gas as it would not react with fluorine if the thin pyrex window was inadvertently broken during the course of an adsorption run. The counter was operated in the proportional region where it was insensitive to any temperature variation.

Pulses were fed to an amplifier, a dis-

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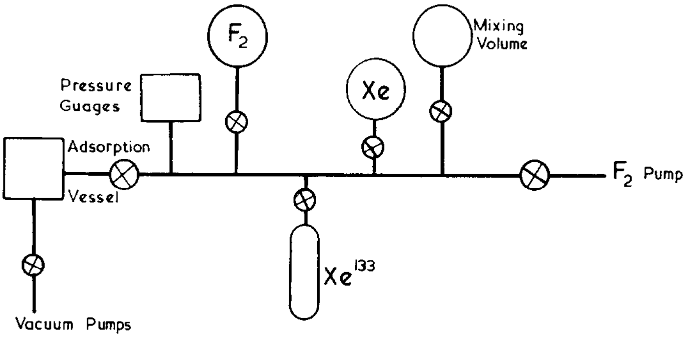

FIG. 1. Schematic diagram of the apparatus.

criminator, and a rate meter, and were displayed on a digital scaler and strip chart recorder. The ^{133}Xe emits a β-particle of energy 0.35 MeV which is absorbed in the glass walls of the apparatus, and a λ ray of energy 0.081 MeV. Hence, the pressure of the krypton counting gas was adjusted to 20 torr, as at this pressure the counter was insensitive to the detection of the λ rays emitted from the ^{133}Xe. This ensured that the detection of background radiation was excluded from all parts of the system other than that contained by the specimen surface and the dead volume (2.5 ml) between this surface and the counter window. As a precaution against β-particles penetrating the Teflon specimen holder from below, a disc of lead sheeting L, 4.5 mm thick, was placed under the specimen holder. The Pyrex glass counter was attached to a stainless steel flange with a graded seal and this flange was located in the base of the specimen holder where it was sealed with a Teflon gasket. The specimen holder consisted of a stainless steel base containing a pumping line V, and a number of electrical leads-through (sealed with a Teflon gland). The base supported a stainless steel rod R, and Teflon piston P, on top of which the specimen S, was located.

Materials

The metal specimens were Pd and Ni foils which had been rolled to a thickness of 0.075 mm and then partially cut so that a continuous electrical path of cross section 0.19 mm^2 was formed. They were heated resistively and a copper-constantan thermocouple (0.25-mm diam. wires) spot-welded to the foil measured the temperature. This design was chosen so that only the metal foil was heated in the presence of fluorine and other parts of the system were thereby protected from excessive attack by fluorine. The design also presented a reasonable surface area to the counter window (5 cm^2). After degreasing, the foils were outgassed strongly at 600–700°C in a vacuum of 10^{-5} torr.

Xenon 133 was obtained from the Radiochemical Centre, Amersham, with a specific activity of 2 Ci/ml at STP. It was purified by distillation and either used at this specific activity or diluted with inactive Xe for use at higher Xe pressures.

Fluorine was prepared and handled as described previously (*1*). It was stored in a reservoir containing a cold finger which was always held at 77.5°K to trap out any HF before admission of fluorine was made to the adsorption vessel.

Procedure

The objective of the adsorption experiments was to obtain data relevant to the catalytic reaction of xenon with fluorine. The metal foil was therefore conditioned by reacting nonactive xenon and fluorine under the previously established reaction conditions (*1*). A stainless steel cylinder with its associated flange, was bolted onto the base of the specimen holder and evacuated. A can, packed with dry ice, surrounded the stainless steel cylinder to condense the reaction products. The Xe/F$_2$ mixtures (ratio 1:1) were admitted to the vessel, the foil was heated to reaction tem-

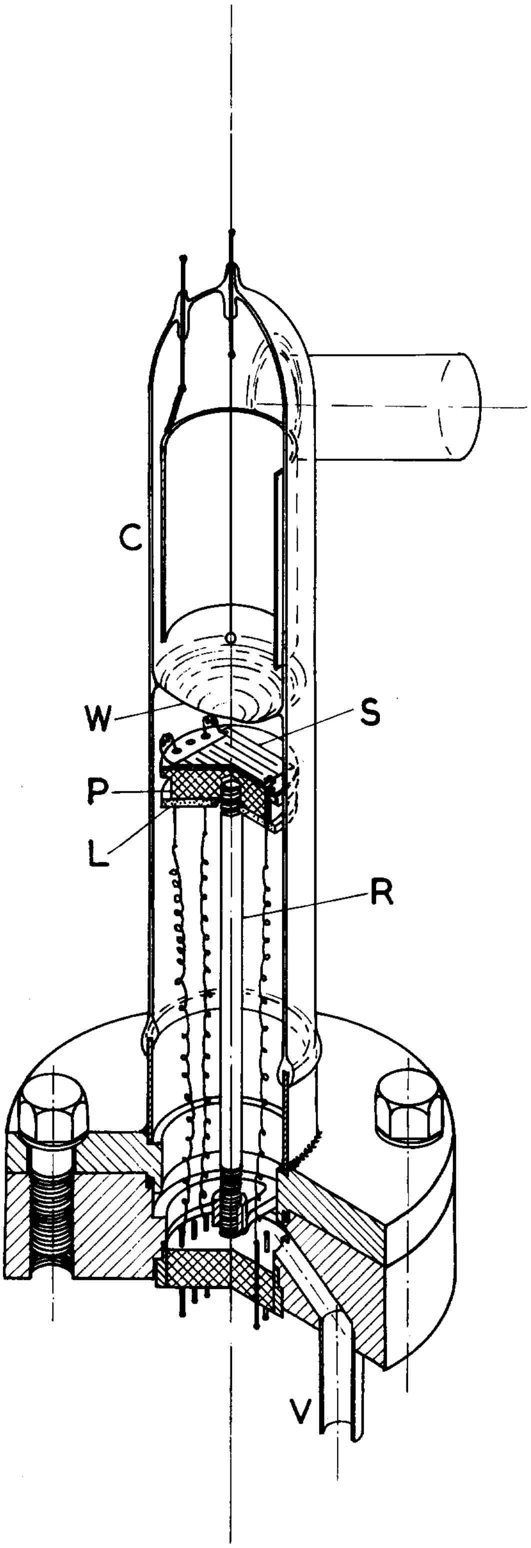

FIG. 2. Adsorption vessel.

perature and the rate was followed by observing the decrease in pressure in the system, on the Bourdon gauge.

For the adsorption experiments, the stainless steel cylinder was replaced by the counter tube. The apparatus was evacuated on both sides of the counter window simultaneously, the counter was isolated, and filled with the counting gas. An external ^{85}Kr source was used as a standard to check on the counter sensitivity. A vacuum of 10^{-5} torr was achieved in the adsorption vessel prior to an adsorption run. Adsorption of Xe was investigated over three ranges of pressure which made it necessary to use different specific activities of ^{133}Xe.

Low pressure range ($1 \rightarrow 8 \times 10^{-3}$ torr of Xe). The vapor pressure of the ^{133}Xe was controlled by immersing the ampoule in a liquid oxygen/nitrogen mixture. In this way a pressure of 8×10^{-3} torr of ^{133}Xe was admitted to the volume of the total system and this was then frozen out at 77.5°K in a cold finger attached to the mixing volume while the fluorine pressure was adjusted to 6×10^{-1} torr. (The vapor pressure of F_2 at 77.5°K = 200 torr.) This pressure was chosen so that the doses of Xe/F_2 mixture admitted to the adsorption vessel could be measured with the capacitance manometer. The mixing volume was isolated and the fluorine was pumped from the line. The cold finger of the mixing volume was warmed to room temperature, about 30 min was allowed for the Xe and F_2 to mix, (Xe/F_2 ratio = 0.08:3) and the temperature of the metal foil was adjusted to the desired value. The adsorption run commenced by admitting the Xe/F_2 mixture to the adsorption vessel in a stepwise manner, the count rate was allowed to reach a steady value between each addition. After the mixture had been expanded from the mixing volume, the total pressure at the end of the run was about 3×10^{-1} torr, and Xe partial pressures were calculated from this value and the known Xe/F_2 ratio at the end of the run.

Medium pressure range ($1 \rightarrow 15 \times 10^{-2}$ torr of Xe). The same procedure was followed except that the ^{133}Xe in the mixing volume was diluted with inactive Xe to a pressure of 3×10^{-1} torr. The diluted ^{133}Xe was frozen out at 77.5°K in a cold finger attached to the mixing volume while the F_2 pressure was built up to 6×10^{-1} torr. A Xe/F_2 ratio of 1:2 was then attained by warming the cold finger to room temperature, and the Xe and F_2 were allowed to mix for 30 min before the adsorption run was commenced. The Xe could be recovered for use in another run by freezing out the Xe in the cold finger of the mixing bulb and then adjusting the F_2 pressure to obtain the desired Xe/F_2 ratio.

High pressure range ($1 \rightarrow 9 \times 10^{-1}$ torr of Xe). The ^{133}Xe was diluted with inactive Xe so that a pressure of about 2 torr was attained in the mixing volume and the Xe/F_2 ratio was adjusted as before to 1:2.

RESULTS

Adsorption on Palladium

A test for catalytic activity was made by heating the palladium foil to temperatures varying from 120 to 200°C in the presence of a mixture of 100 torr of xenon with 100 torr of fluorine. The drop in total pressure was consistent with a reaction rate comparable to the previous data(*1*).

An adsorption experiment was then carried out in the medium pressure range and the count rates were determined as a function of the total pressure. The results for xenon adsorption, which include the contribution from the gas phase, are shown at various temperatures in Fig. 3. Xenon partial pressures were calculated from the total pressure using the known xenon/ fluorine ratio. At the conclusion of an ad-

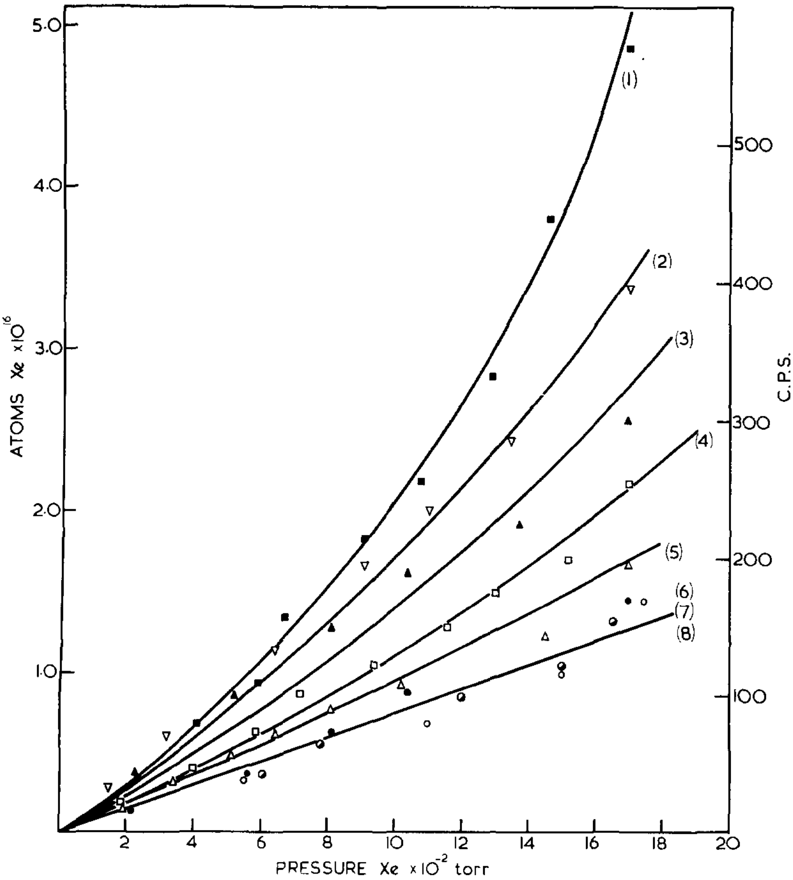

FIG. 3. Adsorption of Xe and F_2 on "conditioned" Pd foil (°K): (1) 243; (2) 278; (3) 293; (4) 333; (5) 373; (6) ●, 413. Adsorption of Xe only on untreated clean Ni (°K): (7) ○, 293; (8) ◒, 247. All isotherms include background contribution from gas phase.

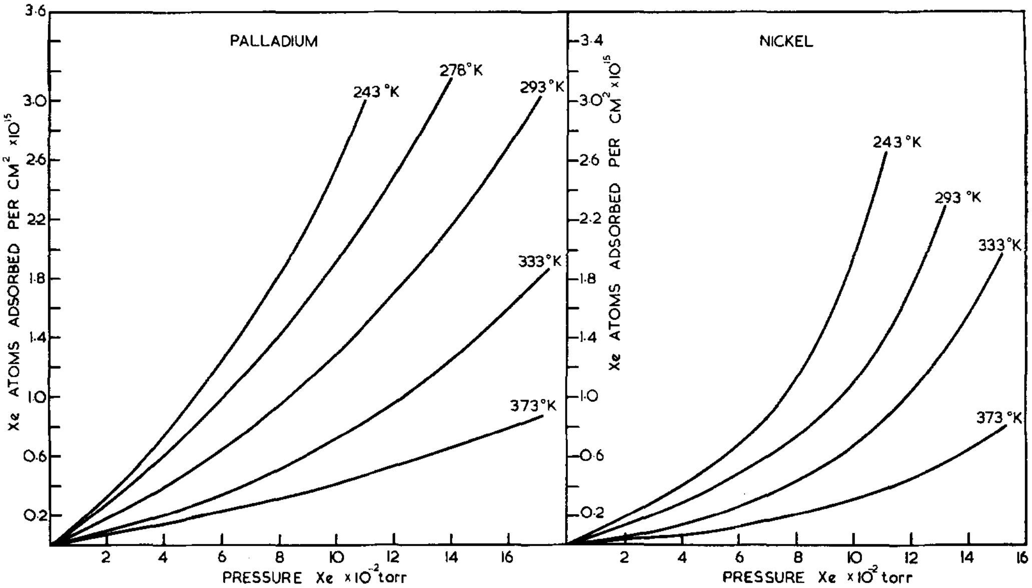

FIG. 4. Adsorption of Xe and F_2 on Pd and Ni at various temperatures. The background contribution from the gas phase has been subtracted.

sorption run, when the gas-phase xenon was removed from the adsorption vessel, the count rate returned to background level which indicated that the adsorption was reversible. A further adsorption run at the same temperature showed that the adsorption result was reproducible.

Gas Phase Contribution

Above 413°K there was no further change in the isotherms, and this suggested that the count rate obtained at this temperature was mainly due to the gas phase. This was tested by replacing the palladium foil with a nickel specimen, and conducting the experiment as before but using xenon only which had been recovered from the previous runs. The thickness of the foils was sufficient to cause saturation back scattering of the ^{133}Xe β-particles. Only a small correction for back scattering (7%), obtained from the results of Jaffe and Justus (*3*), was therefore necessary so that the count rates in the presence of the palladium and nickel foils could be compared. The corrected results on clean nickel are shown in Fig. 3 as plots 7 and 8 at temperatures of 247 and 293°K, respectively. Both these plots are identical to plot 6 in the same Fig. 3, and this confirms that the result at 413°K on the Xe/F_2/Pd system represents no adsorption. This result was the basis of corrections for the contribution to the count rate due to the gas phase at all temperatures. The results for xenon adsorption on palladium, corrected for gas-phase contribution are shown in Fig. 4.

Calibration of Counts per Second

The gas-phase plot 6 in Fig. 3 shows that at a pressure of 10^{-1} torr the count rate is 88 cps. The dead volume between the specimen and the counter window is 2.5 cm^3 and hence the number of atoms present in the dead volume at 10^{-1} torr is 7.5×10^{15} atoms. The equivalence 88 cps $= 7.5 \times 10^{15}$ atoms has therefore been used to convert counts per second to number of atoms and this scale is shown in Fig. 3 together with the scale representing cps. In Fig. 4, the results are presented as the number of atoms adsorbed per square centimeter of the surface assuming a geometric surface area of 5 cm^2. A similar method of conversion was used with other pressure ranges where the specific activity of the ^{133}Xe was an order of magnitude different. In a previous paper (*2*), using a similar apparatus, calibration of the counter was achieved from a standard ^{14}C source to obtain the necessary conversion factor. The same factor is obtained if the present conversion method is applied to the results in that paper, confirming that the difference in counting geometry between the adsorbed layer and gas phase is unimportant.

Adsorption on Nickel

It was concluded [Fig. 3, plots (7) and (8)] that clean nickel did not adsorb xenon at 293°K. A xenon/fluorine mixture was then admitted to the adsorption vessel containing the clean nickel specimen and the catalytic activity of the nickel confirmed, as before with palladium, by observing a pressure drop in the apparatus. Adsorption runs were now conducted, using $^{133}Xe/F_2$ mixtures made up as before, and the results showed that nickel would adsorb xenon at temperatures from 243 up to 373°K. The results are shown in Fig. 4, where they may be compared with the results on palladium.

The extent of uptake of xenon shown in Fig. 4 indicates that an examination of the adsorption at lower pressures is necessary to obtain data below the "monolayer" value. The results also show that it is possible to measure the adsorption of xenon at higher pressures without a large correction being made for the gas phase. A series of adsorption measurements were therefore made over three decades of pressure, using

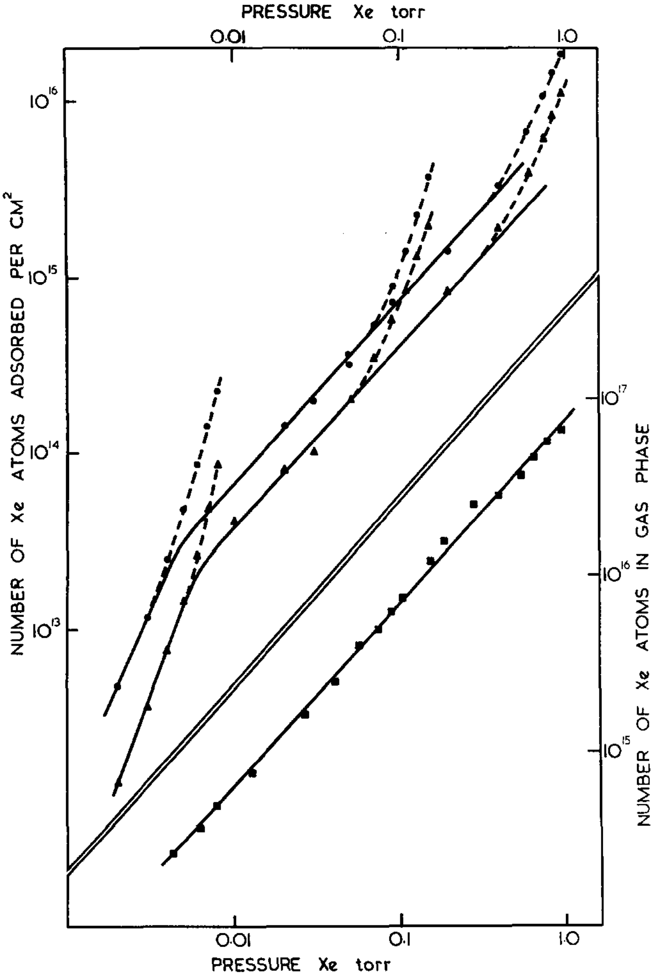

Fig. 5. Adsorption of Xe and F_2/cm^2 of nickel surface at 20°C = ●, and at 60°C = ▲ measured over three decades of pressure; ■ = gas-phase counts over same range of pressure, showing correlation between ranges.

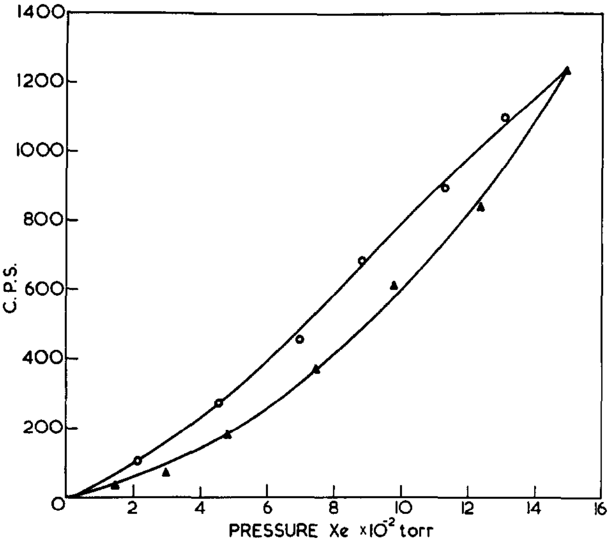

FIG. 6. Adsorption hysteresis: Adsorption = ▲, and desorption = ○, of Xe and F_2 on nickel at 293°K.

three different samples of xenon differing from one another in specific activity by one order of magnitude. The results, corrected for gas phase contribution are shown in Fig. 5 at temperatures of 293 and 313°K. Also shown in the same plot is the correlation of the gas phase results obtained over the three ranges of pressure. Although the correlation of the gas phase results is good, the adsorption results show that a discrepancy is evident at the junction of the ranges, which suggests nonequilibrium behavior.

Desorption of the xenon was therefore investigated, and, at the end of an adsorption run, the xenon/fluorine gas phase was removed from the adsorption vessel in a stepwise manner, and the count rate from the surface was determined as a function of the pressure of the gas mixture until all of the gas phase was removed. Figure 6 shows that adsorption hysteresis occurs,

FIG. 7. Electron micrographs of Pd foils (a) untreated, (b) after heating in F_2, and (c) after heating in Xe/F_2.

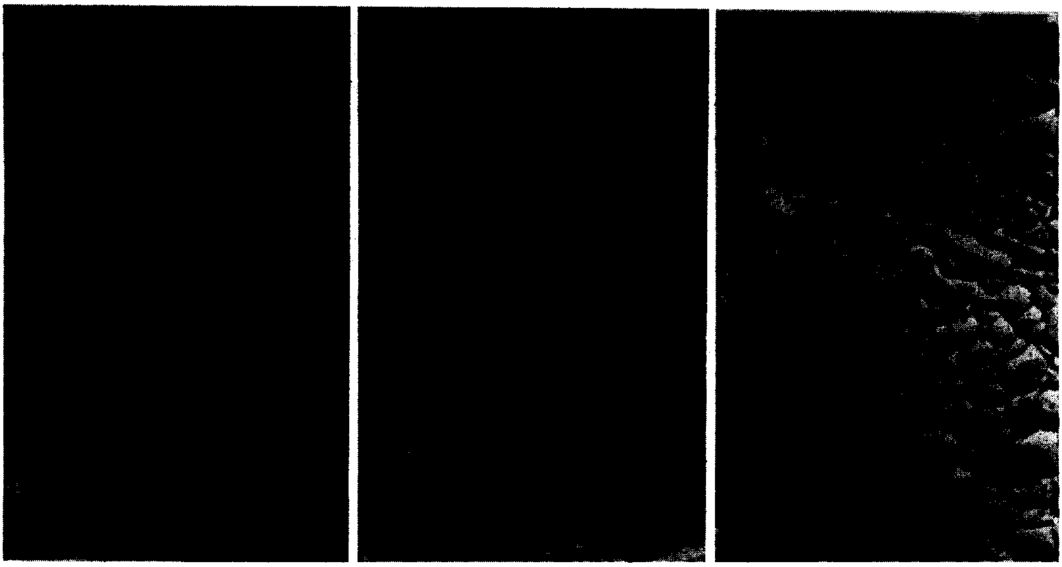

FIG. 8. Electron micrographs of Ni foils (a) untreated, (b) after heating in F_2, and (c) after heating in Xe/F_2.

but also shows that all of the adsorbed xenon is removed when the gas-phase xenon is removed.

Study of Surface Structures

The surfaces of the foils were examined after the catalysis and adsorption experiments. Replicas of the nickel and palladium surfaces were made (a) before any treatment with fluorine or xenon; (b) after heating in the presence of 100 torr of fluorine at 200°C for 5 hr; and (c) after catalysis with 100 torr of xenon and 100 torr of fluorine at 120–200°C for a total of 5 hr. Electron micrographs of these replicas are shown in Fig. 7 for palladium and in Fig. 8 for nickel. Clearly the presence of xenon has caused a marked change in the surface structure of the foils, and there is an enhanced attack of the metal by the fluorine.

Examination of the palladium foil surface with an optical microscope showed that the rapid attack by fluorine in the presence of xenon had caused the formation of a thick deposit. This deposit was stripped from the underlying metal and identified as PdF_2 by X-ray and electron diffraction. Some extra rings appeared in both electron and X-ray diffraction patterns. Grazing incidence electron diffraction patterns from reacted nickel specimens contained rings consistent with NiF_2.

DISCUSSION

The experiments were designed to detect the chemisorption of xenon under the conditions of catalytic formation of xenon difluoride. The metal foils were therefore conditioned by a catalysis experiment before measuring the adsorption. Because the counting of the radioactive adsorbed xenon required that the gas pressure be low, the adsorption data was obtained at temperatures slightly below the catalysis range. Physical adsorption of xenon would be expected to be negligible at these temperatures (243–373°K) (*4*) and in fact no adsorption on pure nickel was detected by the counting technique.

In the presence of fluorine a large uptake of xenon was observed on the conditioned foils. The amount adsorbed was many times that expected for a monolayer. This could be due to either a high surface roughness providing a large area for adsorption, or to the incorporation of xenon into the layer of metal fluoride growing at the surface. The examination of the surface by optical microscopy showed that a deposit, identified as the metal difluoride, covered the surface. It is likely that the true area of this fluoride deposit is large and that xenon is adsorbed only on this surface. The observation that xenon could be removed quickly by pumping suggests that little, if any, is incorporated within the fluoride structure.

The electron micrographs of the foils show that the presence of xenon markedly enhances the attack of fluorine on the metal and results in a very rough surface. It should be noted that the xenon–fluorine bond length in the xenon fluoride is 2.0 Å which is approximately the same as the Ni–F and Pd–F distances in the metal difluoride crystals. It is conceivable therefore that while most of the xenon must remain at the surface, a small amount, not detected here, could be incorporated into the fluoride lattice. In the metal–oxygen system, it is well known that the presence of impurities can cause an enhanced attack of the metal and a very rough surface. A parallel may exist in the Xe–metal–fluorine system with xenon acting as the dopant.

However, the kinetics of such processes have recently been explained on the basis of a rate-controlling surface mechanism (*5*), where the rate-determining step is the transfer from the adsorbed state to the ionized state. It is therefore suggested that xenon, chemically bound to fluorine, assists the formation of F^- ions which can then migrate through the fluoride layer. Enhanced attack of the metal results in a large surface area, and large uptake of xenon.

Removal of the adsorbed xenon is likely to produce an unstable surface, and surface rearrangements would then take place to form a lower surface area. This explains the discrepancy at the junction of the ranges shown in Fig. 5. At the start of a new range the surface area is lower than that at the end of the preceding range due to surface rearrangement on removal of the xenon. The hysteresis shown in Fig. 6 supports this idea.

Clearly there is a large concentration of xenon present on the surface of the foils at pressures considerably lower than, and at temperatures approaching those used in the catalytic experiments (*1*). This is consistent with the zero-order kinetics observed for xenon during xenon/fluorine catalysis.

The adsorption of xenon causes a drastic modification of the surface and hence the isotherms presented here cannot be treated as equilibrium isotherms. However, although the heat of adsorption cannot be calculated, the narrow range of isotherms over a wide range of temperature suggests that the heat is of the order of 5 kcal $mole^{-1}$. Although this heat is low, the temperature range over which xenon is adsorbed in these experiments suggests that the adsorption is chemisorption.

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