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Temperature Programmed Desorption Spectroscopy of N_2H_4 Decomposition on Al_2O_3-Supported Ir Catalyst[1]

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At room temperature the steady-state decomposition of N_2H_4 over an alumina-supported Ir catalyst was found to yield NH_3 and N_2 while at temperatures above 800 K the products were N_2 and H_2. Following exposure of the catalyst surface to N_2H_4 the adsorbed species were studied by the temperature programmed desorption technique at a heating rate of 2 K s^{-1}. The desorption products included N_2, NH_3 and H_2 originating from different binding states. For the more strongly bound nitrogen $[N_2(\beta_2)]$ the kinetics of desorption following exposure to N_2H_4 are of first-order with a desorption rate constant of $3 \times 10^7 \exp(-26{,}800/RT)$ s^{-1}. Adsorption of oxygen on the iridium catalyst was found to decrease the nitrogen binding energy and increase the nitrogen coverage. The surface coverage of all adsorbed species was found to be significantly smaller on catalysts that had been used in pulse mode fuel thrusters. The differences observed were correlated with the loss in metal surface area of the catalyst. However, no differences in the binding energies of the various adspecies were detectable between fresh catalyst and used catalyst.

A. INTRODUCTION

In a preceding study (*1*) of hydrazine decomposition on the surface of polycrystalline iridium it was noted that strongly bound adsorbed species were formed, particularly chemisorbed nitrogen, that led to a gradual reduction of the catalytic activity of the Ir ribbon. In the present study this work is extended to finely dispersed Ir crystallites on an alumina support,[2] as currently used for catalytic decomposition of N_2H_4 in monopropellant thrusters. To elucidate the nature of the surface adsorbate, we carried out temperature-programmed desorption (TPD) spectroscopy after exposure of the powdered catalyst to aliquots of hydrazine in a microreactor. This catalyst is particularly amenable to study of this experimental approach because of its high metal weight loading and relatively large Ir surface area. Analysis of the experimental data permits identification of adsorbed species, their binding state on the surface, and their relative surface coverage. Also, our work on the catalyst allows comparison with another alumina-supported Ir catalyst prepared by Contour and Pannetier (*2*).

The purpose of our work is twofold: (a) to elucidate the causes of catalyst activity loss that occurs in operational monopropellant thrusters, and (b) to determine the mechanism of heterogeneous decomposition of hydrazine on the supported iridium catalyst.

A shorthand notation is adopted for describing the origin of each desorbing gas during TPD. The term A(*x*)/B(*T*) refers to desorption of the *x*-state of gas A

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[1] Support of this research by the Air Force Office of Scientific Research (Contract No. AFOSR F44620-73-C-0069) is gratefully acknowledged.

[2] This catalyst was prepared by Shell Development Co. under the designation "Shell-405."

following adsorption of gas B at temperature T (°C). For adsorption studies carried out at room temperature the temperature designation is omitted from the notation.

B. EXPERIMENTAL DETAILS

The apparatus was designed for continuous or pulsed flow studies, and for TPD experiments following exposure of the catalyst to reactants. The catalyst sample (0.1 g) was placed on a Vycor frit contained in a Vycor reactor (1 cm o.d.). The carrier gas, helium or argon, flowed continuously through the reactor at atmospheric pressure at a flow rate of 100 cm^3/min, corresponding to a catalyst contact time of about 6×10^{-2} s. The reactor was heated electrically by means of a nichrome-wound quartz tube placed around it. The catalyst temperature was measured by a Chromel–Alumel thermocouple in contact with the catalyst. The thermocouple wires (0.005 in. diam) led from the reactor to a feedthrough and a recording instrument. While heating rates (δ) of 0.2 to 4 K s^{-1} were obtainable with this arrangement, most TPD experiments were performed at 2 K s^{-1}. After leaving the reactor the products resulting either from steady-state decomposition or from TPD were continuously analyzed by mass spectrometry (EAI quadrupole mass spectrometer). For this purpose a small fraction of the gas stream leaving the reactor was leaked through an adjustable orifice into the differentially pumped mass spectrometer system operating at a total pressure of 10^{-6} Torr. For TPD studies the supply of reactant was shut off while the inert carrier gas continued to flow through the reactor. After attainment of the "background" gas composition the temperature of the catalyst was raised linearly at a prescribed heating rate. Quantitative analysis of the desorption products as a function of catalyst temperature was carried out by simultaneous recording of the mass spectrometer signal and the thermocouple output.

To obtain an absolute measure of the degree of surface coverage with the various adspecies during TPD and the product stoichiometry during flow experiments, it was necessary to calibrate the mass spectrometer. Empirical calibrations for NH_3, N_2, and H_2 were obtained by injecting known amounts of each of the gases into the carrier stream flowing through the reactor and observing the total signal detected by the mass spectrometer.

Hydrazine was admitted by injecting a pulse of the liquid (0.01–10 μl) through a septum into the reactor, which was continuously swept by the helium stream. In continuous flow experiments N_2H_4 was fed through the septum from a gastight syringe, using a Sage syringe pump to maintain constant mass flow. A small auxiliary nichrome heater kept the inlet portion of the reactor wall sufficiently warm to vaporize the hydrazine so that only vapor contacted the catalyst. A similar procedure was used in experiments with water. Other gases (NH_3, N_2, H_2, O_2) were introduced into the reactor either by continuous flow from a storage cylinder or by injection of small pulses through the septum using a gastight syringe.

To obtain reproducible TPD spectra it was found necessary to reduce the iridium catalyst by exposure to several doses of 5 μl N_2H_4 at room temperature followed by heating to 800°C. The TPD studies were then carried out on the reduced catalyst after varying amounts of liquid N_2H_4 or gaseous NH_3 or H_2 had been injected to obtain different levels of surface coverage.[3] After the mass spectrometer signals had returned to their background levels, the catalyst was subjected to a prescribed heating cycle and the products were monitored as a function of catalyst temperature.

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[3] Approximately 1 μl of liquid N_2H_4 or 250 μl of gaseous NH_3 or H_2 were sufficient to yield saturation coverage. (Additional exposure did not yield any quantitative change in the TPD spectra.)

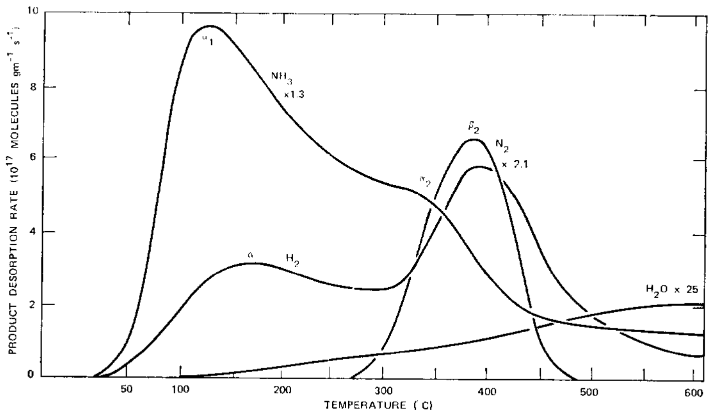

FIG. 1. NH_3, H_2, N_2, and H_2O TPD Peaks for N_2H_4 adsorption (saturation coverage) on fresh Ir/Al_2O_3 catalyst.

The iridium surface areas on the catalysts were measured by "surface titration," similar to that used for platinum (*3*), employing the reaction of chemisorbed oxygen with gaseous carbon monoxide. Oxygen was adsorbed at atmospheric pressure and 25°C after catalyst reduction in H_2 at 300°C for 2 hr and cooling in He to room temperature. Pulses containing known amounts of carbon monoxide in helium were passed over the catalyst. The oxygen adatoms on the Ir sites react to form CO_2. Pulsing of CO was continued until no further sorption of CO occurred. Gas chromatographic measurements of the total CO_2 formed allow calculation[4] of the iridium surface area (*4*).

The iridium catalyst contained 32 wt% iridium on a low surface area alumina. Two samples were studied, one a fresh catalyst (A), and the other (B), a catalyst that had been exposed to about 1100 mol N_2H_4/g of catalyst in pulse-mode operation.[5] The fresh catalyst had a particle size distribution equivalent to 25–30 mesh, while the used catalyst was in the size range of 30–35 mesh because of particle breakup in the thruster.

Hydrazine (Anhydrous-Technical grade from Olin Chemicals), containing 3% water, was used in the initial studies. However, most of the data were obtained with specially purified anhydrous N_2H_4 (obtained from Martin-Denver).[6] Mass spectrometer analysis indicated the presence of less than 1% water and no other detectable impurity. All gases used in our studies were of high purity, and were used directly from the cylinders without further purification.

C. RESULTS

1. *Desorption Studies with Fresh Catalyst (Shell-405)*

After the reduced catalyst (A) had been exposed to hydrazine, it was subjected to TPD, and the concentration of each gaseous product leaving the solid surface was recorded. Figure 1 shows the mass peaks due to N_2, H_2, NH_3, and H_2O following N_2H_4 exposure sufficient to produce saturation coverage. No other desorption products were detected, and no unreacted N_2H_4 desorbed from the surface. At saturation coverage the N_2/N_2H_4 consisted of a

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[4] The ratio of oxygen atoms sorbed per surface Ir atom needs to be known to convert the mass of CO_2 produced to the number of Ir surface atoms. In our calculations we use $O/Ir = \frac{1}{2}$, based on separate adsorption studies with oxygen.

[5] These tests were carried out by Rocket Research Corp., Redmond, Wash.

[6] We are grateful to Mr. L. William, who kindly supplied the purified N_2H_4.

TABLE 1

Temperature-Programmed Desorption Peaks for Ir/Al_2O_3 Catalyst

	Temp (°C)			
Product Adsorbate:	N_2H_4	NH_3	H_2	H_2O
N_2	390 (β_1) ~315 (β_1^1)	390 (β_2) 310 (β_2)	—	—
H_2	400 (β) 175 (α)	400 (β)	135 (α)	—
NH_3	335 (α_2) 140 (α_1)	335 (α_2) 140 (α_1)	—	—
H_2O	Broad peak at 800°C	—	Broad peak at 800	320 (α_2) 107 (α_1)
N_2[a]	355 (β) 180 (α_2) 100 (α_1)			

[a] On catalyst preexposed to oxygen.

single peak $N_2(\beta_2)$ with a peak temperature of 390°C; the H_2/N_2H_4 exhibited a broad peak at 140°C [$H_2(\alpha)$] and a $H_2(\beta)$ peak at approximately 400°C; and the NH_3/N_2H_4 desorbed in two very broad peaks located at 140°C [$NH_3(\alpha_1)$] and 355°C [$NH_3(\alpha_2)$]. The H_2O/N_2H_4 desorption consisted of a very small but broad peak extending to very high temperatures, characteristic of water desorption from the Al_2O_3 support. The peak labels and peak temperatures at initial saturation coverage are listed in Table 1.

To characterize the desorption process more accurately, the desorption peaks were recorded at lower initial surface coverages. Figure 2 shows a series of H_2/N_2H_4 for different intial exposures to N_2H_4. At low coverages only the $H_2(\beta)$ peak was occupied, and with additional hydrazine exposure, the $H_2(\alpha)$ peak became filled. Also, it was noted that with decreasing N_2H_4 exposure, the total mass of NH_3 adsorbate diminished and the NH_3 desorption shifted to higher temperature values. A series of N_2/N_2H_4 desorption studies at

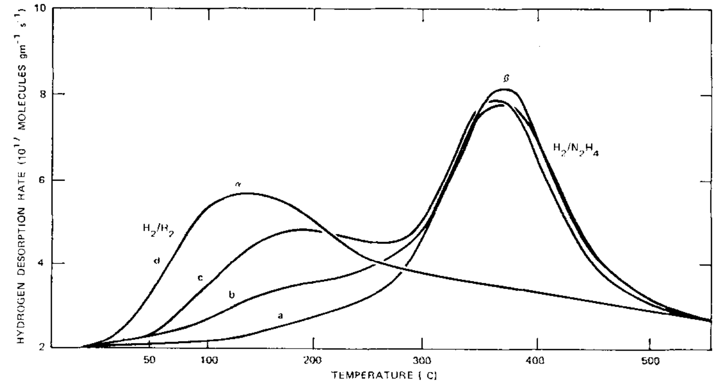

FIG. 2. H_2/N_2H_4 TPD spectra for fresh Ir/Al_2O_3 catalyst. Exposure N_2H_4 (μl): (a) 1, (b) 2, (c) 5, (d) H_2/H_2 flash desorption for saturation exposure.

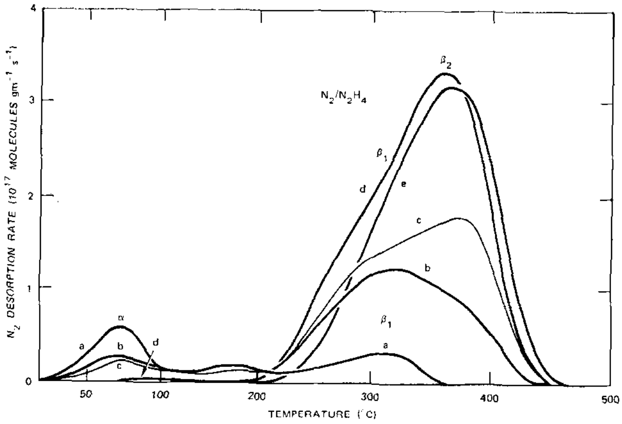

FIG. 3. N_2/N_2H_4 TPD spectra for fresh Ir/Al_2O_3 catalyst. Exposures N_2H_4 (μl): (a) 0.02, (b) 0.05, (c) 0.1, (d) 0.3, (e) 1.0.

different initial coverages demonstrated that lowering of the surface coverages caused the β peak to decrease and the α peak to increase (Fig. 3).

To provide additional detail on the desorption kinetics involved in nitrogen formation, a series of TPD experiments were carried out after N_2H_4 exposure of the catalyst at 275°C. By using such a high initial surface temperature we were able to eliminate the $H_2(\alpha)/N_2H_4$, the $NH_3(\alpha_1)/N_2H_4$, and most of the $NH_3(\alpha_2)/N_2H_4$. The resultant N_2/N_2H_4 (275) TPD spectra, shown in Fig. 4, indicated that the $N_2(\beta_2)/N_2H_4$ peak temperature did not change with initial surface coverage, i.e., the N_2 was formed by a first-order process. Although the $H_2(\beta)/N_2H_4$ (275) peak exhibited a higher peak temperature than the N_2/N_2H_4 (275) peak and a much larger temperature tail, the total mass ratio of $H_2(\beta):N_2(\beta_2)$ was (3.2 ± 0.2):1 after exposure of the Ir catalyst to saturation N_2H_4 coverage at 275°C.

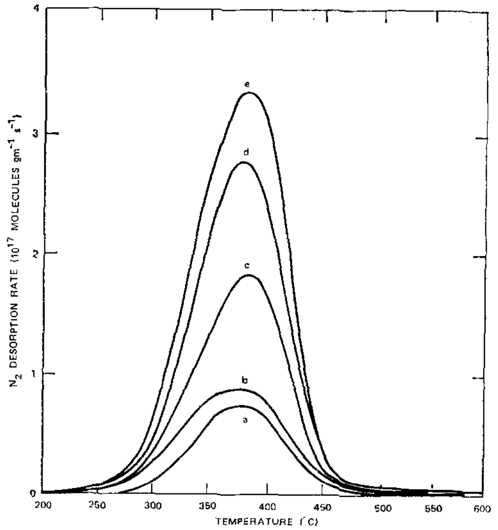

FIG. 4. N_2/N_2H_4 (275) TPD spectra for fresh Ir/Al_2O_3 catalyst. Exposures N_2H_4 (μl): (a) 0.02, (b) 0.035, (c) 0.05, (d) 0.1, (e) 5.0.

By varying the heating rate ($0.25\ K\ s^{-1} \leq \delta \leq 3.6\ K\ s^{-1}$), we determined the activation energy for formation of the well-defined $N_2(\beta_2)/N_2H_4$ at constant initial saturation surface coverage. As the heating rate δ increased, the desorption curves shifted to higher temperatures and increased in amplitude, but the total mass of adsorbate remained the same. From the changes in T_p (peak temperature) and N_p (peak amplitude) with δ, the activation energy, *E*, could be determined without knowledge of the preexponential factor (*5*, *6*). Figure 5 shows the resultant plots of ln (δ/T_p^2) versus $1/T_p$ and ln N_p versus $1/T_p$. From the slope of the lines analyzed by least-squares fit of the data, one obtained activation energies of 27.4 kcal/mol (Fig. 5a) and 26.2 kcal/mol (Fig. 5b).

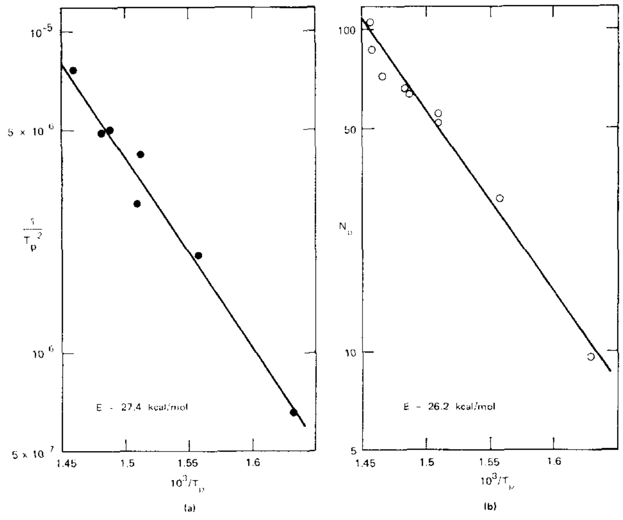

FIG. 5. Activation energy determination from heating rate variation. (a) ln (δT_p^2 vs $1/T_p$ for $N_2(\beta_2)/N_2H_4$; (b) ln N_p vs $1/T_p$ for $N_2(\beta_2)/N_2H_4$.

From the intercept of the curve in Fig. 5a, the preexponential factor can be determined on the basis of a first-order reaction, as indicated by the constancy of the peak desorption temperature with coverage. Using the average value of E $[N_2(\beta_2)/N_2H_4] = 26.8$ kcal/mol, we calculated a preexponential factor of 3×10^7 s^{-1}.

2. *Desorption Studies with Catalyst B*

The TPD spectra obtained for catalyst B exhibited desorption peak temperatures and the relative surface populations of the different adspecies (Fig. 6) similar to those obtained for catalyst A (Fig. 1). However, the total mass of adsorbate, as determined from the integrated areas under the TPD curves, demonstrated marked differences (Table 2). Also, the surface area of these catalysts, measured after the TPD experiments, was found to have decreased appreciably (Table 2).

3. *Effect of Hydrogen Adatoms on Hydrazine Decomposition*

Hydrogen was coadsorbed with hydrazine on catalyst A to obtain a better under-

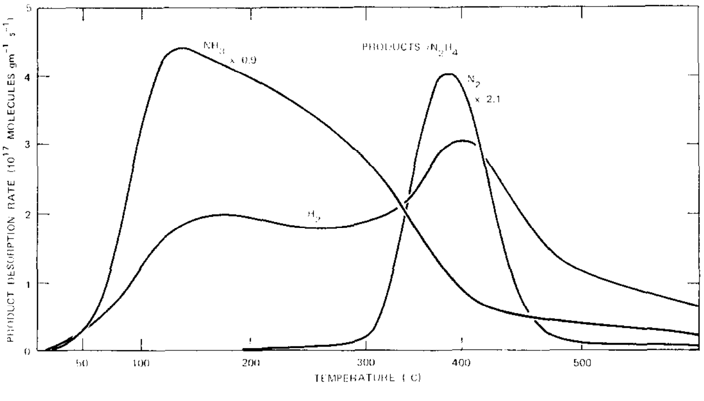

FIG. 6. NH_3, N_2, and H_2 TPD Peaks for N_2H_4 adsorption (saturation coverage) on used Ir/Al_2O_3 catalyst.

TABLE 2

Surface Coverages for Ir/Al_2O_3 Catalyst

Product/ adsorbate	Surface adsorbate ($\times 10^{-19}$ molecules/g catalyst) Catalyst A[a]	Catalyst B[a]	Relative change (%)
H_2/H_2	7.2	4.2	42
H_2/NH_3	—	3.2	—
H_2/N_2H_4	8.2	5.4	34
H_2/N_2H_4 (275)	4.1	3.3	20
N_2/N_2	0	0	—
N_2/NH_3	2.1	1.2	43
N_2/N_2H_4	1.5	0.9	40
N_2/N_2H_4 (275)	1.3	—	—
NH_3/NH_3	9.7	6.1	40
NH_3/N_2H_4	9.7	6.5	35
H_2O/H_2O	21.2	—	—
Iridium surface area (m^2/g Ir)	130[b]	83	39

[a] Samples from Rocket Research Corporation, Redmond, Wash.

[b] This catalyst had been exposed to a series of TPD experiments as a result of which its surface area was somewhat lower than the original value (cf. text).

standing of the decomposition mechanism. A steady flow of H_2 in He was maintained over the surface, while liquid hydrazine was injected through the septum. After a given exposure to reactant, TPD spectra were obtained both in the presence and absence of H_2 in the carrier stream.

For NH_3/N_2H_4, N_2/N_2H_4, and H_2/N_2H_4, the differences in desorption characteristics with and without H_2 coadsorption were found to be within the experimental error (±10%). The products formed from N_2H_4 decomposition also remained unaffected by hydrogen.

4. *Steady-State Flow Experiments*

To examine the product distribution resulting from the Ir-catalyzed decomposition of N_2H_4 over a range of temperatures, 3 μl samples of N_2H_4 were injected into the reactor containing catalysts A or B, and the reaction products were monitored by mass spectrometry. The mass of injected N_2H_4 was large relative to the amount remaining adsorbed on the surface. Steady-state activity was verified by product analysis for repeated injections of 3 μl N_2H_4 at a given temperature, which ranged from 25 to 800°C. Product gases were injected for calibrations at frequent intervals, so that absolute quantities of products could be determined. Figure 7 shows the amounts of N_2, H_2, and NH_3 produced per mole of N_2H_4 in the presence of catalyst A. Below 300°C hydrazine decomposes almost exclusively to form N_2 and NH_3 according to the stoichiometry:

$$3\,N_2H_4 \rightarrow N_2 + 4\,NH_3, \qquad (1)$$

and above 600°C to form N_2 and H_2 with the stoichiometry:

$$N_2H_4 \rightarrow N_2 + 2H_2. \qquad (2)$$

At intermediate temperatures both reactions contribute to the product distributions.

Similar experiments were performed with NH_3 as the reactant by injecting 1000 μl of gaseous NH_3 and observing the decomposition products as a function of catalyst temperature. Figure 8 shows the amount of N_2 formed and the amount of undecomposed NH_3 per mole of injected NH_3. Below 300°C we observed little NH_3 decomposition on catalyst A; however, above 600°C all of the NH_3 decomposed to N_2 and H_2 with a satisfactory mass balance.

A series of runs were carried out in which catalyst A was continuously exposed to N_2H_4 for prolonged time periods at temperatures from 25°C to 435°C. A syringe pump provided continuous feed rates of 2–10 μl liquid N_2H_4/min. The total cumulative exposure was equivalent to 1.1 mol N_2H_4/g of catalyst. Also, the catalyst was given many heating cycles to 750°C after N_2H_4 exposure. For all flow rates used complete reaction occurred at and above room temperature under our experimental conditions. While TPD studies did not reveal any differences in desorption char-

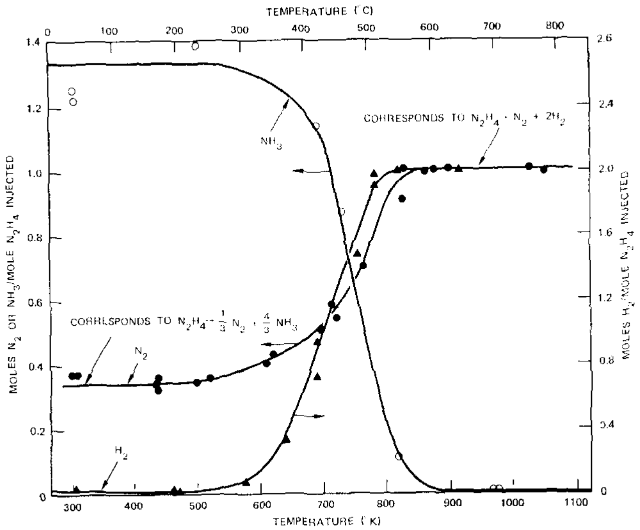

FIG. 7. Products of N_2H_4 decomposition catalyzed by Ir/Al_2O_3 catalyst at different temperatures (data collected during response of catalyst to a series of 3 μl aliquots of liquid N_2H_4).

acteristics of the catalyst after prolonged exposure to N_2H_4, the iridium surface area of catalyst A had decreased from 154 to 134 m^2/g Ir. By way of comparison, catalyst B, which was used in a rocket thruster and had been exposed to 1097 mol N_2H_4/g catalyst, had a surface area of 83 m^2/g Ir.

DISCUSSION

In elucidating the mechanism of the Ir-catalyzed decomposition of hydrazine, it is important to examine the conditions that affect rupture of the N–N bond, i.e., dissociative vs nondissociative adsorption. Thus, to determine whether the TPD products following hydrazine exposure are reaction or desorption limited, a study was carried out of the TPD characteristics of some of the products observed.

The TPD spectra of N_2, H_2, and NH_3 following ammonia adsorption on the Ir/Al_2O_3 catalyst at room temperature are shown in Fig. 9. The NH_3/NH_3 desorption

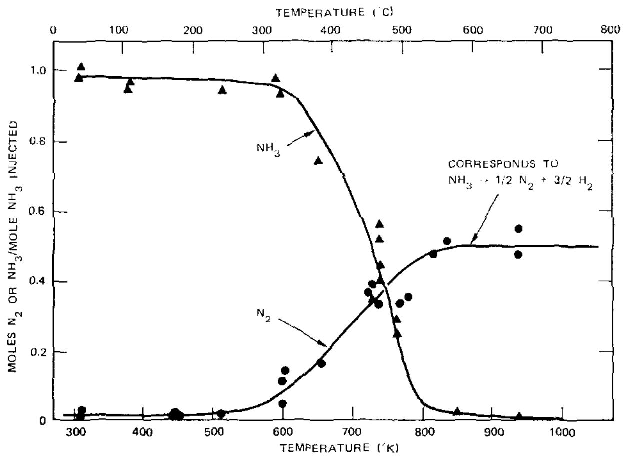

FIG. 8. Products of NH_3 decomposition catalyzed by Ir/Al_2O_3 catalyst at different temperatures (data collected during response of catalyst to a series of 1000 μl aliquots of gaseous NH_3).

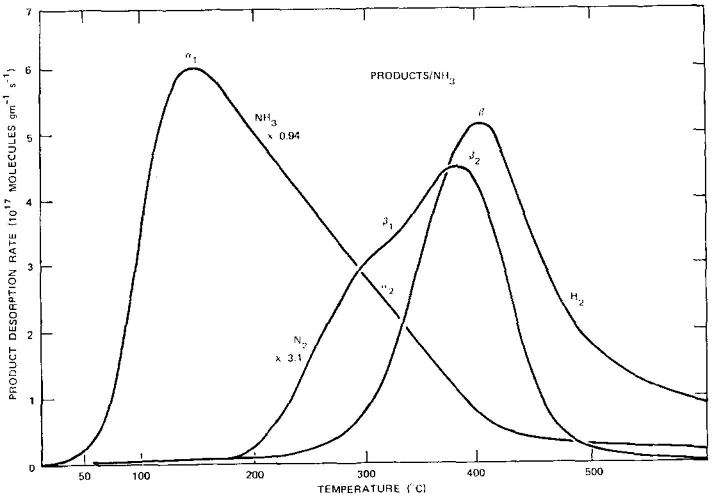

FIG. 9. NH_3, H_2, and N_2 TPD peaks for NH_3 adsorption (saturation coverage) on fresh Ir/Al_2O_3 catalyst.

exhibited a major peak at 140°C and a small peak above 300°C, which became particularly evident at lower NH_3 surface coverages. The N_2/NH_3 and N_2/NH_3 were found to desorb in a 3:1 ratio at nearly the same peak temperature (Table 1). Therefore, one may conclude that they were formed from the same adsorbed species, an ammonia molecule. A comparison of the data in Figs. 1 and 9 indicates strong similarities between the sorption characteristics of NH_3 and N_2H_4 on Ir/Al_2O_3. The NH_3/NH_3 and NH_3/N_2H_4 TPD peaks occur at the same temperature, and the surface coverages with each of these species are nearly the same (Table 2). Also, the $N_2(\beta)/NH_3$ and $H_2(\beta)/N_2H_4$ peaks are similar, especially in comparison with H_2/N_2H_4 at low hydrazine coverages, where the $H_2(\alpha)/N_2H_4$ peak is absent

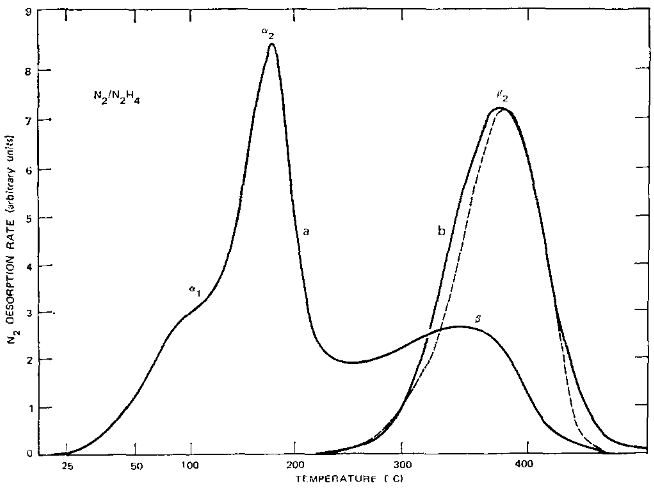

FIG. 10. N_2/N_2H_4 TPD peaks for saturation N_2H_4 coverage on (a) oxidized catalyst (b) reduced catalyst. (— —) Theoretical first-order desorption curve for rate constant of 3×10^7 exp(26,800/RT) s^{-1}.

(Fig. 2). The TPD in Fig. 2 indicates that the $H_2(\alpha)/N_2H_4$ peak corresponds to $H_2(\alpha)/H_2$. Finally, the N_2/N_2H_4 and N_2/NH_3 peaks exhibit similarities, although the N_2/N_2H_4 peak is smaller than the N_2/NH_3 peak at high N_2H_4 exposure (Fig. 3). The strongly bound $N_2(\beta)$, with a peak desorption temperature of 390°C, is essentially the same for N_2/NH_3 and N_2/N_2H_4. But following NH_3 adsorption an additional peak $N_2(\beta_1)$ is observed, which was detected only at low hydrazine coverages. The origin of $N_2(\beta_1)$ is uncertain. It may be due to the existence of an oxygen adsorbate on the Ir surface, which is removed at room temperature by exposure to hydrazine but not reduced by NH_3. As a matter of fact, the two distinct N_2/N_2H_4 spectra shown in Fig. 10 for saturation N_2H_4 coverage at room temperature indicate the effect of adsorbed oxygen on catalyst A. Curve (a) was obtained after the first exposure of the catalyst to N_2H_4. A similar curve was also obtained following N_2H_4 exposure to catalyst A after brief oxygen contact. Curve (b) represents the reproducible spectra obtained for N_2/N_2H_4 on the reduced catalyst. It is identical to the spectra in Fig. 1. Curve (a) corresponds to a total surface coverage of 4.9×10^{19} N_2 molecules/g catalyst, while curve (b) to 1.5×10^{19} N_2 molecules/g catalyst. These results indicate that in the presence of oxygen adatoms the nitrogen coverage is increased and its binding energy reduced.

TPD spectra were also obtained for H_2O/H_2O and H_2O/H_2. Comparison with H_2O/N_2H_4 indicates the H_2O/N_2H_4 was due to hydrogen formed during the hydrazine decomposition. Thus, the H_2O/N_2H_4 did not result from the presence of water in the hydrazine, but more likely from adsorbed hydrogen atoms, which reacted with alumina OH groups or reduced the surface-oxidized iridium with water as a product (*2*).

Using the slope and intercept obtained from the heating rate variation for $N_2(\beta_2)/N_2H_4$, we found that the adsorbed intermediate that yielded N_2 and H_2 products decomposed with a first-order rate constant equal to $3 \times 10^7 \exp(26{,}800/RT)$ s^{-1}. A first-order rate expression with this rate constant was integrated numerically for a 2 K s^{-1} heating rate as a function of temperature to determine the expected desorption curve. The broken curve in Fig. 10 corresponds to that integration, and the agreement with the experimentally observed curve is quite good.

By comparison with the NH_3 experiments we conclude that the H_2- and N_2-peaks formed during N_2H_4 decomposition at room temperature originate from an adsorbed ammonia intermediate, as suggested by the $H_2:N_2$ ratio and the similarity of the H_2/N_2H_4 and N_2/N_2H_4 peaks to H_2/NH_3 and N_2/NH_3. The similarity between N_2/N_2H_4 and N_2/NH_3 strongly suggests rupture of the N–N bond on adsorption of N_2H_4 and formation of an adsorbed intermediate. The decomposition of this intermediate leads to the formation of N_2 and H_2 with a kinetic order of unity. Studies with ^{15}N-labeled hydrazine have indicated the absence of isotope mixing in the N_2 formed from N_2H_4 decomposition on Fe-on-MgO catalyst at temperatures from 26 to 350°C (*7*). Isotope mixing did not occur for labeled N_2H_4 decomposition on quartz at 270–325°C (*8*), nor for liquid phase decomposition on Shell-405 (*9*), nor on Rh(*10*) at room temperature. All these isotopic studies were carried out at relatively low temperatures where N_2 and NH_3 were the predominant products and little NH_3 decomposition took place. Similarly, in our studies at temperatures below 325°C, the amount of NH_3 decomposition, or the amount of H_2 production from N_2H_4, was very small. It appears that in the temperature regime in which reaction (1) predominates, the adsorption does not involve breakage of the N–N bond. However, at higher temperatures where N_2 and H_2 become the predominant products, rupture of the N–N bond prevails. The N_2/N_2H_4 desorption from Shell-405 catalyst requires sufficiently high temperatures to cause dissociation of the surface-adsorbed intermediate. We must conclude that $N_2(\beta_2)/N_2H_4$ is formed by an entirely different pathway from the N_2 produced in reaction (1), as discussed in further detail in Ref. (*1*).

The reaction mechanism on the Al_2O_3-supported Ir catalyst may be similar to that proposed for the polycrystalline iridium foil. But some significant differences are noted. Below 200°C, it was proposed that adsorption on the foil occurs according to Eq. (3)

$$N_2H_4 \rightarrow H\text{-}\underset{*}{N}\text{-}\underset{*}{N}\text{-}H + 2H^*, \qquad (3)$$

where the asterisk indicates adsorbed species. A gas phase N_2H_4 molecule reacted with $N_2H_2^*$ to form NH_3 and N_2.

$$N_2H_2^* + N_2H_4 \rightarrow N_2 + 2NH_3. \qquad (4)$$

This reaction resulted in the formation of N_2 without rupture of the N–N bond in N_2H_4. Also, this mechanism is consistent with the observation that hydrazine decomposition occurs on a surface saturated with adspecies. Indeed, following long exposure to N_2H_4 at room temperature the CO, O_2 titration technique indicated no bare iridium metal. Heating to 300°C in H_2 and then in He removed the adsorbed surface species, and a CO, O_2 titration yielded the same iridium surface area observed before N_2H_4 exposure.

If, as on the foil, reactions (3) and (4) are the pathway to hydrazine decomposition, the subsequent reactions differ for the supported catalyst during steady-state catalysis. On the foil, adsorbed hydrogen atoms recombined and desorbed; on the supported catalyst, almost no gaseous H_2 was formed below 200°C (see Fig. 7). However, adsorbed hydrogen was present on the surface, as indicated by the TPD spectra (Fig. 1). Thus, for the stoichiometry in Eq. (1) to be satisfied, the reaction

$$N_2H_4 \rightarrow 2NH_2^*, \qquad (5)$$

$$NH_2^* + H^* \rightarrow NH_3^*, \qquad (6)$$

may be occurring. The results suggest that below 200°C on the small Ir crystallites of the supported catalyst, reaction (6) is more rapid than hydrogen atom recombination. This may be because the hydrogen is more strongly bound on the supported catalyst than on the foil. The NH_3 formed [Eq. (6)] desorbs as the surface becomes saturated so that the overall result of Eqs. (3)–(6) is reaction (1). Ammonia adsorbed on the surface gave similar desorption characteristics. Since H* is absent in the latter case, the rate-limiting step in NH_3 formation from hydrazine must be the desorption process rather than Eq. (6).

Prolonged exposure of the catalyst to hydrazine and subsequent TPD did not yield the product species in the same ratio as observed during steady-state decomposition. At room temperature, N_2 and NH_3 were the only steady-state reaction products, but during TPD a substantial H_2/N_2H_4 peak was observed in addition to N_2 and NH_3. Apparently, NH_3 and some H_2 formed during steady-state decomposition remain on the Ir surface or on the Al_2O_3 support with a binding energy sufficiently large to prevent desorption at room temperature. Since Ir does not chemisorb nitrogen form the molecular state (*2*, *11*, *12*) the N_2 observed does not arise from readsorption of the nitrogen molecule on the catalyst surface.

In comparing the TPD spectra for catalysts A and B, we observed in the latter case lower surface densities of all the adspecies (H_2, N_2, NH_3), but no change in their respective binding states (Table 2). This decrease in surface population correlates with a diminution in iridium surface area. Assuming that all the desorbed products originate from metal sites, we can calculate a surface coverage per square centimeter of iridium. These values are listed in Table 3 for the fresh and used catalysts. Brooks (*13*) has carried out adsorption experiments on samples of the same catalyst and obtained similar results. In particular, on a used catalyst he observed a decrease in mass of H_2 and O_2

adsorbed. He attributed these changes to increases in the iridium metal crystallite size. The changes in Ir surface area derived from H_2 chemisorption studies (*13*) correspond to those obtained in our study with the CO, O_2 titration technique. However we conclude that for the catalyst employed in our study the accumulation of surface impurities (or irreversibly adsorbed species) during N_2H_4 exposure is responsible for the observed decrease in active surface area. It is rather striking that the relative distribution of adsorbed species does not change during TPD from a fresh or used catalyst (Table 3). Such behavior is more likely to result from gross surface contamination nonspecific to a given binding site. If crystallite growth were to have occurred it would be most surprising to find each binding state diminished in number by the same fractional amount.

TABLE 3

Specific Surface Coverages for Ir/Al_2O_3[a]

Product/ adsorbate	Saturation coverage ($\times 10^{-14}$ molecules/cm^2 Ir)	
	Catalyst A[b]	Catalyst B[b]
H_2/H_2	1.8	1.6
H_2/N_2H_4	2.0	2.1
H_2/N_2H_4 (275)	1.0	1.3
N_2/NH_3	0.5	0.5
N_2/N_2H_4	0.4	0.3
NH_3/NH_3	2.4	2.4
NH_3/N_2H_4	2.4	2.5

[a] Coverages were calculated under the assumption that all the desorption was from the iridium surface and none from the alumina.

[b] Samples from Rocket Research Corp., Redmond, Wash.

Our results with the Ir catalyst are qualitatively similar to the data reported by Contour and Pannetier (*2*) on an Ir/Al_2O_3 catalyst prepared by them. However, their N_2/N_2H_4 desorption results exhibit lower peak temperature (around 200°C) and are interpreted in terms of second-order kinetics with an activation energy of 14 kcal/mol. This discrepancy with our data for $N_2(\beta_2)/N_2H_4$ may be indicative of differences in catalyst preparation and catalyst support.

On the other hand, recent flash desorption experiments with hydrazine adsorbed on a Pd wire (*14*) exhibit interesting differences from the properties of the Ir catalyst. In the case of Pd the N_2/N_2H_4 and H_2/N_2H_4 products desorb at the same temperature (100°C), but experimental difficulties prevented observation of NH_3 desorption. Ertl and Tornau (*14*) postulate that the rate-limiting step is successive hydrogen abstraction to form N_2 and H_2 from adsorbed N_2H_4 without rupture of the N–N bond. Experiments on steady-state decomposition catalyzed by Pd (*14*) demonstrated complete reaction at 180°C. However, similar to the iridium foil, there was no temperature regime in which NH_3 and N_2 were the only reaction products as observed in our study with supported Ir catalyst. A comparison of N_2H_4 decomposition rates and the surface binding states associated with N_2/N_2H_4 on Ir and Pd indicates that a strong adsorbate surface bond is required for efficient N_2H_4 decomposition. Possibly, it is the lifetime of N_2H_4-surface intermediate [Eq. (3)] that governs the catalytic activity for hydrazine decomposition.

The TPD spectra from a polycrystalline iridium foil following N_2H_4 and NH_3 exposure (*1*) exhibit qualitative agreement with the spectra from the supported catalyst. One difference of special interest is the data for N_2/N_2H_4 for which three peak desorption temperatures were recorded for the Ir foil (~150, ~380, and ~546°C). The observation that for the Ir foil the N_2/N_2H_4 peak temperature of 380°C is identical to that for N_2/NH_3 and H_2/NH_3, suggests strongly that this binding state corresponds to $N_2(\beta_2)N_2H_4$ on Ir/Al_2O_3 catalyst. The most strongly bound state corresponding to a peak desorption temperature at 645°C on the Ir foil was not observed on the supported Ir catalyst. However, a small but strongly bound nitrogen species that could not be flashed off at temperature as high as 975°C was detected by AES following exposure of Ir/Al_2O_3 to hydrazine. It must be concluded that surface binding energies are affected by crystal orientation and surface defects, as a result of which quantitative correlation between the properties for polycrystalline Ir and supported Ir crystallites is not to be expected. On the other hand the results for steady-state decomposition of N_2H_4 on the supported Ir catalyst (Figs. 7 and 8) and the polycrystalline foil, exhibit greater similarities. Although the degree of N_2H_4 conversion was smaller on the Ir foil because of differences in metal surface area, the results from low-pressure studies on the polycrystalline foil are consistent with those from the supported catalyst at atmospheric pressure.

The transition in product distribution from reaction (1) (with NH_3 and N_2 as products) to reaction (2) (with H_2 and N_2 as products) is interpretable in terms of the TPD data of the adsorbed surface species resulting from hydrazine decomposition. The rate constant k equal to $3 \times 10^7 \exp(-26{,}800/RT)$ s^{-1} for $N_2(\beta_2)$ formation indicates that at 330°C, where reaction (1) occurs exclusively, the reaction time constant ($1/k$) is 200 s, so that NH_3 desorption would be favored over its decomposition to N_2 and H_2. On the other hand, at 630°C, where reaction (2) occurs exclusively, the reaction time constant is less than 0.1 s, so that N_2 and H_2 formation would be favored over NH_3 desorption, especially since the activation energy for NH_3 desorption[2] is small ($\sim$10 kcal/mol). These results indicate the usefulness of detailed TPD spectra for determination of reaction selectivity.

CONCLUSIONS

Exposure of the alumina-supported Ir catalyst to hydrazine leads to the formation of surface-adsorbed intermediates that yield H_2, N_2, and NH_3 during temperature-programmed desorption. Their binding states are of sufficient magnitude to require elevated temperatures for desorption. The $N_2(\beta_2)$-state, the most strongly bound state observed for Ir/Al_2O_3, exhibits a peak desorption temperature of 380°C. Steady-state catalytic decomposition yields NH_3 and N_2 at temperatures below 300°C, and N_2 and H_2 at temperatures above 500°C, a region in which NH_3 begins to dissociate. Qualitatively, the dispersed Ir crystallites exhibited similar surface properties to those observed for polycrystalline iridium, and crystal structure-sentitive binding states may account for the differences observed.

A comparison of the surface properties of fresh and used Ir/Al_2O_3 catalyst has demonstrated a loss in active metal surface area caused by prolonged exposure of the catalyst to hydrazine in a laboratory reactor or in a monopropellant thruster. This change is accompanied by a decrease in the number density of surface sites available for adsorption during N_2H_4 exposure, without the disappearance of a specific binding state. It has not been ascertained whether this surface area decrease is the result of thermal sintering of the Ir crystallites or the buildup of an irreversibly adsorbed surface species that originates during hydrazine decomposition. The absence of a change in the relative surface density of the various adspecies after prolonged exposure to N_2H_4 favors catalyst poisoning, due to impurities in the N_2H_4 or irreversibly adsorbed intermediate species, such as N adatoms, as the major cause for loss in reactive Ir surface sites.

REFERENCES

1. Wood, B. J., and Wise, H., *J. Catal.* **39**, 471 (1975).
2. Contour, J. P., and Pannetier, G., *J. Catal.* **24**, 434 (1972).
3. Wentrcek, P., Kimoto, K., and Wise, H., *J. Catal.* **33**, 279 (1973).
4. Falconer, J. L., Wentrcek, P., and Wise, H., unpublished data.
5. Redhead, P. A., *Vacuum* **12**, 203 (1962).
6. Falconer, J. L., and Madix, R. J., *Surface Sci.* **48**, 393 (1975).

7. Block, J., and Schulz-Ekloff, G., *J. Catal.* **30**, 327 (1973).

8. Kant, A., and McMahon, W. J., *J. Inorg.-Nucl. Chem.* **15**, 305 (1960).

9. Sayer, C. F., Rocket Propulsion Establishment, Tech. Rep. No. 69/10, December, 1969.

10. Davis, K. M., and Sayer, C. F., *Trans. Faraday Soc.* **68**, 1894 (1972).

11. Mineault, V. J., and Hansen, R. S., *J. Phys. Chem.* **70**, 3000 (1966).

12. Nieuwenhuys, B. E., Meijer, D. T., and Sachtler, W. M. H., *Surface Sci.* **40**, 125 (1973).

13. Brooks, C. S., *J. Colloid Interface Sci.* **34**, 419 (1970).

14. Ertl, G., and Tornau, J., *Z. Phys. Chem. Neue Folge* **93**, 109 (1974).