surface science

The selectivity of hydrazine oxidation on a polycrystalline rhodium surface

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The surface reactions of coadsorbed hydrazine and atomic oxygen have been examined by means of temperature-programmed reaction spectroscopy (TPRS) on a clean polycrystalline rhodium surface over the 90 to 1450 K temperature range. Nitrogen and water are the primary oxidation products observed. In addition, the usual hydrazine decomposition products N_2, NH_3, H_2 and N_2H_2 are observed. Nitrogen oxides (NO and N_2O) were not observed even in the presence of excess oxygen. Preadsorbed atomic oxygen initiates hydrazine oxidation below 140 K indicating that adsorbed hydrazine is quite reactive on a clean rhodium surface. Large initial coverages of coadsorbed hydrazine and atomic oxygen result in the formation of nitrogen and water below 200 K. We suggest that the N–N bond in hydrazine remains intact resulting in "direct" N_2 formation during this low-temperature oxidation process. An analogous "direct" N_2 formation process has been previously reported during hydrazine decomposition on iridium; we have also reported a similar process during hydrazine decomposition on rhodium. For lower hydrazine coverages, two higher temperature water desorption peaks at 270 and 360 K are observed. The water peak at 270 K is limited by reaction of H, O and OH while the water peak at 360 K appears to be limited by surface reaction between coadsorbed oxygen and a NH_y surface intermediate. With increasing initial oxygen coverages the yield of water increases, while the yield of hydrazine decomposition products (NH_3, H_2 and N_2H_2) decreases. The selectivity of nitrogen formation during hydrazine oxidation below 250 K is controlled by direct reaction processes which leaves the N–N bond in hydrazine intact. In this temperature range, hydrogen–oxygen reactions are the dominant mode of interaction with the adsorbed atomic oxygen. Above 250 K, nitrogen–nitrogen recombination is strongly favored over a broad range of temperatures and coverages. No evidence for a nitrogen–oxygen surface was observed even in the presence of excess adsorbed oxygen clearly suggesting the predominance of N atom recombination over N + O atom surface reaction even in the presence of excess adsorbed atomic oxygen.

1. Introduction

This study of hydrazine oxidation is part of a program to characterize the surface chemistry and reactions of adsorbed hydrazine on a wide range of solid surfaces. Hydrazine oxidation on rhodium surfaces may furnish an interesting perspective on simple oxidation processes involving adsorbed N_xH_y species which may be important during ammonia oxidation. Hydrazine is a effective reducing agent which is widely used to selectively hydrogenate unsaturated organic reagents in the liquid phase. Hydrazine oxidation with air at room temperature proceeds spontaneously necessitating anaerobic handling procedures to guard against potential spontaneous combustion. Hydrazine de-

composition on metal surfaces is a rapid exothermic process which led to the development of effective low-temperature monopropellant systems currently used in satellites and high-altitude aircraft.

A number of investigators have characterized the adsorption and decomposition of hydrazine on metal surfaces [1–11]. An extensive study of hydrazine decomposition by Sawin and Merrill focussed on the mechanisms and dynamics of hydrazine decomposition on the Ir(111) surface [10]. Angular resolved TPD studies of hydrazine decomposition have been used to obtain information about decomposition mechanisms and the geometries of the kinetically active surface species. The low-temperature decomposition products are

strongly peaked along the surface normal indicating that the desorbing decomposition products leave with a substantial amount of energy from the decomposition reaction in their translational degree of freedom normal to the surface. Simultaneous formation of the decomposition products along with their strongly forward peaked angular distributions led the authors to conclude that low-temperature pathways were due to direct reaction on the surface [10]. Vibrational spectroscopy has been used to characterize an adsorbed NH species formed during hydrazine decomposition on the Ni(111) surface [9]. This NH intermediate is stable up to 450 K [9].

We have recently characterized hydrazine decomposition on this same Rh foil surface using temperature-programmed desorption [1]. The gas-phase products observed during hydrazine decomposition on a Rh foil surface depend markedly on the initial hydrazine coverage. At low coverage, nitrogen and hydrogen are the only products observed indicating complete decomposition has occurred. At high coverage (near monolayer), nitrogen, hydrogen, ammonia and diimide are all observed during the decomposition reaction. For high coverages, direct decomposition is suggested by simultaneous desorption of ammonia and nitrogen at 220 K. An analogous "direct" N_2 formation process has been previously reported during hydrazine decomposition on iridium by Sawin and Merril [10]. The high-temperature nitrogen peak at

635 K corresponds to the recombination of atomic nitrogen formed during the decomposition process. Initial high hydrazine coverages results in a weakly bound molecular desorption peak of hydrazine which desorbs at 220 K.

2. Experimental

The experiments were performed in a UHV system equipped with Auger electron spectroscopy (AES), low-energy electron diffraction (LEED) and a multiplexed mass spectrometer for temperature-programmed reaction spectroscopy (TPRS) [1]. The base pressure after bakeout was 3.2×10^{-11} Torr. The rhodium foil was mounted on a manipulator which allowed resistive heating to 1500 K and cooling to approximately 80 K. The temperature was monitored by a chromel–alumel thermocouple spot-welded to the back of the sample. The sample was cleaned by repeated heating to 800 K in 2×10^{-7} Torr of oxygen and by argon ion bombardment. The TPRS data were recorded with a linear temperature ramp of 10 K s^{-1}. The sample was placed 2 mm from the mass spectrometer collimator in direct line-of-sight to reduce background effects and eliminate contributions from support wires.

All gases were adsorbed at 80 K through a doser approximately 2.5 cm away from the surface. Hydrazine and oxygen were dosed through two

Table 1
Hydrazine oxidation products on a clean Rh foil surface and their desorption temperatures for various oxygen coverages dosed with low and high hydrazine exposures

Exposure O_2 (L)	N_2H_4 exposure	Hydrazine oxidation products and their desorption peak temperature					
		140–200 K	220–270 K	220–500 K	290–360 K	460 K	600–700 K
0.0	low				H_2	H_2	N_2
0.2	low	N_2	N_2, H_2O		H_2, H_2O	H_2	N_2
0.3	low	N_2	N_2, H_2O		H_2, H_2O	H_2	N_2
0.6	low	N_2	N_2, H_2O		H_2, H_2O	H_2	N_2
1.0	low	N_2	N_2, H_2O		H_2O		N_2
0.0	high		N_2, NH_3	N_2H_2	H_2	H_2	N_2
0.2	high	H_2O	N_2, NH_3, H_2O	N_2H_2	H_2	H_2	N_2
0.3	high	H_2O	N_2, NH_3, H_2O	N_2H_2	H_2	H_2	N_2
0.6	high	N_2, H_2O	N_2, NH_3, H_2O	N_2H_2	H_2	H_2	N_2
1.0	high	N_2, H_2O	$N_2, \quad H_2O$		H_2	H_2	N_2

separate dosers. The hydrazine doser was precon-
ditioned carefully and hydrazine was changed fre-
quently to minimize decomposition inside the
doser. The details of hydrazine dosing are dis-
cussed in ref. [1]. In these oxidation experiments,
the Rh foil surface was first exposed to oxygen gas
at 80 K. The sample was heated to 200 K to
remove molecular oxygen from the surface. The
sample was then cooled to 80 K and dosed with
hydrazine. A series of five representative atomic
oxygen coverages (fig. 1) were reacted with both
high and low hydrazine coverages (fig. 2) to estab-
lish the selectivity of hydrazine oxidation as a
function of the reactant coverages. The results of
hydrazine oxidation are summarized in table 1.

3. Results

Typical oxygen desorption spectra for the rep-
resentative series of five atomic oxygen coverages
used in these N_2H_4 oxidation studies are shown in
fig. 1.

Desorption spectra generated following adsorp-
tion of low and high coverages of hydrazine (no
coadsorbed atomic oxygen) are shown in figs. 2
and 3 respectively. For coverages substantially
smaller than a monolayer, adsorbed hydrazine de-
composes completely (fig. 2) on a clean rhodium
surface during a TPRS cycle. The gas-phase prod-

Fig. 2. A TPRS spectrum illustrating the complete dissociation
of hydrazine adsorbed at 80 K on a clean Rh foil surface. N_2
and H_2 are the only desorbing species observed. The heating
rate was 10 K/s.

ucts observed are H_2 ($T_p = 360$ K and $T_p = 460$
K) and N_2 ($T_p = 635$ K) only. Increasing hy-
drazine coverage results in the formation of NH_3
and N_2H_2 in addition to the low-coverage prod-
ucts (H_2 and N_2) (fig. 3). Ammonia has two
desorption peaks at 220 and 360 K for high cover-
ages of N_2H_4 (fig. 3). The nitrogen peak at 635 K
shifts to lower temperature and a new peak at 220
K appears as the hydrazine coverage increases (fig.
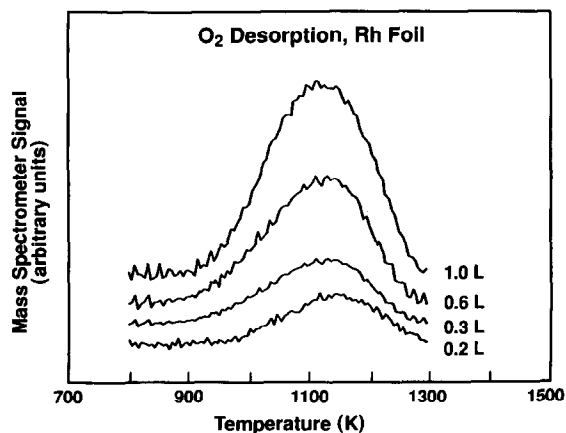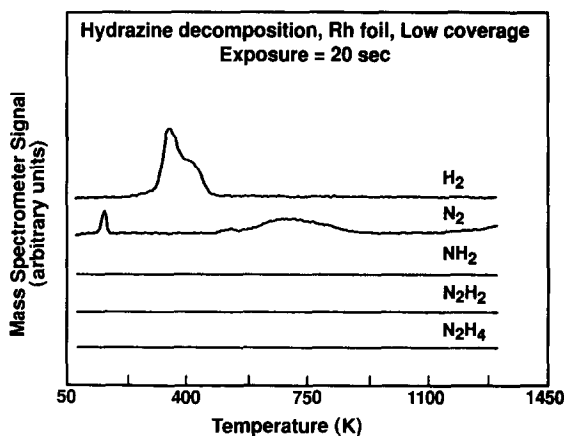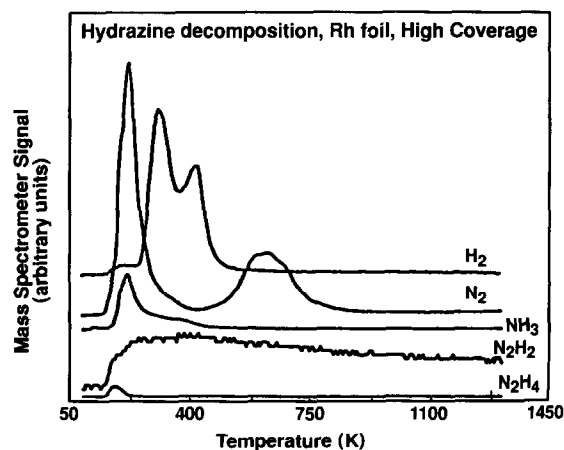3). Diimide formation is observed above 220 K

Fig. 1. Thermal desorption spectra of oxygen from a Rh foil
surface. Oxygen is adsorbed at 80 K and heated to 200 K to
remove molecular oxygen from the surface.

Fig. 3. A TPRS spectrum illustrating the dissociation of hy-
drazine adsorbed at 80 K on a clean Rh foil surface at high
coverage. N_2, H_2, NH_3, N_2H_4 are the desorbing species ob-
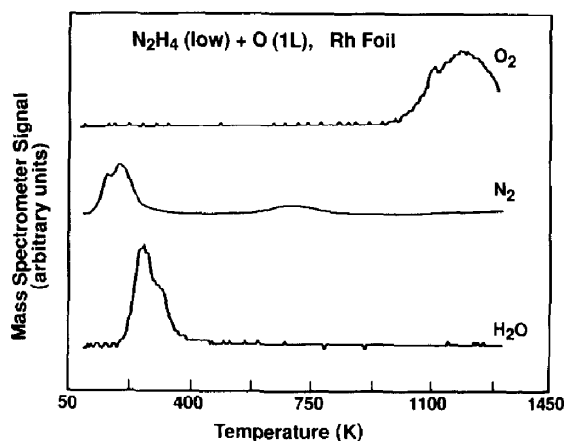served. The heating rate was 10 K/s.

Fig. 4. Thermal desorption spectra of H_2O, N_2, and excess O_2 during N_2H_4 oxidation on a clean Rh foil surface for 1 L of atomic oxygen exposure coadsorbed with low hydrazine exposure.

Fig. 6. Thermal desorption spectra of H_2O during N_2H_4 oxidation on a clean Rh foil surface for various exposures of oxygen coadsorbed with high N_2H_4 exposure.

(fig. 3). High initial hydrazine coverages result in formation of a weakly bound N_2H_4 molecular desorption peak at 220 K (fig. 3). For a more complete discussion of N_2H_4 decomposition see ref. [1].

For low initial coverages of hydrazine coadsorbed with atomic oxygen on a Rh foil surface, two water peaks at 270 and 360 K (fig. 4) and two low-temperature nitrogen desorption peaks at 140 and 220 K (fig. 4) were observed in addition to the expected hydrazine decomposition products (fig.
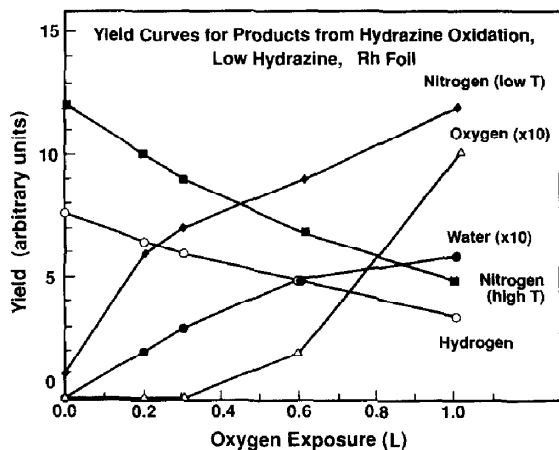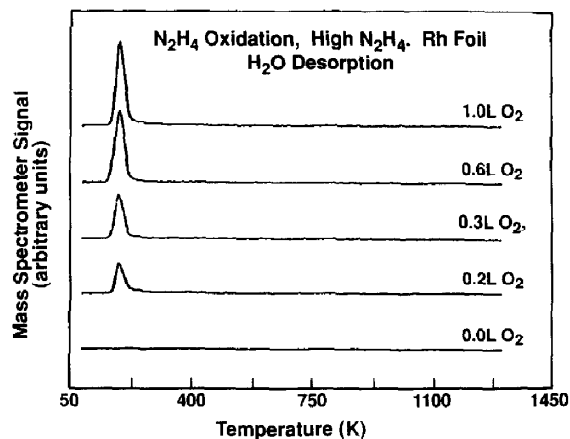
2). The water desorption peak at 270 K increases with increasing coverage of oxygen, while the water peak at 360 K decreases. Yields for all the products of hydrazine (low coverage) reaction with coadsorbed atomic oxygen on a Rh foil surface are shown in fig. 5.

For high initial hydrazine coverages coadsorbed with oxygen, water desorbs at 190 K (fig. 6). The yield of the low-temperature water peak increases with increasing oxygen coverage. The low-temperature nitrogen peak at 140 K also increases with
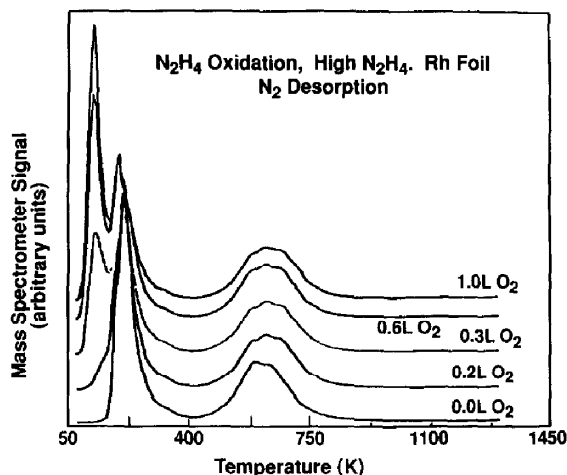

Fig. 5. Yield curves for hydrazine oxidation products H_2, H_2O, N_2, and O_2 as a function of predosed oxygen exposures coadsorbed with low hydrazine exposure.

Fig. 7. Thermal desorption spectra of N_2 during hydrazine oxidation for various exposures of oxygen coadsorbed with high hydrazine exposure.
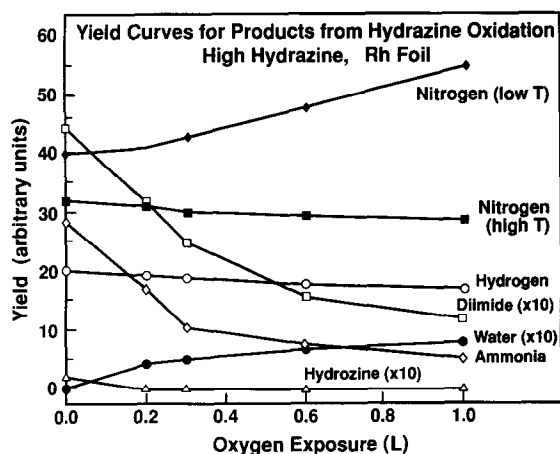
Fig. 8. Yield curves for hydrazine oxidation products H_2, NH_3, H_2O, N_2H_2, and N_2 as a function of oxygen exposures for high exposure of hydrazine.

increasing atomic oxygen coverages, while the nitrogen peak at 635 K decreases (figs. 7 and 8). The yields of hydrogen, NH_3 and diimide decrease with increasing coverage of oxygen (fig. 8).

4. Discussion

Nitrogen and water are the primary products of hydrazine oxidation on rhodium. Oxygen-containing nitrogen products (NO and N_2O) were not observed even in the presence of excess coadsorbed atomic oxygen. Preadsorbed atomic oxygen initiates hydrazine oxidation below 140 K indicating that adsorbed hydrazine is quite reactive on a clean polycrystalline Rh surface. During these TPD studies of hydrazine oxidation we observe that decomposition competes with oxidation reactions over a large range of coverages and temperatures. The yields of the N_2 and H_2O oxidation products increase with increasing oxygen coverage, while the yields of ammonia, hydrogen and diimide (the decomposition products) decrease as oxygen coverages increase. The details of low- and high-coverage hydrazine surface oxidation are discussed separately in the next two sections. The final section of the discussion is focussed on the selectivity of this surface oxidation reaction.

4.1. Low hydrazine coverage

Low coverages of adsorbed hydrazine (no coadsorbed oxygen) decompose completely on a clean Rh surface during a TPRS cycle since only gas-phase H_2 and N_2 desorb from the surface (fig. 2). A single nitrogen recombination peak is observed at 635 K for low hydrazine coverages (fig. 2). This peak is clearly caused by atomic nitrogen recombination as indicated by comparison with previous results reported in the literature for atomic nitrogen recombination on polycrystalline Rh surfaces [5]. Two hydrogen desorption peaks are observed at 360 and 460 K during decomposition of low-coverage hydrazine (fig. 2). The hydrogen peak at 360 K is identical to the desorption-limited peak observed following hydrogen adsorption on the Rh surface, indicating the formation of adsorbed atomic hydrogen below the hydrogen desorption temperature of 360 K. The hydrogen desorption peak at 460 K is limited by thermal dehydrogenation of a hydrogen-containing surface intermediate which we previously suggested is NH [1].

Reaction of low hydrazine coverages with a series of oxygen coverages results in formation of two water desorption peaks at 270 and 360 K (fig. 4). The peak at 270 K is not desorption-limited since the reference water desorption peak from the Rh surface occurs at 180 K [12]. Gurney and Ho [13] have reported that from the reaction of O and H on the Rh(100) surface water desorbs at 275 K. Thus we believe that in this hydrazine oxidation reaction on the Rh surface a water desorption peak at 270 K occurs as a result of O and H reaction via OH according to

$$H(ad) + O(ad) \xrightarrow{\text{below 270 K}} OH(ad),$$

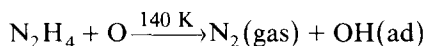$$OH(ad) + OH(ad) \xrightarrow{\text{270 K}} H_2O(gas) + O(ad).$$
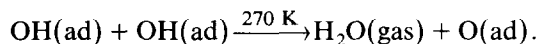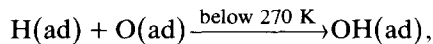
The water desorption peak at 360 K appears to be reaction-limited. The water desorption peak resulting from ammonia oxidation appears at 270 K [4]. Thus the water peak at 360 K observed during hydrazine oxidation cannot be caused by ammonia oxidation. At this time we are unable to determine the exact mechanism of the peak at 360
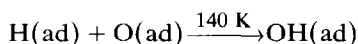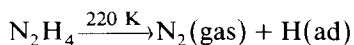
K but suggest that oxidation of a stable surface intermediate (NH) may be involved. Two low-temperature nitrogen desorption peaks at 140 and 220 K are observed for low coverages of hydrazine reacting with coadsorbed oxygen (fig. 4). We believe that the peak at 140 K is due to a direct oxidation reaction and occurs according to N_2H_4 + O (below 140 K) → N_2(gas) + H_2O(ad). We suggest that the hydrogen from hydrazine may be directly transferred to an adjacent adsorbed oxygen atom in analogy with a previous suggestion involving direct hydrogen transfer to adjacent N_xH_y species during hydrazine decomposition [10]. The nitrogen peak at 220 K is due to direct decomposition of hydrazine on the Rh surface as reported previously [1]. For low initial hydrazine exposure, nitrogen does not desorb at 220 K (fig. 2) in the absence of coadsorbed oxygen. This result suggests that the adsorbed atomic oxygen may indirectly increase the surface reactivity and causes direct decomposition according to N_2H_4 (220 K) → N_2(gas) + H(ad). In the case of ammonia oxidation on the same surface, no low-temperature pathway (140 K) for N_2 formation was observed [4]. A comparison of hydrazine oxidation with ammonia oxidation data [4] on the same Rh foil surface indicates that the low-temperature N_2 pathways are characteristic of N_2H_4 oxidation on the Rh surface. The yield curves for the products for low hydrazine coverages (fig. 5) show that water and nitrogen yields increase with increasing coverage of oxygen while the yield of hydrogen decreases.

Thus for low initial coverages of hydrazine coadsorbed with oxygen, we propose the following mechanism for hydrazine oxidation:
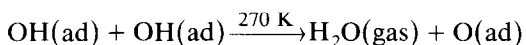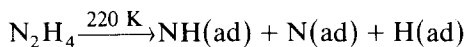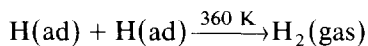
low-temperature oxidation

$$N_2H_4 + O \xrightarrow{140 \text{ K}} N_2(\text{gas}) + OH(\text{ad})$$

direct decomposition

$$N_2H_4 \xrightarrow{220 \text{ K}} N_2(\text{gas}) + H(\text{ad})$$

$$H(\text{ad}) + O(\text{ad}) \xrightarrow{140 \text{ K}} OH(\text{ad})$$

recombination

$$OH(\text{ad}) + OH(\text{ad}) \xrightarrow{270 \text{ K}} H_2O(\text{gas}) + O(\text{ad})$$

dissociative adsorption

$$N_2H_4 \xrightarrow{220 \text{ K}} NH(\text{ad}) + N(\text{ad}) + H(\text{ad})$$

recombination

$$H(\text{ad}) + H(\text{ad}) \xrightarrow{360 \text{ K}} H_2(\text{gas})$$

dissociation of surface intermediate

$$NH(\text{ad}) \xrightarrow{460 \text{ K}} N(\text{ad}) + H_2(\text{gas})$$

recombination

$$N(\text{ad}) + N(\text{ad}) \xrightarrow{635 \text{ K}} N_2(\text{gas}).$$
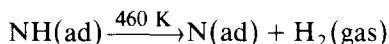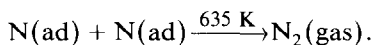
This mechanism is consistent with the data in table 1 for low initial coverage of hydrazine coadsorbed with oxygen on a Rh foil surface

4.2. High hydrazine coverages

Decomposition of a high coverage of N_2H_4 (no coadsorbed oxygen) is shown in fig. 3. Two hydrogen desorption peaks are observed at 360 and 460 K, while ammonia and nitrogen desorb simultaneously at 220 K. As discussed earlier, Sawin and Merril have studied the angular dependence of similar low-temperature nitrogen and ammonia peaks on the Ir(111) surface [10]. From the angular dependence of the peaks and simultaneous formation of reaction products, Sawin and Merril [10] concluded that the low-temperature peak is produced by the direct decomposition of adsorbed hydrazine species. They suggest direct transfer of hydrogen from hydrazine to an adsorbed N_xH_y species resulting in simultaneous N_2 and NH_3 formation [10]. During our recent hydrazine decomposition studies on rhodium we observed simultaneous low-temperature formation of ammonia and nitrogen suggesting that a similar direct decomposition mechanism may dominate at low temperature [1].

Coadsorbed atomic oxygen and hydrazine react on a Rh surface below 200 K. Water (fig. 6) and nitrogen (fig. 7) are the primary low-temperature reaction products. We suggest that the N–N bond in hydrazine remains intact resulting in "direct" N_2 formation during this low temperature process. This hypothesis is supported by the observation that reaction between coadsorbed ammonia and
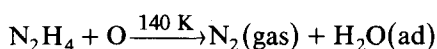
atomic oxygen on this same surface does not result in low-temperature nitrogen formation. Thus this low temperature reaction is clearly characteristic of hydrazine oxidation on a Rh foil surface. This low-temperature reaction may involve direct transfer of hydrogen from the hydrazine to adjacent coadsorbed oxygen atoms. This process may be analogous to the direct decomposition process proposed earlier which involves direct transfer of a hydrogen from adsorbed hydrazine to an adjacent adsorbed N_xH_y species [10].

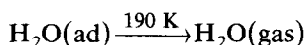$$N_2H_4 + 2O \xrightarrow{\text{below 200 K}} N_2(\text{gas}) + 2H_2O(\text{gas}).$$
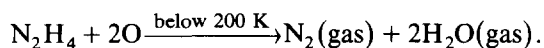
Yields of water and nitrogen increase with increasing oxygen exposure while the yields of hydrogen, ammonia, and diimide decrease as expected (fig. 8). For high coverages of N_2H_4, only a single water peak at 190 K has been observed. The usual desorption-limited peak for water occurs at 180 K. Thus the water peak at 190 K is desorption-limited. This peak indicates the formation of adsorbed water below 190 K.

Thus for high hydrazine coverage coadsorbed with atomic oxygen on a Rh foil surface the results presented in figs. 6–8 and summarized in table 1 lead us to postulate the following mechanism for N_2H_4 oxidation:
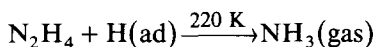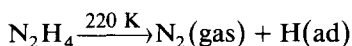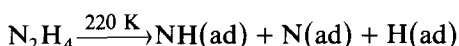
Low-temperature direct oxidation

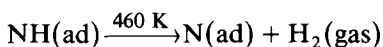$$N_2H_4 + O \xrightarrow{140 \text{ K}} N_2(\text{gas}) + H_2O(\text{ad})$$

desorption

$$H_2O(\text{ad}) \xrightarrow{190 \text{ K}} H_2O(\text{gas})$$

direct decomposition

$$N_2H_4 \xrightarrow{220 \text{ K}} N_2(\text{gas}) + H(\text{ad})$$

$$N_2H_4 + H(\text{ad}) \xrightarrow{220 \text{ K}} NH_3(\text{gas})$$

dissociative adsorption

$$N_2H_4 \xrightarrow{220 \text{ K}} NH(\text{ad}) + N(\text{ad}) + H(\text{ad})$$

dissociation of surface intermediate

$$NH(\text{ad}) \xrightarrow{460 \text{ K}} N(\text{ad}) + H_2(\text{gas})$$

hydrogenation

$$NH(\text{ad}) + 2H(\text{ad}) \xrightarrow{360 \text{ K}} NH_3(\text{gas})$$

recombination

$$NH(\text{ad}) + NH(\text{ad}) \xrightarrow{\text{above 220 K}} N_2H_2(\text{gas})$$

$$N(\text{ad}) + N(\text{ad}) \xrightarrow{635 \text{ K}} N_2(\text{gas})$$

$$H(\text{ad}) + H(\text{ad}) \xrightarrow{360 \text{ K}} H_2(\text{gas}).$$
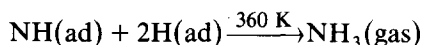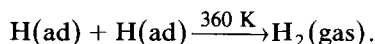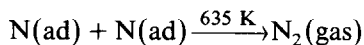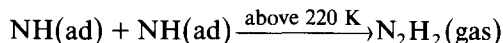
Angular resolved TPD studies may provide more information about direct reaction pathways and the geometries of the kinetically active surface species. We hope to perform a series of angular dependent studies of N_2 and H_2O desorption during N_2H_4 oxidation in order to investigate the nature of low-temperature pathways and the geometries of the active species on the surfaces in the future.

4.3. Selectivity

Two distinct reaction pathways for nitrogen formation are observed during hydrazine oxidation on this Rh surface. We expect that hydrazine oxidation selectivity will be controlled by different factors in these two regions. Below 250 K nitrogen formation is dominated by direct reaction processes which leaves the N–N bond in hydrazine intact. In this temperature range, hydrogen–oxygen reactions are the dominant mode of interaction with the adsorbed atomic oxygen. Above 250 K adsorbed atomic nitrogen and atomic oxygen are the dominant surface species for large initial atomic oxygen coverages. Therefore we expect nitrogen–nitrogen–oxygen surface reactions to compete, yielding molecular nitrogen and nitrogen oxides, respectively. Our results clearly indicate that on this rhodium surface nitrogen–nitrogen recombination is strongly favored over a broad range of temperatures and coverages. No evidence for nitrogen–oxygen surface reactions was observed even in the presence of excess adsorbed atomic oxygen.

In contrast to hydrazine oxidation, no low-temperature pathways are observed either for nitrogen or water formation during ammonia oxidation on

the same Rh surface [4]. These ammonia oxidation results clearly suggest that reaction pathways below 250 K are characteristic of hydrazine oxidation only. Nitrogen formation during ammonia oxidation is clearly dominated by nitrogen–nitrogen recombination at higher temperatures (670 K). A number of previous studies on both supported and unsupported rhodium catalysts have reported nitrogen–nitrogen recombination as primary pathway in agreement with our results. These results are in contrast with the results on the Pt(111) surface where NO formation has been observed [14].

5. Conclusions

In summary, the selectivity of hydrazine oxidation on a Rh foil surface has been studied by means of temperature-programmed reaction spectroscopy. Nitrogen and water are found to be the primary products of hydrazine oxidation at 140 K. Oxygen-containing nitrogen products (NO and N_2O) were not observed even in the presence of excess oxygen. Preadsorbed atomic oxygen initiates hydrazine oxidation below 140 K indicating that adsorbed hydrazine is quite reactive on a clean polycrystalline Rh surface. Large initial coverages of coadsorbed hydrazine and atomic oxygen resulted in the formation of water and nitrogen at temperatures below 200 K. The yields of N_2 and H_2O oxidation products increase with increasing oxygen coverage while the yields of decomposition products (ammonia, hydrogen and diimide) decrease. The selectivity of nitrogen formation during hydrazine oxidation below 250 K is controlled by direct reaction processes which leaves the N–N bond in hydrazine intact. In this temperature range, hydrogen–oxygen reactions are the dominant mode of interaction with the adsorbed atomic oxygen. Above 250 K, nitrogen–nitrogen recombination is strongly favored over a broad range of temperatures and coverages. No evidence for nitrogen–oxygen surface reactions was observed even in the presence of excess adsorbed atomic oxygen, clearly suggesting the predominance of N atom recombination over N + O atom surface reaction even in the presence of excess adsorbed atomic oxygen.

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