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The Synthesis of Butyronitrile from *n*-Butanol and Ammonia over Rhodium (111) and (331) Single-Crystal Surfaces

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The rhodium (111) and (331) single-crystal surfaces selectively catalyze the formation of butyronitrile from *n*-butanol and ammonia without the production of other nitrogen-containing species. The reaction is found to be structure sensitive. The Rh (331) surface is three times more active in the ammonolysis reaction, but poisons faster and produces 8–10 times more cracking products than the Rh (111). Auger electron spectroscopy and thermal desorption spectroscopy results indicate that the reaction takes place on an overlayer which covers 95% of the total surface of the catalyst and contains C, N, and O. On the deactivated catalyst this layer contains more carbon. The mechanism of the reaction is independent of the surface structure of the rhodium catalyst since the apparent activation energies for the two surfaces are practically the same (21–22 kcal/mol). Most of our results are consistent with a model according to which the *n*-butanol is oxidized first to *n*-butanal which then reacts with ammonia and then possibly through an imine intermediate the butyronitrile is produced. © 1989 Academic Press, Inc.

INTRODUCTION

In a time of rapidly expanding knowledge of the surface science of catalytic systems, relatively little work is reported on C–N bond-forming reactions. These include the ammonolysis of alcohols and aldehydes with ammonia (*1*) and the ammoxidation of olefins with ammonia and oxygen.

These reactions produce amines and nitriles of various types. The catalysts used to form them selectively and at high rates have been described in the patent literature. They include a Raney nickel catalyst with a rhodium, ruthenium, or palladium cocatalysts for the production of amines from alcohols and ammonia (*2*); an aluminasilicate catalyst for production of amines via the amination of olefines (*3*); a catalytic complex formed by ammonia addition of copper salt for conversion of unsaturated aldehydes to unsaturated nitriles (*4*); a nickel–copper catalyst to form amines from alcohols or aldehydes (*5*); and a nickel–rhenium catalyst for amination of alcohols (*6*). There are reports on the use of phosphoric acid on alumina, multicomponent cobalt/nickel/copper/silver, nickel/copper/chromium, rhodium/manganese, and molibdenum/bismuth/lead/thallium/iron/arsenic/alkali catalysts (*7–13*). Special attention has been given to the reaction of propylene, oxygen, and ammonia to form acrylonitrile. Grasseli and co-workers have made many important contributions to the study of this reaction over metal oxide catalysts (*14–18*).

Preliminary investigations revealed that rhodium alone can catalyze the formation nitriles from alcohols and ammonia. In order to explore the elementary surface reaction steps leading to C–N bond formation, we studied the reaction of *n*-butanol and ammonia over model rhodium (111) and (331) single-crystal catalysts. This complex reaction system on zinc oxide has been studied by Jodra and co-workers (*19–21*). Our results show that rhodium can very selectively catalyze the formation of butyronitrile from *n*-butanol and ammonia. We are able to provide new insight into the ammonolysis reaction on the basis of ki-

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netic and surface science data provided by a combined high-pressure reactor–ultrahigh vacuum surface science system.

EXPERIMENTAL

All work was performed in a combined ultrahigh vacuum (UHV)–high-pressure catalysis chamber. A schematic of this experimental apparatus has been previously published (*22*). In its UHV mode, the chamber was equipped with a double-pass cylindrical mirror analyzer (CMA) for performing Auger electron spectroscopy. In addition, the system contained a UTI mass spectrometer for temperature-programmed desorption (TPD), an argon ion gun, a molecular doser, and a bake-out lamp. Both the CMA and the mass spectrometer were interfaced to a PET 2001 computer to aid data collection and processing. When TPD was performed up to eight masses could be monitored.

After cleaning and surface analysis the sample was enclosed in a high-pressure batch reactor without removal from the UHV chamber. Using this technique the reactions could be studied at total pressures of 1 atm. The reactants were circulated through a 200-ml reactor with a micropump. The reactor loop was connected to an HP 5890 gas chromatograph via an automatic sampling valve.

The catalysts were rhodium (111) and (331) single crystals. The sample disks were cut to ±0.5° of the desired crystal plane from a single-crystal rod purchased from B. Addis at Cornell University. The polished crystals were initially heated in 1 atm of hydrogen for several days to remove bulk boron. Subsequent cleaning was accomplished in the UHV chamber by argon ion sputtering and oxygen heat treatments. These treatments consisted of heating in 1×10^{-7} Torr of oxygen for 10 min at 973 K and for an additional minute to remove oxygen in 1×10^{-9} Torr. Cleanliness was confirmed with AES.

The crystals were mounted to 4-mm tantalum rods via rhodium- or tantalum-support wires of 0.5 mm. No difference that could be attributed to the support wires was detected in the catalytic properties.

Once the catalyst was prepared in UHV, the catalytic reaction chamber was closed and the reactants were introduced. The ammonia gas, usually 100 Torr, was introduced first with the *n*-butanol or *n*-butyraldehyde added in the liquid phase via a septum to yield a 10-Torr partial pressure. Argon was added to make a total pressure of 300 Torr. In all cases the amounts of liquid added were considerably less than the amount necessary to achieve the vapor pressure of the substance. The reactants were circulated for 30 min to assure good mixing before the reaction was started.

The catalysts were then heated resistively to a constant temperature of ±0.5 K as monitored by a Chromel/Alumel thermocouple spotwelded to the edge of the crystal. Reaction temperatures ranged from 455 to 525 K. The temperature was controlled by a Eurotherm temperature controller.

The reactants and the products were separated on a glass column packed with 4% Carbowax 20M/0.8% KOH on 60/80 Carbopack B. Initial product identification was made with GC/MS. The detector was a flame ionization detector. After reaction, which lasted from 1 to 20 hr, the reaction chamber was evacuated and the catalyst was reintroduced to UHV, where the post-reaction surface characterization was carried out.

In reactions where the catalyst was pretreated, ammonia was introduced with argon, and then the sample was heated to reaction temperature for 30 min prior to the introduction of *n*-butanol.

The ammonia and hydrogen were obtained from Matheson and were introduced via molecular sieve traps cooled to 257 and 77 K, respectively. The *n*-butanol and the *n*-butanal were purchased from Aldrich Chemicals and were used without further purification. The purity of all chemicals was greater than 99.9% as confirmed by gas

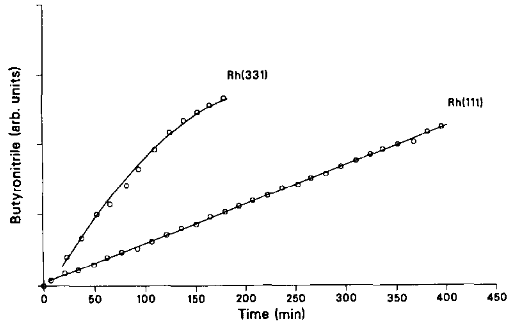

FIG. 1. The accumulation of butyronitrile produced for the reaction of *n*-butanol and ammonia over the Rh (331) and Rh (111) crystal surfaces at 510 K (ammonia : *n*-butanol = 10 : 1, total pressure of reactants 110 Torr).

chromatographic and mass spectral analysis.

RESULTS

1. Reaction Kinetics and Studies of Reaction Mechanism

Our experiments have demonstrated that both Rh (111) and Rh (331) crystal surfaces catalyze the formation of *n*-butyronitrile from *n*-butanol and ammonia:

$$CH_3CH_2CH_2CH_2\text{—}OH + NH_3 \rightarrow CH_3CH_2CH_2CN + H_2O + 2H_2$$

In Fig. 1 two typical product accumulation curves are shown for the two surfaces. The initial rate for the nitrile formation over the clean Rh (331) surface is about three times higher than that over the Rh (111). The activity of the latter is maintained over 6 hr at 515 K. Reactions were carried out for over 12 hr or to about 10% conversion with very little poisoning noted. In the case of the Rh (331) catalyst, a considerable amount of poisoning was evident after 2 hr of reaction time. The reaction on both surfaces is catalytic with a minimum of total turnovers of 500.

To gain some insight into the kinetics of the reaction we determined the pressure dependencies. Within experimental error the results are identical for the two surfaces studied. In Fig. 2 we plot the logarithm of the rate of nitrile formation vs the logarithm of the partial pressure of *n*-butanol and ammonia. The rate of reaction does not depend upon the partial pressure of butanol (Fig. 2a). The dependence of the NH_3 partial pressure was approximately second order up 10 Torr of ammonia; then it became zero order also (Fig. 2b). In the range of zero pressure dependencies we have determined the apparent activation energies for the reaction, which are 21 ± 3 and 22 ± 3 kcal/mol for the (331) and the (111) surface, respectively. Figure 3 shows the Arrhenius plots from which the apparent activation energies were calculated.

In addition to the different reaction and poisoning rates, there is another significant difference between the two surfaces. While the flat (111) crystal produces essentially 100% butyronitrile, the reaction mixture over the stepped catalyst always contains

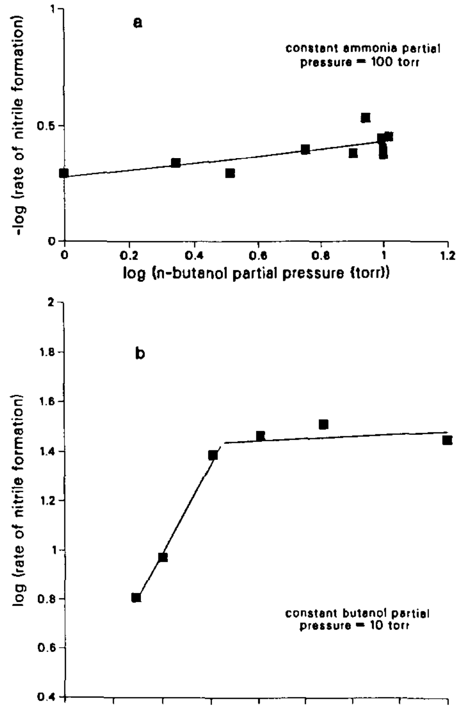

FIG. 2. The *n*-butanol (a) and ammonia (b) pressure dependencies of butyronitrile production from *n*-butanol and ammonia over the Rh (331) catalyst at 510 K.

TABLE 1

The Product Distributions of the Reactions Studied

Reactants	Surface	NTRL[a]	ALD[b]	Amine[c]	C_1	C_2	C_3	C_4
n-Butanol + NH_3	(331)	86	—	—	4	3	3	—
	(111)	98	—	—	—	—	—	—
NH_3 pretreated	(331)	98	—	—	—	—	—	—
n-Butanol → *n*-butanal	(331)	—	48	—	50	—	—	—
	(111)	—	90	—	—	—	10	—
n-Butanal + NH_3	(331)	95	—	—	1	—	4	—
	(111)	98	—	—	—	—	—	—
n-Butanol + NH_3	(331)	4	—	—	10	5	80	—
and hydrogen	(111)	55	—	—	11	1	33	—
n-Butanal + NH_3	(331)	1	—	1	5	—	18	75
and hydrogen	(111)	48	—	1	2	1	7	41
n-Butanol + NH_3	(331)	98	—	—	—	—	—	—
and water	(111)	98	—	—	—	—	—	—
n-Butanal + NH_3	(331)	98	—	—	1	—	1	—
and water	(111)	98	—	—	1	—	1	—

Note. All reactions are at 510 K, 10 : 1 NH_3 : *n*-butanol (or *n*-butanal), and in the presence of 200 Torr argon. For the H_2 reactions 200 Torr of hydrogen was used. Most data are the averages of several experiments.

[a] NTRL, *n*-butyronitrile.

[b] ALD, *n*-butanal.

[c] Amine, *n*-butylamine.

about 10% of C_1, C_2, and C_3 cracking products as well. See Table 1 for product distributions. It is remarkable that the Rh (111) and Rh (331) surfaces selectively produce butyronitrile from *n*-butanol and ammonia and no other nitrogen-containing molecules are observed.

The reaction may proceed via the following two pathways:

$$CH_3CH_2CH_2CH_2{-}OH + NH_3 \rightarrow CH_3CH_2CH_2CH_2{-}NH_2 + H_2O \quad \text{(Ia)}$$

$$CH_3CH_2CH_2CH_2{-}NH_2 \rightarrow CH_3CH_2CH_2CN + 2H_2 \quad \text{(Ib)}$$

$$CH_3CH_2CH_2CH_2{-}OH \rightarrow CH_3CH_2CH_2CHO + H_2 \quad \text{(IIa)}$$

$$CH_3CH_2CH_2CHO + NH_3 \rightarrow \{CH_3CH_2CH_2CHNH\} + H_2O \quad \text{(IIb)}$$

$$\{CH_3CH_2CH_2CHNH\} \rightarrow CH_3CH_2CH_2CN + H_2 \quad \text{(IIc)}$$

To investigate channel I, we performed experiments starting with *n*-butylamine. Under conditions where the nitrile is formed in the reaction of butanol and ammonia, the *n*-butylamine cannot be reduced to butyronitrile on either of the two surfaces. Thus we have ruled out this pathway and in our study we have concentrated on channel II.

The first step of this path is the oxidation of *n*-butanol to *n*-butanal (IIa). On both surfaces we ran this reaction and found that the rate of this reaction is at least a factor of 2 higher than the overall rate of the nitrile formation. Similarly to the ammonolysis re-

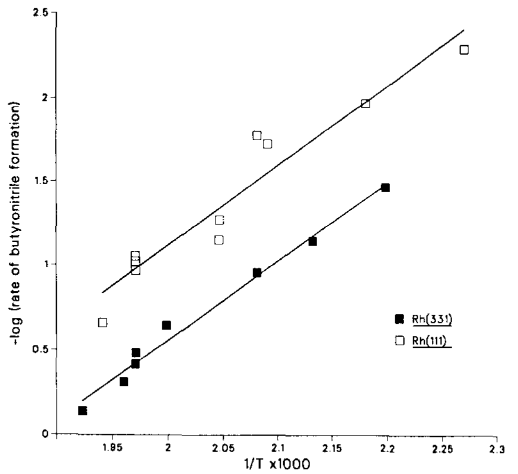

FIG. 3. Arrhenius plots for the formation of butyronitrile from *n*-butanol and ammonia over the Rh (111) and the Rh (331) catalysts. The apparent activation energies are 21 ± 3 and 22 ± 3 kcal/mol for the (331) and the (111) surface, respectively (ammonia : *n*-butanol = 10 : 1, at 110 Torr total reactant pressure).

action the (331) surface is more active than the (111) surface and poisons faster. (See Tables 1 and 2 for rates and product distributions.)

When starting with *n*-butanal (IIb) instead of alcohol, the rate of nitrile production is found to be similar to that of the butanol + ammonia reaction. In these experiments when the ammonia is added to the mixture of *n*-butyraldehyde and argon, suddenly up to 95% of the aldehyde "disappears" from the gas phase as judged by GC analysis. It is interesting to note that with only 5% of the total amount of aldehyde present in the gas phase the rate of nitrile formation hardly changes in comparison with the alcohol + NH_3 reaction. This condensation reaction between the aldehyde and the ammonia is very fast, independent of temperature and the presence of the rhodium catalyst. It can be reversed by addition of water and up to 30% of the aldehyde can be recovered this way. On the basis of the FTIR spectra of the mixture of ammonia and butanal in a glass IR cell one can rule out the possibility of the formation of a gaseous product in this reaction. Thus it seems that the interaction of *n*-butanal and ammonia is mediated by the walls of the reactor and/or the reactor loop.

TABLE 2

Comparison of Rates for Reactions Studied

Reactants	Rates (molecules/ surface Rh atom/sec)	
	Rh (111)	Rh (331)
n-Butanol + ammonia	0.14	0.42
n-Butanol → *n*-butanal	0.44	0.92
n-Butanal + ammonia	0.17	0.13
n-Butanol + ammonia and hydrogen	0.2	0.08
n-Butanal + ammonia and hydrogen	0.5	0.01
n-Butanol + ammonia and water	0.01	0.01
n-Butanal + ammonia and water	0.02	0.01

Note. In the ammonia + *n*-butanol (or *n*-butanal) reactions the total pressure of reactants was 110 Torr (ammonia : aldehyde (or alcohol) 10 : 1). The hydrogen and ammonia partial pressures were 200 and 10 Torr, respectively. Argon was added to attain a total pressure of 300 Torr as necessary. All reaction temperatures were 515 K.

In order to gain more information on this complex reaction system we carried out a number of experiments exploring the effect of addition of some of the products and the effect of a pretreatment of the surfaces with ammonia. The results of these experiments are reported in Tables 1 and 2.

As we showed in the preceding paragraph, the addition of water has a dramatic effect on the concentration of aldehyde in the gas phase. If water is added to the reaction mixture starting from the aldehyde some of the aldehyde is recovered, but the rate of nitrile formation drops. When water is added to the reaction starting from the alcohol, a small amount of aldehyde is detectable, in contrast with the water-free case where no sign of aldehyde is found and the rate of reaction decreases substantially. In both of the above reactions the selectivity to nitrile formation is maintained or increased for the (331) surface.

There are significant shifts in the behavior of the catalyst with the addition of the other product, hydrogen. At first, a very small amount of amine can be detected along with a high-molecular-weight molecule which has been identified as a Shiff

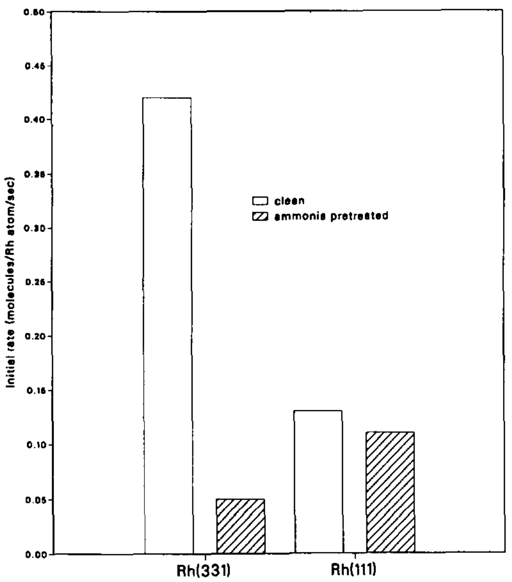

FIG. 4. The rate of formation of butyronitrile from *n*-butanol and ammonia. A comparison between the initial rates of clean and ammonia-pretreated Rh (111) and (331) surfaces (at 510 K, 110 Torr total pressure of reactants, ammonia : *n*-butanol = 10 : 1).

base product of the reaction between the amine and the aldehyde. In addition the selectivity drops and the products are mainly C_1–C_4 hydrocarbons.

Another interesting comparison between the (331) and the (111) catalysts is the effect of ammonia pretreatment. The selectivity and the rate over the (111) surface is essentially unaffected. The behavior of the (331) surface, however, is modified by this treatment. The selectivity of butyronitrile increases and reaches the level of selectivity of the (111) surface, but the rate decreases by a factor of 8. In addition the poisoning rate of the (331) surface is decreased and reactions that poisoned in 1–2 hr work for 10–15 hr after pretreatment. The results of these experiments are shown on Fig. 4 and in Table 1.

2. *Surface Science Studies*

After reactions the gases were pumped down and the high-pressure cell was opened to the UHV. Auger spectra taken from the postreaction catalysts showed that its surface is covered with an overlayer containing carbon, oxygen, and nitrogen. As an example, in Fig. 5 we present an Auger spectrum obtained from an active catalyst. On a working catalyst the stoichiometry implied is approximately C : N : O = 4 : 2.5 : 1. This ratio remained constant within ±10% for both Rh (331) and Rh (111) active catalysts. For the poisoned Rh (331) the ratio changed to C : N : O = 6 : 2.5 : 1, indicating carbon accumulation. A higher amount of carbon is also found on the Rh (111) catalyst when the reaction is carried out at temperatures higher than 550 K and in reactions where the alcohol-to-ammonia ratio is high. In these cases the poisoning is more rapid.

The ammonia pretreatment changes the properties of the (331) surface considerably. Auger electron spectra taken after reactions on pretreated catalysts do not show an increase in the amount of nitrogen present. Furthermore, in accordance with the kinetic data, the carbon content of the overlayer remains unchanged for a longer period of time.

Temperature-programmed desorption (TPD) is a useful tool to obtain information on the reactivity of adsorbed molecules on surfaces. We determined the thermal desorption spectra (TDS) of the reactants (*n*-butanol, *n*-butanal, and ammonia) and butyronitrile. The molecules were adsorbed

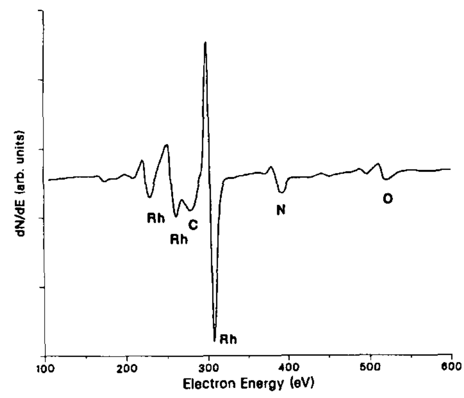

FIG. 5. Auger electron spectrum taken from the postreaction surface of an active Rh catalyst.

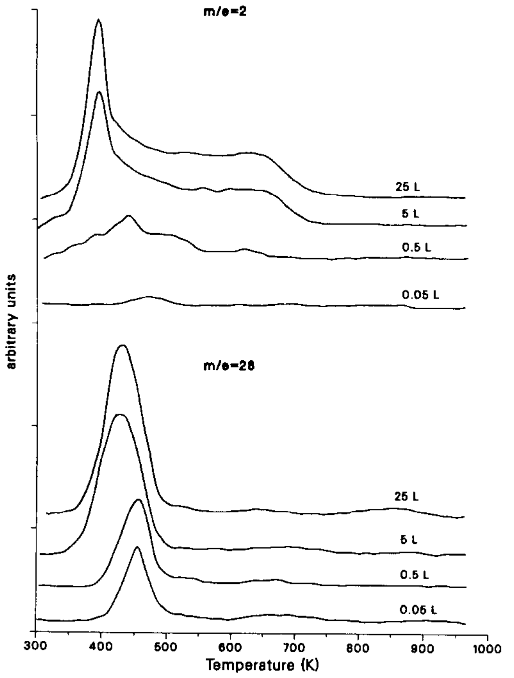

FIG. 6. Temperature-programmed desorption spectra from a clean Rh (111) surface dosed at 300 K with *n*-butanol (1 L = 10^{-6} Torr · sec).

on the clean surfaces of Rh (111) and (331) at room temperature and desorbed using a heating rate of 15 K/sec.

None of the molecules tested produced any molecular desorption features in any of the experiments performed on the clean (111) and (331) surfaces which indicates a strong interaction between the reactants and the clean rhodium surface. Both the alcohol and the aldehyde give very similar desorption spectra and only H_2 and CO leave the surface. In Fig. 6 we show the spectra for the *n*-butanol adsorbed on a clean Rh (111) as a function of exposure. In the *m*/*e* = 28 desorption one peak around 450 K is seen at low exposures and shifts to lower temperatures with increasing dosage. The *m*/*e* = 2 desorption was also equivalent for the two molecules with a major desorption peak around 385 K followed by a long tailing desorption that continued to about 650 K. Very similar desorption spectra were obtained on the Rh (331), but on this surface another desorption feature appeared around 870 K for both the alcohol and the aldehyde.

Neither butyronitrile nor *n*-butylamine adsorbs on either surface at 10^{-6} Torr at 300 K. The sticking probability for ammonia is also very small since 10,000 L of exposure is necessary to produce a detectable amount of nitrogen by TDS and AES.

To investigate what kinds of species desorb from an active catalyst surface we cooled the sample to room temperature in the reaction mixture, then pumped down the gases, introduced the sample in UHV, and performed temperature-programmed desorption experiments. The principal desorbing masses are 2, 12, 14, 27, 28, 29, and 42. An example of these desorption spectra from the Rh (331) surface is shown in Fig. 7. No obvious differences are noted for the experiments carried out on the Rh (111) surface and none of the spectra contained

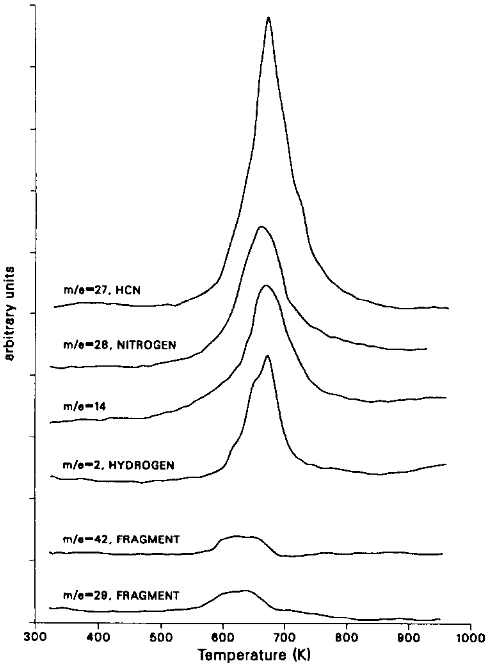

FIG. 7. Temperature-programmed desorption spectra from an active postreaction surface following the reaction of *n*-butanol and ammonia over the Rh (331) surface (at 510 K, 110 Torr total pressure of reactants, ammonia : *n*-butanol = 10 : 1).

masses corresponding to molecular desorption of either of the reactants or the products. The desorption peaks at the lowest temperature are at 630 K, some 100 K above the reaction temperature, and are very small amounts of $m/e = 29$ and 42. This 630 K desorption was closely followed by much larger peaks at $m/e = 27$, 2, 28, and 14. The peaks at $m/e = 28$ and 14 are assigned to molecular nitrogen desorption because their intensity ratio is very similar to the cracking pattern of N_2 observed. The assignment of the peak at 27 to HCN is based on the absence of any other matching desorptions and the amount of nitrogen observed in the AES compared to other works (*26, 27*).

To determine the fraction of the surface that is not covered with the overlayer, the surface of the active catalyst was exposed to ^{13}CO and then in a TDS experiment the labeled carbon monoxide was desorbed. On both catalyst surfaces we found that only 5% of the total number of CO sites, that is Rh atoms, are available.

DISCUSSION

We have found that both Rh (111) and Rh (331) single-crystal surfaces selectively catalyze the formation of butyronitrile from *n*-butanol and ammonia at around 500 K. The (331) surface is three times more active, but poisons faster and produces 8–10 times more C_1–C_3 cracking products. Thus it seems that the *n*-butanol + $NH_3 \rightarrow$ butyronitrile is structure sensitive on rhodium, and the step sites on the (331) surface are more active for the ammonolysis and much more active in the cracking reaction. This observation is consistent with other studies that have previously reported that stepped surfaces are more active in hydrogenolysis reactions than flat surfaces (*23, 24*).

The apparent activation energies are practically the same for both surfaces (21–22 ± 3 kcal/mol), indicating that the mechanism of the nitrile formation is likely the same and independent of the surface structure of the rhodium catalyst. Since we can rule out the reaction of ammonia with the alcohol to produce the amine as a first step, on the basis of our experimental results one can conclude that the reaction follows the dehydrogenation path to produce the aldehyde first:

$$\underset{n\text{-butanol}}{CH_3CH_2CH_2CH_2\text{—}OH} \rightarrow \underset{n\text{-butanal}}{CH_3CH_2CH_2CHO} + H_2 \quad \text{(a)}$$

This is supported by the observations that (i) both rhodium surfaces oxidize *n*-butanol readily, with a higher rate than the overall reaction to form nitrile, and (ii) starting from the *n*-butyraldehyde one obtains butyronitrile with similar rates and product distributions.

Imine intermediates in the reaction of aldehydes and ammonia have been proposed both in the literature and in the patent disclosures (*6, 30–34*). Our effort to identify the product of the condensation reaction between the aldehyde and the ammonia at room temperature by FTIR has failed but it is possible that this interaction leads to a precursor which at higher temperatures and on the rhodium surface transforms to the imine intermediate. To understand the nature of this condensation reaction further investigation is necessary. Nevertheless, the reaction-inhibiting role of water does imply that an imine intermediate is likely to form:

$$\underset{n\text{-butanal}}{CH_3CH_2CH_2CHO} + NH_3 \rightarrow \underset{n\text{-butylimine}}{\{CH_3CH_2CH_2CHNH\}} + H_2O \quad \text{(b)}$$

$$\underset{n\text{-butylimine}}{\{CH_3CH_2CH_2CHNH\}} \rightarrow \underset{n\text{-butyronitrile}}{CH_3CH_2CH_2CN} + H_2 \quad \text{(c)}$$

In our kinetic studies we have found that rate of the nitrile formation is independent of the partial pressure of the alcohol. This zero-order pressure dependence and the high rate of oxidation to *n*-butanal indicate that the rate-limiting step in the overall reaction is either the reduction of the imine intermediate or the desorption of the product.

Due to the fast oxidation of the alcohol to aldehyde it is expected that an overlayer builds up on the working catalyst. Indeed, as we have shown in our ^{13}CO titration experiment the surface of the active Rh catalyst is covered with an overlayer and only 5% of the Rh atoms are exposed. Auger electron spectra obtained from the active surface also support that the reaction probably occurs on an overlayer containing carbon, nitrogen, and oxygen. The role of this overlayer is critical in understanding the action of the catalyst. The temperature-programmed desorption of the reactants adsorbed on clean surfaces can provide hints as to what species this overlayer might contain.

Our TPD data obtained by dosing the *n*-butanol and *n*-butanal indicate that both of these molecules dissociate readily on the clean (331) and (111) surfaces since there is no molecular desorption. The only desorption products are CO and H_2 indicating that a hydrogen-deficient C_3 overlayer is left behind. The position of the CO desorption peak at 455 K is very similar to the CO desorption reported by Solymosi *et al.* (*29*) for methanol desorption from Rh (111). It seems that both the alcohol and the aldehyde undergo α–β C–C bond scission, the CO leaves the surface, and the C_3 fragment remains to form one part of the overlayer. These species are unlikely to participate in the principal reaction as no C_3 nitriles or amines have been detected.

The active overlayer contains nitrogen and oxygen as well, implicated by both the AES and the TDS. The desorbing molecules from the active catalyst are mainly small molecules such as H_2, HCN, N_2, and fragments of longer C_4 molecules involved in the reaction. No molecular desorption of either the products or the reactants has been observed.

The hydrogen desorption is most likely due to organic fragments bound to the surface losing H_2 because molecular H_2 desorbs from rhodium at a much lower temperature (325 K). Among the desorbing molecules, there is no CO or if there is its amount must be very small since the ratio of peaks m/e = 14 and 28 closely corresponds to the ratio found for dinitrogen. This indicates that on the active surface there can be only a very small amount of alcohol/aldehyde present; in other words it is possible that equilibrium (IIb) in our scheme is shifted to the right, at least during the desorption experiment in UHV.

It is interesting that the nitrogen on the active catalyst exists in at least two forms leading to the desorption of HCN and N_2. Here the unusual high-temperature HCN desorption suggests that the molecule is a decomposition product. Similarly there are different species containing carbon in the overlayer: (i) C_4 molecules, although in very small quantities; (ii) hydrogen-deficient C_3 residues from the decomposition of the alcohol, the aldehyde, and/or N-containing intermediates; (iii) C_1 species which are produced in the α–β C–C bond breaking in the C_4 molecules and are possible sources of HCN desorption; and (iv) carbon deposits that are eventually formed from (ii) and (iii). Types (ii), (iii), and (iv) carbons are most likely the species that slow the nitrile formation by covering the surface with an inactive layer. In accordance with this, the Auger spectra of deactivated surfaces exhibit a higher carbon concentration than the active catalyst surfaces.

The step sites on the Rh (331) surface are more effective at breaking C–C bonds and as a consequence this catalyst poisons faster than the Rh (111). This behavior can be altered by pretreating the surfaces in ammonia at reaction temperature. After this treatment, the reactivity of the (331) surface is significantly different. The ammonia treatment eliminates the cracking activity, making the product distribution the same as that of the (111) surface. Although the rate of nitrile production dropped by 85%, this activity was maintained five times longer than that of the untreated (331) surface. The effect of pretreatment seems to be irreversible since the altered catalyst remains stable.

The influence of the pretreatment could be explained if one assumes that nitrogen-containing species formed during the decomposition of ammonia during the pretreatment are blocking step sites which are responsible for the cracking and poisoning reactions. Examples of this type of selective poisoning have been noted in the literature (*27, 28*). In the AES and the TDS spectra, however, there are no detectable differences between the (331) and the (111) surfaces. Neither can we see indications of a more pronounced nitrogen buildup than that of untreated surfaces after reaction. Another effect of the pretreatment could be that it restructures the (331) surface. This restructuring on a macroscopic scale was reported by Hasenberg *et al.* for the (331) surface of rhodium caused by high-pressure ammonia treatment, observed by SEM (*25*). We have been unable to see any macroscopic changes on our pretreated samples using SEM. Certainly we cannot rule out the possibility of an atomic level reconstruction of the (331) surface of rhodium caused by the ammonia pretreatment and a detailed LEED study should address this question in the future.

ACKNOWLEDGMENT

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