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Concerted Reaction Mechanism in Deuteration and H/D Exchange of Nitriles over Transition Metals

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In acetonitrile hydrogenation the selectivity to primary amine decreases in the order of Ru, Ni, Rh, Pd, Pt. Ruthenium is highly selective for primary amine and platinum for tertiary amine. The selectivity of the metals is related to their propensity for multiple bond formation. The metal known for the highest propensity to form multiple bonds has the highest selectivity to primary amine. In the deuteration of nitriles both D addition and H/D exchange take place. Most of the primary and secondary amine molecules that are formed when acetonitrile and D_2 mixture is passed over the catalysts have fewer D atoms than predicted by stoichiometry. D atoms are added to the C atom of the CN group, but H atoms are preferentially added to the N atom. For instance, for diethylamine the preferred isotopomers are $(CH_3CD_2)_2NH$, (CH_3CD_2)–NH–(CD_2CD_3), and $(CD_3CD_2)_2NH$. Many of these H atoms originate from isotope exchange of D_2 with the methyl group. A concerted mechanism is proposed in which dissociation of C–H bonds of some CH_3CN molecules results in H transfer to other CH_3CN molecules that are adsorbed with their C≡N bond parallel to the surface. Particularly with Ru it is also conceivable that this H transfer is instrumental in the amine desorption step when strong C–Ru bonds have to be broken. A second source of H atoms is a surface overlayer that is formed over all metals and will, initially, have a H/D ratio different from the overall ratio in the feed. © 1999 Academic Press

INTRODUCTION

Amines are widely used in industry as intermediates for polymers, pesticides, and other chemicals. One important route for the production of amines is hydrogenation of the corresponding nitriles. This is often done in the liquid phase in batch experiments. As to the reaction mechanism, Sabatier and Senderens (1) proposed in 1905 that primary amines are formed in two steps; first two H atoms are added to the nitrile, resulting in an aldimine, which is subsequently hydrogenated to the primary amine. In 1920, Mignonac (2) proposed that a secondary amine is formed from three molecules of aldimine, followed by hydrogenolysis to a Schiff base and its hydrogenation. In 1923, von Braun *et al.* proposed (3) that secondary amines are formed by interaction between aldimine and a primary amine, leading to an 1-aminodialkylamine or a Schiff base. Hydrogenolysis of the former or hydrogenation of the latter forms the secondary amine. Juday and Adkins (4) assumed that in the hydrogenation of aromatic nitriles dimerization of an imine followed by hydrogenolysis leads to the Schiff base. In the same general logics, Kindler and Hesse (5) proposed in 1933 that tertiary amines are formed by the interaction of an imine with a secondary amine, leading to 1-amino-trialkylamine; again hydrogenolysis is required to form the final product. Greenfield (6) proposed in 1967 that 1-aminotrialkylamine undergoes deamination to an enamine that is subsequently hydrogenated to a tertiary amine.

Most of the proposed unsaturated products, e.g., Schiff bases and enamines, have been identified. The selectivity of nitrile hydrogenation depends on a number of factors, among which the nature of the metal is the most important, but also the least understood. There is a consensus that the selectivity to primary amines is high over Ru and Ni, whereas Cu and Rh tend to form secondary amines, while Pd and Pt have a high propensity to form tertiary amines (7–9). No mechanistic explanation is known for this pattern. A naive concept assuming that those metals known to catalyze the fission of strong chemical bonds will also lead to secondary and tertiary amines is obviously at variance with the experimental facts: ruthenium which has the highest propensity to catalyze bond fissions has also the lowest selectivity toward higher amines. One motivation of the present work is to shed some light on this issue.

Nitrile hydrogenation in the gas phase in flow reactors has been extensively studied in our group. For the hydrogenation of acetonitrile and butyronitrile over NaY-supported Pd and Pt catalysts under flow conditions we reported that the selectivities to secondary products change little with conversion; with butyronitrile hydrogenation over NaY-supported Ru, Ni, Rh, Pd, and Pt under flow and static conditions, the same selectivity pattern is obtained as reported in the literature for autoclave experiments in the presence of a liquid phase. Since it was verified that no capillary condensation occurred in the pores of the support, this shows that all reaction steps up to the formation of the

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tertiary amine can take place on the catalyst surface, no liquid phase is required (10). The same conclusion was drawn previously by Kemball and Moss who studied the reaction of methylamine and ethylamine with H_2 over evaporated films of Ni, Fe, Pd, Pt, and W and found that all steps leading to the formation of secondary or tertiary amine take place at the metal surface (11).

Significant evidence on the chemistry of nitriles and amines at the surface of transition metals has been obtained from H/D exchange of these molecules with D_2 (12). With acetonitrile it was found that the multiplicity of the H/D exchange over a variety of metals at 75°C decreases in the order of Ru, Ni, Rh, Pd, Pt. As we shall show, this multiplicity can be correlated with the selectivity of these metals to form primary amines.

In the present work, mixtures of acetonitrile and D_2 or butyronitrile and D_2 with large excess of D_2 are passed over the supported transition metal. In the absence of any secondary H/D exchange, the following stoichiometry might be expected for the three overall reactions ($R = CH_3$– or $CH_3CH_2CH_2$–):

$$RCN + 2\,D_2 = RCD_2ND_2 \qquad [1]$$

$$2\,RCN + 4\,D_2 = (RCD_2)_2ND + ND_3 \qquad [2]$$

$$3\,RCN + 6\,D_2 = (RCD_2)_3N + 2ND_3. \qquad [3]$$

In this "naive stoichiometry" the prevailing isotope will be d_4 for the primary amine, for the secondary amine it will be d_5, and for the tertiary amine d_6. (Here we use the conventional nomenclature indicating a molecule containing x D atoms as d_x). In an excess of D_2, additional H/D exchange will take place, leading to higher d_x fractions. Any abundant formation of molecules with *lower* D content than predicted by Eqs. [1] through [3] is evidence that the actual processes taking place at the surface of these catalysts are insufficiently described by these conventionally considered reaction steps.

In the present work, products have been analyzed by a combination of GC and mass spectrometry. To identify the position of the H and D atoms in the amines, selected products were subjected to a secondary isotopic exchange in liquid D_2O; this reaction specifically exchanges the hydrons bonded to the N atoms. TPD has been used to estimate overlayers and to identify conditions of temperature and partial pressure, under which capillary condensation is insignificant.

EXPERIMENTAL

M/NaY (M = Ru, Ni, Rh, Pd, Pt) catalysts were prepared by ion exchange, as described previously (12). Ru/NaY (UOP, Y-54) was used as received. Ru/NaY was prepared by ion exchange of a $Ru(NH_3)_6Cl_3$ solution with NaY zeolite at room temperature for 24 h. Rh/NaY was prepared by ion exchange of $Rh(NH_3)_5Cl_3$ with NaY at 80°C for 72 h. Pd/NaY was prepared by ion exchange of $Pd(NH_3)_4(NO_3)_2$ with NaY at room temperature for 24 h. Pt/NaY was prepared by ion exchange of $Pt(NH_3)_4(NO_3)_2$ with NaY at 80°C for 12 h. Ni/NaY was prepared by ion-exchange of $Ni(NO_3)_2$ with NaY at room temperature at pH ∼6 for 24 h followed by a NaOH treatment. All M/NaY catalysts have a metal loading of about 3%.

Two batches of Ru/SiO_2 catalysts were prepared. Ru/SiO_2(A) was made by impregnation of silica with $Ru(NH_3)_6Cl_3$; the Ru loading is 1.41%. Ru/SiO_2(B) was prepared by impregnation of silica with $RuCl_3 \cdot xH_2O$; the Ru loading is about 3%. Pt/SiO_2 was prepared by impregnation of silica with $Pt(NH_3)_4Cl_2$; the Pt loading is 2.71%.

Prior to reduction, the Ru/NaY and Ru/SiO_2 catalysts were subjected to calcination in an Ar flow of 60 mL/min at 450°C for 20 min, all other catalysts were calcined in a flow of oxygen of 100 mL/min at 500°C for 2 h. *In situ* reduction was carried out in a hydrogen flow of 30 mL/min at a specified temperature for 30 min: 300°C for Ru/NaY, Ru/SiO_2, and Pd/NaY, 350°C for Rh/NaY, 400°C for Pt/NaY and Pt/SiO_2, and 500°C for Ni/NaY.

Deuteration of Ru/SiO_2 with D_2O was carried out by exposure of the catalyst to a flow of D_2O/He at 300°C for 30 min, this process is known to transform the OH groups of the support into OD groups (13). This D_2O/He flow was obtained by passing a flow He of 30 mL/min through a saturator of D_2O (23°C), the partial pressure of D_2O in the mixture was 36 Torr. After that treatment, the catalyst was purged at 300°C with He of 30 mL/min for 30 min and with D_2 of 30 mL/min for 10 min, followed by cooling to the reaction temperature in flowing He.

The "deuteration" of the nitriles was preceded by purging the freshly reduced catalysts for 10 min with flowing D_2 of 30 mL/min at the reaction temperature. One hundred milligrams of catalyst was used in all cases unless otherwise indicated. In the hydrogenation of acetonitrile, less than 100 mg of Rh/NaY, Pt/NaY, and Ni/NaY were tested in order to keep the conversion below 16%. In this case, the catalyst was diluted with quartz (Fluka, <200 mesh) to obtain a total mass of 100 mg. In butyronitrile deuteration, 50 mg of Pt/SiO_2 mixed with 50 mg quartz was used.

The reaction was carried out in a microflow fixed-bed reaction system. The diameter of the reactor was about 10 mm, the catalyst bed was about 1 mm thick. At a flow rate of 30 mL/min, the contacting time thus amounts to about 0.15 s. The feed stream was obtained by passing a H_2 flow of 30 mL/min or a D_2 flow of 40 mL/min through an acetonitrile (−4°C) or butyronitrile saturator (25°C). The partial pressures of the nitriles in the feed stream were about 20 Torr.

A HP-5890 gas chromatograph equipped with a HP-1 capillary column (5 m × 0.53 mm) was used for on-line analysis of hydrogenation. A GC-MS (HP-G1800A GCD system) equipped with a HP-PONA column (50 m × 0.2 mm) was used for mass spectral analysis on-line or off-line. A

Varian Unity Plus 400 NMR system with a 5-mm probe was used for ^{1}H NMR analysis. NMR analysis was run at 5°C since ethylamine has a low boiling point (16.6°C).

The products of nitrile deuteration were analyzed online. In some cases, the products were condensed in a liquid nitrogen cooled trap and subsequently analyzed by ^{1}H NMR. These products were then subjected to a secondary exchange with liquid D_2O by adding a few drops of heavy water. A small amount of deuterated chloroform (CD_3Cl) was added in this stage and the mixture was shaken vigorously. The secondary exchange products were analyzed by GC-MS and ^{1}H NMR. As reported previously (12), the GC-MS analysis permits identification of isotopomers, as molecules with higher deuterium numbers have shorter retention times. For the calculation of the isotopic distribution, the mass signals were averaged, and the usual corrections were made for the natural abundance of isotopes and the fragmentation in the MS.

RESULTS

1. *Hydrogenation of Acetonitrile over M/NaY Catalysts*

In the gas phase hydrogenation of acetonitrile at 75°C, all catalysts initially deactivate with time, but after 5 h conversion and selectivity no longer change. In Table 1 the steady state conversions and selectivities over a variety of *M*/NaY catalysts at 75°C are compiled. The catalyst quantities were adjusted to keep conversions below 16%. The results show that Ru/NaY is highly selective to ethylamine, while Pd/NaY and Pt/NaY are highly selective to triethylamine. These selectivities are in line with previous results of gas and liquid phase hydrogenation of butyronitrile (10).

TABLE 1

Acetonitrile Hydrogenation over *M*/NaY Catalysts (M = Ru, Ni, Rh, Pd, Pt)

Catalyst	Amt. catal. (mg)	Conv. (%)	Sel (mol %)			
			EA	EEA	DEA	TEA
Ru/NaY	100	4.6	81.8	15.2	3.0	0
Ni/NaY	50	10.5	18.5	35.1	27.2	19.2
Rh/NaY	30	5.9	9.7	4.9	27.8	57.6
Pd/NaY	100	1.8	3.5	0	7.1	89.4
Pt/NaY	20	15.8	0.9	0	2.8	96.2

Note. 75°C, $H_2 = 30$ mL/min, $P(AN) = 20$ Torr, when less than 100 mg catalysts is used, quartz (Fluka, >200 mesh) is used as dilutant. The final mixture for testing is 100 mg. Data were taken after 5 h TOS reaction. AN, acetonitrile; EA, ethylamine; EEA, ethylidene–ethylamine; DEA, diethylamine; TEA, triethylamine.

In a previous paper (12), we reported that in the H/D exchange of acetonitrile over *M*/NaY catalysts at 75°C under the same flow conditions the "multiplicity" depends on the metal: Ru/NaY, 1.79; Ni/NaY, 1.28; Rh/NaY, 1.21; Pd/NaY, 1.06; Pt/NaY, 1.10. In Fig. 1 the selectivity to ethylamine in

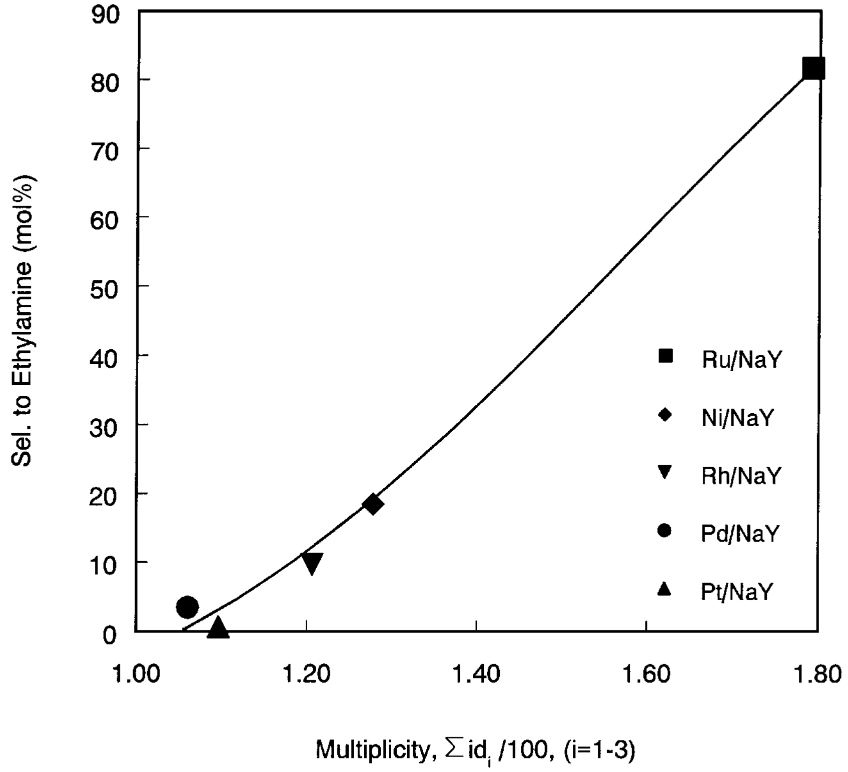

FIG. 1. Relationship between multiplicity in acetonitrile/D_2 exchange and selectivity to primary amine in acetonitrile hydrogenation.

the CH_3CN hydrogenation at 75°C is plotted against this multiplicity of the CH_3CN/D_2 exchange. Clearly, two extreme situations exist: Ru has the highest multiplicity and the highest selectivity to primary amine, while Pd and Pt have the lowest multiplicity and the lowest selectivity to primary amine.

2. *Acetonitrile Deuteration over M/NaY*

Deuteration of acetonitrile is carried out at 75°C over *M*/NaY catalysts ($M = $ Ni, Rh, Pd, Pt). A kinetic isotope effect is observed; the rate of deuteration is lower than that for hydrogenation but the same selectivity pattern is found in both cases. Over Pd/NaY, the relative ratio of hydrogenation to deuteration is 1.8.

Over Rh/NaY and Ni/NaY ethylamine is formed in low concentrations; the MS signal is weak. The pattern is shown in Fig. 2 for the isotopic distribution of ethylamine. For Rh/NaY maxima are observed at d_0, d_2, and d_5 and for Ni/NaY at d_0, d_4, and d_5. The d_6 and d_7 yields are very low.

The isotopic distribution strongly deviates from that expected on the basis of the "naive stoichiometry." Most remarkably, even perproto-ethylamine, d_0, is formed when acetonitrile reacts with D_2 over Rh/NaY and Ni/NaY catalysts.

Diethylamine is formed in substantial amounts over Rh/NaY, Ni/NaY, and Pd/NaY. Figure 3 shows the isotopic distributions. Maxima are observed at d_7 for Ni/NaY and at d_8 for Rh/NaY and Pd/NaY. Over Ni/NaY and Rh/NaY d_{10} has also a high abundance. Again, the product contains the *perproto* molecule diethylamine d_0. The most spectacular phenomenon is the very low abundance of d_{11}, i.e., a precipitous decrease from d_{10} to d_{11}.

Large amounts of triethylamine are produced over Ni/NaY and Rh/NaY; over Pd/NaY and Pt/NaY the selectivity to triethylamine is even higher than 90%. Figure 4 shows the isotopic distribution of the triethylamine produced over these metals. There is a maximum abundance at d_{12}. Over Rh/NaY, a large amount of d_{15} is also detected; evidently all methylene and all methyl groups are deuterated in this product.

Over a fresh batch of Ru/NaY acetonitrile deuteration was carried out at and above 100°C in order to get detectable activity. Over Ru/NaY, the selectivity to the various amines changed dramatically with temperature. At 100°C and 25 min time on stream (TOS) primary amine is formed with a selectivity as high as 85 mol%. At 125°C, this selectivity decreases to 46.4 mol% and the selectivity to secondary amine is as high as 39.7 mol%. At 150°C, the selectivity to tertiary amine is as high as 15.3 mol% and appreciable amounts of ethane are formed.

The isotopic distribution within the fraction of primary amine formed over Ru/NaY changes significantly with

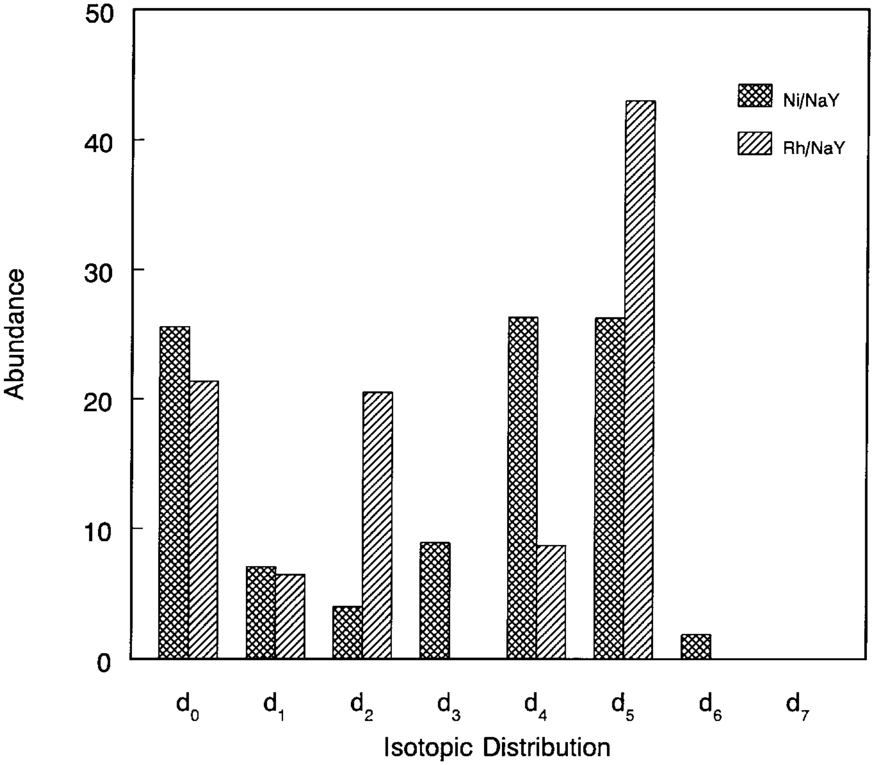

FIG. 2. Isotopic distribution of ethylamine from acetonitrile deuteration over Ni/NaY and Rh/NaY. 75°C, 100 mg catalyst, $D_2 = 40$ mL/min, $P(\mathrm{AN}) = 20$ Torr, 25 min TOS.

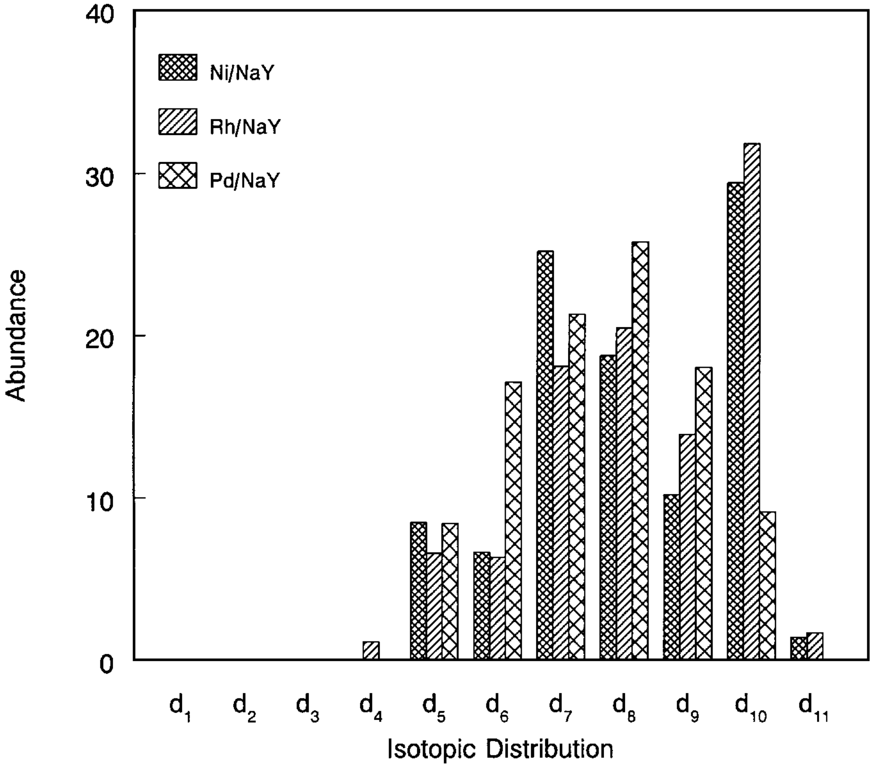

FIG. 3. Isotopic distribution of diethylamine from acetonitrile deuteration over Ni/NaY, Rh/NaY, Pd/NaY. 75°C, 100 mg catalyst, $D_2 = 40$ mL/min, $P(\text{AN}) = 20$ Torr, 25 min TOS.

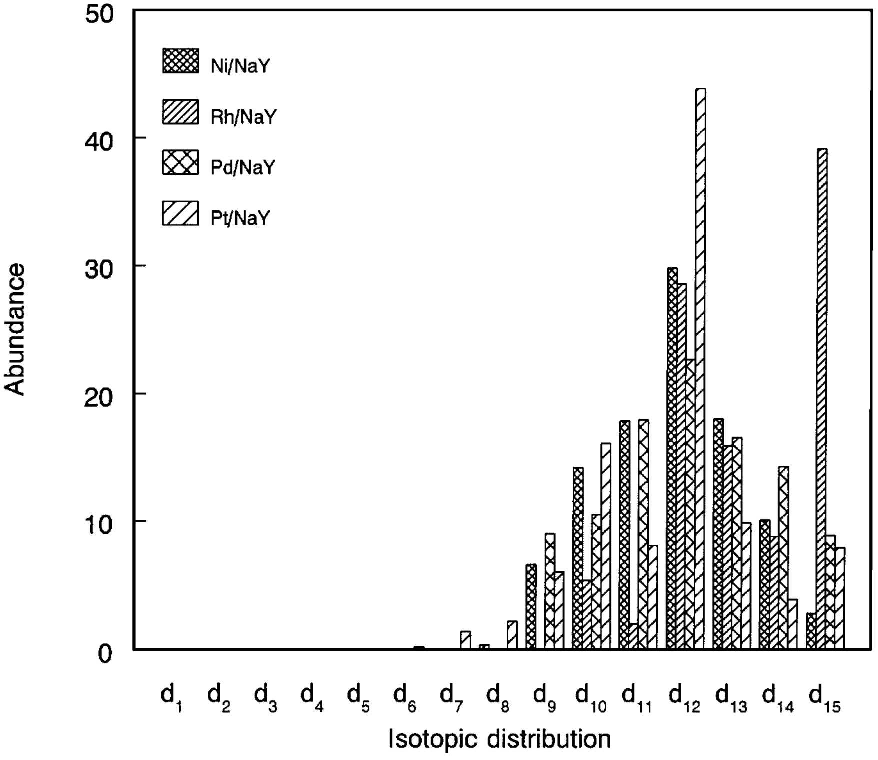

FIG. 4. Isotopic distribution of triethylamine from acetonitrile deuteration over Ni/NaY, Rh/NaY, Pd/NaY, and Pt/NaY. 75°C, 100 mg catalyst, $D_2 = 40$ mL/min, $P(\text{AN}) = 20$ Torr, 25 min TOS.

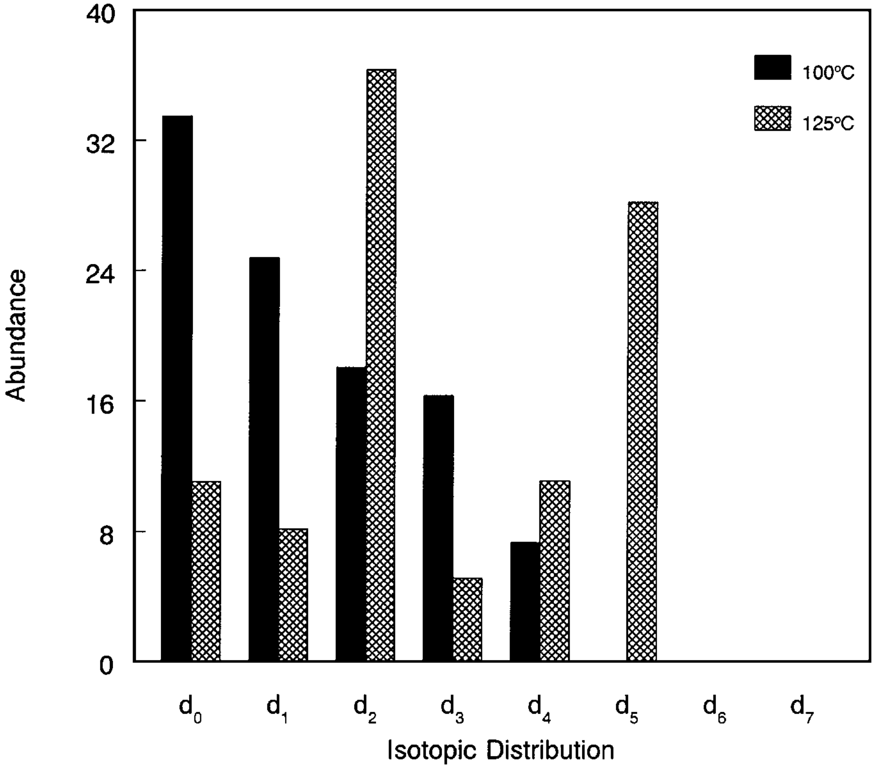

FIG. 5. Isotopic distribution of ethylamine from acetonitrile deuteration over Ru/NaY at 100°C and 125°C. 100 mg catalyst, $D_2 = 40$ mL/min, $P(\text{AN}) = 20$ Torr, 25 min TOS.

temperature, as shown by the data in Fig. 5. At 100°C, the most abundant species is d_0 and the relative abundances decrease in the order $d_0 > d_1 > d_2 > d_3 > d_4$. No product molecules with more than 4 D atoms are detected at this temperature. At 125°C, the maximum abundance is observed at d_2 and d_5, while d_0, d_1, d_3, and d_4 are formed in low concentrations only. The largest number of D atoms in any molecule is five.

Over Ru/NaY at 125°C, the formation of diethylamine is detectable by MS. The isotopic distribution obtained is similar to that formed over Rh/NaY, Ni/NaY, and Pd/NaY at 75°C. The maximum abundance is observed at d_7 while the abundance at d_{11} is very low.

The d_0 content of ethylamine and diethylamine is higher over Ru/NaY at and above 100°C than over NaY-supported Ni, Rh, and Pd at 75°C.

3. *Acetonitrile Deuteration over Ru/SiO$_2$*

For the deuteration of acetonitrile over Ru/SiO$_2$(A) the selectivity to diethylamine and triethylamine and ethane increases with temperature. Compared with Ru/NaY, the selectivity to primary amine is always lower while the selectivity to ethylidene–ethylamine is always higher.

With acetonitrile deuteration over Ru/SiO$_2$ at 125°C, the isotopic distribution of the ethylamine has two maxima at d_2 and d_5, whereas the concentrations of d_6 and d_7 are very low. For diethylamine, a maximum is observed at d_7 and the contents of d_4 and d_{10} are also high. Again, there is a sharp drop from d_{10} to d_{11}. With ethylidene ethylamine, a maximum is observed at d_6. The d_0 content of the reaction product is significant though lower than over Ru/NaY.

4. *Position of the D Atoms in the Acetonitrile Deuteration Product Molecules*

The above results clearly show that the isotopic distributions of ethylamine, diethylamine, and triethylamine formed over *M*/NaY (*M* = Ni, Rh, Pd, Pt) at 75°C and over Ru/NaY and Ru/SiO$_2$ at 125°C have similar characteristics. Therefore, it is important to determine the position of D atoms in the product molecules. A few samples are taken for detailed analysis.

Figure 6 shows the mass spectrum of triethylamine formed over Pt/NaY at 75°C. The most abundant parent molecular ions are observed at $m/e = 113$. The most abundant main fragmentation ions, which have lost one methyl group (14), are observed at $m/e = 95$ and 98. The abundance at $m/e = 95$ is almost two times that at $m/e = 98$. The results clearly indicate that this triethylamine contains predominantly molecules of the composition CH_3CD_2–N–$(CD_2CD_3)_2$.

Figure 7 shows the mass spectrum of ethylidene–ethylamine formed over Ru/SiO$_2$ at 125°C. The molecular ion and the main fragmentation ion after losing one methyl

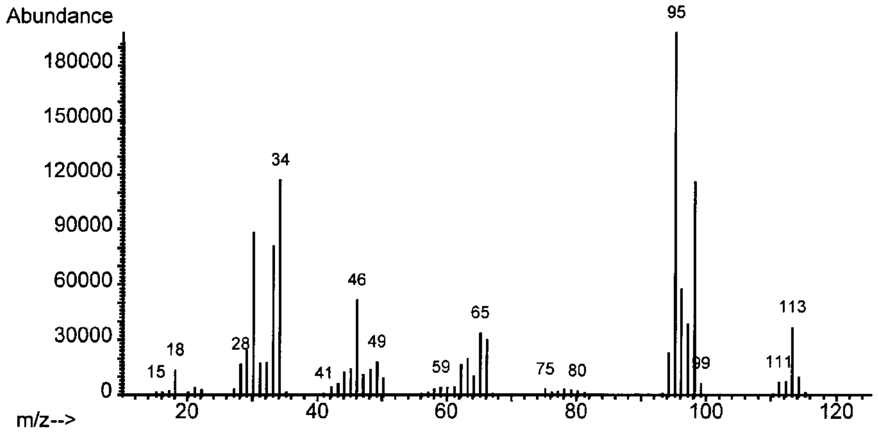

FIG. 6. Mass spectrum of triethylamine from acetonitrile deuteration over Pt/NaY at 75°C. 100 mg catalyst, $D_2 = 40$ mL/min, $P(\mathrm{AN}) = 20$ Torr, 25 min TOS.

group are observed at $m/e = 77$ and 62, respectively. This suggests $CH_3CD{=}N{-}CD_2CD_3$ as the dominant product.

In ethylamine and diethylamine, H atoms preferentially attached to the N atom. The position of the D atoms inside a given molecule has been derived from the analysis of the products formed in the secondary exchange with liquid D_2O. It is known that this secondary exchange leads exclusively to replacement of the N-bonded H atoms by D atoms (15–17). This secondary exchange is easily detected by ^{1}H NMR spectra or by the fragmentation pattern in the mass spectrometer. In our previous paper, we had used the combination of ^{1}H NMR and GC-MS to determine the location of D atoms in amine/D_2 exchange products (12). The same technique is used here. Figure 8 shows the ^{1}H NMR spectra of the primary product from acetonitrile deuteration over Ru/SiO_2 at 125°C and the secondary exchange product with D_2O. The signals of the $-CH_2-$ group and the $-CH_3$ group in the amines and the signal of the $-CH_3$ group in CH_3CN are well separated. As for amines, the chemical shift of $-CH_2-$ is higher than that of a $-CH_3$ group. There is no separate signal of an $-NH_2$ or $=NH$ group in the spectra. However, the change of the relative ratio of the signal at about 2.8 ppm to the signal at about 1 ppm reveals the presence of hydrogen in the amine group. With the primary product, the ratio of the signal at 2.8 ppm to the signal at 1 ppm is 1 : 11.0. After the secondary exchange with D_2O, the ratio changes to 1 : 6.5. The results clearly show that the amine group ($-NH_2$ or $=NH$) in the primary product contains mainly H atoms, not D, and that the signal of amine H atoms is merged with that of the $-CH_3$ group. As a consequence, the ratio (1 : 6.5) deviates greatly from the normal ratio of H atoms in a methylene group to the H atom in the methyl group for D-free molecules. With ethylamine or diethylamine, this ratio is 1 : 1.5. The deviation indicates that in the present deuteration products (ethylamine or diethylamine), D atoms are mainly located in the $-CH_2-$ groups and not in the $-CH_3$ groups.

With GC-MS we succeeded in separating ethylamine from diethylamine. Figure 9 shows the MS spectra of ethylamine in the primary product of acetonitrile deuteration

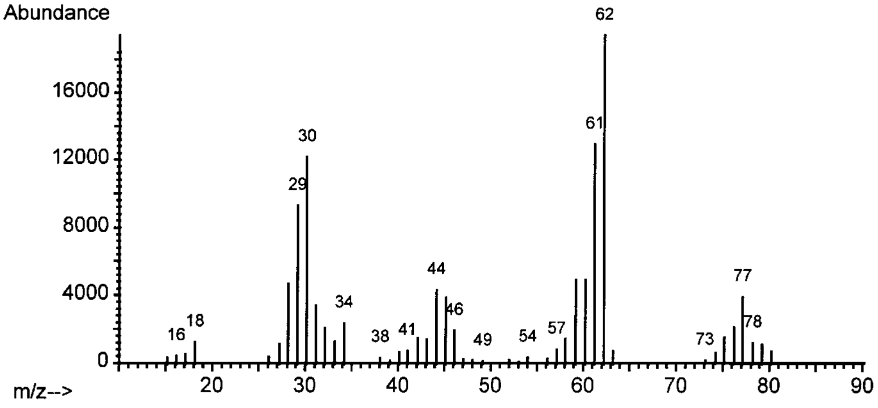

FIG. 7. Mass spectrum of ethylidene–ethylamine from acetonitrile deuteration over Ru/SiO_2 at 125°C. 100 mg catalyst, $D_2 = 40$ mL/min, $P(\mathrm{AN}) = 20$ Torr, 25 min TOS.

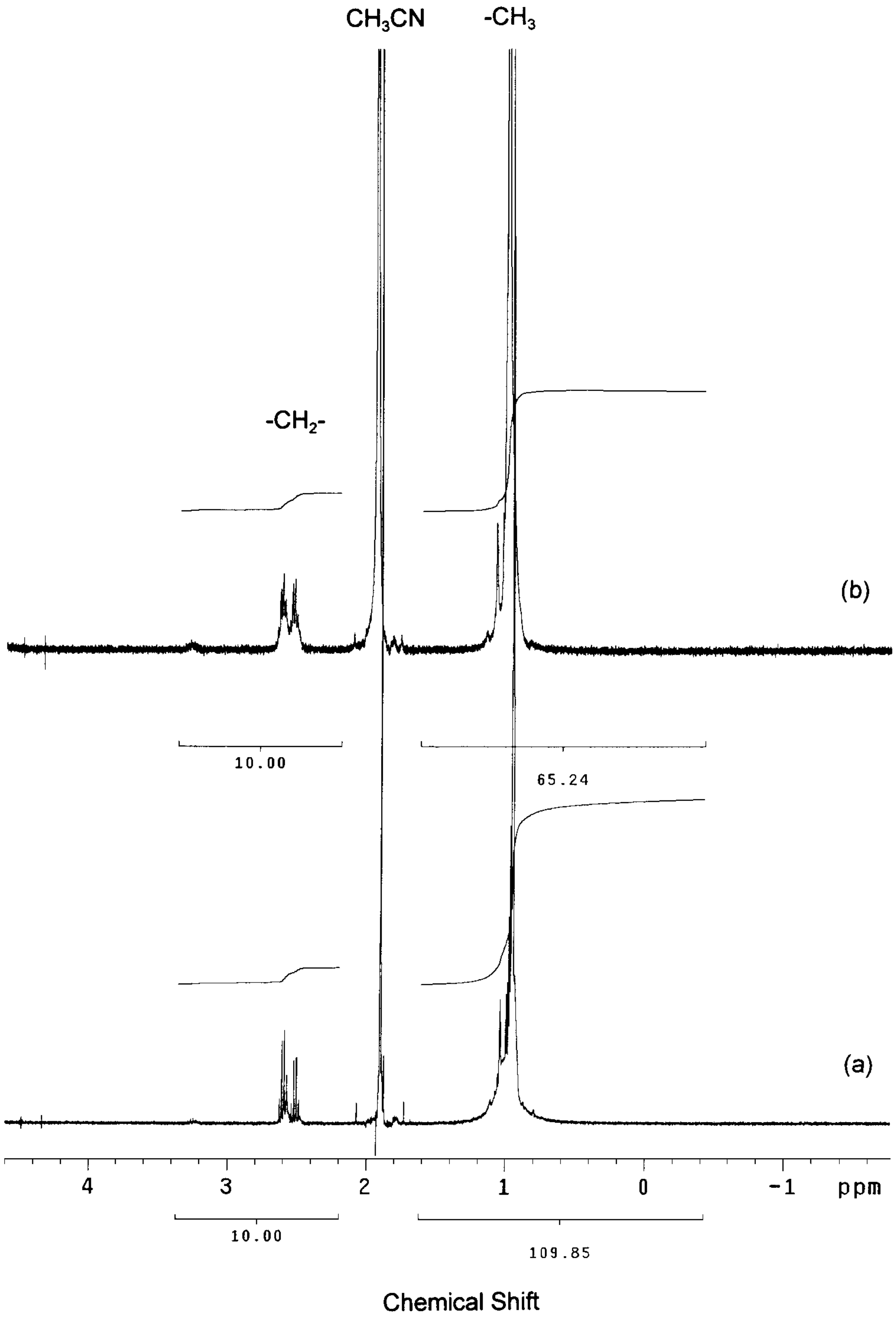

FIG. 8. ^{1}H NMR spectra of acetonitrile deuteration products over Ru/SiO_2 at 125°C in first 30 min. (a) Fresh product, (b) after secondary exchange with D_2O.

over Ru/SiO_2 at 125°C and after secondary exchange with D_2O. In the original ethylamine, the main fragmentation ion, at $m/z = 32$, is due to the loss of one methyl group. After exchanging with D_2O, this has been shifted to $m/z = 34$, while a peak at $m/z = 33$ is also observed. Likewise, the fragmentation peaks at $m/z = 47$, 48, and 50 are shifted to 49, 50, and 52, respectively. From these results it is clear that the methylene groups and the methyl groups contain mainly D atoms but the amino group contains mainly H atoms. The formed ethylamine has preferentially a formula

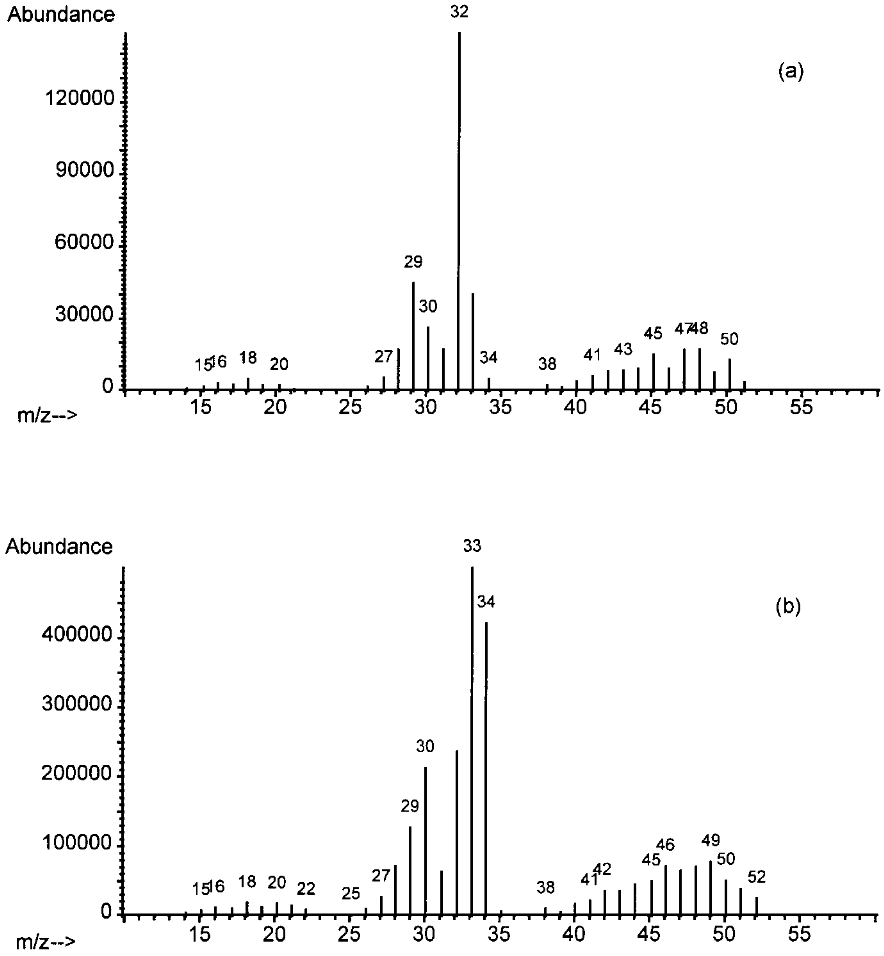

FIG. 9. Mass spectra of ethylamine from acetonitrile deuteration over Ru/SiO_2 at 125°C in first 30 min. (a) Fresh product, (b) after secondary exchange with D_2O.

of $CH_3CD_2NH_2$ and $CD_3CD_2NH_2$. The main fragmentation ion at $m/z = 33$ after exchanging with D_2O is probably due to the exchange equilibrium. The poor separation of GC for ethylamine isotopomers is another reason for the appearance of the main fragmentation ion at $m/z = 33$.

The diethylamine isotopomers d_0, d_4, d_7, and d_{10} are detected by CG-MS in the primary reaction product of acetonitrile deuteration over Ru/SiO_2 at 125°C. The d_4 molecule is not well separated from the others. Figure 10 shows the mass spectrum of d_{10} in the primary reaction product and after secondary exchange with D_2O. The most abundant molecular ion and main fragmentation ion by losing a methyl group are observed at $m/z = 83$ and 65. After exchanging with D_2O, the molecular ion and main fragmentation ion both shift up by one unit. The same result is observed with d_0, d_4, and d_7. The results clearly show that the D atoms in diethylamine are located in the alkyl group, but the H atoms are located in the amino group. The preferential formulas are $(CH_3CD_2)_2NH$, (CH_3CD_2)–NH–(CD_2CD_3), and $(CD_3CD_2)_2NH$.

5. *Acetonitrile Deuteration over Predeuterated Ru/SiO_2*

After *in situ* reduction, one Ru/SiO_2(B) sample was deuterated with D_2O/He and purged with D_2 at 300°C in order to completely transform the OH groups on the silica into OD groups. When such deuterated Ru/SiO_2 was tested for CH_3CN and D_2, the products ethylamine or diethylamine have the same mass spectra as those formed on nondeuterated Ru/SiO_2. Therefore, the present results indicate that the H atoms which are added to the N atom of the CN group do *not* stem from the silica surface.

6. *Hydrogenation of CD_3CN over Ru/SiO_2*

The reversed labeling reaction $CD_3CN + H_2$ was carried out over Ru/SiO_2 at 125°C under the same conditions as $CH_3CN + D_2$. The same selectivity is found in both cases. The primary reaction product of $CD_3CN + H_2$ was subjected to GC-MS analysis, collected in a liquid nitrogen trap, and subjected to the secondary exchange with D_2O, followed by analysis with GC-MS. With ethylamine in the

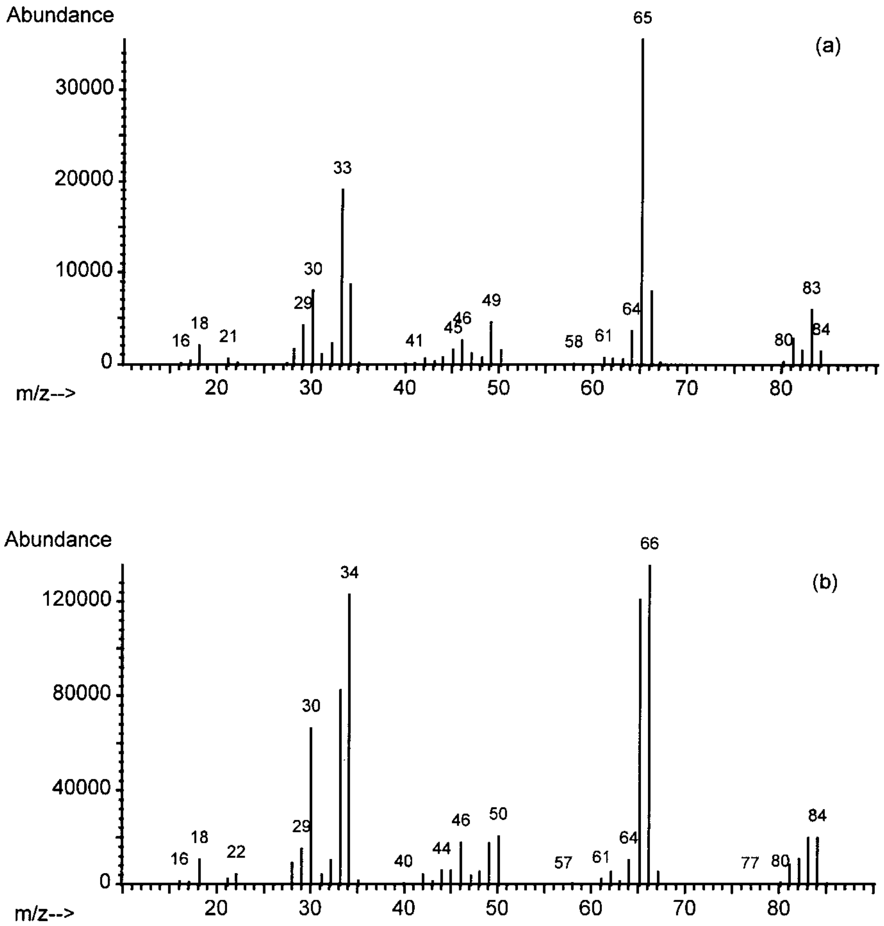

FIG. 10. Mass spectra of diethylamine of d_{10} from acetonitrile deuteration over Ru/SiO_2 at 125°C in first 30 min. (a) Fresh product, (b) after secondary exchange with D_2O.

primary product, the molecular ion and the main fragmentation ion are at $m/e = 50$ and 32. After secondary exchange with D_2O, the molecular and fragmentation ions do not shift. The results clearly indicate that the predominant primary product is $CD_3CH_2CD_2$. The results are also consistent with those reported above for $CH_3CN + D_2$.

7. Potential Sources of H Atoms in $CH_3CN + D_2$ Runs over Ru/SiO_2

The findings that (1) significant amounts of deuteration products contain less protons than predicted by the "naive stoichiometry" and (2) in the deuteration of acetonitrile the hydrons attached to the N atom are almost exclusively H, not D atoms, require some estimate of the potential source of these N-bonded H atoms. In the case of zeolite-supported metals, significant amounts of adsorbed acetonitrile are present; this overlayer can deliver an appreciable number of H atoms in exchange for D. In the case of SiO_2 supported metals a major source of H atoms is dissociative adsorption of acetonitrile molecules that are not hydrogenated but leave the surface as partially deuterated acetonitrile. Likewise, amine molecules can exchange some of their H atoms against D atoms. An estimate of the material balance is, therefore, desirable, comparing the H atoms lost by exchanging acetonitrile and D-rich amines with the H atoms required to be attached to the N atoms of the primary amine molecules. For this purpose acetonitrile was deuterated over Ru/SiO_2(B) at 125°C for an extended period. It was found that in the first 1.5 h, the isotopic distribution patterns of each product show no significant change. Therefore, an estimate of the isotope material balance has been made by integrating the most prominent products over the time from 15 to 90 min TOS. The reaction forms ethylamine and diethylamine.

For ethylamine, we calculate from our measured conversions and selectivity values for the N-bonded H atoms:

$$2 \int A_o \times \mathrm{CONV} \times \mathrm{SEL(EA)} \times dt = 15.5 A_o$$

Here A_o is the total number of acetonitrile molecules fed per minute, CONV is the conversion, and SEL is the selectivity.

With diethylamine, the N-bonded hydron is an H atom. The amount of H atoms required to produce such diethylamine is calcualted to be

$$\int A_o \times \mathrm{CONV} \times \mathrm{SEL(DEA)} \times \mathrm{d}t = 2.3A_o.$$

In the reaction, some acetonitrile molecules undergo H/D exchange on the surface and desorb from the surface. H atoms of methyl group are exchanged against D atoms. The total amount of H released in this way is estimated by

$$\int A_o \times (1 - \mathrm{CONV}) \times \mathrm{EX} \times (\mathrm{d}_1 + 2\mathrm{d}_2 + 3\mathrm{d}_3) \times \mathrm{d}t = 23.3A_o.$$

Here d_1, d_2, and d_3 are relative abundance of CDH_2CN, CD_2HCN, and CD_3CN, respectively. EX is the exchange ratio of acetonitrile.

Second, in the formed ethylamine, the abundance of d_2 and d_5 is very high and ethylamine of d_5 has a formula of $CD_3CD_2NH_2$. Therefore, each d_5 molecule will release three H atoms upon its formation through secondary H/D exchange. The total number of H atoms released this way is estimated by

$$3\int A_o \times \mathrm{CONV} \times \mathrm{SEL(EA)} \times [\mathrm{d}_5/(\mathrm{d}_2 + \mathrm{d}_5)] \times \mathrm{d}t = 9.4A_o.$$

Third, in the formed diethylamine, the maxima are observed at d_4, d_7, and d_{10}. Each d_7 or d_{10} molecule will release at least three hydrogen atoms upon formation through secondary H/D exchange. The total amount of H atoms released this way is estimated:

$$3\int A_o \times \mathrm{CONV} \times \mathrm{SEL(DEA)} \times [(\mathrm{d}_7 + \mathrm{d}_{10})/(\mathrm{d}_4 + \mathrm{d}_7 + \mathrm{d}_{10})] \times \mathrm{d}t = 5.1A_o.$$

For the hypothetical case where no H atoms leave the catalyst as HD, the above results indicate that the total amount of H atoms released by H/D exchange processes is larger than the amount needed for the formation of ethylamine and diethylamine with exclusively H atoms bonded to N atoms.

8. *Deuteration of Butyronitrile over Pt/SiO$_2$*

Deuteration of butyronitrile was carried out over Pt/SiO_2 at 80°C. The catalyst shows the highest selectivity to tertiary amine but the selectivity to primary and secondary amine is also appreciable. Under the present conditions, the conversion at 30 min TOS is 69.4%, the selectivity (mol%) is 20.4 to butylamine, 3.8 to butylidene-butylamine, 38.2 to dibutylamine, and 37.6 to tributylamine.

The deuteration products were analyzed on line by GC-MS. Primary products were condensed in a liquid nitrogen trap and subjected to secondary exchange with D_2O and analyzed again by GC-MS. The mass spectra are not presented here but are available upon request. With butylamine in the primary products, the molecular ion and the main fragmentation ion formed by loss of one propyl group ($CH_3CH_2CH_2$–, $MW = 43$) are at $m/e = 75$ and 32, respectively. After exchange with D_2O, the molecular and main fragmentation ions shift by two m/e units to $m/e = 77$ and 34, respectively. It follows that the butylamine molecule in the fresh product has the approximate formula $CH_3CH_2CH_2CD_2NH_2$.

With diethylamine, the molecular ion and the main fragmentation ions, due to loss of one propyl group, are at $m/e = 133$ and 90, respectively, in the primary product. After secondary exchange with D_2O, they shift by one unit to 134 and 91, respectively. This indicates that the dibutylamine in the fresh product is predominantly $(CH_3CH_2CH_2CD_2)_2NH$.

Little d_0 butylamine and d_0 dibutylamine are formed under the present conditions.

Tributylamine has no N bonded hydrogen. No secondary exchange is observed with D_2O. The molecular ion is at $m/e = 193$ but the main fragmentation ions, again by losing one propyl group, are at $m/e = 150$ and 149 with high abundance. After losing another propyl group the secondary fragmentation ion is at $m/e = 106$. This indicates that the lost propyl group has the formula $CH_3CH_2CH_2$– ($MW = 43$) or CH_3CH_2CHD– ($MW = 44$). Therefore, the primary triethylamine product appears to be $(CH_3CH_2CH_2CD_2)$–N–$(CD_2CDHCH_2CH_3)_2$.

The present results indicate that in the “deuteration” of butyronitrile over platinum, D atoms are added to C atoms, but H atoms are added to the N atom.

DISCUSSION

1. *Isotope Composition of Reaction Product; Deviations from “Naive Stoichiometry”*

The simple model which assumes that only D addition and H/D exchange occur predicts the following isotopic distributions: d_{4+} for the primary amine, d_{5+} for the secondary amine, and d_{6+} for the tertiary amine. The present results show that only tertiary amines, which have no N-bonded hydrons, qualitatively follow this simple stoichiometry under certain conditions. Usually, triethylamine has a maximum abundance of d_{12}, indicating that H/D exchange is rather extensive, before the product molecules leave the catalyst. This suggests a long residence time at the surface for adsorbed precursors of triethylamine. MS analysis shows that the formula CH_3CD_2–N–$(CD_2CD_3)_2$ correctly describes the predominant d_{12} product. Tributylamine formed over Pt/SiO_2, has the composition $(CH_3CH_2CH_2CD_2)$–N–$(CD_2CDHCH_2CH_3)_2$. Due to its longer chain length, the extent of H/D exchange is much lower than with triethylamine. Molecules with fewer D atoms than predicted by the naive stoichiometry are negligible in the triethylamine.

Ethylidene-ethylamine, a Schiff base formed over Ru/SiO_2 also follows this stoichiometry. The isotopic distribution has a maximum at d_6 with a composition $CH_3CD{=}N–CD_2CD_3$. Both addition of D atoms and H/D exchange take place.

In contrast, the primary and secondary amines show very significant deviations from the "naive stoichiometry," in particular for ruthenium catalysts. Some D-free amines are formed in "nitrile deuteration" with all catalysts. For NaY-supported Rh, Ni, and Pd at 75°C and over Ru/NaY and Ru/SiO_2 above 100°C, the isotope distribution of the product still shows a maximum abundance of d_5 with ethylamine and d_7 with diethylamine, but the prevailing molecules have the compositions $CD_3CD_2NH_2$ and $(CD_3CD_2)–NH–(CD_2CH_3)$, respectively. This shows a clear preference of H addition to the N atoms and addition of D atoms to the methylene C atoms. Large quantities of products with less D atoms are formed, such as d_2 for ethylamine and d_4 for diethylamine. Their formulas are $CH_3CD_2NH_2$ and $(CH_3CD_2)_2NH$.

With butylamine and dibutylamine formed on Pt/SiO_2 at 80°C, it seems that little secondary H/D exchange takes place and D addition is limited to the methylene group. The molecular formulas are $CH_3CH_2CH_2CD_2NH_2$ and $(CH_3CH_2CH_2CD_2)_2NH$, respectively. Again, only C-bonded hydrons have a high D content, in particular those in the methylene group in α-position to the amine group; the N-bonded hydrons are dominantly H atoms.

NaY and silica surfaces contain many OH groups at their surface, but the CH_3CN deuteration over Ru supported on deuterated SiO_2 gives rise to amines with the same isotopic abundances as that over nondeuterated Ru/SiO_2. A significant contribution of the OH groups on the support to the H content of the reaction product is therefore ruled out. The reversed isotopic labeling reaction, $CD_3CN + H_2$, confirms that the reaction takes place at the metal surface.

Capillary condensation of the nitrile is ruled out on the basis of temperature programmed desorption (TPD) results of acetonitrile on NaY. Two TPD peaks were observed at 101°C and 256°C if adsorption was carried out at room temperature and the same partial pressure of acetonitrile as used in the catalytic tests. The former peak is attributed to physisorbed nitrile, it is absent if adsorption was carried out at 75°C. The 256°C peak shows that chemical interaction took place at some zeolite sites. This chemisorbate is a potential source of H atoms in the runs with zeolite supported metals, but this reservoir of H atoms will be exhausted after prolonged reaction times.

The dispersion of the metals inside NaY was determined by H adsorption and by EXAFS in previous work of this group. It shows that metal/zeolite systems as described in the present paper have the vast majority of the metal clusters inside zeolite cavities. For the particular case of Ru/NaY we refer to a paper dedicated to this system (18).

No enamine formation is observed in the reaction under the present conditions, but enamines were previously identified in the hydrogenation of butyronitrile in the presence of pentylamine and in the hydrogenation of benzylcyanide in the presence of diethylamine (10).

2. *Acetonitrile Adsorption and H/D Exchange*

The adsorption of acetonitrile on well-defined metal crystal surfaces, e.g., Ru(001) (19), Ni(111) (20), Pt(111) (21), or on films of nickel or palladium (22), and Raney Ni (23) has been studied by a number of researchers. A semiempirical theoretical study was conducted for the adsorption of acetonitrile on Ni(111), Ni(100), and Ni(110) (24). From this it appears that CH_3CN is adsorbed on most metal surfaces with the CN group parallel to the metal surface. On Ni(111) and Pt(111), the adsorbed CN group is assumed to be diadsorbed in the configuration $M–C{=}N–M$, with the carbon and nitrogen atoms having sp^2 hybridization.

Addition of H or D atoms to an adsorbed acetonitrile molecule, positioned parallel to the surface, is assumed to lead to the formation of amines, but H/D exchange of acetonitrile apparently makes use of CH_3CN molecules in a position more or less perpendicular to the surface. In this case chemisorption is dissociative and the molecule is adsorbed through the C atom of the methyl group. This follows from our previous H/D exchange results (12) revealing a prevailing multiple exchange, i.e., α,α-bond formation between this C atoms and the metal. The formation of d_3 in the H/D exchange of CH_3CN on Ru suggests intermediate adsorbates such as $Ru{=}CHCN$. In this respect Ru is different from the other transition metals, which show stepwise exchange, indicating formation of a single C–*M* bond. This result is in good conformity with the known activity patterns of transition metals in exchange and hydrogenolysis, as pointed out by Kemball, Bond, Burwell, and others (25–29). The propensity of metals to form multiple metal–carbon bonds decreases in the order Ru, Ni, Co, Rh, Pd, Pt.

On Ru we thus have two chemisorption complexes of acetonitrile: (i) with the $C{\equiv}N$ bond parallel to the surface; these are precursors of amines: (ii) with the $C–C{\equiv}N$ axis vertical to the surface; they form multiple C–Ru bonds, for instance $Ru{=}CHCN$, and are thus a continuous and inexhaustible (in flow experiments) source of H atoms.

Strong adsorption of acetonitrile will lead to formation of an overlayer containing C, H, and N atoms on transition metal surfaces in the steady state. This $C_xN_yH_z$ layer may consist of chemisorbed molecules or oligomers. It is thought to be responsible for the TPD peak at 256°C. This overlayer is a potential source for the H atoms which are added to the nitrile molecule under a flow of CH_3CN/D_2 mixture. The overlayer model is in accordance with the concept proposed by Hansen *et al.* (30) and Thomson and Webb (31) for the hydrogenation of ethylene and confirmed by Hoek *et al.* (32, 33) for the enantioselective hydrogenation of methyl acetoacetate to methyl hydroxy butyrate over asymmetrically modified Ni catalysts.

It follows that an exhaustible and a nonexhaustible source of H atoms are both involved. The first reservoir appears to be an overlayer, the second source comprises acetonitrile molecules which release H atoms as part of their H/D exchange. At the steady state, the overlayer will be in isotope equilibrium with the feed and no longer cause deviations of the isotope distribution of the product from that of the feed. Only the "vertical" acetonitrile molecules can provide the H atoms which have been found in this work to preferentially bond to the N atoms. We will focus the present discussion on this phenomenon. The effects of the overlayer on the reaction mechanism will be discussed in a separate paper (34).

During the first hours, catalyst deactivation is always observed in gas phase, but not in liquid phase hydrogenation. Increasing the H_2 partial pressure does not eliminate the deactivation in the gas phase reactions. Apparently, a strongly adsorbed overlayer is formed that is dissolved in the solvent when present. Carbide formation is unlikely, as our previous work on CO hydrogenation showed that ruthenium carbide is formed only at much higher temperatures (above 260°C) (35, 36). Accordingly, temperature programed reduction of Ru/NaY that was covered with preadsorbed acetonitrile revealed that methane is formed only at 563°C.

3. *Hypothetical Models for Specificity of N–H and C–D Formation*

The overlayer model and the quantitative estimates of H transfer from CH_3CN or some primary reaction products to other CH_3CN molecules which are converted into a primary amine, can rationalize the deviation of the overall isotopic composition of the reaction product from that predicted by the naive stoichiometry. This still leaves open the tantalizing problem of why the amino groups in the primary and secondary amines produced from nitrile and D_2 have such a remarkable preference for H atoms, whereas the adjacent methylene groups are preferentially $-CD_2-$.

This finding indicates that one of the following two mechanistic principles has to be invoked: *either*

(i) the first addition of a hydron to the N atom of the nitrile or

(ii) the rupture of the $M{=}N$ or $M{-}N$ chemisorption bond requires a *concerted mechanism involving a hydrogen donor molecule*:

Re-1. The addition of the first H atom from a donor molecule $[H]$:

$$CH_3CN + [H] \Rightarrow CH_3{-}\underset{|}{C}{=}NH$$

results in a chemisorbed α-adsorbed aldimine which could isomerize to the tautomeric enamine,

$$CH_3{-}\underset{|}{C}{=}NH \Rightarrow CH_2{=}\underset{|}{C}{-}NH_2.$$

Addition of three D atoms to the enamine produces $CDH_2{-}CD_2{-}NH_2$, but if these D atoms are added to the aldimine, $CH_3{-}CD_2{-}NHD$ will be formed. The predominance of the d_3 isomer, after extended TOS, is in agreement with this model.

Re-2. Amine precursors will be bonded to the surface with a multiple $M{=}N$ bond, in particular for $M{=}Ru$. This strong bond will be broken by transfer of H atoms from a donor molecule $[H]$. This transfer occurs in one step over Ru or two steps over other metals:

$$CH_3{-}CD_2{-}N{=}Ru + 2[H] \Rightarrow CH_3{-}CD_2{-}NH_2$$

or

$$CH_3{-}CD_2{-}N{=}M + [H] \Rightarrow CH_3{-}CD_2{-}NH{-}M$$

$$CH_3{-}CD_2{-}NH{-}M + [H] \Rightarrow CH_3{-}CD_2{-}NH_2.$$

This concept, which assumes a specific path for the transfer of H atoms to the N atoms of adsorbed acetonitrile, is reminiscent of earlier work by Otvos *et al.* (37). They observed that in D_2SO_4, isobutane readily exchanges all nine primary protons for deuterons but not the 10th H atom, which is provided by "hydride ion transfer" from another isobutane molecule. It appears to the present authors that in the hydrogenation of nitriles over a metal surface, the most probable rate-limiting step will be the desorption step, for which hydrogen transfer is plausible.

4. *Mechanistic Cause for Selectivity to Primary, Secondary, or Tertiary Amines*

The present results show that the selectivity toward primary amines can be correlated with the multiplicity of the H/D exchange pattern. As this multiplicity is known to be a consequence of the different propensity of metals to form multiple bonds with adsorbed molecules, it is suggested that this propensity is also at the root of the selectivity for primary amines. For hydrocarbons it is well known that metals with high propensity for multiple $M{=}C$ bond formation display also a high activity for hydrogenolysis, i.e., C–C bond fission. Over such metals also C–N bond cleavage is fairly easy. It is well known that disproportionation of aliphatic amines is catalyzed by transition metals even at mild conditions.

On the basis of these general relations it is still surprising that ruthenium, an active hydrogenolysis catalyst, displays a high selectivity for the primary amine, whereas platinum, a good hydrogenation and poor hydrogenolysis catalyst, forms 90% tertiary amine (see Table 1). While it may be expected that under the very mild conditions of the present work no methane formation is detected, it remains remarkable that ethane, a typical hydrogenolysis product, is detected over Ru/NaY only at 150°C, but over Pt/NaY, ethane formation is detected at 50°C in the product of acetonitrile hydrogenation.

A possible explanation for these unexpected findings is provided by the model, discussed in the previous section, that Ru=N bonded precursors are preferentially desorbed from the surface by a concerted reaction with a hydrogen donor, such as acetonitrile. As the Ru=N bond is stronger than the bonds between the N atoms and other transition metals, it is plausible that this desorption mode prevails on Ru, in particular at low temperature. It has been found that adsorption of small molecules on Ir, another metal with high activity for hydrogenolysis, gives immobile species at low temperature, while over Pt the adsorbed species is highly mobile (38, 39). Formation of secondary and tertiary amines requires mobility of adsorbed groups which can react with each other, this mobility of Ru=N bonded species is minimal on the Ru surface. The same holds for Ru=C bonded species. Surface mobility increases, however, with temperature and so does indeed the selectivity toward higher amines.

An alternative explanation assumes that the strongly chemisorbed molecules, held by Ru=N bonds to the surface are mere spectators. Over ruthenium at low temperature, the hydrogenation of acetonitrile would then exclusively take place at the overlayer/gas interface, following the Thomson Webb model. On metals with weaker N–*M* bonds, the metal surface remains the locus of the hydrogenation step; adsorbed groups are sufficiently mobile that they can react with each other also at low temperature to form a new C–N bond. While it is not possible to exclude this model, the concerted mechanism model appears to be a better base for rationalizing the preferential formation of N–H bonds in the "deuteration" of nitriles over metal catalysts.

CONCLUSIONS

(i) The nature of metals, i.e., their propensity for multiple bond formation correlates with the selectivity of acetonitrile hydrogenation. One extreme is Ru, which has a high propensity to form multiple adsorption bonds and shows a high selectivity to primary amine. At the other extreme, Pt and Pd, having a high propensity to form single adsorption bonds, show a high selectivity toward tertiary amines.

(ii) Isotopic labeling shows significant formation of product molecules which receive hydrons from other sources than the D_2 of the feed. There is a dramatic discrepancy between isotopic product composition and the stoichiometry expected on the basis of straightforward addition of D atoms. With CH_3CN and D_2 mixture as the feed, the amine groups in the product contain predominantly H atoms, but the methylene groups adjacent to the $-NH_2$, are almost pure CD_2. Secondary and tertiary amines have much deuterium in the methyl groups, indicating a longer residence of their precursors at the surface, favoring secondary H/D exchange.

(iii) One source of H atoms under conditions of CH_3CN deuteration are CH_3CN molecules which dissociate C–H bonds and undergo isotopic exchange. A second source of the hydrons added to acetonitrile is a $C_xN_yH_z$ overlayer. Its effect dominates in the initial stage of the reaction, but dissociation of C–H bonds of "vertically" chemisorbed acetonitrile molecules remains a source of H atoms also in the steady state.

(iv) Formation of amines is not a simple addition of chemisorbed D atoms to the C≡N triple bond, but a *concerted reaction* takes place with a H-donor molecule. An overlayer and the alkyl groups in the nitrile, or in some reaction products, can act as H donors.

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