Preparation and Characterization of a Novel Catalyst for the Hydrogenation of Dinitriles to Aminonitriles

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Highly dispersed rhodium on a high-surface-area magnesia support is a very selective and efficient catalyst for the partial hydrogenation of aliphatic α,ω-dinitriles to the corresponding ω-aminonitriles. In this catalyst the content of rhodium is 4–5%. The conditions needed for reproducible preparation of the high-surface-area magnesia are described. The role of the high-surface-area magnesia and the steps leading to the preparation of this catalyst are discussed. © 1988 Academic Press, Inc.

INTRODUCTION

Recently, we studied new potential routes for the production of caprolactam from simple aliphatic feedstocks. A careful examination of various options led to the conclusion that propylene or its ammoxidation product, acrylonitrile, is the most desirable raw material. This approach was further strengthened by our recently reported discovery of a selective polystyrene-bound catalyst for the dimerization of acrylonitrile to the desired mixture of *cis*- and *trans*-1,4-dicyanobutenes (*1*). Hydrogenation of this neat mixture catalyzed by a Pd/C catalyst leads to adiponitrile. The next step in the proposed process is the selective hydrogenation of adiponitrile to 6-aminocapronitrile.

The hydrogenation of adiponitrile has been extensively studied. However, the main focus of this work has been the conversion of adiponitrile to 1,6-diaminohexane, a monomer for Nylon 66 (*2*). A literature search and preliminary screening of a number of catalysts convinced us that a catalyst which allows conversion of adiponitrile to 6-aminocapronitrile with high selectivities at moderate to high conversions remains to be found. Our screening also re-

vealed that rhodium metal dispersed on basic supports such as alkaline earth metal oxides gives better selectivities than rhodium supported on neutral (carbon) or acidic supports such as silica and alumina. We hypothesized that the higher yields are the result of a substantially decreased tendency of the basic support to adsorb amines. This effect should be further enhanced by a high dispersion of rhodium on the support. Our efforts, therefore, centered on a study of rhodium supported on magnesia. This type of catalyst with a low surface area and unknown dispersion has previously been used for the selective hydrogenation of CO to methanol (*3*). When a similar catalyst is utilized to hydrogenate adiponitrile its initial high selectivity to 6-aminocapronitrile and moderate activity falls after only a few hundred turnovers; the catalyst cannot be recycled. These difficulties have been overcome, and an effective and selective catalyst has been developed. The preparation, characterization, and use of this new catalyst for the hydrogenation of aliphatic dinitriles are reported in this paper (*4*).

EXPERIMENTAL

Apparatus and Procedures

Surface areas were measured on a Quantachrome instrument using the standard

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BET method for nitrogen adsorption at −196°C with desorption at room temperature. Chemisorption experiments were conducted on a Micrometrics Accusorb Model 2100E at a final hydrogen pressure of 100 Torr. Before the measurement, hydrogen adsorbed on the catalyst was removed by heating the sample for 20 min at 200°C. Thermal analyses were performed on a Mettler TA-1 instrument in air at a heating rate of 10°C/min. GC analyses were carried out on a Hewlett–Packard 5880A chromatograph equipped with a flame ionization detector and a 6-foot (1.83-m) stainless-steel column packed with 5% of OV225 on 80/100 mesh GHP chromosorb. GC–MS data were collected on a Finnigan 3300 instrument. Using Cu$K\alpha$ radiation a Phillips 3400 automated diffractometer in the parafocus mode between $2\theta = 6$ and 90° was employed for determining the ratio and the size of MgO and Mg(OH)$_2$ crystallites. Chloride ion concentration was measured on a Corning Model 110 digital pH meter equipped with an Orion Model 94-47 chloride selective electrode and with an internal Calomel reference electrode. The samples were first acidified with nitric acid to pH 3 and then titrated with 0.1 M silver nitrate. Transmission electron microscopy was carried out on a sample which was first suspended in alcohol and then sprayed on a graphite substrate using a Phillips 400T instrument.

Reagents

Magnesia was purchased from Harshaw Chemical Co. as magnesia catalyst MgO601 T1/8 lot 9. Rhodium(III) chloride hydrate (Ventron Corp.), anhydrous ammonia (Matheson Gas, 99.99% purity), and hydrogen (Matheson Gas, 99.95% purity) were used as received. Adiponitrile, succinonitrile (both from Aldrich), glutaronitrile, and 1,5-dicyanopentane (both from Eastman-Kodak) were fractionated on a Vigreaux column at 0.1 Torr. The first and last 10% of the distillate were discarded. The purity of the center cuts was checked by GC and

found to be at least 99.5% in all cases. Triglyme (Aldrich) was distilled from LiAlH$_4$ at 0.1 Torr and stored under nitrogen. Tetrahydrofuran (Fisher) was stored over 20/80 Na/K alloy and vacuum transferred immediately prior to use.

Catalyst Preparation

Hydration of magnesia. Magnesia pellets were ground and sieved to >80 mesh. The powder was then heated in distilled water (10 ml of water per 1 g of magnesia) in an oil bath for the periods indicated in Table 1.

TABLE 1

Preparation of High-Surface-Area Magnesia[a]

Hydration[b] hours	MgO/ Mg(OH)$_2$[c] ratio	DTA peak[d]	Calcination[e] hours	Surface area (m^2/g)
3	0.33	437	1	91
3	0.33	437	8	167
3	0.33	437	24	204
3	0.33	437	96	194
22	0.15	450	1	245
22	0.15	450	8	234
22	0.15	450	24	270
22	0.15	450	80	224
96	—	—	16	273
22[f]	0.13	424	0	38
0	—	—	0	15

[a] Commercial magnesia is used as the starting material.

[b] Magnesium oxide is suspended in water, stirred, and heated to 95°C.

[c] The size of the MgO crystallites before hydration and after calcination is in the range of 30 to 168 Å. The average size of the remaining MgO crystallites after 3 and 22 h of hydration is 218 and 253 Å, respectively. The size of the remaining Mg(OH)$_2$ crystallites after calcination is 30 to 70 Å; it decreases with prolonged hydration and calcination times.

[d] At a constant rate of temperature increase the peak temperature is reproducible within 1°C. However, the peak temperature is extremely dependent on the rate of temperature increase. The data listed above were obtained at a rate of temperature increase of 10°C/min.

[e] Calcined at 400°C and atmospheric pressure in a static oven.

[f] The magnesia was hydrated for 22 h and then calcined for 24 h.

After filtration the solids were dried overnight at 100°C/100 Torr.

Calcination of hydrated magnesia. A sample of hydrated magnesia (3 g) was spread evenly in a 165 × 65-mm evaporating dish and placed in an oven preheated to the required temperature (Table 1). Parts of the sample were periodically removed and analyzed.

Adsorption of rhodium chloride. High-surface-area magnesia (22 g) obtained as above was added under vigorous stirring to a solution of $RhCl_3 \cdot 3H_2O$ (2.86 g) in distilled water (200 ml). After 1 h the colorless aqueous phase was removed on a rotary evaporator at 40°C. The resulting beige solid was dried for 15 h in a vacuum oven at 100°C.

Treatment with sodium hydroxide. A sample of rhodium chloride on magnesia (30 g) prepared as above was slurried in distilled water (150 ml) and then treated with 1 *M* NaOH (38 ml). After being stirred for 3 h at 90°C the formed yellow solid was isolated by filtration, washed three times with 100-ml portions of distilled water, and dried for 18 h at 100°C in a vacuum oven. This material was then stirred in distilled water (125 ml) for 3 h at 95°C. It was filtered, washed with three 100-ml portions of water, and dried under vacuum.

Reduction and calcination. The rhodium hydroxide on magnesia from above (400 mg) was placed in a 22-mm-id glass tube equipped with a course glass frit and a stopcock at one end. This end was connected to a compressed air-driven reciprocating motor with a 300 arc (Aldrich); the second end (exit) was attached to an oil bubbler. The tube was flushed with hydrogen, and the exit end was closed with a stopper and inserted through a muffle furnace preheated to 300°C. After reconnecting the bubbler and tilting the whole assembly about 10° from horizontal, the motor was started, and the hydrogen flow continued at a rate of 2–3 bubbles/s. The exit of the tube was heated to prevent water condensation. After 1 h the tube was closed with a stopper, removed from the furnace, and emptied into a

hydrogenation reactor in a dry box. The weight loss from the catalyst was approximately 25% due to water removal. *Caution!* The Rh/MgO catalyst will ignite hydrogen if the reduction tube is opened to the air.

Hydrogenation of Dinitriles

A. In ammonia. A Parr minireactor was equipped with a mechanical stirrer, a glass liner, a $\frac{1}{16}$-in. stainless-steel sampling device, and a check valve installed between the reactor and the hydrogen line. The check valve does not allow ammonia to escape from the reactor but enables hydrogen to flow into the reactor. In a dry box the catalyst (400 mg) was first poured into the reactor. This was followed by the addition of degassed adiponitrile (22.67 g) and triglyme (9.902 g) using a syringe under a nitrogen blanket. The reactor was then attached to a pressure/vacuum manifold, cooled in a dry ice/acetone mixture to −78°C, and evacuated. A measured amount of ammonia (59 ml at −78°C) was transferred into the reactor. After this was warmed to room temperature, stirring was started and the reactor pressure was increased by an additional 100 psi with hydrogen. When the reaction temperature (90 to 110°C) was reached the pressure was adjusted with hydrogen and held constant (Table 4). *Caution!* The reactor must not be brought to the operating pressure before it reaches the reaction temperature since the check valve prevents pressure relief. Samples were periodically withdrawn and analyzed by GC. Conversion and selectivities are defined by Eqs. (1) and (2), respectively,

Conversion(%)

= [moles of dinitrile consumed]

× 100/[moles of dinitrile charged

into the reactor]   (1)

Selectivity(%) = [moles of one product]

× 100/[moles of dinitrile consumed].   (2)

Selectivities for all products at exactly 70% conversion, as reported in Table 4, were

TABLE 2

Partial Hydrogenation of Dinitriles[a]

Dinitrile[b]	Conversion[c] (%)	Selectivity[c] (%)			
		Aminonitrile	Cyclic imine	Diamine	Dimer
C4	85.5	85.5	0	0	14.5
	89.4	87.3	0	0	13.3
C5	60.9	92.9	1.0	0	3.9
	92.0	81.6	4.1	0.2	12.9
C6	70.0	86.5	0.5	12.0	1.0
	90.0	74.0	2.0	21.0	3.0
C7	73.9	82.2	0	17.7	0
	92.7	65.4	0	34.0	0

[a] The hydrogenations were run in THF at 100°C with 750 psi of H_2 and 21% (w/v) of adiponitrile; the NH_3/dinitrile molar rato was 13, and the dinitrile/Rh molar ratio was 300.

[b] Number of carbon atoms in the chain of the straight chain dinitrile.

[c] Conversion and selectivities were calculated using Eqs. (1) and (2), respectively, from GC data. Triglyme was used as the internal standard.

obtained from selectivity/conversion plots for each run.

B. In a THF–ammonia mixture. A 30-ml Parr reactor was equipped with a glass liner, magnetic stirrer, a $\frac{1}{16}$-in. stainless-steel sampling device, and a 100-ml high-pressure hydrogen reservoir. Adiponitrile (2.10 g), triglyme (0.900 g), and THF (10 ml) were placed into the reactor. Nitrogen was bubbled through this mixture for 1 min. A sample of freshly reduced catalyst (160 mg) was removed from the dry box in a sealed vial. This vial was opened and its contents were added to the reactor while nitrogen purging continued. The bomb was sealed, attached to a pressure/vacuum manifold, and cooled in a dry ice/acetone bath. After evacuation (10^{-3} Torr), ammonia (5.9 ml, measured at −78°C) was vacuum transferred into the reactor. The reactor was warmed to room temperature and pressurized with an additional 750 psi of hydrogen. It was then placed into an oil bath preheated to 100°C. Samples were periodically withdrawn and analyzed by GC and reported in Table 2. All of the dinitriles reported in Table 2 were hydrogenated in an identical manner.

RESULTS AND DISCUSSION

Catalyst Preparation

Commercial magnesia is a very low-surface-area (10–15 m^2/g) support. Our study shows that this commercial magnesia is composed of hexagonal platelets with an average crystallite size of 168 Å. This crystallite size should give a moderately high surface area (greater than 100 m^2/g). Thus, the observed low surface area suggests a very high degree of crystal agglomeration. Attempts to adsorb rhodium salts on this support met with difficulties due to a slow rate of adsorption, a rise in the pH of the aqueous salt solution, and precipitation of the metal oxides from this solution. This can be partially circumvented by the use of methanol as the solvent for impregnation of the support (3). Nevertheless, the resulting catalyst exhibits a low surface area (40–50 m^2/g), similar to that of our initial catalyst prepared from aqueous solution (50–60 m^2/g). This material lost its activity very rapidly or was found to be completely inactive from the start.

Several groups have demonstrated that catalysts with a very high degree of metal

dispersion may be obtained by first reacting organometallic complexes with the hydroxide groups of silica or alumina supports followed by chemical and thermal treatment (5). Similar effects might be achieved in the case of magnesia by an exchange of the metal salt anion for the surface oxide ion. However, a simple calculation revealed that the surface area found in commercial magnesia is not sufficient for adsorption of a monomolecular layer of a rhodium salt in quantities sufficient for the preparation of approximately 5% Rh on the support. It became obvious that the above problems can be eliminated only by adsorption of the rhodium salts onto high-surface-area magnesia.

Preparation of high-surface magnesia. This can be achieved in two steps (6). Commercial magnesia is first hydrated to form magnesium hydroxide which is then calcined to high-surface-area magnesia. The temperature and duration of each step are the major variables which are not well defined. Correspondingly, these variables, together with the size of crystallizes, ease of dehydration, and surface area development, have been examined. The results are summarized in Table 1. The hydration is best carried out in water just below its boiling point (approximately 95°C). During this treatment MgO was progressively converted into $Mg(OH)_2$ as shown by the change in the $MgO/Mg(OH)_2$ ratio from 0.33 to 0.15 after 3 and 22 h of hydration, respectively. The crystallite size of the remaining MgO gradually increased from 168 Å in the initial sample to 218 and 253 Å after 3 and 22 h of treatment. This is expected since the smaller particles with larger surface area react faster leaving the remaining magnesia enriched in larger crytallites. Interestingly, the size of the hexagonal $Mg(OH)_2$ crystallites remains unchanged at approximately 184 Å. DTA analysis shows that all the water gained during hydration can be removed between 350 and 500°C, in agreement with the previous observation (6). However, with increasing hydration

time, the DTA peak maximum, which is a qualitative measure of the ease of water removal from hydrated magnesia, shifts to higher temperatures (7). This may reflect an increasing degree of $Mg(OH)_2$ crystallite perfection with time. Complete hydration and disappearance of MgO has never been achieved, and in most of the samples the reaction stops when about 85 to 90% of the magnesia is hydrated.

The calcination of hydrated magnesia has been studied at temperatures between 300 and 400°C in a static oven in air. Under these conditions the optimum surface area was achieved at 400°C. The optimum reaction time depends on the degree of magnesia hydration. If the hydration step is carried out for the minimum time of 3 h, then 24 h of calcination is required. After this time no improvement in the surface area is observed even after 90 h at 400°C. If the hydration step is carried out for 24 h to yield the maximum $Mg(OH)_2/MgO$ ratio, water removal is far more facile and even after 1 h a near optimum surface area of 240 m^2/g can be observed. However, removal of the last portions of water as measured by the $MgO/Mg(OH)_2$ ratio with formation of the highest surface area of approximately 270 m^2/g requires 24 h of calcination. Again treatment longer than 24 h does not lead to further improvement even after 96 h at 400°C. Correspondingly, all magnesia samples needed for the catalyst preparation were hydrated and then calcined for 22 and 24 h, respectively. The size of the formed hexagonal plate-like MgO crystallites is in the range of 30 to 150 Å and the size of the remaining $Mg(OH)_2$ crystallites is in the range of 30–40 Å.

This high-surface magnesia is sensitive to atmospheric moisture and carbon dioxide. When exposed to air it absorbs water with a concomitant decrease in surface area. Therefore, it should be used immediately for the next step or it must be stored under vacuum or in an inert atmosphere.

Adsorption of rhodium chloride on high-surface magnesia. An aqueous solution of

rhodium trichloride when brought in contact with high-surface magnesia decolorizes quantitatively and rapidly. Since the step is accompanied by a rapid and exothermic magnesia hydration, it is assumed that the rhodium species are bound to the $Mg(OH)_2$ rather than to the MgO. During this stage very little chloride ion is released to the aqueous phase. This is not changed substantially even by stirring this suspension at room temperature overnight (this releases only approximately 0.5 mole of chloride ion per mole of rhodium chloride adsorbed). Control experiments show that if magnesium chloride were formed it would not remain adsorbed on magnesia but would be released into water. The color of the adsorbed rhodium species remains reddish suggesting that at least two chloride ions remain associated with each rhodium atom (8). The remainder of the chloride ion can be bound to the support in the form of a mixed chloride–oxide phase. At this stage the magnesia is fully hydrated with a MgO/$Mg(OH)_2$ ratio of 0.13. The surface area of this rehydrated magnesia is in the range of 35–50 m^2/g, substantially higher than the surface area (approximately 10 m^2/g) of the hydrated, commercial magnesia.

Calcination followed by reduction of this material with hydrogen leads to a catalyst which either is inactive for hydrogenation of aliphatic dinitriles or loses its activity after a few turnovers. The same behavior has been observed in the case of rhodium nitrate. Further study revealed that these properties can be ascribed to the chloride or nitrate ions left on the support. This is not a surprising conclusion in view of the results reported by Leofanti et al. who studied the preparation of Ru/MgO catalysts from $RuCl_3$(aq) and MgO (6e). They found that chloride ion left on the support prevented formation of small pores during the subsequent calcination step; the resulting catalysts have a low surface area.

Chloride ion removal from rhodium chloride adsorbed on hydrated magnesia. Heating of the rhodium chloride adsorbed on hydrated magnesia in water at 95°C gradually liberates the remaining chloride ion into the aqueous phase. However, this process is very slow and requires more than 60 h. When "aged" (6e) $RhCl_3$(aq) is used in the adsorption step, the chloride ion removal is accelerated. Nevertheless, at least 24 h of treatment is needed. This prolonged heating is, however, detrimental to the subsequent calcination step which must be carried out at the lowest possible temperature. Simulation of the calcination step in a TGA cell shows that hydrated magnesia containing rhodium salts dehydrates in two well-defined steps in sharp contrast to pure high-surface magnesia, rehydrated for 3 h, which exhibits only one symmetrical peak (Fig. 1). With prolonged heating in water both peaks shift to higher temperatures, well above the peak temperature for the pure rehydrated magnesia; the area below the second peak becomes more pronounced. This effect is more noticeable for nitrate than for chloride ion. This observation strongly suggests the presence of two distinct magnesium hydroxide phases with different thermal behavior. Based on this thermal behavior, the composition and morphology of the phase with the lower DTA peak temperature seem to be the same as those for the pure hydrated magnesia. The composition and morphology of the second phase are not known at this time.

A careful examination of various procedures for chloride ion removal revealed that addition of slightly more (approximately 5%) than the theoretical amount of sodium hydroxide to a suspension of the $RhCl_3$/$Mg(OH)_2$ in distilled water followed by heating at 95°C for not more than 3 h removes most of the remaining chloride ion and yields a material which on examination in a TGA cell exhibits behavior very close to that of pure rehydrated magnesia (Fig. 1). This finding also holds in the case of rhodium nitrate.

At this stage the reddish color of the adsorbed rhodium salt has changed to yellow suggesting the presence of rhodium hydrox-
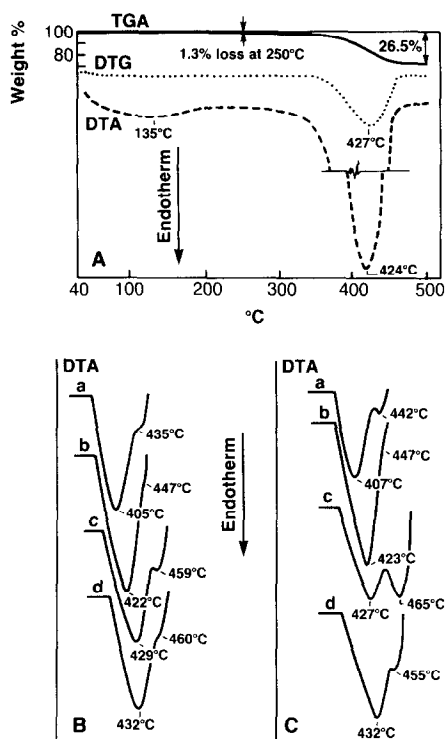
FIG. 1. DTA of magnesia in air at various stages of catalyst preparation. Heating rate is 10°C/min. (A) High-surface-area magnesia after 3 h in water at 95°C. (B and C) High-surface-area magnesia treated with $RhCl_3$ and $Rh(NO_3)_3$, respectively. (a) As obtained. (b) After 3 h at 95°C in diluted aqueous NaOH with 5 mole% excess of NaOH over Cl^-. (c) After 19 h of heating in water at 95°C. (d) As in (b) with an additional 19 h in water at 95°C.

ide. This color is very analogous to rhodium hydroxide powder and clearly distinct from the brown rhodium oxides. It is believed that the rhodium is chemically bound to the surface via Rh–O–Mg bonds.

The small amount of the remaining chloride ion may be completely removed by an additional 3 h of heating in water. This additional treatment seems to be beneficial for the preparation of a high-activity catalyst.

Calcination and reduction of Rh(III) on hydrated magnesia. Both reactions are carried out in one step in a hydrogen flow. We have demonstrated that calcination of hydrated commercial magnesia at the optimum temperature of 400°C yields a high-

surface-area (270 m^2/g) magnesia. Unfortunately, calcination and reduction of Rh(III) on hydrated magnesia under the same conditions leads to a high-surface-area catalyst which exhibits low selectivity to 6-aminocapronitrile and loss of activity after a few hundred turnovers. This is true even if the reduction time is limited to 1 h. This catalyst was examined by EDX and TEM. The presence of rhodium in about 4% concentration has been confirmed by EDX. The rhodium clusters, which on TEM micrographs appear denser than the MgO, range in size from 3 to 10 nm. Assuming cubic crystallites, these aggregates should on average contain from 500 to several thousand rhodium atoms (9). Apparently, a substantial agglomeration of the rhodium atoms has occurred in the course of this step (Fig. 2).

Examination of a range of temperatures between 300 and 400°C and various arrangements of the reduction cell revealed that a very active and selective catalyst with a surface area of 100–180 m^2/g can be obtained if this last step is carried out at 300°C with good mixing. This is possibly due to the fact that loss of water from rehydrated high-surface magnesia is far more facile than that from hydrated commercial magnesia. This difference is kept at a minimum and the calcination is carried out in a flow of gas. Thus, the use of high-surface magnesia serves two purposes: it allows both fast and efficient adsorption of rhodium salts from aqueous solutions and reduction/calcination at temperatures at which agglomeration of rhodium into large clusters is prevented.

The rhodium in a sample calcined and reduced at 300°C with only a moderate surface area of 101 m^2/g can again be confirmed by EDX. Examination by TEM showed that the rhodium clusters, observable at a magnification of 1.1×10^6, are not larger than 1.8 nm (Fig. 3). Chemisorption experiments determined an uptake of 0.76 H atom per rhodium atom.

Our data represent the first direct demon-

FIG. 2. TEM of rhodium on magnesia reduced at 400°C.

stration that rhodium on magnesia under-
goes facile agglomeration at a temperature
of approximately 400°C and that this is not
caused by a dimensional changes of the
support. Our observation is also in agree-
ment with the reported large increase in the
Rh–Rh coordination number after reduc-
tion of Rh(III) oxide on magnesia at the
same temperature when compared with a
sample reduced at 200°C (3). This high mo-
bility of rhodium atoms on magnesia at
400°C strongly contrasts with the complete
stability of highly dispersed rhodium on sil-
ica and alumina under the same conditions
(3, 10).

This catalyst is sensitive to moisture.
When in contact with air it gradually loses
its activity. It must, therefore, be used im-
mediately after preparation or it must be
stored under an inert atmosphere or under
vacuum.

Hydrogenation of Aliphatic Dinitriles

A series of aliphatic α,ω-dinitriles, con-
taining four to seven carbon atoms, has
been hydrogenated under arbitrarily chosen
conditions without any attempts to opti-
mize the yields. Tetrahydrofuran was
selected as the solvent since the use of tolu-
ene and methanol (representatives of non-
polar and polar solvents) resulted in inferior
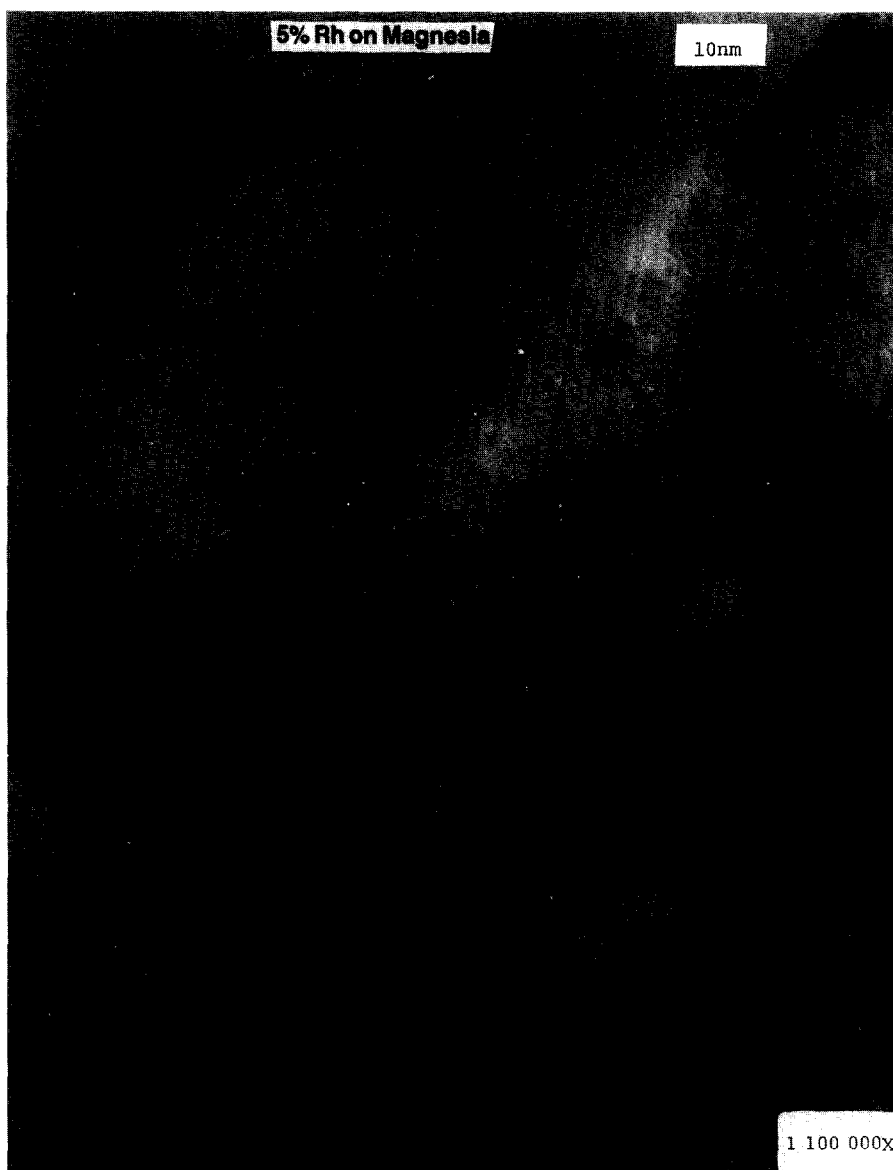selectivities. In agreement with our work-

FIG. 3. TEM of rhodium on magnesia reduced at 300°C.

ing hypothesis, the results summarized in Table 2 reveal that the selectivities to ω-aminonitriles remain high even at conversions as high as 90% and decrease with increasing chain length between the nitrile groups of the starting α,ω-dinitriles. There are striking differences in the amount and type of by-products formed. Thus, in the case of succinonitrile and glutaronitrile, the corresponding α,ω-diamines are not formed even at 90% conversion. The absence of a cyclic imine among the hydrogenation products of succinonitrile is also noteworthy. This happens despite the fact that the five-member cyclic imine, expected to be formed from succinonitrile, is more stable than the six- and seven-member cyclic imines found among the hydrogenation

Catalyst	Conversion (%)	Selectivity (%) to aminonitrile
5% Rh/C	78	55
5% Rh/Al$_2$O$_3$	80	76
5% Rh/MgO	82	89

[a] The hydrogenations were carried out in THF at 100°C with 500 psi of H$_2$ and 21% (w/v) of adiponitrile; the NH$_3$/adiponitrile molar rato was 11, and the adiponitrile/Rh molar ratio was 240. Conversions and selectivities are defined by Eqs. (1) and (2), respectively.

products of glutaronitrile and adiponitrile. The only by-product in the case of succinonitrile is a dimer. In contrast to other dinitriles which yield typical dimers [bis(ω-cyanoalkyl)amines], hydrogenation of succinonitrile results in imine dimer **6**,

$$NC(CH_2)_2CH=N(CH_2)_3CN.$$

6
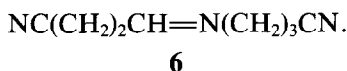
Both the tendency for this dimer's formation and its preservation in the reaction mixture are a consequence of a facile ammonia and amine addition to imine intermediates activated by close proximity to the cyano groups.

In contrast to succinonitrile, the only by-product of 1,5-dicyanopentane hydrogenation is the corresponding 1,7-diaminoheptane. In the studied series the remaining dinitriles of intermediate chain length exhibit behavior between the above two extremes. They form an array of by-products which includes cyclic imines, α,ω-diamines, and bis(ω-cyanoalkyl)amines. The selectivities, for unoptimized conditions at which data for the whole series of dinitriles is available, are summarized in Table 2. Clearly, the selectivity to the desired ω-aminonitrile decreases with increasing chain length. Although it is very high for succinonitrile and glutaronitrile, it is only moderate for 1,5-dicyanopentane. Nevertheless, under similar conditions, rhodium

dispersed on other neutral or acidic supports exhibits lower selectivities (Table 3) and a substantial loss of activity mainly at concentrations of ammonia necessary to suppress the formation of cyclic imines and bis(ω-cyanoalkyl)amines. We believe that the enhanced selectivity of our catalyst is a consequence of (a) the basic magnesia support which facilitates desorption of basic compounds such as amines, and (b) the high dispersion of rhodium which allows a strong interaction between the active metal and the adsorbed species with the support.

Conditions for partial hydrogenation of adiponitrile were only partially optimized and further improvement is feasible. Nevertheless, the following conclusions can be drawn. The concentration of adiponitrile has a minimal effect on the formation of 1,6-diaminohexane and azacycloheptane. However, production of bis(5-cyanopentyl)amine increases significantly with increasing adiponitrile concentration. Thus, the best selectivities are obtained at the lowest possible adiponitrile concentrations. However, for practical purposes, further optimization has been done for 10% (w/v) adiponitrile concentrations in the reaction mixture. Ammonia suppresses formation of the cyclic imine and the dimer which leads to a higher yield of 6-aminocapronitrile (Fig. 4). Hydrogenation of adiponitrile in neat ammonia should then give the best
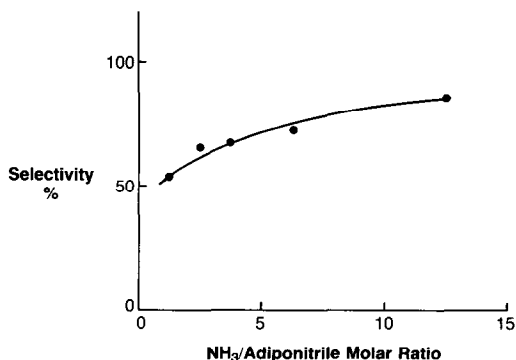

FIG. 4. Selectivity of adiponitrile hydrogenation to 6-aminocapronitrile as a function of ammonia/adiponitrile molar ratio.

TABLE 4

Partial Hydrogenation of Adipontrile in Ammonia[a] at 70% Conversion

Pressure[b] (psi)	Selectivities (%)			
	Aminonitrile	Diamine	Cyclic imine	Dimer
910	86.0	6.4	2.9	4.9
960	90.2	6.6	1.2	1.7
1500	94.1	5.0	0.5	0.3

[a] The hydrogenations were carried out at 100°C with an NH_3/substrate molar ratio of 12 and with a substrate/Rh molar ratio of 1340. Conversion and selectivities were calculated according to Eqs. (1) and (2), respectively.

[b] This represents the total pressure of H_2 and NH_3.

FIG. 5. Selectivity of adiponitrile hydrogenation to 6-aminocapronitrile as a function of adiponitrile/rhodium molar ratio.

results. Indeed, this has been demonstrated (Table 4). Importantly, hydrogenation of dinitriles in neat ammonia is feasible only with our highly dispersed catalyst. Even after 10,000 turnovers, this catalyst shows no substantial decrease in its activity. Less dispersed catalysts, prepared in the early stages of this project, deactivated quickly when used under the same conditions. In-
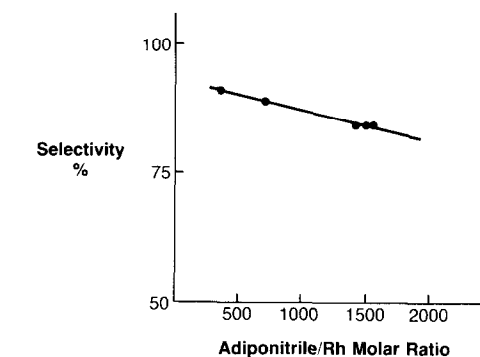
creased hydrogen pressure is also beneficial (Table 4) since it increases the rate of the intermediate imine hydrogenation at the expense of its reaction with the amino group of 6-aminocapronitrile (Scheme 1). Higher hydrogen pressure also increases the rate of imine 7 (Scheme 1) hydrogenation and thus increases formation of 1,6-diaminohexane at the expanse of cyclic imine 4. For similar reasons the selectivity to 6-aminocapronitrile increases with decreasing molar sub-
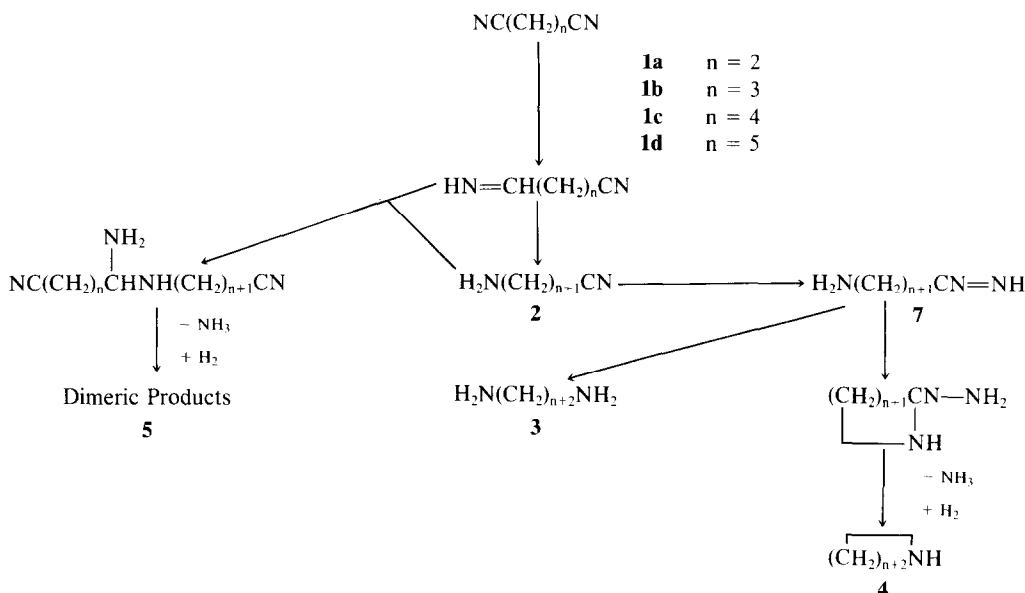
SCHEME 1. By-product formation in the hydrogenation of aliphatic dinitriles.

strate to catalyst ratio (Fig. 5). However, for economical reasons the mole ratio of adiponitrile to catalyst was kept at approximately 1300.

Thus, the yield of 6-aminonitrile is favored by high dilution, neat ammonia as the reaction medium, and higher hydrogen pressure. Under the best reaction conditions (Table 4, run 3) a selectivity of 94% can be reached at 70% adiponitrile conversion.

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