The selective hydrogenation of acetonitrile on supported nickel catalysts

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The catalytic behavior of several supported nickel catalysts in the hydrogenation of acetonitrile was studied. It was established that the selectivity of this process is greatly influenced by the nature of the support used. Catalysts consisting of nickel supported on acidic supports catalyzed the formation of condensation products, diethyl- and triethylamine. Nickel supported on basic supports was highly selective with respect to the formation of the primary amine, ethylamine. It was shown that modification of the intrinsic acidity of alumina-based supports by the application of alkaline additives has a large impact on the selectivity of the resulting catalyst. Based on the results obtained from measurements on a basic catalyst diluted with either an acidic or a basic support, a dual-function mechanism is suggested. The mechanism implies that the hydrogenation function of the catalyst is located on the metal, while the acid function, responsible for the condensation reactions, is located on the support. A mechanism, accounting for the occurrence of the acid-catalyzed condensation reactions, is proposed.

Keywords: nickel catalysts; hydrogenation; nitriles; amines; selectivity; acidity

1. Introduction

Amines can be prepared by a large number of methods, but commercially the most commonly used procedure is the hydrogenation of nitriles [1,2]. An example is the hydrogenation of adiponitrile producing hexamethylenediamine, a starting compound for nylon 6,6 production [3,4]. The industrial process of nitrile hydrogenation is usually carried out in the presence of a heterogeneous transition metal catalyst at elevated temperatures and hydrogen pressures. Because of the high reactivity of partially hydrogenated reaction intermediates, imines or Schiff bases, a conventional hydrogenation leads to a mixture of primary, secondary, and tertiary amines. For the production of primary amines a nickel-based catalyst is commonly used. Further tuning of the catalytic reaction for the production of primary amines is accomplished by application of a high ammonia (partial) pressure to suppress the side reactions. Even under these conditions the primary amine yield is never complete. Therefore, it was our objective to study the parameters responsible for the formation of secondary and tertiary amines in nitrile hydrogenations.

It seemed rather obvious to study the acid–base properties of the medium in which the hydrogenation is performed, because in the numerous patents dealing with nitrile hydrogenations either application of a high partial ammonia pressure and/or addition of (in)organic bases to the catalytic system is mentioned (e.g. refs. [5–7]). Modification of the nickel *catalysts* themselves with respect to their acid–base properties has, however, not been reported and studied in such detail as yet. In a review paper on nitrile hydrogenation, Volf and Pašek [8] even state that the support does not have any influence on the selectivity of the hydrogenation process but merely helps to create a well-dispersed catalyst. According to these authors, the selectivity is determined for the greater part by both the catalytic metal and the reaction conditions employed.

All products of the nitrile hydrogenation (primary, secondary, and tertiary amines) are basic species that will interact more strongly with an acidic than with a basic catalyst. It has therefore to be expected that, on changing the character of the support from acidic to basic, a change in selectivity will be observed in favor of primary amines. To study this hypothesis, the research described in this paper is aimed at the investigation of a possible influence of the acid–base properties of supported nickel catalysts on the product selectivity in nitrile hydrogenations. In a previous paper the acidity of a variety of supported nickel catalysts was determined using the temperature-programmed desorption of ammonia [9]. A set of catalysts was prepared ranging from highly acidic (nickel-on-aluminum phosphate), to only slightly acidic (nickel-on-potassium-promoted-γ-alumina). This set of well-characterized catalysts was studied in the hydrogenation of acetonitrile producing ethyl-, diethyl-, and triethylamine.

2. Experimental

2.1. PREPARATION OF THE CATALYSTS

Promoted and unpromoted nickel catalysts supported on various inorganic oxides were prepared by means of impregnation of powdered support materials with a nickel nitrate solution, as described elsewhere [9]. Several silica-supported nickel catalysts were also prepared by means of a homogeneous precipitation method using the decomposition of urea at 90°C.

Magnesia-supported nickel catalysts were prepared through the precipitation of a nickel magnesium mixed oxalate using the injection of ammonium oxalate into a solution containing both nickel and magnesium nitrate at 50°C as described by Langenbeck et al. [10].

Catalysts are encoded by taking the first character of the support material (i.e., S for silica, A for alumina, M for magnesia, AS for aluminosilicate and AP for aluminophosphate) and attaching the nickel weight loading (i.e., 5 or 25 wt%) to it. Sometimes a -d is attached to indicate a diluted catalyst. The nickel loading was adjusted to 5 wt% with all catalysts (based on a complete reduction), except for the catalysts encoded S25U (the U indicates prepared by urea decomposition) and M25 that were loaded with 25 wt% of nickel. Samples of catalyst S25U were diluted with silica to obtain formally a 5 wt% Ni-loaded catalyst after reduction. To that end the dried precursor was powdered in a mortar and diluted with aerosil 200 in the ratio precursor-to-silica of 1/4: The code of this catalyst is S25U-d. The catalyst M25 was diluted with magnesia (Merck, p.a.) to obtain formally a 5 wt% Ni-loaded catalyst after decomposition. The code of this catalyst is M25-d.

After preparation, the catalyst precursors were air-dried at 120°C overnight, and subsequently powdered. The powdered (diluted) precursors were pressed at 1000 kg/cm^2, crushed, and finally sieved. The sieve fraction 0.50–0.85 mm was used in all kinetic experiments.

2.2. GAS-PHASE HYDROGENATION OF ACETONITRILE

The gas-phase hydrogenation of acetonitrile to primary, secondary, and tertiary amines was studied in a fully automated micro-flow apparatus, operating at atmospheric pressure, as described elsewhere [11]. Prior to the catalytic experiments, the precursors were dried in situ at 125°C for 30 min in flowing hydrogen. Following the drying step, reduction was performed by raising the reactor temperature to 450°C at a rate of 2°C/min and maintaining this temperature for 10 h. It was shown earlier that this reduction procedure results in high levels of reduction (80–100%) and well-dispersed nickel catalysts (60–120 m^2/g Ni) [9]. After reduction, the catalyst sample was cooled to room temperature in flowing hydrogen. The hydrogen flow was subsequently saturated with acetonitrile (Merck, p.a.) by bubbling the gas stream through a saturator, held at −4°C by means of a cooled circulator, resulting in a concentration of 2.5 vol% acetonitrile in the gas stream [12]. The gas mixture was passed downflow through the fixed catalyst bed that initially consisted of 0.25 g of the dried catalyst precursor (i.e., before reduction). The catalyst was contained in a Pyrex® reactor with an internal diameter of 10 mm. The temperature was measured just below the catalyst bed with a chromel–alumel thermocouple.

In the Arrhenius-type experiments the reactor temperature was first raised from room temperature to 40°C (where the catalytic activity of most catalysts developed) and then the temperature of the catalyst bed was stabilized for 25 min. Following the stabilization, the bed temperature was raised in steps of 5°C to 140°C with a 20 min stabilization time between two measurements. The same procedure was followed with decreasing bed temperatures. In one isothermal experiment, performed with catalyst M25-d, the reactor temperature was first raised from room temperature to 128°C as described for the Arrhenius measurement. Then, the bed temperature was stabilized for 25 min and, subsequently, the performance of the catalyst was followed as a function of time on stream.

Sampling of the reactant and product gases was performed with pneumatically controlled six-way valves and the gas samples were analyzed by means of GLC using a gas chromatograph equipped with a flame ionization detector. Data points were collected every 20 min. A typical run consisted of the analysis of a product sample ($\text{acetonitrile}_{\text{out}}$) and of a reference sample withdrawn from the reactant gas entering the reactor ($\text{acetonitrile}_{\text{ent}}$). The conversion is defined as

$$\text{conversion (\%)} = \left(1 - \frac{\text{acetonitrile}_{\text{out}}}{\text{acetonitrile}_{\text{ent}}}\right) \times 100\% .$$

Product selectivities have been calculated from peak areas corrected for different response factors in the flame ionization detector and normalized to moles of product. Since the carbon balance was always near 100%, the selectivity for product i is defined as

$$\text{selectivity}^{i}\text{(mol\%)} = \frac{\text{corrected area}^{i}}{\text{summed area of all peaks}} \times 100\% .$$

In table 1 the general test conditions adapted in the kinetic measurements are summarized.

Preliminary experiments ruled out the existence of transport limitations. To that end the usual experimental checks were performed [13]. The sieve fractions 0.212–0.50 mm and 0.50–0.85 mm produced identical conversion patterns indicating the absence of intra-particle transport limitations. Variation of the bed depth and gas flow rate at constant space velocity also resulted in similar conversion pat-

Table 1
General test conditions for the hydrogenation of acetonitrile

catalyst weight	0.25 g
reactor nickel loading [a]	about 11 mg
grain size	0.50–0.85 mm
gas flow rate	75 ml/min
feed	97.5 vol% hydrogen 2.5 vol% acetonitrile
H/C-ratio [b]	39
total pressure	1 bar
temperature range for Arrhenius measurements	40–140°C
analysis	gas chromatography column: CP-Sil 5CB detector: FID (carrier N_2)

[a] Amount of nickel present in the reactor.

[b] Ratio of molar concentrations of hydrogen and acetonitrile in the feed.

terns, and thus inter-particle heat and mass transfer limitations were absent too. It was also verified that the bare, nickel-free supports did not have any activity in the conversion of acetonitrile in the temperature range 20–250°C. Above this temperature no tests were performed.

Because the selectivity of all catalysts toward primary, secondary, and tertiary amines changed with temperature, a large number of graphics would be required to describe the performance of the various catalysts. However, an inspection of the selectivity patterns learned that the selectivity *change* as a function of temperature was very much comparable for all catalysts measured. The primary amine selectivity always increased with temperature in the temperature range measured, whereas the selectivity toward tertiary amines always decreased in the same range. We therefore decided to describe the selectivities of the catalysts at a fixed temperature of 125°C. At this temperature the primary amine selectivity is always near its maximum value.

3. Results and discussion

3.1. HYDROGENATION OF ACETONITRILE: NICKEL SUPPORTED ON SILICA

By means of acidity measurements using TPD of ammonia other work demonstrated that the unreduced catalyst S25U possessed a high acidity [9]. It was found that reduction of the nickel precursor both decreased the total acidity and caused the desorption of ammonia to proceed within a more narrow temperature range. From the combination of those results with data from the literature on the structure of the catalyst [14], it was concluded that acidic nickel hydrosilicate formed during precipitation, was responsible for the acid–base properties of nickel-on-silica catalysts prepared by urea decomposition. Because the amount of nickel hydrosilicate in the reduced catalyst is affected by the extent of reduction, it seems possible to change the acidity of these catalysts gradually and in situ by progressively increasing the degree of reduction. Richardson and Dubus described that an increase of the degree of reduction can be achieved by either raising the temperature of reduction or increasing the reduction time [15].

Because the unreduced catalyst did not have any hydrogenating activity it was necessary to reduce some of the nickel to the metallic state prior to the kinetic measurements. Several reduction temperatures were used to obtain nickel-on-silica catalysts of varying degrees of reduction and thus varying degrees of acidity. All following measurements were performed on the same sample of catalyst S25U-d. Prior to the first measurement, precursor S25U-d was reduced at 350°C for 1 h. Between the first and second Arrhenius measurement, the already slightly reduced catalyst was reduced further at 375°C for 30 min. Then, prior to the third measurement, the catalyst was reduced at 400°C for 30 min, and the final reduction, prior to the fourth measurement, was performed at 450°C for 10 h. After each reduction procedure, and, hence, with each different degree of reduction, an Arrhenius measurement was carried out between 40 and 140°C. The selectivity of the catalyst at 125°C was taken as a representative base for comparison, as explained. It was observed that with increasing reduction temperatures the selectivity toward primary amines increased and toward condensation products decreased. The following selectivities were observed: MEA 39%, DEA 40%, SCB (Schiff base) 10%, TEA 11% (reduction at 350°C), MEA 48%, DEA 41%, SCB 3%, TEA 8% (reduction at 375°C), MEA 56%, DEA 37%, SCB 0%, TEA 7% (reduction at 400°C), and MEA 70%, DEA 25%, SCB 0%, TEA 5% (reduction at 450°C). It can be concluded that the extent to which the condensation reactions proceeded decreased with increasing degrees of reduction of this catalyst. When the reduction temperature is increased, the free nickel surface area and the amount of nickel hydrosilicate in the catalyst change. A more reduced catalyst contains less nickel hydrosilicate and using TPD of NH_3 it was shown that nickel hydrosilicate possesses a high acidity [9]. If the acid–base properties of the catalyst are indeed responsible for the product selectivity, then it is highly probable that the primary amine selectivity is increased because of an increased degree of reduction of catalyst S25U.

To verify this hypothesis, the performances of two silica-supported catalysts are compared in the hydrogenation of acetonitrile. One catalyst was prepared by means of urea decomposition and the precursor thus contained nickel hydrosilicate, the other catalyst was prepared by the impregnation of silica with an acidic nickel nitrate solution. These catalysts, S5U (urea decomposition) and S5I (impregnation), both contained the same amount of nickel and were reduced at the same temperature and for the same period of time (450°C, 10 h). The selectivities toward MEA, DEA and TEA for both catalysts at 125°C were 80, 17 and 3% for catalyst S5I and 56, 35 and 9% for catalyst S5U. It is apparent that the more acidic catalyst (prepared by urea decomposition, S5U [9]) was less selective indeed toward the primary amine than the less acidic, impregnated catalyst, S5I. During preparation of catalyst S5I hydrosilicate formation has been suppressed and the lower acidity of this catalyst as compared to catalyst S5U accounts for the higher selectivity toward ethylamine.

3.2. HYDROGENATION OF ACETONITRILE: NICKEL SUPPORTED ON MAGNESIA

The precursors of the nickel-on-magnesia catalysts were prepared by the simultaneous precipitation of nickel and magnesium ions with ammonium oxalate. Using thermogravimetric analysis (TGA) it was determined that when the nickel loading in the catalysts is adjusted to a value larger than about 20 wt% Ni, a nickel–magnesium mixed oxalate is formed. The nickel and magnesium ions in the precipitate are mixed on an atomic scale, because the ionic radii of nickel and magnesium are similar, and the lattice structure of both nickel and magnesium oxalate, monoclinic, is the same [16]. The resulting mixed oxalate has the following general formula: $Ni_xMg_y(C_2O_4)_{x+y}\cdot 2H_2O$. Depending on the nickel content, an excess nickel or magnesium oxalate is present in the structure. Following the preparation, the mixed oxalate precursor is first dehydrated and subsequently decomposed to the nickel-on-magnesia catalyst in either inert or hydrogen [17]. The decomposition temperature of the mixed oxalates depends on their nickel content; catalysts of high nickel loadings were shown to decompose at a lower temperature than catalysts containing only a small amount of nickel. Furthermore, it was determined using TGA that the decomposition of the mixed oxalates proceeds at a temperature between the decomposition temperature of pure nickel oxalate on one hand and of pure magnesium oxalate on the other. TGA is therefore an appropriate technique to indicate whether a mixed oxalate phase has been formed.

The use of mixed oxalates as catalyst precursors, however, has a serious drawback. During decomposition of the precursor, the solid disintegrates and the resulting nickel-on-magnesia catalyst consists of an extremely fine powder that renders fixed bed applications troublesome. However, we observed that if the precursor oxalate was mixed with magnesia prior to the decomposition, a solid was obtained that exhibited still a good mechanical strength after the activation procedure. The diluted catalyst M25-d was therefore well-suited for use in the fixed bed reactor. With catalyst M25-d (as well as with nickel–magnesium mixed oxalates having either higher or lower nickel loadings) a quite unusual effect was observed in the hydrogenation of acetonitrile. During operation the catalyst appeared to be activated. This phenomenon, that was observed only with the nickel–magnesium mixed oxalate catalysts, is shown in fig. 1.

It is clear that at increasing temperatures the conversion of acetonitrile, as indicated by the arrow pointing up, was always lower than the conversion at decreasing temperatures, indicated by the arrow pointing down. The activation of the

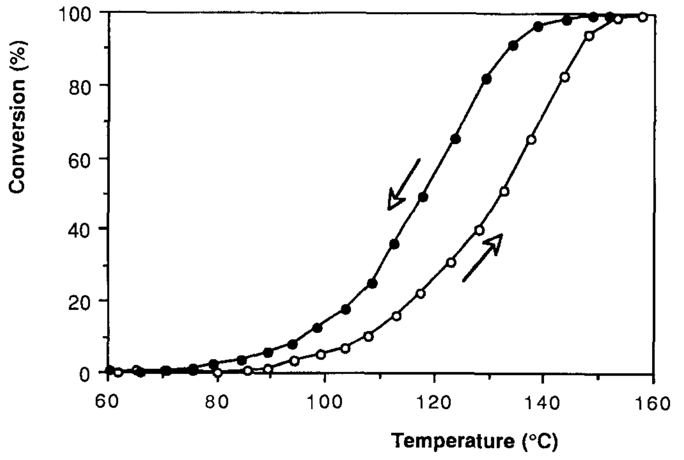

Fig. 1. The conversion of acetonitrile as a function of temperature, catalyst M25-d. The arrow near the lower curve indicates conversions measured at increasing reaction temperatures, whereas the arrow near the upper curve indicates conversions measured at decreasing temperatures.

catalyst during operation is obvious. To investigate this phenomenon more closely, the activity of a freshly reduced catalyst was followed isothermally at 128°C as a function of process time. Fig. 2 shows the results.

The plot on the left-hand side of fig. 2 indicates the conversion of acetonitrile as a function of temperature until a temperature of 128°C was reached, at which temperature the isothermal measurement was started. The data on the right-hand side of fig. 2 demonstrate that the catalyst was indeed activated, also during isothermal operation. During the isothermal measurement, which lasted about 20 h, the conversion rose from the initial value of 45% to the final value of 65%. The low activity of this catalyst in the first run with increasing temperature (fig. 1 and the left-hand plot in fig. 2) agrees with the extremely low value of its specific nickel surface area, viz., 11 m^2/gram nickel [9]. Figs. 1 and 2 show that the onset of acetonitrile conversion is located near a temperature of 90°C. Compared with catalyst S25U-d, for example, that converted already more than 90% of the acetonitrile feed at this temperature, catalyst M25-d has a relatively low activity. Both figures (1 and 2) demonstrate, however, that the latter catalyst was activated during the process. Presumably this activation was brought about by an in situ increase of the free nickel surface area during operation. It is speculated that during operation nickel atoms are extracted from some positions encapsulated by the magnesia support in the reduced catalyst through the action of the organic molecules in the feed.

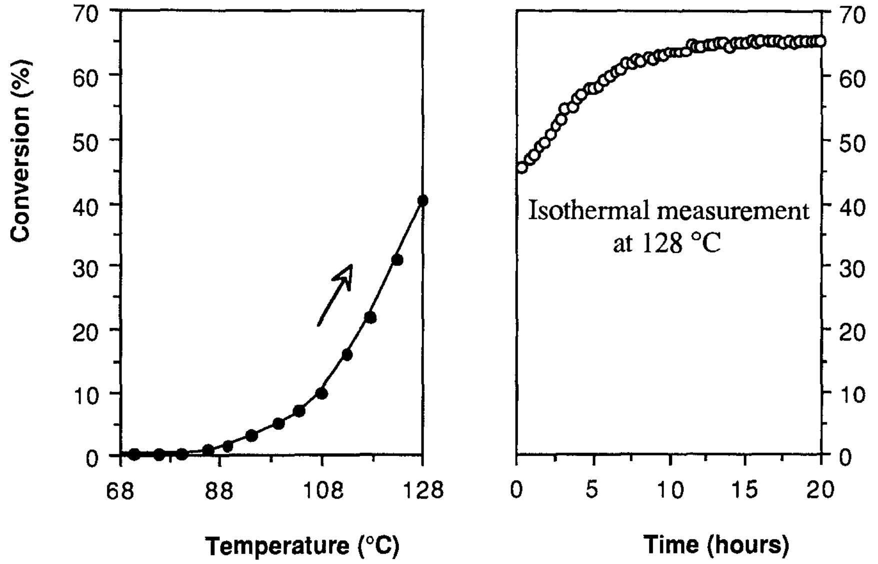

Fig. 2. The conversion of acetonitrile as a function of temperature (left) and, measured immediately after the experiment indicated in the left-hand plot, the conversion of acetonitrile at 128°C as a function of time (right).

3.3. HYDROGENATION OF ACETONITRILE: NICKEL SUPPORTED ON ALUMINA-BASED CARRIERS

Several catalysts consisting of nickel supported on supports of a different intrinsic acidity were studied in the hydrogenation of acetonitrile. Fig. 3 displays the selectivity toward ethyl-, diethyl-, and triethylamine at 125°C for the catalysts AP5, AS5, S5U, A5 and, S5I. The magnesia-supported catalyst M25-d, described in the previous section, is included for comparison.

It is evident that the more acidic the catalyst is, the more condensation products (di- and triethylamine) are formed. Going from left to right in fig. 3, the acidity *de*creases, whereas the selectivity toward ethylamine *in*creases. In this sequence, the selectivity toward the primary amine ranges from 25 mol% (catalyst AP5) to 98 mol% (catalyst M25-d). The basic catalyst M25 (nickel-on-magnesia) is thus highly selective in the formation of the primary amine even in the absence of ammonia. The use of a basic catalyst therefore seems to make the application of the (high) ammonia (partial) pressure normally encountered in technical operations superfluous.

The above set of catalysts contained nickel on supports that differed in intrinsic acidity. Another set of increasingly less acidic catalysts, containing nickel and potassium on γ-alumina, was also studied. With these catalysts, the intrinsic acidity of the alumina support was modified by covering its acidic sites with increasing amounts of potassium. Fig. 4 shows the selectivity toward ethylamine at 125°C for the potassium-promoted catalysts encoded A5, A5K-1, A5K-2, and A5K-3. In the codes the suffix K-1, K-2, or K-3 indicates the K weight loading.

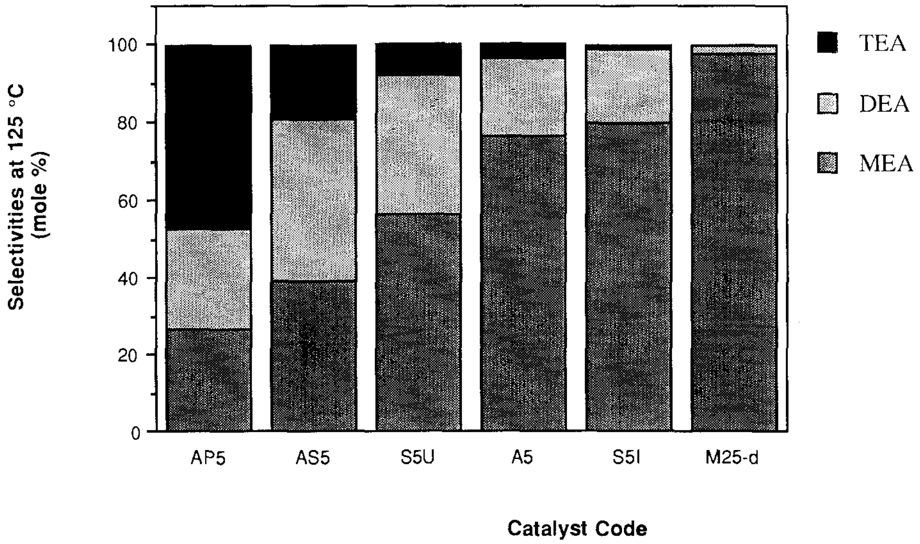

Fig. 3. Selectivities in the hydrogenation of acetonitrile at 125°C for several nickel catalysts containing supports of different intrinsic acidity. MEA = monoethylamine, DEA = diethylamine, and TEA = triethylamine.

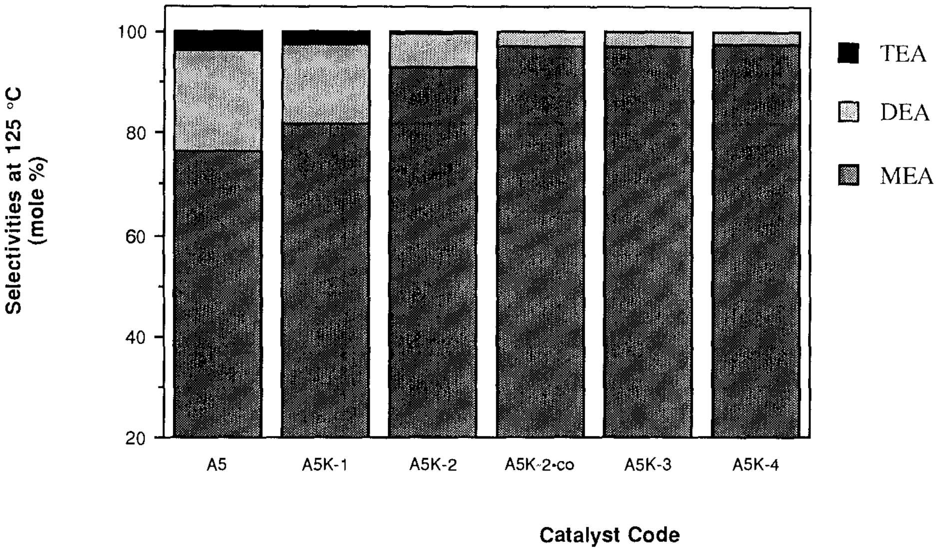

Fig. 4. Selectivities in the hydrogenation of acetonitrile at 125°C for several potassium-promoted nickel-on-alumina catalysts. A5 (0% K), A5K-1 (1% K), A5K-2 (2% K), A5K-2-co (2% K, prepared by co-impregnating K and Ni), A5K-3 (3% K), and A5K-4 (4% K). MEA = monoethylamine, DEA = diethylamine, and TEA = triethylamine.

Fig. 4 shows that higher potassium loadings induced a higher catalytic selectivity for the production of ethylamine. The increased amount of ethylamine produced was, of course, accompanied by a decreased amount of condensation products, diethyl- and triethylamine. Whereas the unpromoted catalyst A5 and the potassium-promoted catalysts A5K-1 and A5K-2 produced both the tertiary amine and an appreciable amount of the secondary amine, the potassium-promoted catalysts containing more potassium and the co-impregnated catalyst A5K-2-co were all extremely selective toward the primary amine and did not produce tertiary amines at all. It is demonstrated that the least acidic catalysts are the ones most selective for the production of primary amines in nitrile hydrogenations. Also with these catalysts a high selectivity toward ethylamine was achieved without the addition of ammonia to the reaction system. However, in spite of the improved selectivity at high K-loadings, the activity is affected negatively on increasing the amount of potassium in the catalyst. At low K-loadings, i.e., 1 wt% K, the activity was not affected by the promotion as compared to the unpromoted catalyst. At higher K-loadings, however, the decline of activity is severe as represented in fig. 5.

It is generally found that alkali promoters decrease the activity of nickel catalysts in various catalytic reactions. Promotion of nickel-on-alumina and nickel-on-silica catalysts with increasing amounts of potassium decreased the turnover numbers (TON) in the hydrogenation of carbon monoxide [18]. In another study Huang and Richardson [19], observed a maximum TON for carbon monoxide hydrogenation when a Ni/SiO_2–Al_2O_3 catalyst was doped with an increasing

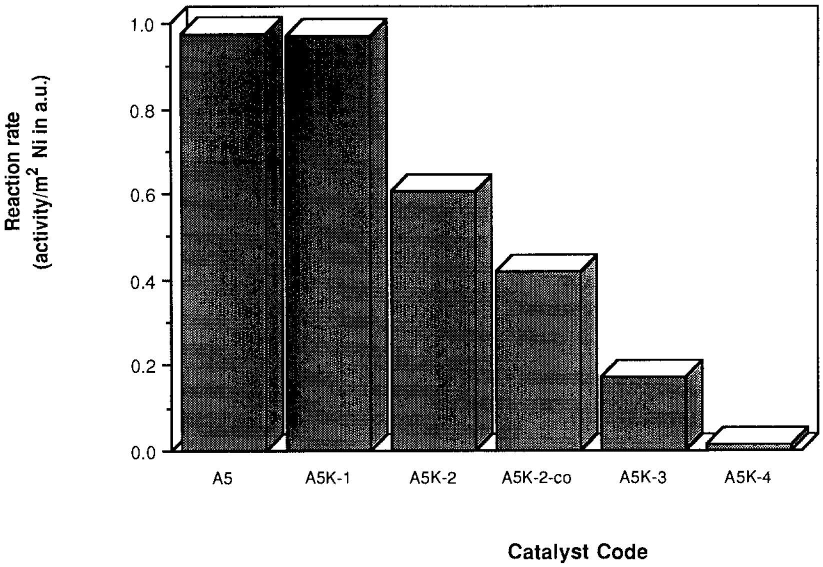

Fig. 5. The activity of several potassium-promoted nickel-on-alumina catalysts, expressed as areal reaction rates (activity/m^2 Ni surface area) in arbitrary units.

amount of sodium. The maximum was positioned at 0.3 wt% Na. When the amount of sodium in the catalyst was increased beyond this value, a drop in TON was observed. In a similar study Chai and Falconer determined the influence of potassium on supported nickel catalysts [20]. Their nickel-on-silica catalysts showed a continuously decreasing TON in the CO-hydrogenation with increasing amounts of K, while K-promoted Ni/SiO_2–Al_2O_3 catalysts exhibited a maximum TON at 0.5 wt% K. Modification of a platinum reforming catalyst by the addition of alkali or alkaline earth dopes also decreased the activities [21]. In the literature there is little agreement on the mechanism by which alkaline additives modify the catalytic activity. In most cases, the hydrogenation of carbon monoxide is used to study the effect of the promoter. Based on a shift of the carbon–oxygen stretching vibration in infrared experiments with CO adsorbed on potassium-promoted nickel, it is usually assumed that potassium functions as an electronic modifier of the metal (e.g., ref. [22]). We speculate that alkali promoters might influence the morphology of the individual nickel crystallites. The exposure of different, less active crystal planes in a K-promoted nickel catalyst could be responsible for a decreased activity. Because this was not studied in this work, further research is needed to answer this question.

It was shown that the potassium-promoted nickel-on-alumina catalysts were highly selective to ethylamine in the hydrogenation of acetonitrile. These catalysts, however, exhibited a lower activity when the K-loading was raised beyond 2 wt%. To evaluate the performance of the catalysts, it is therefore preferred to use yield values instead of selectivities. Multiplication of the molar selectivities (in %) by the conversions renders the yield. Fig. 6 shows the yield of ethylamine at 125°C for the various potassium-promoted nickel-on-alumina catalysts.

From the inspection of fig. 6 it is apparent that addition of more than 3 wt% K overpromoted the catalyst, leading to a drop in the ethylamine yields. In spite of its decreased activity, catalyst A5K-4 still exhibited a high selectivity toward ethylamine. Furthermore, the conclusion can be drawn that it is more efficient to apply K and Ni onto γ-alumina simultaneously, i.e., by co-impregnation, since less potassium is required, a one-step procedure can be used, and the ethylamine yield is high. In this set of K-promoted catalysts, catalyst A5K-2-co is preferred for the selective production of primary amines.

The addition of potassium to nickel-on-alumina catalysts is thus highly efficient to decrease the acidity of the catalysts. Besides potassium, also the effect of the application of sodium, calcium, and zinc onto γ-alumina was studied. It was found that sodium also raised the selectivity toward ethylamine, whereas both calcium and zinc were less efficient for this purpose, in accordance with the acidity measurements using temperature-programmed desorption of ammonia [9]. It can be concluded that alkali metal promoters are preferred to reduce the surface acidity of alumina-based supports. To illustrate the effect of alkali metal additives still more clearly, the acidic aluminosilicate support was also doped with potassium prior to the application of nickel. Because the surface area of this material was much larger (225 m^2/g) than the surface area of γ-alumina (100 m^2/g), more K was applied. An amount of 10 wt% K was added. The selectivity toward ethylamine measured at 125°C was raised from 40 mol% (catalyst AS5, no K) to 95 mol% with the K-

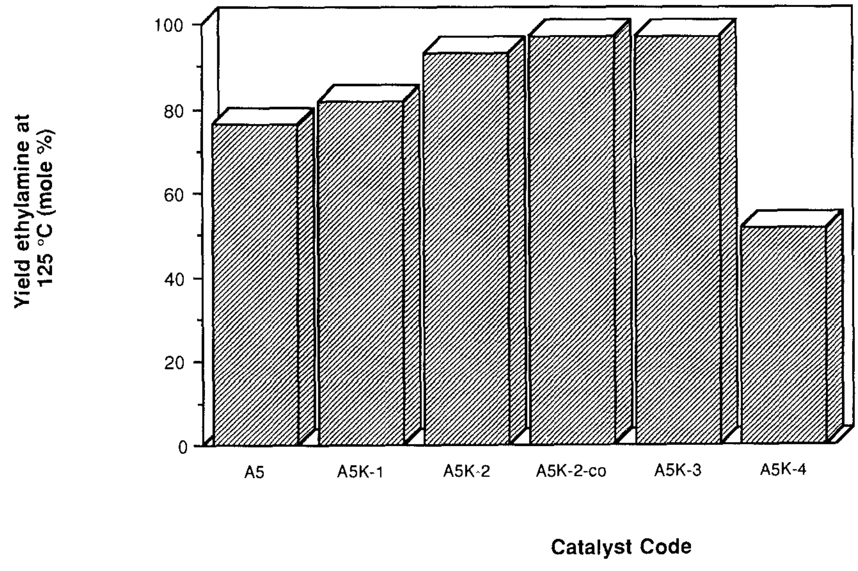

Fig. 6. Ethylamine yields at 125°C for several K-promoted nickel-on-alumina catalysts.

promoted catalyst, AS5K-10. These experiments therefore demonstrate that the chemical composition of the catalyst influences the product distribution in nitrile hydrogenations to a great extent.

3.4. THE REACTION MECHANISM

With the above results, a relation between the acidity of the catalyst and its selectivity in the hydrogenation of acetonitrile has been established. Because the acidities of a large number of catalysts were quantified in other work using temperature-programmed desorption of ammonia [9], it is now possible to visualize the effect of an increasing acidity on the selectivity to ethylamine in the hydrogenation of acetonitrile. Fig. 7 shows the ethylamine selectivity at 125°C as a function of catalyst acidity calculated from the ammonia desorption profile by partially integrating the curve between 20 and 150°C. A linear relation results. Therefore it is apparent that the acidity of the catalyst is directly responsible for the occurrence of the condensation reactions leading to secondary and tertiary amines. This would imply some dual-function mechanism. Hydrogenation and dehydrogenation proceed on the metal surface, while the acid-catalyzed condensation reactions occur on the surface of the support. The following experiment was performed to establish unambiguously that a dual-function mechanism is operative. The only slightly acidic catalyst, M25, was used to prepare two physical mixtures. The first mixture was prepared by mixing powdered fractions of catalyst M25 and the highly acidic aluminosilicate support in equal amounts. The other physical mixture was prepared analogously by mixing powdered fractions of catalyst M25 and the (basic)

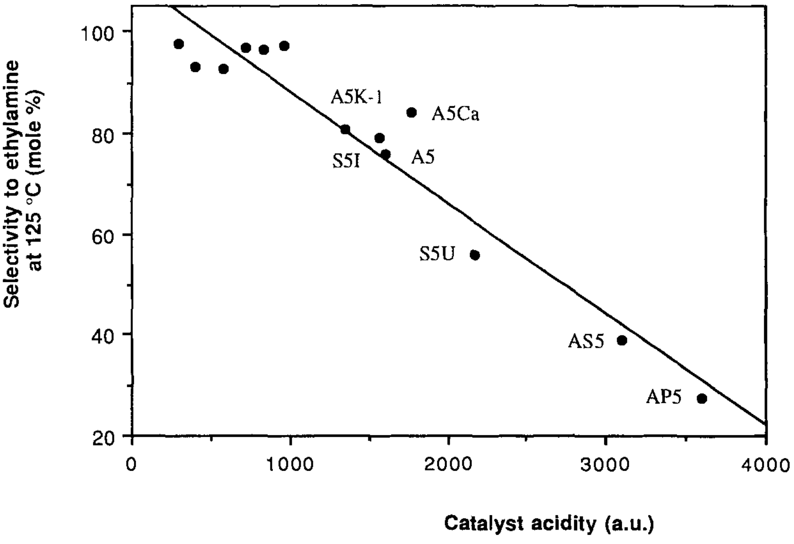

Fig. 7. Relation between catalyst acidity, as measured by the desorption of NH_3, and selectivity toward ethylamine in the hydrogenation of acetonitrile at 125°C.

potassium-promoted aluminosilicate support (10 wt% K/aluminosilicate). Samples are coded respectively M25-da (da stands for diluted with acidic support) and M25-db (where b stands for basic support). Catalyst M25-d was prepared as described under Experimental. After mixing, the physical mixtures were pressed into tablets, crushed and sieved. At 125°C the following selectivities toward MEA, DEA and TEA were observed: MEA 98% and DEA 2% (catalyst M25-d), MEA 59%, DEA 37% and TEA 4% (catalyst M25-da) and MEA 97% and DEA 3% (catalyst M25-db). It is obvious that a dual-function mechanism is involved. By adding acidity to the basic catalyst M25 through mixing with an acidic oxide, higher amounts of condensation products result. Because the samples are not mixed on a microscopical scale, the experiments demonstrate that the location of acid sites is not restricted to the direct neighborhood of the nickel crystallites for condensation reactions to occur. Therefore, intermediate reaction products can travel over relatively long distances before condensation actually occurs. The transport out of the catalyst bed makes detection of the intermediates possible.

The reactions in nitrile hydrogenation are accomplished in the following way. On the metallic component of the catalyst nitriles undergo hydrogenation to imines and amines. These compounds then migrate, probably through the gas phase, to acidic sites where the imines become protonated and react with amines coming from the gas phase. The resulting "α-amino amine" is then deprotonated and loses ammonia. A Schiff base is formed that after desorption from the support migrates back to the metal, where it is hydrogenated to the secondary amine. This sequence of steps is outlined in fig. 8.

At this point it is illustrative to compare the mechanism of carbinolamine formation in the reactions of carbonyl compounds with amines, with the condensation reactions of amines and imines. Since the carbonyl bond and the N-unsubstituted imine bond are isoelectronic we expect their reactions to be very similar. The condensation of carbonyl compounds with amines is normally carried out with the assistance of an electrophilic catalyst, most commonly the proton [23]. The function of the catalyst is to coordinate with the carbonyl group making it more subject

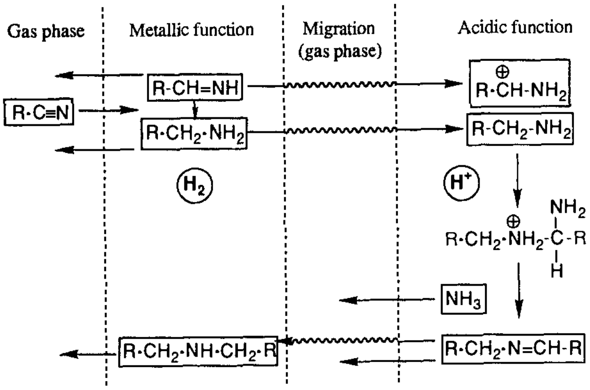

Fig. 8. Bifunctionality in the hydrogenation of nitriles.

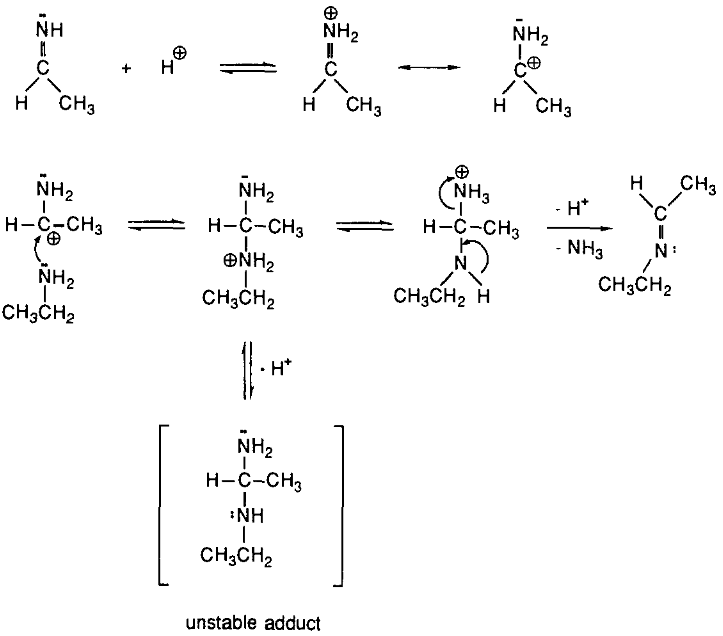

Fig. 9. Mechanism for the acid-catalyzed condensation of amines and imines.

to attack by a nucleophile. After the nucleophilic attack, proton transfer and 1,2-elimination of water produce the final product. When the analogy is drawn to the reaction of imines with amines (because bonds are isoelectronic), the acid-catalyzed addition of the amine to the imine and the consecutive elimination of ammonia will produce the Schiff base. This proposed reaction sequence is outlined in fig. 9 for the reaction of ethylidene amine (Schiff base) with ethylamine (that functions as the nucleophile).

All results point in the same direction. The acidity of the catalyst determines the selectivity in the hydrogenation of acetonitrile. When the active (transition) metal has been selected, the support can therefore be used to optimize the selectivities. It was shown that nickel on a basic support is both active and highly selective in the production of primary amines, even in the absence of ammonia.

4. Conclusions

The nature of the support greatly influenced the course of vapor-phase hydrogenation of acetonitrile by modifying the extent to which condensation reactions proceeded. With catalysts that consisted of nickel on acidic supports, the supports catalyzed the condensation of amines with imines. As a result, catalysts with acidic supports exhibit a low selectivity toward primary amines. Basic nickel catalysts, on the other hand, were highly selective with respect to the formation of ethylamine because, due to their basic nature, acid-catalyzed side reactions were suppressed. Because the acidity of the supported nickel catalysts is determined by the properties of the support, modification of the support creates a means to manipulate its acidity.

Both sodium and potassium were highly efficient in decreasing the acidity of the catalysts, which manifested itself in high selectivities toward ethylamine. In spite of their high selectivity toward the primary amines, potassium-promoted nickel-on-alumina catalysts exhibited an activity decreasing with increasing potassium loading. Since all the hydrogenation experiments were performed in the absence of ammonia, it can further be concluded that the addition of ammonia to the reaction system for the selective production of primary amines is superfluous when a basic nickel catalyst is used. The advantage to be able to omit ammonia is obvious.

Because the selectivity of a magnesia-supported catalyst toward ethylamine dropped when this catalyst was physically mixed with an acidic support, the conclusion was drawn that a bifunctional mechanism is operating. Furthermore, a mechanism was proposed that accounts for the occurrence of acid-catalyzed side reactions. The discussion about the acid-catalyzed condensation reactions will be taken up in a following paper when the disproportionation of *n*-propylamine will be investigated.

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