

Hydrogenation of Acetonitrile on Nickel-Based Catalysts Prepared from Hydrotalcite-like Precursors

Francisco Medina Cabello,¹ Didier Tichit, Bernard Coq,² Angelo Vaccari,³ and Nguyen Thy Dung⁴

Laboratoire de Matériaux Catalytiques et Catalyse en Chimie Organique, CNRS, UMR 5618, 8 Rue Ecole Normale, 34296 Montpellier Cedex 1, France

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Various solids with a hydrotalcite-like structure and containing $\text{Ni}^{2+}/\text{Mg}^{2+}/\text{Al}^{3+}$ cations in different amounts were prepared. These solids were calcined at 623 K and reduced at 723 K to give Ni/Mg(Al)O catalysts, with metallic Ni particles between 7 and 9 nm. The properties of Ni and the support for the adsorption of monoethylamine, acetonitrile, CO, and H_2 were evaluated by calorimetric and temperature-programmed desorption experiments. These catalysts were tested in the gas phase hydrogenation of acetonitrile between 350 and 450 K and with a $\text{H}_2/\text{CH}_3\text{CN}$ molar ratio of 6.75. The main product is monoethylamine (MEA). Secondary products are *N*-ethylethylamine at low conversion and diethylamine and triethylamine at high conversion. The MEA selectivity and, to a much lesser extent, the rate depend on the Mg/(Mg + Ni) ratio. An optimal Mg content ($\text{Mg}/(\text{Mg} + \text{Ni}) \approx 0.23$) exists for which the MEA selectivity goes through a maximum value of 92.6% at 99% CH_3CN conversion. The occurrence of this optimal Mg content is due to a compromise between the reducibility of Ni and the acidity/basicity of the material, both decreasing with the introduction of Mg. The acid sites are partly responsible for the formation of secondary products. The heat of MEA adsorption, which is 40 kJ mol⁻¹ lower for the Mg-containing sample ($\text{Mg}/(\text{Mg} + \text{Ni}) \approx 0.23$) than for the Mg-free sample, provides evidence of a decrease in the acidity for the composite Ni/Mg(Al)O. This is further confirmed by the disappearance of the high temperature peaks of MEA desorption for the latter sample. © 1997 Academic Press

INTRODUCTION

Amines can be prepared commercially by hydrogenation of nitriles (1–5). A typical example is the hydrogenation of adiponitrile, which is hydrogenated to 1,6-hexanediamine for the manufacture of nylon-6,6 (6, 7). The industrial synthesis of these amines is usually carried out in the liquid phase at elevated temperatures and hydrogen pressures

in the presence of a heterogeneous transition metal catalyst (8).

Raney nickel and Raney cobalt are probably the most frequently used catalysts for primary amine production from nitrile hydrogenation (9–14). Other catalysts based on Rh, Mn, and Fe have also been reported (15–17). Due to the high reactivity of partially hydrogenated reaction intermediates, imines or Schiff bases, a conventional hydrogenation process leads to a mixture of primary, secondary, and tertiary amines (6, 18–21). Promotion by bases of the reaction medium was found to decrease the formation of secondary and tertiary amines, though the primary amine yield was never complete (16, 22). The promoting effect of NH_3 can come from (i) a thermodynamic influence on the reaction between primary imine and amine, leading to secondary imine and NH_3 ; (ii) a modification of the electronic properties of the hydrogenating metal; and (iii) a poisoning of the surface acid sites which would be mainly responsible for the coupling reaction between primary imine and primary amine to secondary amine (23). All products of the nitrile hydrogenation, imines and amines, are basic species which will interact more strongly with acid than with basic sites. It has therefore to be expected that, on tuning the acid–base character of the support, a change in selectivity should be found in favor of primary amines (23–25). Thus, it has been reported that, by adding alkali metals, the modification of the intrinsic acidity of catalysts promotes the selectivity to primary amines (5, 17, 23, 26). However, Volf and Pasek (4) stated that the support does not have a great influence on the selectivity of the hydrogenation process but merely helps to create a well-dispersed catalyst; these authors claim that the selectivity is determined for the most part by the nature of the metal and by the reaction conditions.

Lamellar double hydroxides (LDHs) of the hydrotalcite type are interesting materials as precursors for mixed oxides with basic properties. LDHs consist of lamellar structures whose sheets can associate, in an appropriate ratio ($1.5 < \text{M}^{2+}/\text{M}^{3+} < 4$), different types of divalent (Mg^{2+} , Ni^{2+} , Ca^{2+} , Zn^{2+} , Cu^{2+} . . .) and trivalent cations (Al^{3+} , Fe^{3+} , Cr^{3+} . . .). The interlayer space contains exchangeable anions (NO_3^- , SO_4^{2-} , CO_3^{2-} , Cl^- . . .) and water. These

¹ Present address: Departament d'Enginyeria Química, Universitat Rovira i Virgili, Carretera de Salou, 43006 Tarragona, Spain.

² To whom correspondence should be addressed.

³ Present address: Dipartimento Chimica Industriale e dei Materiali, Viale del Risorgimento 4, Bologna, Italy.

⁴ Present address: Institute of Chemical Technology, 1 Mac Dinh Chi, Q. I., Ho Chi Minh City, Vietnam.

compounds easily decompose into a mixed oxide of the $M^{\text{II}}(M^{\text{III}})\text{O}$ type upon calcination (27). Strong basic properties were identified on some of these mixed oxides (28). Moreover, they give rise to well dispersed metallic particles, and this class of supported metal catalysts has been reported to exhibit unusual properties, similar to those of hydrogenation or steam reforming catalysts (see Ref. (28) for a review).

The final basicity of these catalysts and the electronic state of the metallic phase depend on a wide variety of parameters such as the Ni, Co, Mg, Zn/Al ratio, the presence of alkali dopes, the nature of compensating anions, and thermal treatments. Actually, the ways in which these parameters affect the surface properties and define the catalytic behavior of the active metallic phase have been scarcely studied and are not well understood.

It was, therefore, the aim of this work to synthesize LDH materials of the hydrotalcite type in which the divalent cations are both Ni^{2+} and Mg^{2+} . They constituted the parent structure giving access to the $\text{NiMg}(\text{Al})\text{O}$ mixed oxides which, after reduction, transformed to $\text{Ni}^0/\text{NiMg}(\text{Al})\text{O}$. Catalysts were thus prepared with a $\text{Mg}/(\text{Mg} + \text{Ni})$ molar ratio from 0 to 1 and calcination temperatures ranging from 393 to 973 K. Details of the preparation and characterization are given elsewhere (29). Their catalytic properties were evaluated in the gas phase hydrogenation of acetonitrile.

EXPERIMENTAL

Preparation and Characterization of the Catalysts

Two samples corresponding to the takovite mineral with Ni/Al ratios of nearly 2 and 3 and four samples containing $\text{Ni}^{2+}/\text{Mg}^{2+}/\text{Al}^{3+}$ cations with a large range of compositions were prepared (Table 1). They were obtained by coprecipitation at constant pH 8 ± 0.2 of an aqueous solution containing appropriate amounts of $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$. The dropwise addition of a solution of NH_4OH and $(\text{NH}_4)_2\text{CO}_3$ was

performed at 353 K under vigorous magnetic stirring. The precipitated gels were heated in air at 353 K for 14 h and then filtered and washed several times with distilled water at 353 K. The solids were finally dried in an oven at 393 K for 72 h.

Heats of hydrogen, carbon monoxide, acetonitrile, and monoethylamine adsorption were determined with a modified SETARAM microcalorimeter DSC-111. The flowing gas passes through the catalyst bed (5–10 mm height) inside a silica reactor, which is placed in the calorimetric cell. The sample was first activated *in situ* as described below for the catalytic tests. After outgassing under flowing He at 723 K, the sample was cooled to room temperature. The temperature was then set at 313 ± 0.01 K, and micropulses of the probe molecules were fed to the catalyst using a six-way sampling valve flushed with He. The thermal event in the calorimetric cell was then recorded as a function of the adsorbate uptake, which was monitored by a catharometer. All the gases were of ultrahigh purity and further purified by a molecular sieve and MnO traps.

After the reactant adsorption followed by calorimetry had been achieved, the temperature-programmed desorption (TPD) of the adsorbate was performed under ultrapure argon for hydrogen TPD or helium flow for the others TPD. The temperature was raised from 313 to 800 K at 10 K min^{-1} .

Catalytic Test

The catalytic tests were performed in a microflow reactor operating at atmospheric pressure. Prior to any measurement, 40 mg of catalyst was activated *in situ*. The sample was first calcined in an O_2/N_2 mixture (20/80, vol/vol) for 2 h at 623 K (ramp, 2 K min^{-1}) and then cooled to room temperature under nitrogen. After that, the sample was reduced in a diluted hydrogen flow (H_2/N_2 , 10/90, vol/vol) at 723 K for 2 h (ramp, 2 K min^{-1}). The reaction temperature ranged from 343 to 453 K. Acetonitrile was fed by means of a positive displacement pump, and diluted with hydrogen in a mixing chamber to obtain different acetonitrile/ H_2

TABLE 1

Some Characteristics of the Ni-Based Catalysts

Sample	Chemical formulae	Mg/(Mg + Ni)	S_{BET}^a ($\text{m}^2 \text{ g}^{-1}$)	S_{Ni}^b ($\text{m}^2 \text{ g}^{-1}$)	dp_{Ni}^b (nm)
HA	$\text{Ni}_{2.82}\text{Al}_1(\text{OH})_{7.64}(\text{CO}_3)_{0.09}(\text{NO}_3)_{0.82} \cdot 2.46\text{H}_2\text{O}$	0	193	13	8.9
HD	$\text{Mg}_{0.23}\text{Ni}_{2.4}\text{Al}_1(\text{OH})_{7.26}(\text{CO}_3)_{0.19}(\text{NO}_3)_{0.62} \cdot 2.15\text{H}_2\text{O}$	0.09	202	13	7.9
HC	$\text{Mg}_{0.42}\text{Ni}_{1.43}\text{Al}_1(\text{OH})_{5.7}(\text{CO}_3)_{0.19}(\text{NO}_3)_{0.62} \cdot 2.15\text{H}_2\text{O}$	0.23	210	8	7.4
HE	$\text{Ni}_{1.99}\text{Al}_1(\text{OH})_{5.98}(\text{CO}_3)_{0.22}(\text{NO}_3)_{0.56} \cdot 2.36\text{H}_2\text{O}$	0	236	12	7.0
HG	$\text{Mg}_{1.56}\text{Ni}_{1.52}\text{Al}_1(\text{OH})_{8.16}(\text{CO}_3)_{0.5} \cdot 2.15\text{H}_2\text{O}$	0.51	210	—	—
HF	$\text{Mg}_{2.1}\text{Ni}_{0.35}\text{Al}_1(\text{OH})_{6.9}(\text{CO}_3)_{0.5} \cdot 2.4\text{H}_2\text{O}$	0.86	220	—	—

^a After calcination at 623 K.

^b After calcination at 623 K and reduction at 723 K.

molar ratios. The reaction mixture was then passed through the catalyst and the effluent was analyzed by sampling on line to a gas chromatograph (Perkin Elmer) equipped with a capillary column (30 m \times 0.25 mm i.d., apolar phase) and a flame ionization detector. The products were identified by GC-MS. All connecting lines, commutation, and sampling valves were placed in a hot box heated at 373 K in order to prevent any condensation. The following parameters were determined to evaluate the catalytic properties: acetonitrile conversion (mol%) = $100 \times (\text{acetonitrile}_{\text{in}} - \text{acetonitrile}_{\text{out}}) / \text{acetonitrile}_{\text{in}}$ selectivity_{*i*} (mol%) = $100 \times (\text{corrected area})_i / (\text{sum of all corrected areas})$.

The selectivities were calculated from peak areas taking into account the different sensitivity factors in the flame ionization detector.

RESULTS

Some of the main characteristics of the catalysts are summarized in Table 1; details are given elsewhere (29). The main points are the following:

(i) The NO_3^- and CO_3^{2-} counteranions originate from the starting salts and the different treatments. Before calcination, all samples show the typical XRD patterns of hydrotalcite-type phases. The specific surface areas, in the range of 15–35 m² g⁻¹ in the uncalcined samples, increase up to a maximum value of 190–240 m² g⁻¹ after calcination at 623 K. No micropore was identified in the samples.

(ii) Upon calcination, the crystallinity of the lamellar structure progressively decreases, while a mixed oxide phase appears for every sample. Only the mixed oxide of the NiO type is observed after calcination at 623 K.

(iii) TPR experiments showed that the reducibility of the nickel oxide particles decreases when the calcination temperature increases or the Mg and Al contents of the samples increase. This could explain the decrease in the Ni⁰ crystal size measured by XRD in sample HC and the lack of these particles in samples HF and HG calcined at 623 K and reduced at 723 K (Table 1). The reduction of the NiO is, therefore, hindered by the presence of the Mg and Al species in the structure of the LDHs.

Figures 1–4 present the heats of H₂, CO, acetonitrile, and monoethylamine (MEA) adsorption as a function of adsorbate coverage on HA, HD, and HC samples. The TPD profiles of H₂, acetonitrile, and MEA, carried out after the calorimetric experiments, are shown in Figs. 5–7.

First, there are no great differences in the heats of H₂, CO, and acetonitrile adsorption on the three samples; they remain within $\pm 10\%$ (Figs. 1–3). However, tendencies are apparent. The heats of H₂ adsorption are 5–10 kJ mol⁻¹ higher on the HD and HC samples than on the HA sample, while the reverse is true for the heats of acetonitrile adsorption. On the other hand, the heat of CO adsorption is 20 kJ mol⁻¹ greater on the HD sample. There is general

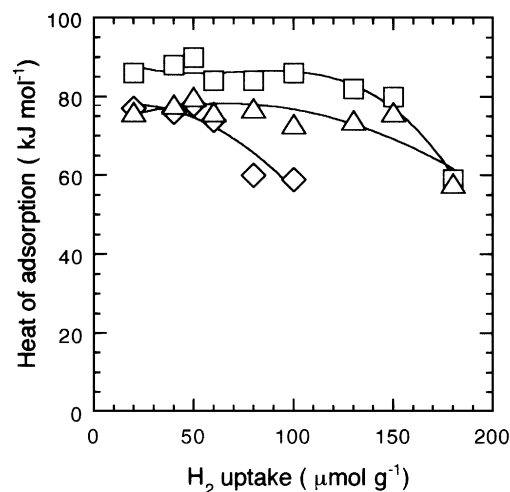


FIG. 1. Differential heat of adsorption as a function of H₂ uptake on HA (□), HD (△), and HC (◇) samples at 313 K.

agreement in the literature that the promotion of transition metals by alkali metals leads to more tightly bound CO. This is reflected by an increase in the heat of CO adsorption upon addition of K to Fe (30, 31), Pd (32), or Pt (33). As far as the heat of H₂ adsorption is concerned, the agreement is not so general (30–35). In addition, the values of $\Delta Q(\text{H}_2)$ that we found for the various samples, i.e., 80–85 kJ mol⁻¹ at half hydrogen coverage, are similar to the reported value of 82 kJ mol⁻¹ for the adsorption of hydrogen on Ni/SiO₂ (36). From calorimetric studies on silica-supported Ni catalysts, Prinsloo and Gravelle (37) reported a differential heat of H₂ adsorption decreasing from 100 to 70 kJ mol⁻¹ from low to high H₂ coverage. Actually, and within the experimental errors, the heat of H₂ adsorption is only slightly affected by the addition of alkali metals, and this remains true when promoting Ni by Mg.

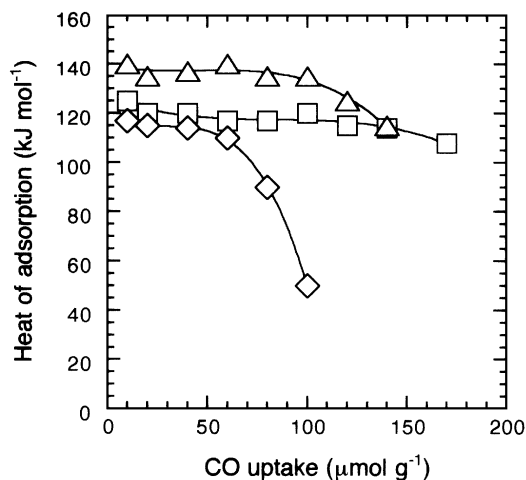


FIG. 2. Differential heat of adsorption as a function of CO uptake on HA (□), HD (△), and HC (◇) samples at 313 K.

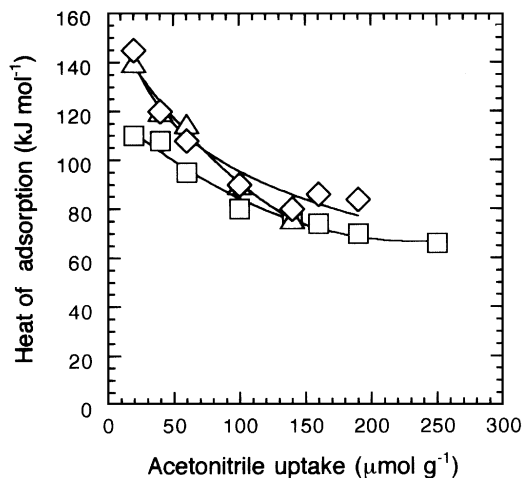


FIG. 3. Differential heat of adsorption as a function of acetonitrile uptake on HA (□), HD (△), and HC (◇) samples at 313 K.

The TPD of hydrogen (Fig. 5) shows that at least two bound states of hydrogen exist which desorb around 530 and 600 K. Besides a weakly bound state which desorbs at room temperature, two strongly bound states were identified for hydrogen adsorbed on Ni/Al₂O₃, desorption of which occurred at approximately 600 and 700 K (36). The behavior of hydrogen desorption from Ni/Mg(Al)O is similar, but with a shift to lower desorption temperatures. Moreover, it seems that the presence of Mg slightly modifies the proportion of weakly and more tightly bound states of hydrogen on Ni, though these possible changes were not reflected by clear change of the heat of H₂ adsorption (Fig. 1).

Figure 3 shows the heat of acetonitrile adsorption on different samples, which increases slightly upon Mg addition. However, the case of acetonitrile adsorption is more complex, because this compound not only adsorbs on reduced

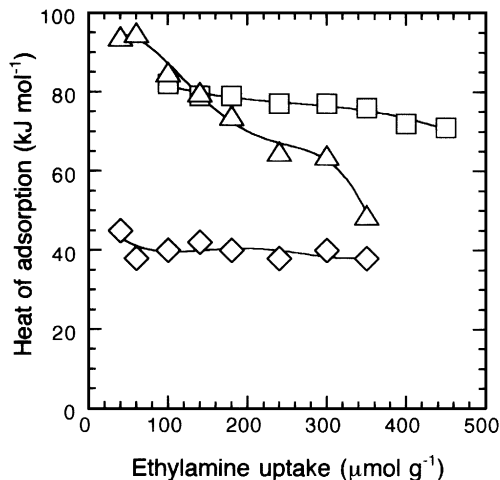


FIG. 4. Differential heat of adsorption as a function of ethylamine uptake on HA (□), HD (△), and HC (◇) samples at 313 K.

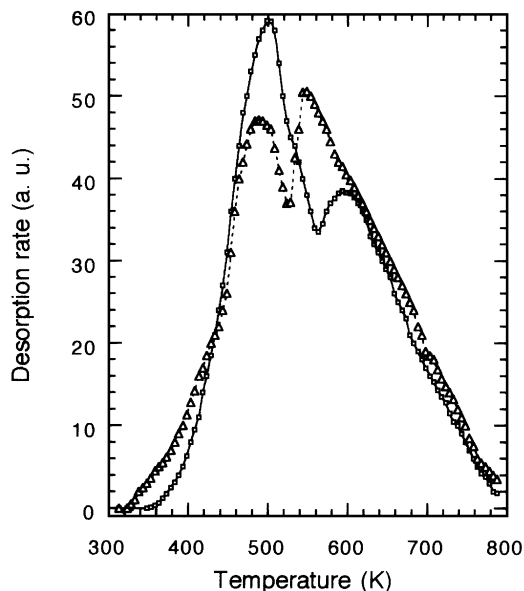


FIG. 5. Temperature programmed desorption profiles of H₂ from HA (□) and HD (△) samples.

Ni particles (38, 39), but also on basic or acid sites of the support (40). Therefore, it is difficult to assign unambiguously the changes in the heat of adsorption to a modification of the Ni or the support surfaces by Mg. On the other hand, TPD experiments show that weakly bound states of acetonitrile, which desorb from 340 to 440 K for the HA catalyst, disappeared for HD and HC samples. In contrast, desorption of strongly bound states shifted to higher temperatures upon the addition of Mg.

The differential heat of MEA adsorption is 40 kJ mol⁻¹ greater on the HA than on the HC sample, and HD exhibits

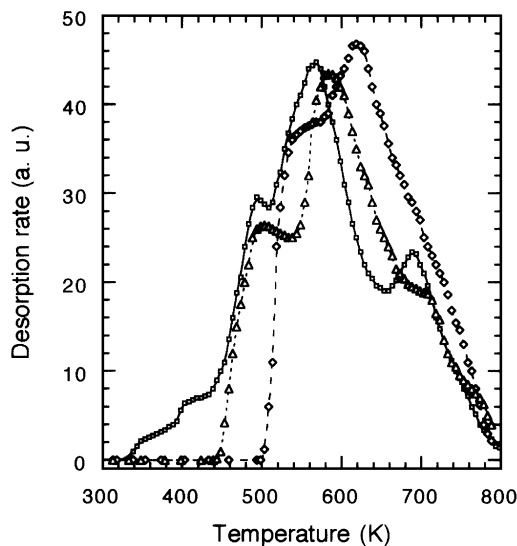


FIG. 6. Temperature programmed desorption profiles of acetonitrile from HA (□), HD (△), and HC (◇) samples.

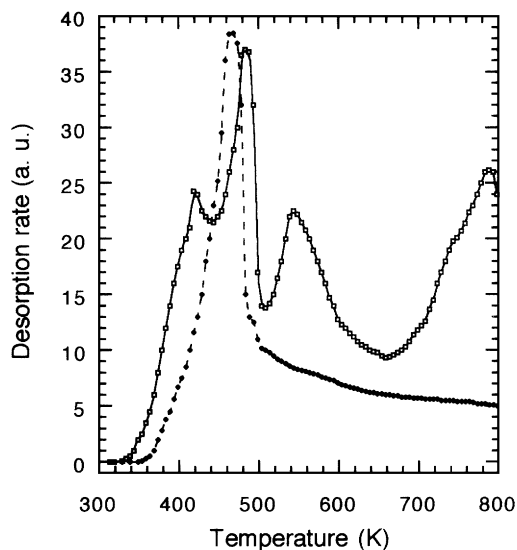


FIG. 7. Temperature programmed desorption profiles of ethylamine from HA (\square) and HC (\diamond) samples.

an intermediate behavior (Fig. 4). The TPD of MEA from the HC sample exhibits only one desorption peak at low temperature (≈ 430 K), whereas two additional desorption peaks around 550 and 780 K appear on the HA sample (Fig. 7). Gardin and Somorjai (41) reported that the thermal desorption of MEA from the Ni(111) surface (ramp, 8 K s^{-1}) occurred in two steps, a molecular desorption at temperatures lower than 300 K and a dehydrogenating desorption to acetonitrile at 350 K. On the other hand, a molecular MEA desorption at 430 K (ramp, 50 K min^{-1}) from Raney Ni was assigned to MEA in interaction with acid sites associated with alumina residues (38).

In the course of the acetonitrile reaction with hydrogen over Ni-based catalysts, MEA was the main organic compound formed, with selectivity normally higher than 70%. Diethylamine (DEA), *N*-ethylethylimine (EEI), and triethylamine (TEA) usually appeared as by-products, and trace amounts ($<1\%$) of ethane, methane, and oligomeric products were sometimes detected at high reaction temperatures.

In a preliminary set of experiments, the catalysts were tested by a temperature-programmed reaction from 353 to 453 K in steps of 10 K for 2 h. The plots of acetonitrile conversion and MEA selectivity as a function of reaction temperature are shown in Fig. 8. These results call for the following comments:

(i) Whatever the catalyst, the by-products are mainly EEI at low temperature and conversion, but DEA and TEA at high temperature and conversion.

(ii) The HA and HE samples, which contain Ni only as divalent cations, exhibit a similar MEA selectivity though the reactivity is different.

(iii) When replacing part of Ni by Mg as divalent cations, there is first an increase in both reactivity and MEA selectivity at low Mg content (HD, HC) and, thereafter, the samples become unreactive and less selective at higher Mg content (HG, HF).

However, deactivation of the samples occurred during these screenings of the catalysts in a temperature-programmed reaction. To circumvent these drawbacks and to focus more precisely on the most interesting HA, HD, and HC samples, these catalysts were reacted at 393 K overnight in the reaction medium. Figure 9 shows, for the HC sample, the evolution of acetonitrile conversion and MEA selectivity as a function of time as well as the effect of two different reactivation procedures. At the end of the first run, the catalyst was reactivated *in situ* directly in diluted hydrogen at 723 K for 2 h (ramp, 10 K min^{-1}). At the end of the second run, the sample was reactivated *in situ*, first by calcination at 623 K and then by reduction at 723 K according to the initial activation protocol. During the first run, after a steep initial decrease, the activity

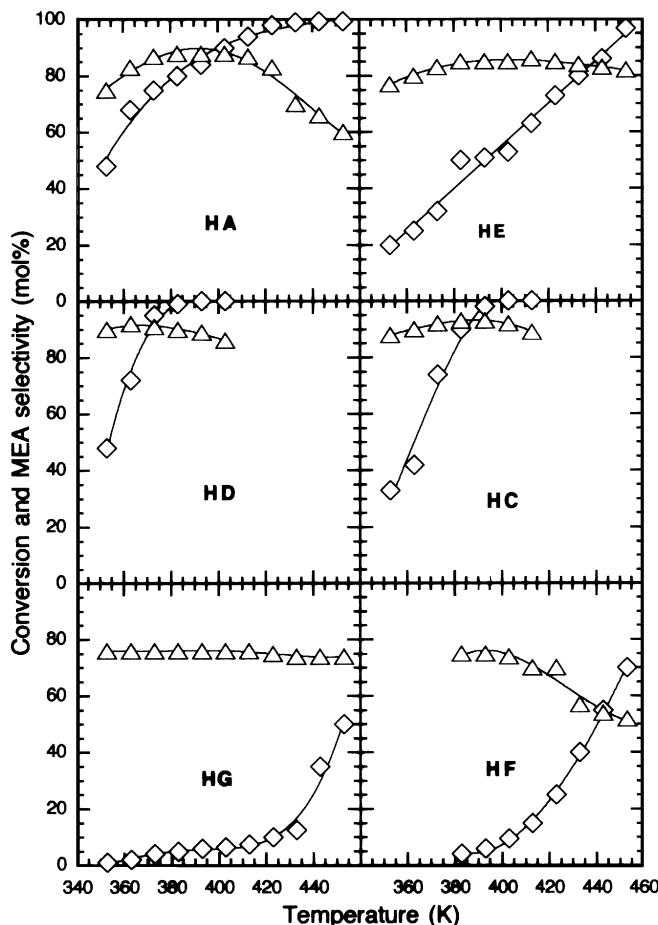


FIG. 8. Acetonitrile conversion (\diamond) and MEA selectivity (\triangle) as a function of reaction temperature on HA, HC, HD, HE, HG, and HF samples; $P(\text{H}_2) = 88 \text{ kPa}$, $P(\text{acetonitrile}) = 13 \text{ kPa}$.

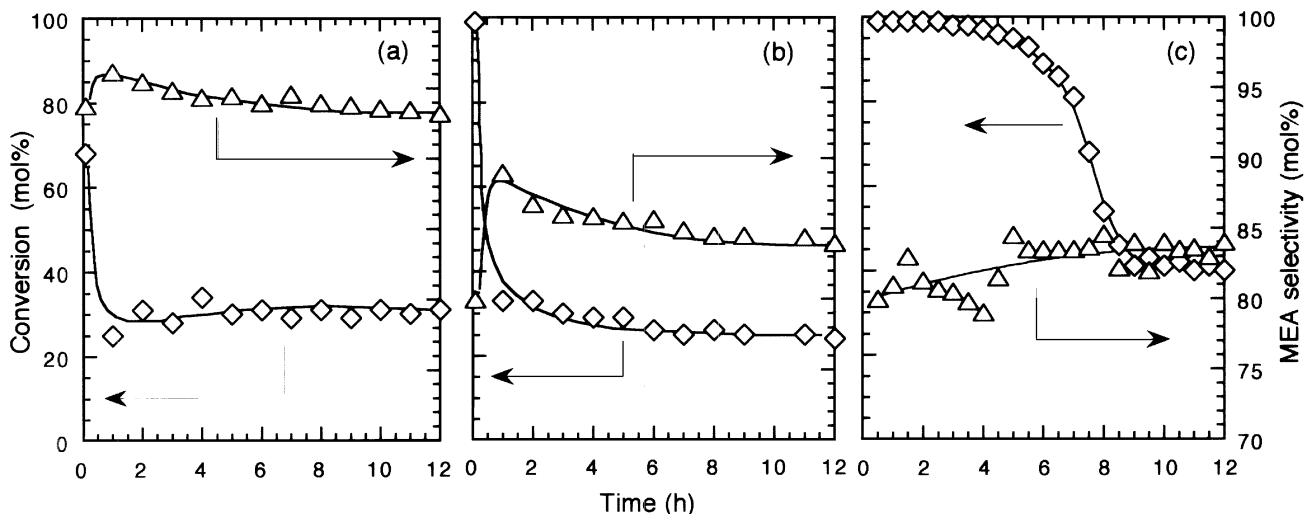


FIG. 9. Acetonitrile conversion (\diamond), and MEA selectivity (\triangle), as a function of time on HC sample; $P(\text{H}_2) = 88$ kPa, $P(\text{acetonitrile}) = 13$ kPa. (a) Fresh sample, (b) after regeneration by hydrogen treatment at 723 K, (c) after regeneration by calcination at 623 K and reduction at 723 K.

remained stable; the same occurred for the MEA selectivity which showed a constant value close to 94%. After reactivation under hydrogen, the initial reactivity was recovered, though the steady state conversion was slightly lower. However, the salient point is the clear decrease from 94 to 85% of the MEA selectivity. This decrease in MEA selectivity was stable after the second regeneration procedure though an increase in reactivity occurred.

The reaction orders with respect to hydrogen and acetonitrile pressures were determined at the steady state for the HC sample in the ranges $13.3 < P(\text{H}_2) < 97$ kPa and $0.9 < P(\text{acetonitrile}) < 28.7$ kPa. The slopes of the rate dependency as a function of hydrogen and acetonitrile pressures are 1.1 ± 0.1 and 0.6 ± 0.03 , respectively (Fig. 10). These reaction orders are very similar to those reported by Hochard *et al.* (38) for the gas phase hydrogenation of acetonitrile over Raney Ni catalysts under similar conditions; they found 1.2 and 0.55 for hydrogen and acetonitrile pressures, respectively. Hereafter, the following reactant pressures were chosen: $P(\text{H}_2) = 88$ kPa and $P(\text{acetonitrile}) = 13$ kPa.

In order to study in detail the behavior of the HA, HD, and HC samples, the catalysts were first passivated for 12 h at 393 K in the reaction medium. The hydrogenation of acetonitrile was then carried out by alternating high and low reaction temperatures between 340 and 400 K. Table 2 lists the main catalytic properties of the samples. These results, obtained under steady state and isothermal conditions, are in good agreement with those previously found by the temperature-programmed reaction (Fig. 8). The MEA selectivity of the investigated samples increases with both acetonitrile conversion and Mg content. Moreover, EEI is the main by-product which appears at low conversion. On the other hand, disregarding the rate values

obtained at conversions higher than 50%, which might be affected by heat and mass transfer phenomena, the intrinsic rate expressed on a per m_{Ni}^2 basis are of the same order of magnitude for the three samples, though the Mg-promoted catalysts seem to exhibit a slightly higher reactivity. The apparent activation energies found for the different samples are lower than those reported by Hochard *et al.* (38) for the same reaction on Raney Ni. Finally, the MEA selectivity obtained at medium conversion on the HA sample, i.e., 80–85%, compares well with the values reported by Verhaak *et al.* (23) for the gas phase hydrogenation of acetonitrile on Ni/Al₂O₃ but with a H₂/acetonitrile molar ratio of 39.

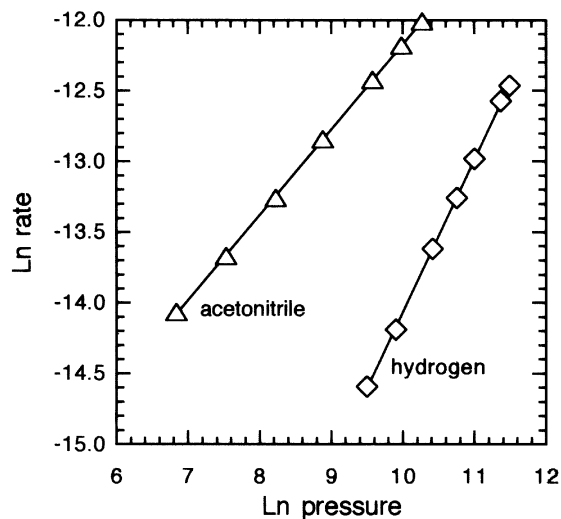


FIG. 10. Acetonitrile hydrogenation rate on HC sample as a function of hydrogen (\diamond) and acetonitrile (\triangle) pressures.

TABLE 2
Main Catalytic Properties of Ni-Based Catalysts for the Reaction of Acetonitrile with Hydrogen

Sample	Temp. (K)	Conv. (mol%)	Rate		E_a (kJ mol ⁻¹)	Product selectivity (mol%)				
			(mol g ⁻¹ s ⁻¹) × 10 ⁶	(mol m _{Ni} ⁻² s ⁻¹) × 10 ⁶		MEA	DEI	DEA	TEA	Others ^a
HA	387	50	36.8	2.8	51	90.4	1.8	7.8	0.2	0.1
	371	29	21.3	1.6		87.3	5.5	6.8	0.2	—
	360	18	13.2	1.0		84.5	8.3	6.6	0.3	—
	349	10	7.5	0.55		79.2	15.0	5.5	—	—
	339	6	4.6	0.35		71.0	22.5	4.9	—	—
HD	387	99	72	5.5	66.5	86.9	—	10.9	1.1	0.3
	380	64	47	3.6		92.0	0.1	6.0	0.15	0.1
	371	53	38.4	3.0		91.2	1.1	6.9	0.3	0.1
	361	21	15.2	1.2		87.2	4.7	6.8	0.2	—
	351	11	8.2	0.65		85.2	7.5	6.3	0.3	—
	340	8	6.3	0.5		81.5	12.0	6.5	0.2	—
HC	402	99	72	9.0	67	92.6	—	6.7	0.4	0.1
	392	47	34.4	4.3		93.8	1.2	4.7	0.1	0.1
	371	16	11.6	1.5		93.9	2.2	3.4	—	—
	353	5	3.8	0.5		93.9	4.7	1.2	—	—
	340	2	1.5	0.2		91.0	8.6	—	—	—

Note. $P(\text{H}_2) = 88$ kPa, $P(\text{acetonitrile}) = 13$ kPa.

^a Methane + ethane.

DISCUSSION

As pointed out above, two factors are predominant. First, the MEA selectivity often increases with acetonitrile conversion and second, it passes a maximum value as a function of Mg content of the catalyst.

As far as the increase in MEA selectivity with reaction temperature is concerned, the same occurred when the contact time under isothermal conditions was increased. EEI is the main by-product observed at low conversion. The for-

mal reaction scheme for the formation of higher amines in the hydrogenation of nitriles is now well-established, even if several elementary steps are still controversial (4, 5, 8, 18–21, 42). On the one hand, the nitrile is hydrogenated to the very reactive imine and thus leads to the amine by a further hydrogenation step (Fig. 11). On the other hand, the by-products, such as secondary and tertiary amines, result from a transamination reaction (Fig. 11). Secondary amines are formed in a three-step pathway: (i) nucleophilic addition of the primary amine to the imino carbon atom to produce the

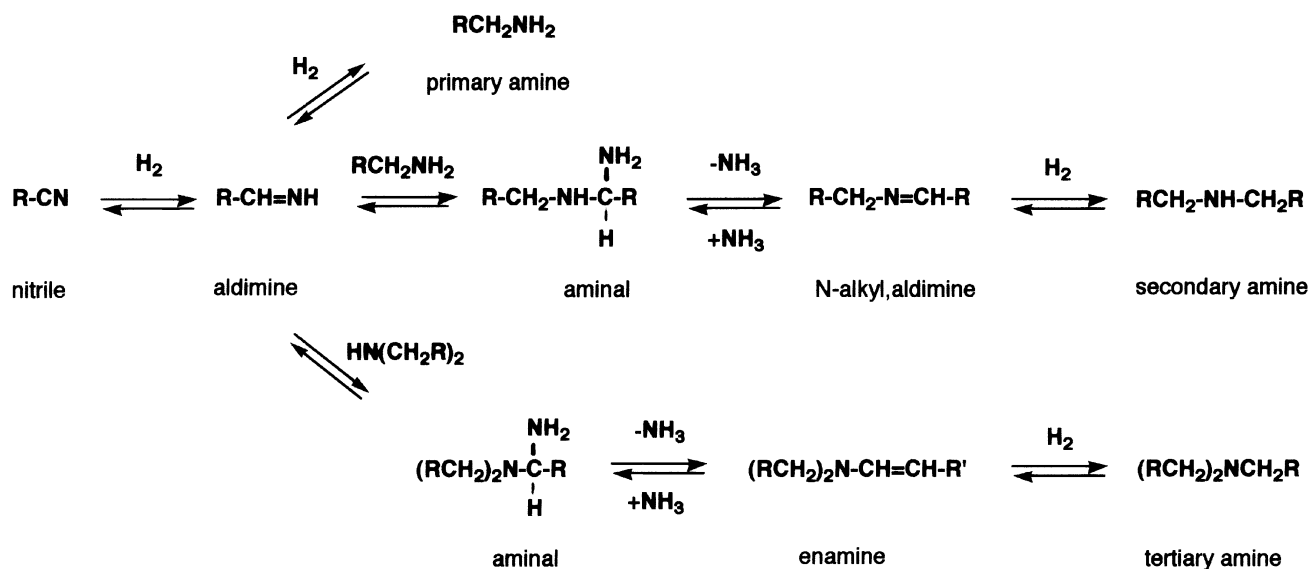


FIG. 11. Formal reaction scheme for nitrile hydrogenation.

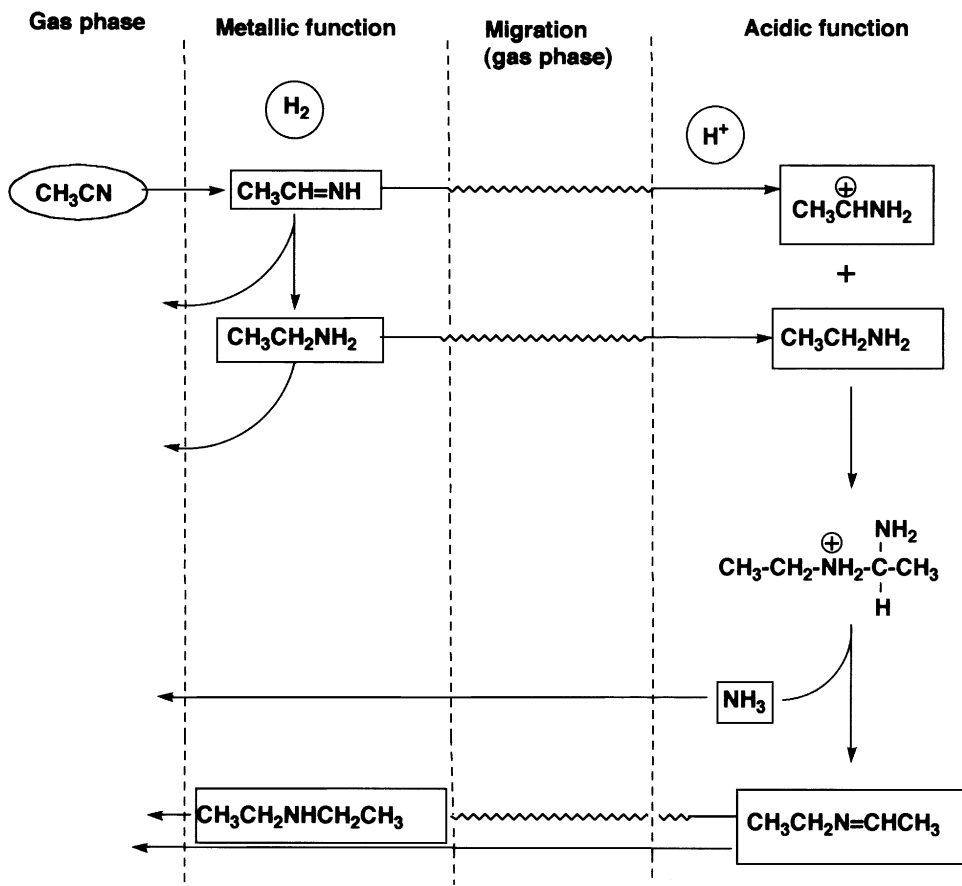


FIG. 12. Reaction scheme of the gas phase hydrogenation of acetonitrile as proposed by Verhaak *et al.* (Ref. 23).

aminal, (ii) elimination of an ammonia molecule to yield the *N*-alkylaldimine, and (iii) hydrogenation of the C=N group to afford the secondary amine. The side reaction leading to tertiary amines has been discussed analogously, taking into account that no hydrogen is available on the proimino nitrogen atom, thus implying the participation of an enamine intermediate.

Hydrogenation steps obviously need a catalyst, which is not strictly necessary for the condensation step. In their pioneering work on the liquid phase hydrogenation of nitriles, Braun *et al.* (18) claimed that this condensation step occurs in the homogeneous phase. From kinetic experiments in the liquid phase, Dallons *et al.* (42) concluded that the transamination reaction takes place on the catalyst surface. The duality between reactions occurring at the surface of the catalyst (heterogeneous) and those in the liquid phase (homogeneous) is still a matter for challenging research (5).

Assuming that the formation of by-products occurs on the catalyst surface during gas phase hydrogenation, two pathways may exist for supported metal catalysts:

(i) The condensation reaction between imine and amine proceeds on the metal surface before desorption of the intermediate imine. Such a process could be invoked for

unsupported metal catalysts such as Ni-black and Raney Ni (25, 38). However, traces of alumina residues exist on Raney Ni, which initiates the presence of acid sites.

(ii) According to Verhaak *et al.* (23), a bifunctional mechanism operates for the formation of secondary and tertiary amines in the hydrogenation of nitriles over supported Ni catalysts (Fig. 12). Acetonitrile undergoes hydrogenation to ethylimine and MEA at the Ni sites. These compounds then migrate through the gas phase or, by spill-over, to acid sites where the transamination reaction occurs between the protonated ethylimine and MEA from the gas phase. Within this framework, the acidity of the support is a key factor which determines the selectivity in primary amines during nitrile hydrogenation. It was indeed shown that inhibition of the acid sites in Ni/Al₂O₃ by K improves the MEA selectivity (23). Freidlin *et al.* (24) also reported enhanced selectivities to secondary amines for a metal supported on an acid support.

Bifunctional catalysis for the formation of secondary amines receives support from acetonitrile hydrogenation on mechanical mixtures of HC samples with γ -Al₂O₃, a slightly acidic support (Fig. 13). Upon addition of alumina the reactivity of the catalyst mixtures remains the same,

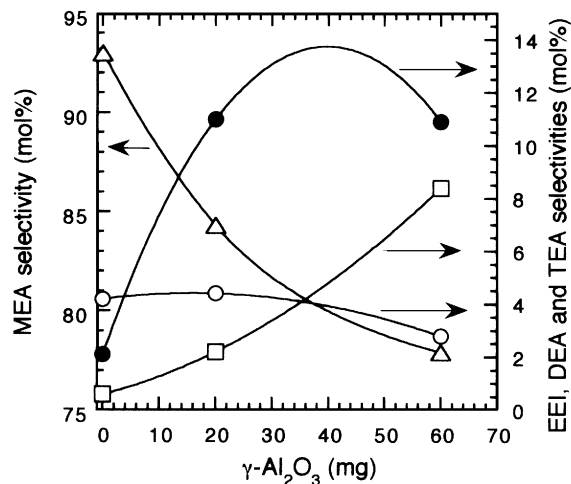


FIG. 13. Product selectivity as a function of $\gamma\text{-Al}_2\text{O}_3$ content for the acetonitrile hydrogenation in HC + $\gamma\text{-Al}_2\text{O}_3$ mechanical mixtures; $m(\text{HC}) = 40$ mg, $P(\text{H}_2) = 88$ kPa, $P(\text{acetonitrile}) = 13$ kPa, reaction temperature = 363 K; (Δ) MEA, (\circ) EEI, (\bullet) DEA, (\square) TEA.

whereas the selectivity to higher amines increases. Similar experiments were carried out by Verhaak *et al.* (23) involving hydrogenation of acetonitrile on two physical mixtures, constituted by a Ni/MgO catalyst mixed with either an aluminosilicate (acidic) or a K-promoted aluminosilicate (basic). The MEA selectivity decreased upon mixing with the acidic support, while it remained the same with the basic support. This is proof that the rate of the overall process is determined by the hydrogenation of the nitrile to the imine, but that the selectivity depends on the further hydrogenation of imine to primary amine on Ni sites and on the transamination reaction which can occur on acid sites. However, with heavy amines, capillary condensation might occur in the narrow pores of the catalyst, even for a gas phase process. Homogeneous transamination could then be possible in the microporosity (43). The results obtained by Verhaak *et al.* (23) on the physical mixture with basic support give evidence that for acetonitrile hydrogenation, which leads to volatile amines, the occurrence of homogeneous transamination in the narrow pores is unlikely. Moreover, it should be pointed out that the extent of microporous volume is very low in our samples. Obviously, the occurrence of a bifunctional mechanism for secondary and tertiary amines formation does not preclude that a monofunctional mechanism on the Ni surface intervenes as well.

The inhibition of the acid sites, which can be obtained by alkali metal addition, can also be successfully achieved not only by the partial pressure of NH_3 (16, 22), but also by inhibition by MEA formed in the course of the reaction. For this reason, the effect of "support" on Ni based HA, HD, and HC samples will be shown more clearly when comparing the MEA selectivity at low acetonitrile conversion.

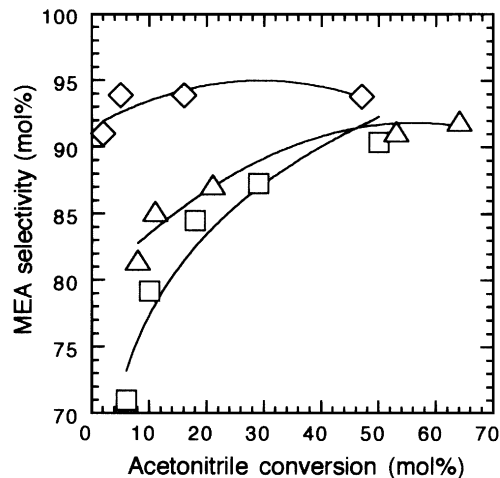


FIG. 14. MEA selectivity as a function of acetonitrile conversion on HA, HD, and HC samples; $P(\text{H}_2) = 88$ kPa, $P(\text{acetonitrile}) = 13$ kPa; (\square) HA, (Δ) HD, (\diamond) HC.

Figure 14, where the MEA selectivity is plotted as a function of acetonitrile conversion, clearly shows that the Mg content in catalyst precursor has an influence. Therefore, by comparing HA, HD, HC, and HG catalysts at about 5% conversion (Fig. 15), it is found that the MEA selectivity goes through a maximum for a $\text{Mg}/(\text{Mg} + \text{Ni})$ molar ratio of 0.23. It was shown elsewhere that the reducibility of Ni remains roughly the same for the first additions of Mg, but suffered a steep decrease for $\text{Mg}/(\text{Mg} + \text{Ni})$ values higher than 0.4 (29). This low MEA selectivity, which also parallels a low reactivity, can be ascribed to the low reduction degree of the HG sample. As far as the improvement of MEA selectivity at low Mg addition is concerned, a modification of the acid-base properties of the catalyst surface can be postulated. We think that the chemisorption of MEA, followed by DSC and TPD experiments, gives interesting

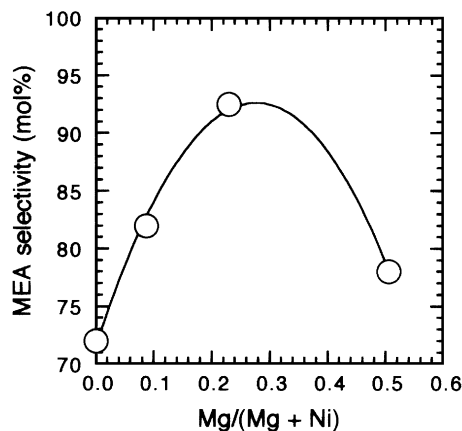


FIG. 15. MEA selectivity as a function of $\text{Mg}/(\text{Mg} + \text{Ni})$ molar ratio; $P(\text{H}_2) = 88$ kPa, $P(\text{acetonitrile}) = 13$ kPa.

information. Adsorption of MEA on supported Ni catalysts can occur on both the Ni surface and the support. The studies of the Somorjai group (41, 44) show us that MEA adsorption on Ni(111) is relatively weak, with molecular desorption occurring below 300 K, and that two or three Ni atoms are involved in the binding. The amount of surface Ni sites were probed by H₂ adsorption (Fig. 1) and ranges from 200 to 400 μmol g⁻¹. These sites are thus covered by 60–140 μmol g⁻¹ of MEA. Therefore, the adsorption of MEA during DSC experiments, with an uptake of 300 to 500 μmol g⁻¹ depending on the catalyst, occurred mainly on the support, very likely on residual acid sites, owing to the basic properties of MEA. The strength of remaining acid sites, if any, of HC samples is lower than that of HA. This conclusion is furthermore substantiated by the results of the TPD of MEA (Fig. 7), which shows the disappearance of strongly bound states of MEA on the HC sample with respect to HA sample. This higher strength of interaction of MEA with HA sample favors the coupling reaction between [CH₃CHNH₂]⁺ and CH₃CH₂NH₂ to form an unstable adduct which, after elimination of NH₃, desorbs as EEI. The decrease in the acidity of the Ni-based catalyst after a small Mg addition can be compared to that observed on Ni/Al₂O₃ upon K promotion (23).

On the other hand, part of the transamination reaction could take place on the Ni surface. It is usually assumed that alkali promoters, such as K, can modify the Ni *d*-band (23, 45). The same might be expected for the Mg-promoted HD and HC samples. An increase in the electron density at Ni sites due to a charge transfer should, therefore, decrease the strength of the interaction of the electron donor compounds, such as imine and amine, with the Ni surface. Their faster desorption rate will thus slow down the transamination reaction. This electron enrichment of Ni upon Mg addition would explain the 20 kJ mol⁻¹ increase in the heat of CO adsorption on the HD sample as compared to the HA sample. Higher electron density at Ni sites enhances the electron back donation from Ni *d*-band to the antibonding π* orbital of CO, thus strengthening the interaction with the Ni surface.

CONCLUSION

Ni/Mg(Al)O catalysts, prepared by calcination and reduction of Ni-containing precursors with hydrotalcite-like structures, are very efficient for the gas phase hydrogenation of acetonitrile. The MEA selectivity and, to a lesser extent, the rate depend on the Mg/(Mg + Ni) molar ratio. An optimal Mg content (Mg/(Mg + Ni) ≈ 0.23) exists for which the MEA selectivity goes through a maximum value of 92.6 at 99% acetonitrile conversion. This behavior can be accounted for by a balance between two antagonistic effects, the reducibility of Ni and the amount of residual acid sites, both of which decrease with increasing Mg con-

tent. The two main secondary products, EEI and DEA, are formed by the coupling reaction between (CH₃CHNH₂)⁺ and CH₃CH₂NH₂ on these acid sites. Calorimetric and TPD studies provide evidence of the weaker interaction of CH₃CH₂NH₂ with the HC sample which contains the optimal Mg content. The heat of MEA adsorption is indeed 40 kJ mol⁻¹ lower on the HC than on the HA sample which does not contain Mg. In contrast, the heats of adsorption of CH₃CN, CO, and hydrogen are modified to a much lesser extent.

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