The Formation of Nickel–Copper Alloys in Zeolite Y as Studied by the Ferromagnetic Resonance Method

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Samples of zeolite Y with part of their Na^+ ions exchanged by Ni^{2+} and Cu^{2+} ions were dried and reduced by H_2. The resulting samples were investigated by the ferromagnetic resonance method, and by measuring their catalytic properties in *n*-hexane conversion. The results led to the conclusion that during reduction performed above 690 K part of the Ni^{2+} and Cu^{2+} ions form large-sized metal particles at the outer surface of the zeolite crystals and that these are responsible for the magnetic behavior and the catalytic activity. In almost all bimetallic samples two types of metal particles are formed, namely, ferromagnetic particles with a high Ni content and paramagnetic particles with a high Cu content. The bulk composition of the ferromagnetic alloy particles was found to be nearly constant but the surface composition proved very sensitive to the reduction temperature. The formation of the NiCu alloy was found to influence the catalytic properties for *n*-hexane conversion. Compared with NiY, NiCuY was less active but more selective for the isomerization because of suppressing the hydrogenolysis reaction.

INTRODUCTION

It has been shown in previous papers (*1–3*) that the reduction by H_2 of zeolite X or Y with part of their Na^+ ions exchanged by Ni^{2+} and Cu^{2+} ions leads to the formation of nickel–copper alloy particles. However, several questions about the circumstances of the alloy formation and the properties of the alloy particles have not so far been answered.

The nickel–copper system has been studied by numerous workers. Most studies were made on unsupported systems (films or powders). Depending on the conditions either a continuous series of solid solutions or a two-phase system is observed. In the latter case, a copper-rich phase envelops a nickel-rich phase (*4, 5*). For supported nickel–copper systems with a low metal loading, where the metal particles are usually smaller than 5.0 nm, the composition of the alloy particles was found to be nonuniform and the two-phase model could not be

applied (*6, 7*). However, Burton *et al.* (*8*) suggested that even in highly dispersed metal alloy particles the more volatile component can segregate to a site of lower coordination number.

In the present work, we have tried to obtain information about alloy formation in zeolite Y by studying the magnetic properties and catalytic behavior of nickel, copper, and several nickel–copper–zeolite Y samples by ferromagnetic resonance.

EXPERIMENTAL

A. Catalyst Preparation

All samples were prepared from the same batch of NaY zeolite as supplied by the Linde Division of the Union Carbide Corporation (SK 40, Lot 3607-411). The SiO_2/Al_2O_3 molar ratio of this material was stated to be 4.9.

The standard procedure for the preparation of the catalysts was as follows. First the sodium ions were partly exchanged by nickel and/or copper ions by suspending about 30 g of NaY in 400 ml of a 0.2 M solution of nickel and/or copper acetate (Merck p.a.) in water and stirring for 90 min

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at room temperature. After that the zeolite was filtered, washed with water (2 × 40 ml), and dried in air during 17 h at 390 K. The nickel and copper contents of the so-obtained Ni–Cu–Y zeolites were determined polarographically and are presented in Table 1. After drying, dehydration of the samples (H) was performed in air by heating for 2 h at the respective temperatures of 520, 620, 720, and 820 K. Reduction (Red) was carried out by heating in a stream of hydrogen with the temperature increasing at a rate of 4 K min^{-1} starting at room temperature. At the desired final temperature, the sample was held for 3 h, and subsequently cooled down in the hydrogen stream.

B. Magnetic Measurements

The ferromagnetic resonance (FMR) measurements were performed with a Varian EPR spectrometer Type V 4500 A at a frequency of about 9.6 GHz. A special high-temperature dual-sample cavity (8a) was used enabling the measurement at temperatures up to 800 K. The reduced samples were transferred in the sample tubes under exclusion of air and then evacuated at a pressure of 10^{-4} Torr during 2 h at room temperature and 2 h at the temperature of reduction.

The FMR spectra were recorded from 0 to 5000 Oe in the temperature range from about 100 to 700 K. The signal intensities were calculated by twofold integration of the recorded spectra. Because the so-obtained signal intensities strongly depend on the Q-factor of the cavity, the intensity of the strong-pitch signal was used as an internal standard. By dividing the signal intensity of the sample by the signal intensity of the strong-pitch reference sample we obtain the "normalized" total ferromagnetic absorption A, expressed in arbitrary units.

The g-factor and linewidth ΔH were calculated from the field strength of the external magnetic field as measured with an AEG nuclear resonance magnetic field meter type 11/5045/6. From repeated measurements we estimate a relative error of ±10% for the linewidth and ±0.5% for the g-factor.

C. Activity Measurements

To study the catalytic activity we chose the isomerization of n-hexane. This reaction was carried out in a conventional pulse microreactor connected to a gas chromatograph. Two hundred milligrams of the catalyst sample was packed in the reactor and held by plugs of quartz-glass wool. The catalyst was reduced for 3 h at the specified temperature between 690 and 800 K in a stream of hydrogen.

After adjusting the reaction temperature the reactant, n-hexane, was injected into the carrier gas by means of a microsyringe. The reactant volume was 2 mm^3. The n-hexane (Merck Uvasol) was used without further purification. The reaction temperature was varied between 470 and 820 K. The reaction pressure was 2 × 10^4 N m^{-2}. The gas-chromatographic separation of the reaction product was effected with a column filled with 25 wt% squalane on 60/80-mesh Chromosorb W at 341 K.

RESULTS AND DISCUSSION

A. The Effect of the Ni and Cu Content
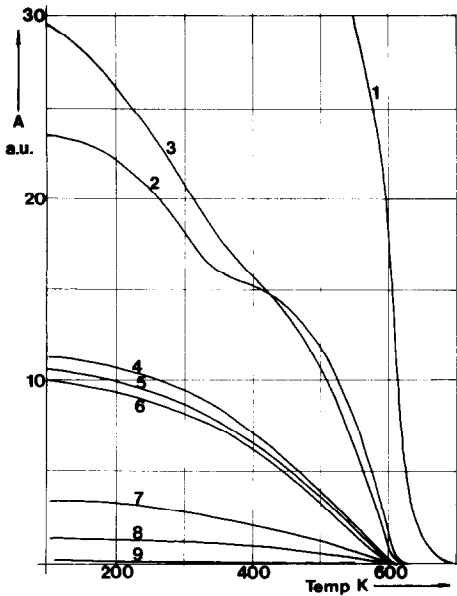
Figure 1 presents the temperature de-

TABLE 1

Chemical Composition of the Catalyst Samples

Sample No.	Ni wt%	Cu wt%	Total degree of exchange (%)
1	7.55	—	58.6
2	6.14	0.30	49.8
3	5.97	0.61	50.7
4	5.70	1.29	53.5
5	5.12	1.92	53.5
6	4.98	2.12	53.8
7	3.87	3.33	53.9
8	3.40	4.00	55.0
9	1.52	5.96	54.5
10	—	7.94	56.9
11	1.39	—	10.8

FIG. 1. The "normalized" total ferromagnetic absorption A in arbitrary units as a function of temperature for NiY and NiCuY samples Nos. 1–9 dried at 390 K and reduced at 720 K.

pendence of the total ferromagnetic absorption A for catalyst samples Nos. 1–10. It is seen that the value of A decreases with increasing temperature, analogous to the variation of the saturation magnetization in classical constant-field measurements. It is clear that the addition of Cu to Ni leads to a drastic decrease of the total ferromagnetic absorption A, but does not greatly influence the Curie temperature T_c. The Curie tem-

peratures of the different samples were determined from Figs. 2A and B where the relative total ferromagnetic absorption A/A_{max} is plotted as a function of temperature. The Curie temperature of the Ni-containing zeolite No. 1 is about 635 K, in good agreement with the values for pure Ni mentioned in the literature. The Curie temperatures of Ni–Cu zeolites Nos. 2–8 vary from 585 to 605 K: we assume that they are approximately constant within experimental error. Sample No. 9 was found to be paramagnetic and sample No. 10 gave no resonance signal. It is noteworthy that the shapes of the curves of samples Nos. 2 and 3 indicate the existence of another ferromagnetic phase, with T_c at 350 and 333 K, respectively. This will be discussed later.

Figures 3 and 4 show linewidths, ΔH, and g-factors as a function of temperature for the Ni- and NiCu-containing zeolites. All ΔH and g-factors obtained for samples Nos. 2 and 9 are assembled in the hatched areas. From Fig. 3 it can be seen that for sample No. 1 an increase in temperature to about 580 K is accompanied by a substantial decrease in ΔH.

The main reason for the increase in linewidth for polycrystalline samples at lower temperatures is the magnetic anisotropy. The presence of differently oriented crystallites with different directions of the internal anisotropy field causes broadening of the FMR signal since in each crystallite
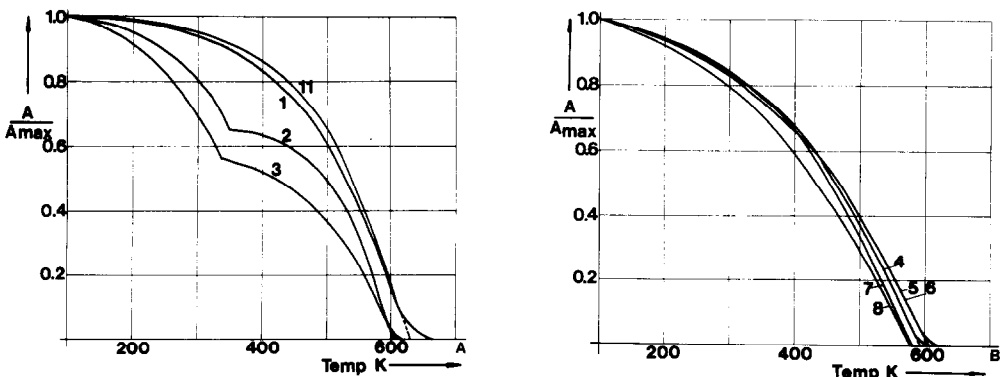

FIG. 2. The relative total ferromagnetic absorption A/A_{max} as a function of temperature for NiY and NiCuY samples dried at 390 K and reduced at 720 K. (A) Nos. 1–3, 11. (B) Nos. 4–8.
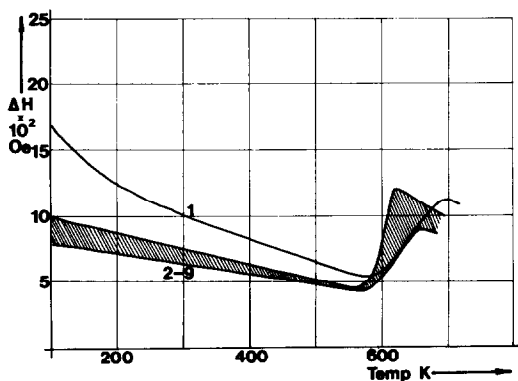
FIG. 3. The linewidth ΔH as a function of temperature for NiY and NiCuY samples Nos. 1–9, dried at 390 K and reduced at 720 K.

resonance occurs at a different value of the external magnetic field. A minimum linewidth is observed at about 580 K. At this temperature the anisotropy vanishes and the line broadening due to the differences in orientation with respect to the external magnetic field is eliminated. Near T_c the linewidth shows a rise with increasing temperature, which is continued beyond the Curie point into the paramagnetic region. A small maximum is observed at about 700 K. The curves representing samples Nos. 2 to 8 show a similar shape, but the broadening near T_c is steeper and the maximum of ΔH appears at lower temperatures. It is interesting that a similar broadening of ΔH near the Curie temperature was earlier observed by other authors for the case of nickel (11–13) and was attributed to the influence of
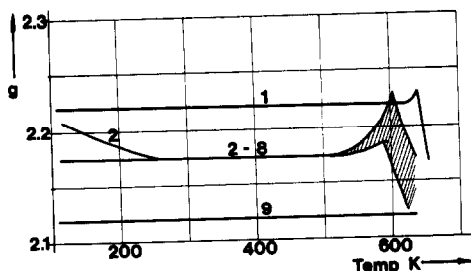

FIG. 4. The g-factor as a function of temperature for NiY and NiCuY samples Nos. 1–9, dried at 390 K and reduced at 720 K.

the spin fluctuations at the magnetic phase transition (see the theories of Huber (14) and of Tomita and Kawasaki (15)). In the case of nickel single crystals Spörel and Biller (16) for deformed or rough crystals and polycrystals found a very sharp maximum of ΔH at T_c, which had not been observed before. In our work, the ΔH maximum occurs appreciably higher than T_c and this may be the reason that the ΔH maximum has not been mentioned in earlier works. At low temperature (110 K) the lineshape is very unsymmetrical, especially for the Ni-containing zeolite Y, but becomes more symmetrical at higher temperatures. This fact is connected with the great difference in linewidth between the Ni and NiCu samples at low temperatures. Similar phenomena were previously observed by Lloyd and Bhagat (17) who found that when working with Ni and NiCu single crystals the observed large increase in linewidth in pure Ni could be suppressed by the addition of 5.4% Cu.

Figure 4 shows that the g-factor of the Ni and NiCu samples remains constant at the values of 2.22 and 2.175, respectively, up to the Curie temperature. The g-factor of pure Ni is very sensitive to the size, shape, and surface configuration of the Ni particles and many different values ranging from 2.09 to 2.8 are given in the literature (18–23). At T_c g slightly increases to 2.23 for the Ni sample and to 2.18–2.23 for the NiCu samples, and falls off rapidly above T_c to about 2.12. In our case this value was characteristic for the paramagnetic region and the same value was found for paramagnetic sample No. 9. As also indicated by other authors (26–28), it must be concluded that the g-factor changes in the phase transition region.

All these results taken together indicate that alloy formation occurred in our NiCu samples. It is then noteworthy that the Curie temperatures of all these NiCu alloys are rather similar and are found in the narrow range from 585 to 605 K. Moreover, by alloy formation the decrease of T_c from 635 to about 600 K might also be caused by

the decreasing amounts of nickel when going from pure Ni to Ni–Cu systems with less than 20% of nickel. However, this possibility can be excluded on the basis of a comparison of A/A_{max} as a function of temperature for zeolites containing 7.55 wt% Ni (sample No. 1) and 1.39 wt% Ni (sample No. 11). As shown in Fig. 2A both samples have the same T_c value.

On the basis of the correlation between Curie temperature and alloy composition given in the literature (29–31) we can derive the composition of the ferromagnetic NiCu alloy with T_c between 585 and 605 K. This composition is found to be 2–4.5% Cu and 95.5–98% Ni. In the case of samples Nos. 2 and 3 a second ferromagnetic alloy is formed with T_c = 333–350 K which corresponds to a composition of about 25% Cu and 75% Ni.

These results can be understood in the following way. During the reaction of the NiCuY zeolites with H_2 the Ni^{2+} and Cu^{2+} ions are reduced to Ni and Cu atoms, which in that situation are no longer bonded to the zeolite lattice. They therefore can diffuse to the surface of the zeolite crystallites to form metal–alloy particles. The composition of these alloy particles is determined by thermodynamics. According to Raap and Maak (32) and Vecher and Gerasimov (33) two alloys can be formed under the reaction conditions we used. These are a ferromagnetic alloy I, with a composition of 98% Ni and 2% Cu, and a paramagentic alloy II, with a composition of 20% Ni and 80% Cu. The presence of alloy I can indeed be observed in samples Nos. 2–8. Because this alloy contains only 2% Cu and the Cu content of the NiCuY zeolites is considerably higher in all samples, a second NiCu alloy will also be formed. In the case of samples Nos. 4–8 this will be the paramagnetic alloy II, but in the case of samples Nos. 2 and 3 the amount of Cu is too small to form this alloy. In these cases the remaining possibility is the formation of a second ferromagnetic alloy, which according to the observed T_c must have a composition of about 75% Ni and 25% Cu.

The results of the catalytic activity measurements on samples Nos. 1–10 are presented in Figs. 5A and B. They show the total conversion (5A) and that leading to isomerization (5B) both as a function of the reaction temperature. NiY (No. 1) demonstrates a high total conversion. The reaction starts at approximately 470 K and up to 570 K hydrogenolysis and isomerization take place. Above 570 K a decay in activity presumably caused by coke formation is found.

NiCuY (Nos. 2–8) is less active than NiY (No. 1) and the range of activity of these catalysts has moved to higher temperatures. Up to the temperature corresponding to maximum activity, isomerization is
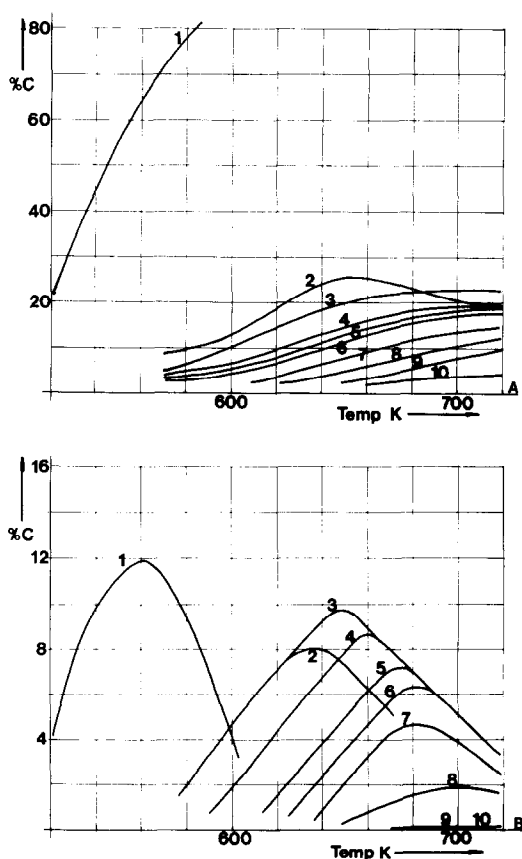

FIG. 5. The total conversion (A) and the isomerization activity (B) as a function of reaction temperature for NiY and NiCuY samples Nos. 1–10.

found to occur at relatively high selectivity. At higher temperatures this selectivity decreases in favor of an increasing selectivity for the hydrogenolysis reaction. Catalyst decay, i.e., coke formation, is evident only in the case of catalyst No. 2.

The paramagnetic sample No. 9 and the CuY sample No. 10 behave like acid catalysts. The reaction starts at about 670 K and cracking is found to occur with propane and propene as the main products.

B. The Effect of Previous Dehydration and of the Temperature of Reduction on Catalyst Properties

In the preceding section we concluded that reduction at 720 K of dried NiCuY samples (Red) resulted in the formation of Ni–Cu alloy particles at the surface of the zeolite crystallites. We can now ask ourselves how this alloy formation depends on previous dehydration and on the temperature of reduction. To answer this question we measured the total ferromagnetic adsorption A_{max} at $T = 110$ K as a function of the reduction temperature for samples Nos. 1 (NiY) and 4 (NiCuY) in the series Red and HRed. The results are shown in Fig. 6.

Sample No. 1 shows an increase of A_{max} with increasing reduction temperature. This is probably due to the higher degree of reduction and the larger particle size after reduction at higher temperatures. The effect is more pronounced for the Red sample (only dried before reduction) than for the HRed sample (dehydrated before reduction). This may be explained on the basis of the behavior of the Ni^{2+} ions in the Y zeolite during dehydration (34). In the hydrated state, the Ni^{2+} ions are mainly present in the supercages (S_{II} sites), which are undoubtedly the best positions for the reduction.

During reduction performed at temperatures above 710 K, these cations form metal particles with dimensions of 10–40 nm which are responsible for the magnetic behavior and the catalytic activity. During dehydration the Ni^{2+} ions become redistrib-
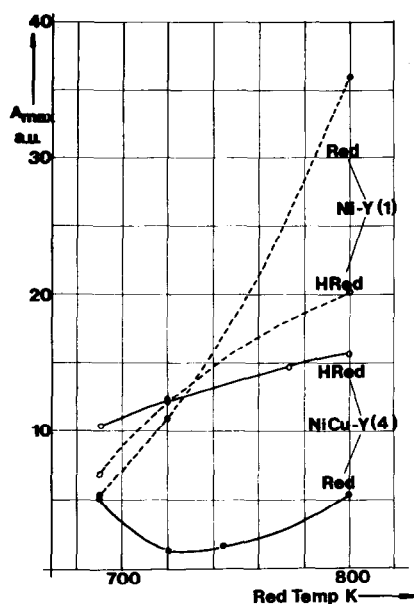

FIG. 6. The "normalized" total ferromagnetic absorption A_{max} in arbitrary units as a function of the temperature of reduction for NiY sample No. 1 and NiCuY sample No. 4 ($T = 110$ K).

uted over the various sites, with a preference for the hexagonal prisms (S_I sites) where they are nonreducible up to 820 K (35). For sample No. 4 prepared by reduction after dehydration at 820 K (HRed) the dependence of A_{max} on the reduction temperature is rather similar to that of sample No. 1. The large value of A_{max}, comparable to that of pure NiY, indicates the formation of mainly pure Ni particles also in this case. However, sample No. 4, for which the reduction was done after drying at 390 K (Red) behaves differently; A_{max} has much lower values with a minimum for the samples reduced at about 720–740 K.

Additional information can be obtained from Fig. 7 which presents the linewidth (ΔH) of samples measured at 110 K. The linewidth of the NiY samples varies from 1200 to 1900 Oe and increases with increasing reduction temperature. The effect of the reduction temperature is different for the case of the NiCuY samples; a contraction of the resonance signal can be observed here. In agreement with the data presented
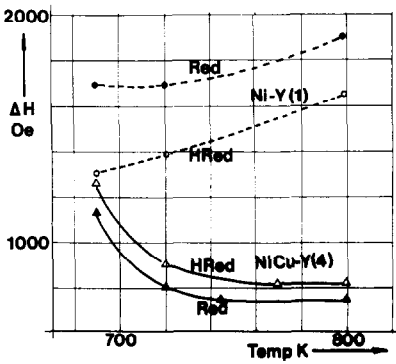
FIG. 7. The linewidth ΔH as a function of the temperature of reduction for NiY sample No. 1 and NiCuY sample No. 4 ($T = 110$ K).

in Fig. 3, the formation of a NiCu alloy suppresses the large increase in linewidth observed with pure Ni. From this is can be concluded that in the case of the Ni–Cu

samples reduced at temperatures above 690 K NiCu alloy particles are formed. However, to explain the large value of A_{max} in the case of the HRed sample in Fig. 6, a large part of these alloy particles must consist of the ferromagnetic alloy I. This conclusion is supported by the results of the catalytic activity measurements in the n-hexane reaction.

Figures 8A and B present the total conversion and the isomerization activity as a function of temperature for sample No. 4 pretreated in different ways. The fact that, compared to the NiY sample No. 1, the n-hexane isomerization is slower, because it occurs at higher temperatures while hydrogenolysis is only a minor reaction, indicates that the surface of the metal particles consists of a NiCu alloy. It is interesting to note that an increase of the reduction tempera-
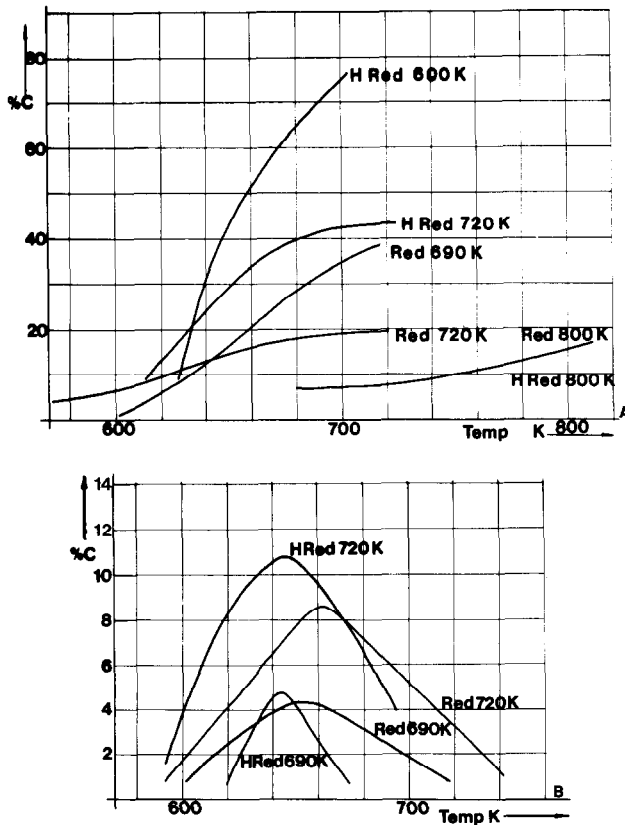

FIG. 8. The total conversion (A) and the isomerization activity (part B) as a function of reaction temperature for NiCuY sample No. 4.

ture causes a decrease of the catalytic activity, so that samples reduced at 800 K show a very low activity. This indicates that the surfaces of the metal particles formed at higher temperatures become richer in copper, and that reduction at 800 K or higher leads to the formation of the nonactive paramagnetic CuNi alloy at the surface of the particles.

CONCLUSIONS

The reduction by H_2 of a Y zeolite in which part of the Na^+ ions are exchanged by Ni^{2+} or Ni^{2+} and Cu^{2+} ions leads to the formation of relatively large metal particles at the outside of the zeolite crystals. The size of these particles should be at least 15 nm because for NiY they behave as real ferromagnetic crystals. The composition of the ferromagnetic particles, formed by *reduction at 720 K of dried NiCuY*, is found to be independent of the Ni and Cu contents of these zeolites. The Curie temperatures of the ferromagnetic alloys in all cases are in the range between 585 and 595 K. This fixes the composition of the alloy at 2–4.5% Cu and 95.5–98% Ni.

According to the two-phase model we suppose the formation of two different types of metal alloy particles:

i. particles consisting of the ferromagnetic alloy (98% Ni and 2% Cu) and

ii. particles consisting of the paramagnetic alloy (20% Ni and 80% Cu).

Only in the case that the amount of Cu is too small to form the paramagnetic alloy is a second ferromagnetic alloy (75% Ni and 25% Cu) formed. The metal particles so formed are homogeneous with similar bulk and surface composition.

The catalytic activity of the NiCu samples does not change much over a large range of compositions, indicating that only the number of the ferromagnetic particles or their particle size decreases when the Ni content decreases.

At *higher reduction temperatures (>720 K)* the microstructure of the NiCu particles

is changed. It can be deduced from the catalytic measurements that high reduction temperatures facilitate the diffusion of the more volatile component (copper) to the surface of the metal particles. As a consequence the ferromagnetic alloy will form the core of the particles and will be covered by an outer layer of the paramagnetic alloy.

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