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Alloy Formation on Zeolite Y

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Samples of zeolite Y in which part of the Na^+ ions were exchanged by metal ions such as Ni^{2+}, Cu^{2+}, or others were subjected to a reduction by H_2 at 550°C. The resulting samples were investigated by magnetic and ESR methods. The results led to the conclusion that the metal atoms produced by the reduction diffuse out of the pores and form relatively large sized crystals at the outer surface of the zeolite particles. If, previous to the reduction, two types of metal ions are present, for instance Ni^{2+} and Cu^{2+}, reduction may, under favorable circumstances, lead to the formation of crystals of alloys. Alloy formation was found to have a profound influence on the type of conversion of *n*-hexane. Ni-on-zeolite catalysts show a hydrogenolytic reaction producing CH_4 and straight chain paraffins of lower molecular weight. Ni–Cu zeolite catalysts are less active, but show considerable isomerization to singly branched isoparaffins. Small amounts of 2,2-dimethylbutane were also found in the products. The pattern of the reaction thus becomes more similar to that demonstrated by Pt-on-zeolite catalysts. A similar influence on the reaction pattern was demonstrated by the admixture of Ag although to a lesser degree.

INTRODUCTION

Since the discovery that zeolites can exert a catalytic action, many investigations have been made on these systems. The majority of these are concerned with the problem of the nature of the acidic properties of ionic and decationated forms of zeolites, while only relatively small attention has been given to the properties of metal ions during and after reduction, although the first experiments were performed with platinum loaded zeolites (*1–4*). This is the more remarkable since it was suggested early that for instance platinum might be atomically dispersed in the zeolite; no further investigations on this subject were made, however, until recently Lewis (*5*) published results of X-ray absorption studies on platinum loaded zeolite. Two other studies (*6*, *7*) dealt with reduced nickel on zeolites.

Similar experiments were also performed by us, and the general impression remains that for Ni^{2+} as the cation, reduction does not lead to atomically dispersed systems but instead to relatively large, ferromagnetic crystals. Since their size far surpassed the pore diameter, the conclusion is that reduction leads to formation of metal atoms that diffuse out of the pores to conglomerate to crystals in the voids between the zeolite-crystals.

At first sight this is a somewhat disappointing conclusion, but on further consideration it leads to an interesting question. Suppose that there are two types of reducible cations present in the zeolite, for instance Cu^{2+} and Ni^{2+}. Does such a system after reduction form alloy-crystals in the voids or do the phases remain separated? And if the first alternative happens to be true, what is the influence of alloy formation on the conversion of hydrocarbons?

It is this problem that has been investigated by us for the case of *n*-hexane as the hydrocarbon. The results are of a preliminary character but they appear sufficiently

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interesting to warrant a publication at this time.

Experimental Methods

A. Catalyst Preparation

The zeolite used in these experiments was a zeolite type Y with a ratio SiO_2/Al_2O_3 = 4.7. Sodium ions in the zeolite were exchanged by stirring a suspension of the zeolite in a metal salt solution. The salts used were all Merck pA nitrates. Mixtures of metals were prepared by stirring in a solution, containing mixtures of metal salts. A platinum catalyst was prepared by stirring with a solution of platinum(II) chloride in ammonia. A HY-zeolite catalyst was prepared by exchanging with an ammonium chloride solution and subsequently heating of the exchanged zeolite. After the ionexchange the catalysts were washed with water until the wash water was nitrate free. Then they were treated with ethanol and finally ether, and dried in air during 2 hr at 110°C. The reduction and activation of the catalysts were performed *in situ*, by heating in a stream of hydrogen at 550°C for 3 hr.

B. Magnetic Measurements

Static magnetic measurements were performed with a Newport Variable-Temperature Gouy-balance system, which was adapted for the Faraday measuring method (*8*). Ferromagnetic resonance measurements were performed with a Varian EPR-spectrometer type V 4500A at a frequency of ca. 9.6 GHz. A special high temperature equipment was used to reach temperatures up to 450°C. Field strength was measured with an AEG nuclear-resonance magnetfieldmeter 11/5045/6, and the frequency with a Hewlett-Packard microwave frequency converter 2590 B in combination with a electronic counter type 5245 L and a plug-in unit type 5253 B.

C. Activity Measurements

The continuous flow system used is schematically shown in Fig. 1. A stream of hydrogen is purified by means of a deoxo- and drying-unit (a and b). The flow rate was adjusted with a pressure and flow regulator (c) and measured by a flow meter (d). Pressure was measured by means of a manometer (e). The stream then passes a saturator system, consisting of three bubble-vessels (f) filled with *n*-hexane; the first one is kept at room temperature, the other two are placed in a melting ice-bath (g). For activation purposes a sideline (h) is available. From the saturator onward the tubing is heated to prevent condensation of hexane.

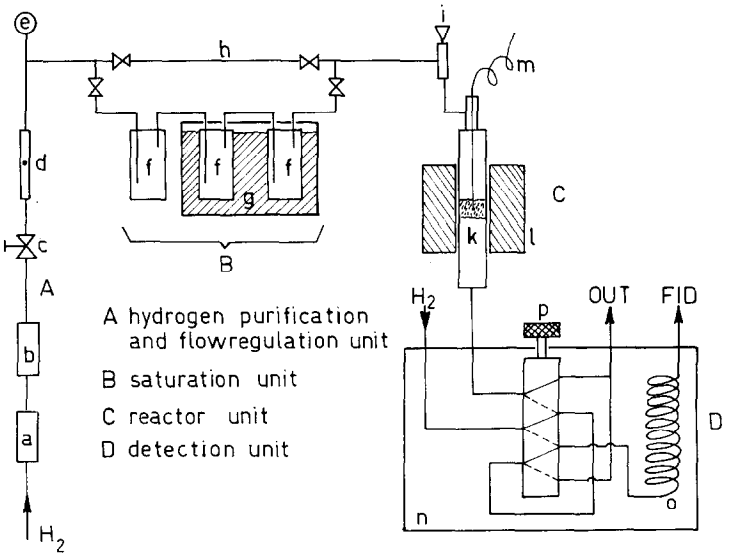

Fig. 1. Schematic representation of the continuous flow system used for the activity measurements.

The stream then passes the quartz reactor (k) heated by a movable furnace (l). The temperature is measured with a chromel-alumel thermocouple (m) placed in the catalyst bed. The catalyst can be poisoned by injection of poisoning substances via the injection port (i).

The reactor was placed on top of a gas thermostat (n) in which were suspended the chromatographic column (o) and the gas sampling valve (p). As stationary phase for the column 25 wt % squalane on Chromosorb S 60/80 mesh was used. Detection was made with a flame ionization detector (FID).

D. Experimental Conditions

0.5 g (dry wt base) of catalyst was used. The hydrogen flow rate was 60 ml/min. Reaction occurred at atmospheric pressure at temperatures ranging from 200–700°C. Blank tests were made to ascertain the inactivity of the system at these temperatures. The *n*-hexane used was Merck Uvasol and was used without further purification.

Experimental Results

A. Magnetic Measurements

The results of the magnetization measurements of some nickel-containing catalysts at 20°C are shown in Table 1 and in Fig. 2. From these results the saturation magnetization (I_m) for each catalyst was calculated with the approximate formula:

$$\frac{I}{I_m} = 1 - \frac{kT}{\mu H}. \qquad (1)$$

This formula can only be used for large values of $\mu H/kT$. By linear extrapolation of the $I_{sp} - 1/H$ graphs to $1/H = 0$, the values of I_m are found.

Comparison of the I_m values for the nickel-containing catalyst with the value of pure nickel leads to the conclusion that the nickel particles must be rather large. This was sustained by ferromagnetic resonance measurements on the Ni(I) catalyst. The results are shown in Fig. 3, which gives the ferromagnetic resonance absorption and the peak width of the resonance signal as a function of temperature. The absorption is a measure for the magnetization of the nickel particles. The temperature dependence of the magnetization is typical for larger particles (curve 1), and it can especially be seen in the case of the sintered catalyst (curve 2) that the magnetization is higher and the decrease with temperature is even more pronounced.

From the magnetization measurements,

TABLE 1

Specific Magnetization of Some Nickel-Containing Catalysts at 20°C (cgs units) and the Calculated Values of the Saturation Magnetization [H (gauss)]

H	Ni(I)[a]	Ni(II)[a]	Ni(III)[a]	NiAg[a]	NiCd[a]	NiCu(I)[a]	NiCu(II)[a]
341.2	11.71	12.79	14.65	13.20	12.81	3.20	0.401
614.6	16.88	18.06	22.15	18.62	19.05	4.64	0.593
888.7	19.05	20.11	25.43	20.98	21.42	5.20	0.623
1162.7	20.77	21.74	27.62	22.69	23.27	5.67	0.739
1445.6	22.06	23.34	29.45	24.24	24.81	6.04	0.815
1725.6	23.12	24.58	30.96	25.52	26.06	6.34	0.842
1984.8	24.71	25.75	32.47	26.83	27.27	6.66	0.909
2240.9	25.29	26.51	33.36	27.63	28.03	6.85	0.967
2503.0	25.83	27.15	34.17	28.29	28.67	7.00	1.018
2979.6	28.28	28.63	36.01	29.81	30.41	7.39	1.115
3378.7	29.08	30.10	37.41	31.24	31.56	7.68	1.162
3706.4	29.67	30.77	38.36	32.03	32.30	7.87	1.207
3986.4	30.12	31.16	38.90	32.41	32.57	7.98	1.251
I_m[b] ∞	35.39	35.97	47.69	39.64	39.24	9.46	1.637

[a] For chemical composition see Table 2.

[b] For pure nickel I_m = 54.39 at 20°C.

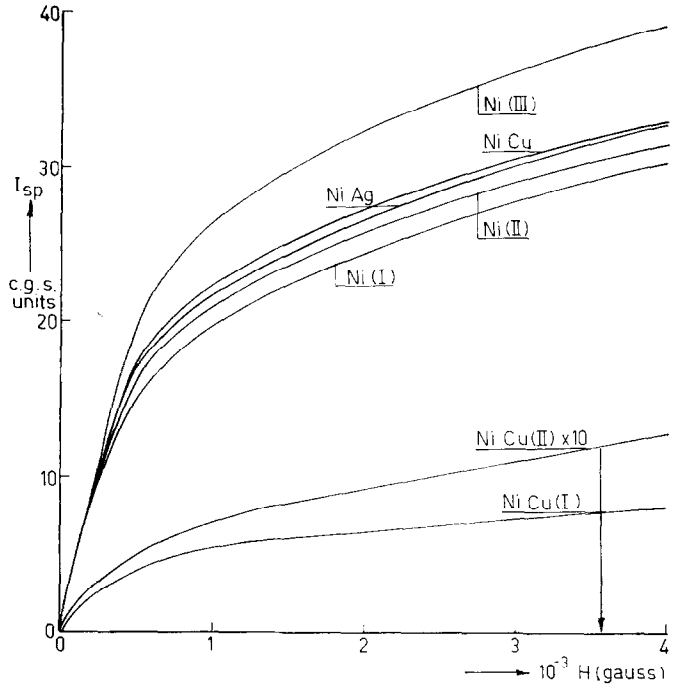

FIG. 2. The specific magnetization (I_{sp}) of some nickel-containing catalysts as a function of field strength (H).

particle sizes were also calculated using Eq. (1). Therefore these values can be considered as a lower limit for the average particle size and they amount to ca. 70 Å in diameter. Since particle size turns out to be much larger than the pore diameter of the zeolite Y (9 Å with voids of 12–13 Å), we think that the metal crystals are formed at the surface of the zeolite crystallites.

The values of the saturation magnetization of the other catalysts shown in Table 1 are interesting and in particular those of the two Ni–Cu catalysts. The large decrease in magnetization with rising copper content can only be due to alloy formation between nickel and copper, because it is known that alloying of nickel with copper diminishes the specific magnetization of nickel (*9*).

The specific magnetization of the NiAg catalyst and the NiCd catalyst do not show such a decrease. Both alloys are reported to consist of two phases, one of these being nickel rich (*10*). Therefore high values of the specific magnetization are always found. Whether, therefore, alloy formation occurs or not, cannot be answered from magnetic measurements. In the case of the NiCd catalyst however, we have an additional argument for alloy formation. Normally at 550°C cadmium is distilled out of the zeolite, and a cadmium mirror is formed on the wall of the quartz reactor. With the NiCd catalyst, however, no such phenomena were observed.

B. Activity Measurements

The catalysts tested are listed Table 2, in which also gives the composition of the catalysts. They are divided into four groups. Each group contains catalysts with the same characteristic reaction pattern. Short descriptions of the catalysts are given below.

Group 1. The catalysts of group 1 all possess those characteristics that are usually connected with acid properties. Reaction starts at about 400°C. Only cracking is found to occur and the main reaction products are propane and propene. The activity depends on the degree of exchange of the sodium ions of the zeolite. With the Zn^{2+}Y catalyst, appreciable amounts of benzene

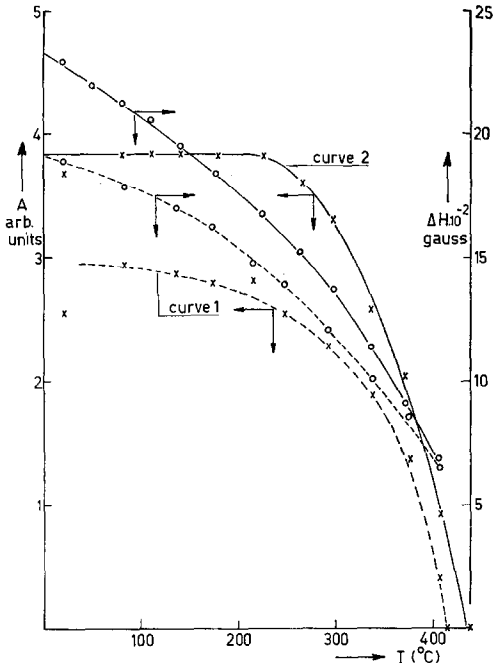

FIG. 3. Ferromagnetic resonance absorption (A) and peak width (H) of the Ni(I) catalyst as a function of temperature: (– –) reduced during 0.5 hr at 550°C and evacuated during 3 hr at 450°C; (—) reduction the same as above, but evacuated during 16 hr at 450°C.

were observed in the reaction products at temperatures over 600°C. The reaction can be poisoned by pyridine, while self-poisoning by coke formation was found to occur, especially at higher temperatures.

Group 2. Group 2 consists of the three nickel catalysts. They demonstrate a product pattern that is entirely different from that described above, although acid properties might also be expected. Reaction starts at approximately 200°C. The main reaction is hydrogenolysis and the main product is methane, while small amounts of isomers are found. All reaction products are saturated, in contrast to those observed for the group 1 catalysts. The reaction is not poisoned by pyridine, but here thiophene poisons the catalyst; the thiophene-poisoned catalyst showing similar properties as that group 1 catalysts. At higher conversions self-poisoning by coke formation takes place, especially with the Ni(III) catalyst. The activity of the catalysts depends on the amount of nickel present.

Group 3. The platinum-containing catalyst forms a group in itself. Reaction starts at about 300°C and the activity is only moderate, which is probably due to the low platinum content of the catalyst; it possesses a high selectivity for isomerization of n-hexane. The reaction is poisoned by thiophene only. This means that this type of isomerization is a reaction occurring at the metal surface, as demonstrated earlier by previous investigations (*11*, *12*). In the re-

TABLE 2
CATALYSTS TESTED IN ACTIVITY MEASUREMENTS

Group	Catalyst	Composition (dry wt base) (%)	Character and main products
1	HY	70 exchanged	Acidic properties; cracking catalysts; propane/propene
	$Zn^{2+}Y$	8.30 Zn	
	$Cu^{0}Y$	7.14 Cu	
	$Ag^{0}Y$	6.82 Ag	
2	Ni(I) Y	6.04 Ni	Hydrogenolysis; methane
	Ni(II) Y	4.25 Ni	
	Ni(III) Y	2.03 Ni	
3	Pt Y	0.44 Pt	Isomerization; C_6-products
4	NiCu(I) Y	4.12 Ni 2.54 Cu	Depending on chemical composition
	NiCu(II) Y	2.07 Ni 4.18 Cu	
	NiAg Y	2.55 Ni 4.48 Ag	
	NiCd Y	3.50 Ni 3.98 Cd	

action products also methylcyclopentane, and at higher temperatures (over 400°C) benzene are found.

Group 4. Although all the alloy catalysts are placed in group 4, their behavior in the reaction of *n*-hexane is quite different. Therefore a separate description for each catalyst is needed.

The NiCd catalyst, although of slightly lower activity, behaves similarly to the Ni(II) catalyst. The principal reaction is hydrogenolysis and it seems that cadmium has little or no influence on the reaction pattern demonstrated by the pure nickel catalyst.

The NiAg and NiCu(I) catalysts possess similar catalytic properties. Reaction starts at about 250°C. Up to temperatures of 325–350°C isomerization is the main reaction, while only saturated products are found at these temperatures. The NiCu(I) catalyst shows a somewhat higher selectivity for the isomerization. For this particular catalyst the main by-product is propane in contrast with the NiAg catalyst, where methane is the main by-product. The isomerization could not be poisoned by pyridine.

The NiCu(II) catalyst is the least active of the alloy catalysts. Reaction starts at about 350°C. Although at low conversion levels isomerization is found, the main reaction is cracking and at higher temperatures the catalyst behaves like the acid catalysts of group 1. The reaction is poisoned by pyridine at these temperatures.

After having obtained a preliminary impression of the activity and the product pattern of these catalysts, the most interesting specimens were tested in a somewhat more extensive study. We also changed the conditions; conditions now were: hydrogen pressure 2 atu, and hydrogen flow rate of of 40 ml/min. The catalysts were the Ni(I), NiCu(I), NiAg, and Pt catalysts. The results are shown in Figs. 4–7. The amounts of reaction products as well as the activity are expressed in percentages of hexane fed into the reactor.

General remarks on the patterns of reactivity: up to 425°C the platinum-containing catalyst shows excellent isomerization properties. The selectivity is over

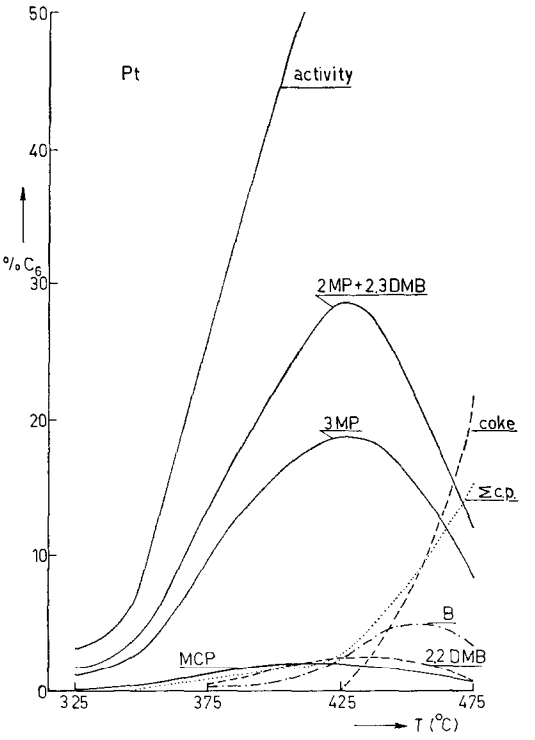

FIG. 4. Product pattern of Pt–Y catalyst as a function of temperature. In Figs. 4–7, the following abbreviations have been used: 2MP = 2-methylpentane; 3MP = 3-methylpentane; 2,2DMB = 2,2-dimethylbutane; 2,3DMB = 2,3-dimethylbutane; MCP = methylcyclopentane; B = benzene; Σc.p. = sum of cracking products; Σisom. = sum of isomers.

95%.* At higher temperatures coke formation occurs and the activity appears to come to a limit (ca. 63%). Cracking also becomes more important, the main cracking product being propane (and propene). The catalyst can be poisoned by thiophene but not by pyridine.

On the nickel-containing catalyst, hydrogenolysis of *n*-hexane is found: only very small amounts of isomers are formed (maximal selectivity 7.3% at 240°C). The product distribution shows a characteristic pattern. From the curves, consecutive maxima for pentanes, butanes, propane, and ethane

* Selectivity = [amount of C_6 in reaction product (hexane excluded)]/[amount of converted *n*-hexane (= activity)].

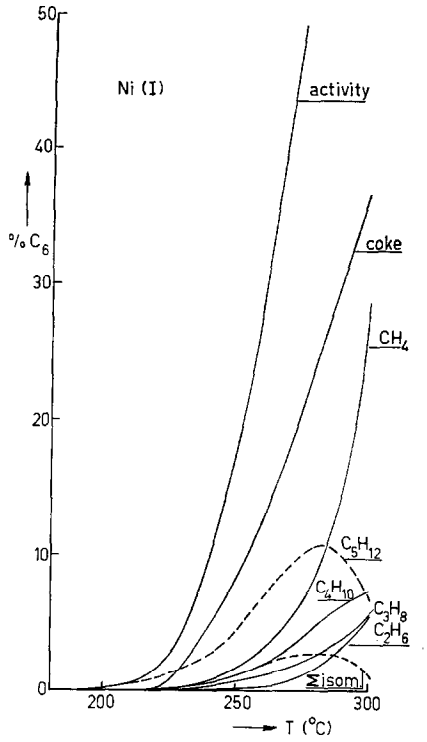

FIG. 5. Product pattern of Ni(I) catalyst as a function of temperature.

seem to occur with increasing temperature. The high coke formation is surprising, because the catalyst activity decreases only slowly with time on account of self-poisoning.

Typical for the NiCu(I) catalyst is the break of the activity line at 325–350°C, also found for the NiAg catalyst. Below these temperatures both catalysts possess good isomerization activity (NiCu over 90% at 325°C and NiAg about 70% at the same temperature). Above 325°C the rise in activity is slower. Probably the catalysts become more sensitive to poisoning by coke formation than the pure nickel catalyst. A striking difference between the NiCu and NiAg catalyst is formed by the distribution pattern of the cracking products. In the case of nickel–silver, methane is the major cracking product; while for nickel–copper, it is propane. In the products of both catalysts small amounts of methylcyclopentane and benzene are found. Neither of the two catalysts can be poisoned by pyridine, although they are poisoned by thiophene.

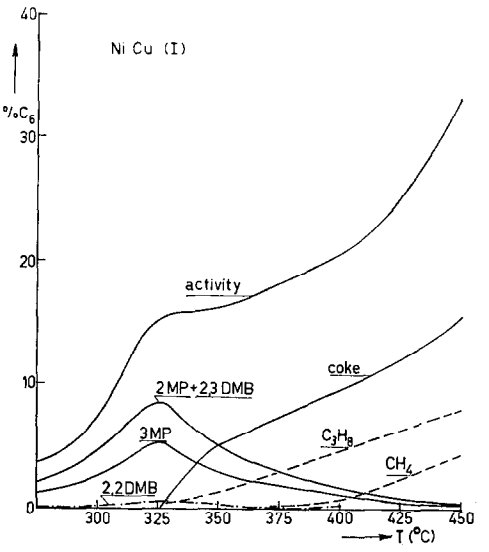

FIG. 6. Product pattern of NiCu(I) catalyst as a function of temperature (pentanes, butanes, and ethane omitted).

DISCUSSION

The reduction by H_2 of a zeolite Y sample in which part of the Na^+ ions are exchanged by Ni^{2+} leads, as is evident from magnetic and ESR measurements, to the formation of

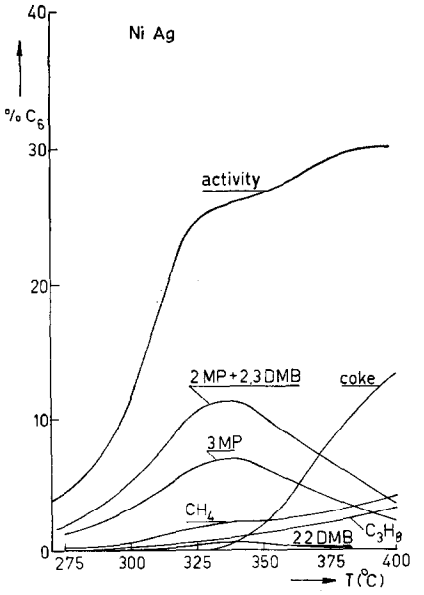

FIG. 7. Product pattern of NiAg catalyst as a function of temperature (pentanes, butanes, and ethane omitted).

systems in which the metal is present in the form of metal crystals. The crystals are surprisingly large, certainly larger than the size of the pores in the zeolite matrix. The reduction does not, however, destroy the zeolite structure as evident from the X-ray diagrams of the reduced samples. The only conclusion that can be drawn from these results is that Ni atoms formed by the reaction:

$$Ni^{2+} + H_2 \rightarrow Ni + 2H^+,$$

diffuse out of the pores to form crystals at the outer surface of the zeolite particles. If two reducible metal ions are present in the unreduced sample, the reduction may lead, if circumstances permit, to the formation of alloy crystals. This process of alloy formation has been demonstrated here by the considerable decrease in ferromagnetism for the case of Ni and Cu. The metal-on-zeolite catalysts formed in this way are therefore presumably similar to the metal alloy films as studied extensively by Sachtler and Van der Plank (*11*) or the granular alloy systems investigated by Cadenhead and Wagner (*12*). Their catalytic behavior may, however, demonstrate some characteristics that are derived from the protons supposedly present in the zeolite matrix.

As far as their catalytic behavior towards the conversion of *n*-hexane is concerned Ni-on-zeolite systems show a considerable similarity to the Ni-on-SiO_2 catalysts as studied by Kikuchi and Morita (*13*). The main reaction is a hydrogenolysis that operates in steps. In every step a terminal C atom is dissociated from the paraffin under the production of CH_4 and a paraffin molecule with one C atom less. A minor difference between the results of Kikuchi and Morita and our observations is that we find a small amount of paraffinic isomers in our product while they do not mention the presence of isomers.

Alloy formation leads to a major change in the pattern of the reaction. The rate of conversion declines notably as a consequence of the inclusion of, for instance, Cu in Ni. Simultaneously the dominant reaction products, at least at moderately high temperatures, are singly branched paraffins while small amounts of 2,2-dimethylbutane could also be identified. This represents a type of inhibition that is fundamentally different from that demonstrated, for instance, by the injection of thiophene, which leads to a decrease in the rate of conversion without, however, the formation of substantial amounts of isomers. Actually, the type of hexane conversion observed over the Ni–Cu and Ni–Ag systems shows a marked similarity to that observed over Pt-on-zeolite catalysts. Now, Barron *et al.* (*14*) working with supported Pt catalysts and Anderson and Avery (*15*), working with Pt metal films have shown convincingly that isomerization occurs at the surface of the platinum metal. The important question confronting us, therefore, is whether this is also true for the alloy catalysts. If so, an interesting example would have been found for the often suspected possibility of a change in the catalytic properties of a metal by varying the number of *d*-electrons by alloying one metal with another. An alternative explanation to account for the facts observed is given by the assumption that the isomerization proceeds along the classical bifunctional route. Now, in this case, the isomerization would have to be liable to a poisoning by pyridine, because this would eliminate the acid centers, and by thiophene, since this eliminates the necessary dehydrogenation over the metal. If the isomerization were confined to the metal surface only thiophene would act as a poison. Since it was found that pyridine does not act as a poison, but thiophene does, it appears probable that indeed the isomerization occurs at the surface of the alloy crystals. Whether this applies also for the isomerization leading to doubly branched isomers remains undecided by the data presently available. Gault and his collaborators never observed the formation of doubly branched isomers on their supported Pt catalysts and similar observations were made by Dautzenberg and Platteeuw (*16*) for Pt-on-Al_2O_3 catalysts, where great care was taken to remove all acid properties from the Al_2O_3 carrier. However, Anderson and Avery did observe the formation of doubly branched isomers over Pt films. If the surface conditions at the metal systems applied by us happen to be similar to those for the supported catalysts

mentioned above, the formation of 2,2-dimethylbutane as observed by us must be due to the influence of the acid sites in the zeolite. If they resemble those of the metal films of Anderson and Avery all the isomerization reactions are confined to the metal surface. Further work is necessary to settle this point.

Acknowledgments

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References

1. Rabo, J. A., Pickert, P. E., Stamires, D. N., and Boyle, J. E., *Actes Congr. Int. Catal., 2nd, 1960* **1961**, 2055–2073.
2. Rabo, J. A., Pickert, P. E., and Mays, R. L., *Ind. Eng. Chem.* **53**, 733–736 (1961).
3. Pickert, P. E., Rabo, J. A., Dempsey, E., and Schomaker, V., *Proc. Int. Congr. Catal., 3rd, 1964* **1965**, 714–728.
4. Rabo, J. A., Schomaker, V., and Pickert, P. E., *Proc. Int. Congr. Catal., 3rd, 1964* **1965**, 1264–1276.
5. Lewis, P. H., *J. Catal.* **11**, 162–174 (1968).
6. Brooks, C. S., and Christopher, G. L. M., *J. Catal.* **10**, 211–223 (1968).
7. Bredikhina, T. N., and Evdokimov, V. B., *Russ. J. Phys. Chem.* **41**, 1601–1604 (1967).
8. Lipsch, J. M. J. G., thesis, Eindhoven, 1968.
9. Kittel, C., "Introduction to Solid State Physics," p. 581. Wiley, New York, 1968.
10. Hansen, M., "Constitution of Binary Alloys." McGraw-Hill, New York/London, 1969.
11. Sachtler, W. M. H., and Van der Plank, P., *Surface Sci.* **18**, 62 (1969).
12. Cadenhead, D. A., and Wagner, N. J., *J. Phys. Chem.* **72**, 2775 (1968).
13. Kikuchi, E., and Morita, Y., *J. Catal.* **15**, 217–223 (1969).
14. (a) Barron, Y., Maire, G., Cornet, D., and Gault, F. G., *J. Catal.* **2**, 152 (1963); (b) Barron, Y., Maire, G., Muller, J. M., and Gault, F. G., *J. Catal.* **5**, 428 (1966).
15. Anderson, J. R., and Avery, N. R., *J. Catal.* **5**, 446 (1966).
16. Dautzenberg, F. M., and Platteeuw, J. C., *J. Catal.* **19**, 41–48 (1970).