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COMPLEX STUDY OF NICKEL SKELETON CATALYSTS

V. STUDY OF NOVEL NON-PYROPHORIC NICKEL SKELETON CATALYSTS BY DERIVATOGRAPH

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ABSTRACT

The structure and properties of non-pyrophoric skeleton catalysts prepared from Ni–Si, Ni–Al–Si, Ni–Mg and Ni–Zn alloys have been studied—apart from other thermal methods—by means of the derivatograph.

Our experimental results have contributed to the explanation of the non-pyrophoric behaviour of these catalysts. We demonstrated that the desorption of the hydrogen content in our catalysts is not accompanied by the oxidation of active nickel. This oxidation takes place only at higher temperatures, above 200 °C, at a rate proportional to the amount of active nickel.

Other constituents of the catalysts (adsorbed water, hydroxide content) were also determined from the experimental data. The outstandingly high $Mg(OH)_2$ content of the Ni–Mg catalyst indicates that its structure is dissimilar: $Mg(OH)_2$ also acts as support for the catalyst.

INTRODUCTION

Changes in industrial catalysts caused by the effect of heat largely affect their behaviour. Such changes, the structure, the surface state and incidental adsorbed substances can be studied using thermal methods. We investigated the novel nickel skeleton catalysts by means of several thermal methods. In our earlier papers[1,2] we reported on our thermal desorption and thermomagnetic results. In the present paper, measurements using the derivatograph[3] will be discussed.

Skeleton catalysts developed on the basis of Raney's activity[4,5] are of great importance in various fields of organic chemical industry for liquid-phase hydrogenations. Such catalysts are prepared by alloying a catalytically active metal (usually nickel) with a catalytically inactive metal (mostly aluminium). The latter is then selectively removed, e.g., by alkaline dissolution, and the active component is thus obtained in the form of a very finely dispersed powder. When the inactive component is dissolved, hydrogen is released, and a substantial part of this hydrogen will be sorbed on the surface of the catalysts. Owing to their large surface area and to the hydrogen content, Raney catalysts are pyrophoric, so that their use requires increased precaution.

Csűrös and co-workers[6,7] used thermal analysis for studying traditional Raney nickel prepared from Ni–Al alloy. Difficulties in measurement arose owing to the pyrophoric nature of the catalyst. A silicone oil layer was applied to prevent rapid oxidation of the surface when sudden desorption of hydrogen takes place. After removal of the silicone oil, measurement was continued at a higher temperature. The authors[6,7] stated that part of the dissolved aluminium remains in the catalyst in the form of hydrargillite–$Al(OH)_3$. An exothermic process, namely the desorption of chemisorbed hydrogen and its simultaneous recombination partly overlaps the decomposition process of $Al(OH)_3$. From the ratio of $Al(OH)_3$ to the amount of sorbed hydrogen, optimum conditions for the dissolution of aluminium were obtained.

Flóra et al.[8] used the derivatograph to study the properties of Raney copper and its change in the course of the reaction. The catalyst prepared from the Cu–Al–Zn alloy contained both aluminium hydroxide and zinc hydroxide, both acting as promoters in the studied furfural → methylfurane reaction. The amount of hydroxides remaining in the catalyst was found to increase—in agreement with the observations of Csűrös and co-workers[6,7]—with increasing concentrations of the dissolving alkali.

Our work led to the development of a novel group of nickel skeleton catalysts. Instead of the traditional Ni–Al alloy, we used Ni–Si, Ni–Al–Si, Ni–Mg and Ni–Zn alloys as starting material[9–13]. These catalysts are non-pyrophoric or substantially less pyrophoric than classical Raney nickel, while their performance attains or, in some cases, exceeds that of Raney nickel. They can be dried in air, the dry powders can conveniently be stored for an indefinite period, and reactivated in a few minutes. A similar treatment can be used to reactivate exhausted catalysts.

The structure and properties of our catalysts were investigated in order to throw light on the reasons for their non-pyrophoric nature. To find the differences as compared to classical pyrophoric Raney nickel, our studies were extended to a commercial catalyst prepared from Ni–Al alloy (B 113, product of Degussa).

EXPERIMENTAL

Before derivatographic measurements, our novel catalysts stored under water were dried by letting them stand overnight in air. Owing to its pyrophoric nature, the Degussa catalyst could not be measured without particular precautions. We therefore dehydrogenated this catalyst under silicone oil, similar to the technique applied by Csűrös et al.[6]. 40–50 g of the catalyst were washed several times with ethanol. Subsequently the major part of the alcohol was distilled off in vacuum, letting argon flow through the apparatus, and the catalyst was covered with silicone oil (Silorol). Then the catalyst, still with argon flowing through, was heated for 2 h to 180–200 °C.

After this period, a slight release of gas was still noticeable. After cooling, the silicone oil was washed off with benzene, and the powder dried at ambient temperature was used for further studies. This substance was not pyrophoric any more.

Derivatograms were taken with samples weighing 0.5–1 g, at a heating rate of 5 °C min^{-1}. The reference standard was α-Al_2O_3. Some samples were also tested in an inert atmosphere, viz., under argon at a flow-rate of 25 l h^{-1}. For comparison, the alloys used as starting material for the catalysts were also measured in all cases.

RESULTS

Ther derivatograms of a Ni–Si alloy and of the catalyst prepared from this alloy are shown in Fig. 1. Oxidation of the alloy powder in air starts at 380 °C. Under argon, no change takes place up to 700 °C. The oxidation process involves nickel only, since under such conditions silicon is still stable. At 720–740 °C, endothermic peaks without changes in weight are observable on the DTA curve. However, the phase diagram of the alloy shows no change in this temperature range[14].

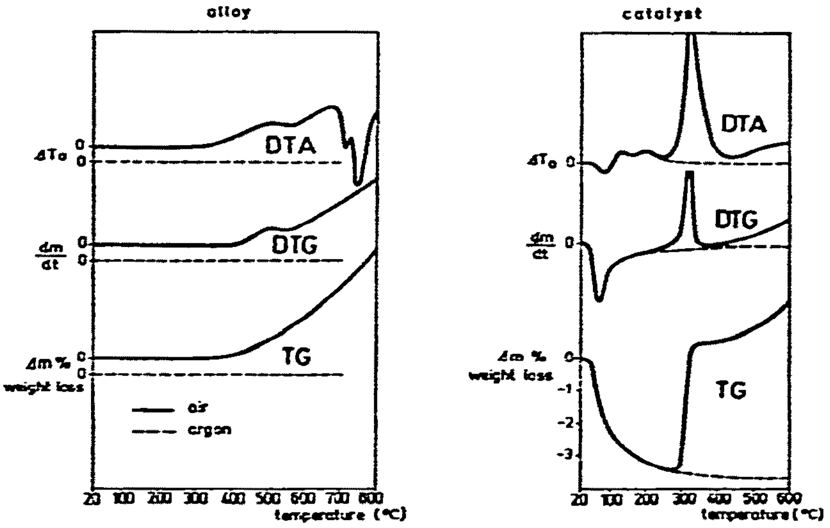


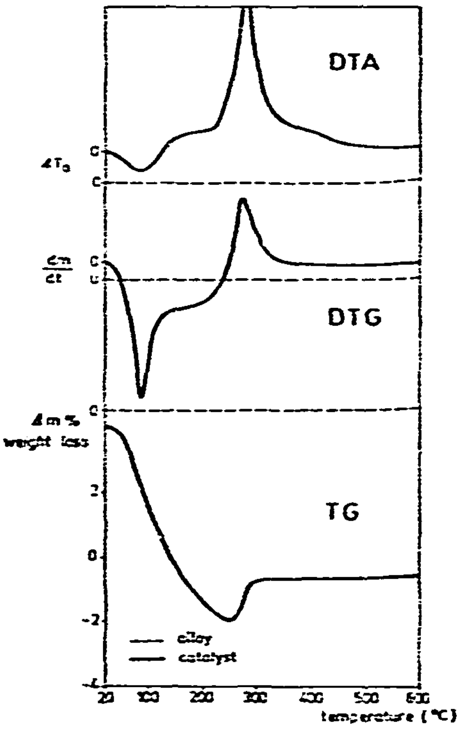
Fig. 1. Derivatogram of a Ni–Si alloy and catalyst.

The derivatogram of the catalyst indicates that its water content is removed rather slowly. The flat extended curve is characteristic of silica formed and precipitated during the dissolution process and the splitting-off of its constitutional water. The removal of adsorbed and constitutional water cannot be distinguished. Partly overlapping with the loss of water, a rather rapid increase in weight occurs between 290 and 340 °C, together with a strong exothermic reaction.

This reaction does not take place under argon, hence it is presumably the oxidation of the active surface nickel content of the catalyst. This nickel content is not necessarily identical with the amount of catalytically active nickel, therefore it is more correct to term it "oxidizable active nickel". The oxidation of active surface nickel was observed to proceed similarly, however, at somewhat different temperatures, with all types of our catalysts, at maximum rates between 220 and 330°C. This general observation appears particularly important in view of the non-pyrophoric nature of our catalysts.

At 120 and 220°C, two small indistinct exothermic peaks are found on the DTA curve. Since they appear identically both in air and in argon, the process involved cannot be an oxidation. Thermal desorption tests[1] indicated that a small amount of hydrogen is also present on the dry catalyst powder, and its desorption starts in this temperature range. The thermal effect measured is presumably that of the recombination of a part of the sorbed hydrogen. The released heat is substantially less than that at the oxidation of nickel.

At 390°C, slow, uniform oxidation of a further part of the nickel begins. In argon, of course, no such reaction takes place.



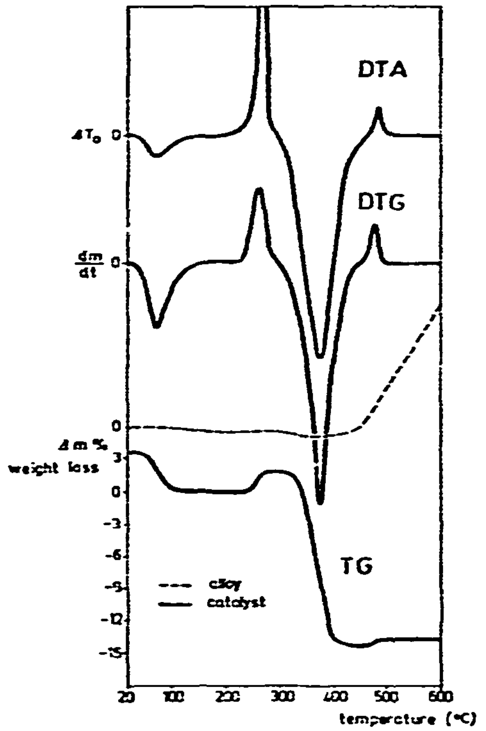


Fig. 2. Derivatogram of a Ni–Al–Si alloy and catalyst in air.

Fig. 3. Derivatogram of a Ni–Mg alloy and catalyst in air.

The behaviour of the Ni–Al–Si alloy and of the catalyst prepared from it (Fig. 2) is much similar to that of Ni–Si and the Ni–Si catalyst, respectively. The slight oxidation of the alloy starts at a somewhat higher temperature, around 500°C. With the catalyst, the process following the loss of adsorbed water (from 120°C on) is more distinct. Presumably the effect is due to the loss of constitutional water of silica. The exothermic effect indicating recombination of sorbed hydrogen appears between 130 and 230°C on the DTA curve. After the reaction of oxidizable active nickel, the catalyst is stable up to 500°C. Further oxidation starts very slowly and at higher temperatures only.

For the sake of lucidity, only the TG curve of the Ni–Mg alloy is shown in Fig. 3. Between 100 and 150°C a small amount of adsorbed water is removed. Subsequently, around 330°C, a further small loss in weight, corresponding to an exothermic reaction, is observed. We were unable to explain this process. It cannot be due to accidental oil contamination in the milling operation, since washing the powder with petroleum ether had no effect. Oxidation of the metal starts at 360°C and becomes very fast from 440°C on. Apparently this is the well-known violent oxidation reaction of magnesium.

On the catalyst, the oxidation of oxidizable active nickel takes place at 260°C, after the loss of adsorbed water between 40 and 100°C. Immediately after the oxidation, from 290°C, a substantial weight loss begins, corresponding to the loss of water of $Mg(OH)_2$ present in the catalyst. The exothermic reaction taking place at 480°C and accompanied by an increase in weight is the oxidation of unalloyed magnesium whose presence in small amounts had been indicated by the X-ray diffraction pattern[15].

The Ni–Zn alloy and the catalyst prepared from it were measured both in air and in argon (Fig. 4). The alloy is stable in air up to 300°C, then a very intense exothermic reaction starts: zinc is oxidized. Under argon, the substance remains unchanged up to 790°C, after which a decrease in weight starts which becomes very strong at 1000°C: the alloy is decomposed and zinc sublimates. A small endothermic peak on the DTA curve at 680°C indicates a phase transformation. At 860°C the substance begins to melt.

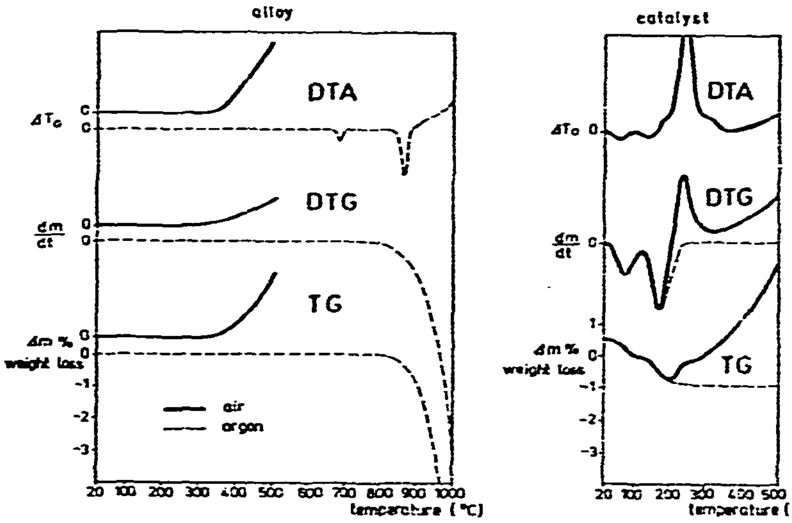


Fig. 4. Derivatogram of a Ni–Zn alloy and catalyst.

From the catalyst, a relatively small amount of adsorbed water is removed. At 160°C, a further small weight loss presumably indicates the decomposition, i.e., water loss of $Zn(OH)_2$. However, an unequivocal statement is made difficult as the decomposition temperatures of both $Zn(OH)_2$ and $Ni(OH)_2$ lie in this range, with a difference of only 20°C. However, the formation of $Ni(OH)_2$ under the conditions of catalyst preparation is highly improbable, and no $Ni(OH)_2$ was found in the other catalysts investigated. These facts appear to confirm the correctness of our presumption. Almost immediately after the oxidation of oxidizable active nickel, at 240°C, the oxidation of the rest of the substance starts. In argon, the first two processes take place in the same way, while no oxidation occurs of course. On both sides of the DTA peak indicating the oxidation of active nickel, a small exothermic shoulder is observable. They are difficult to evaluate because of overlapping. However, it appears probable that both correspond to the recombination of sorbed hydrogen. The shoulder at 330°C is in good agreement with the peak observed at the same temperature in the thermal desorption experiments[1].

The question may arise whether drying of the catalysts does not change the state of the sample. Our novel catalysts can be dried from their water-wet state at ambient temperature without releasing heat, and our thermal desorption measurements[1] demonstrated that only traces of hydrogen are left after drying. It appears

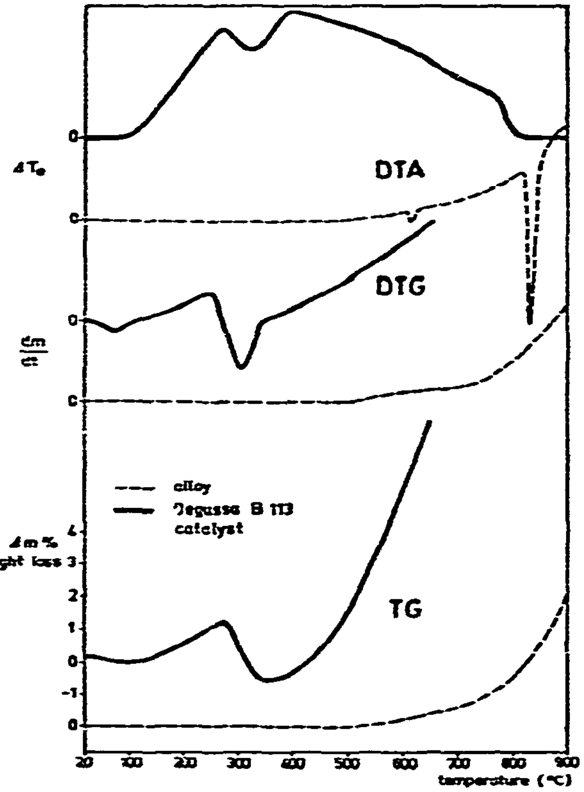


Fig. 5. Derivatogram of a traditional Raney nickel alloy and catalyst in air.

that in the course of the drying operation, simultaneously with hydrogen desorption, active surface nickel is oxidized to a slight extent only, since—in the presence of water—$Ni(OH)_2$ would be formed in the oxidation process, whereas no $Ni(OH)_2$ was found in the catalysts. Oxidation to a major extent— in agreement with the non-pyrophoric nature of our catalysts—takes place only at substantially higher temperatures. Hence, it may be assumed that thermal analysis was carried out on samples in a state close to the original.

The derivatogram of Degussa Raney nickel dehydrogenated under silicone oil (Fig. 5) differs in several respects from those of our catalysts. After the removal of adsorbed water, oxidizable active nickel is oxidized within a rather broad temperature range and shows a relatively small thermal effect. Its DTG peak temperature is lower (215°C) than those of our novel catalysts. Dehydration of $Al(OH)_3$ takes place only after the oxidation of active nickel, while the oxidation of the bulk of the nickel starts at 360°C. Oxidation of the Ni–Al alloy powder begins very slowly at 530°C only.

DISCUSSION

The data obtained from the derivatograms for individual components of our catalysts are summarized in Table 1. Adsorbed water and constitutional water of silica could not be distinguished satisfactorily in the derivatograms of silicon-containing catalysts, and silcas with different degrees of hydration could not be accounted for with an unequivocal reaction equation. Therefore in the case of these catalysts we listed the total water loss as sorbed solvent.

TABLE 1

CATALYST CONSTITUENTS DETERMINED FROM DERIVATOGRAMS

Type	*Nickel content (wt.-%)*[a]	*Oxidizable active nickel*		*Adsorbed water (wt.-%)*	*Hydroxide content (wt.-%)*
		wt.-%	*% of total Ni*		
Ni–Si	65.0	14.4	22.1	3.4	
Ni–Al–Si	47.6	5.1	10.7	6.0	
Ni–Mg	35.7	7.0	19.6	3.6	48.7 $Mg(OH)_2$
Ni–Zn	47.6	1.5	3.1	0.6	2.2 $Zn(OH)_2$
Ni–Al Degussa B 113	82[b]	4.8	5.8	0.2	5.3 $Al(OH)_3$

[a] Determined polarographically after dissolution of the catalyst. [b] Taken from Degussa-Mitteilung (no identifying number).

The amount of $Mg(OH)_2$ in the Ni–Mg catalyst is outstandingly high. This is due to $Mg(OH)_2$—in contrast to the hydroxides of the other inactive metals—not being amphoteric. Hence, $Mg(OH)_2$ is not dissolved in the alkali during the alkaline treatment of the alloy, so that only some of it is removed from the surface, while a substantial part remains in the catalyst.

The amount of oxidizable active nickel, as determined from the derivatograms, is significantly (in some cases by one order of magnitude) smaller than the total nickel content of the catalysts. This can be explained by NiO formed in oxidation constituting a massive, well-sealing layer that will prevent the diffusion of oxygen into the deeper layers of the catalyst. Therefore the oxidation of active nickel will take place on the surface, and total oxidation will proceed at higher temperatures only. This assumption is supported by the finding that the trend of the change in oxidizable nickel content is the same as that of the change in specific surface area (Table 2).

Comparison of the derivatograms of our novel catalysts demonstrates that the rates of oxidation of oxidizable active nickel and DTG peak temperatures vary largely, and that these values are the higher, the higher the percentage of oxidizable nickel. The relating data are also summarized in Table 2.

TABLE 2

SOME CHARACTERISTICS OF THE OXIDATION OF THE CATALYSTS

Type	*Oxidizable active nickel (wt.-%)*	*Specific surface area ($m^2 g^{-1}$)*	*Oxidation of active nickel*		
			Peak temperature (°C)	*Temperature range (Δ°C)*	*Temperature leap (Δ°C)*
Ni–Zn	1.5	13.5	220	$190 \rightarrow 235 = 45$	+5
Ni–Al–Si	5.1	48	280	$250 \rightarrow 320 = 70$	+10
Ni–Mg	7.0	55	265	$240 \rightarrow 280 = 40$	+25
Ni–Si	14.4	61	320	$290 \rightarrow 340 = 50$	+35
Ni–Al Degussa B 113	4.8	4[a]	215	$110 \rightarrow 270 = 160$	<+5

[a] After removal of hydrogen.

The differences in the rate of oxidation are related to the pyrophoric properties, to the propensity to take fire. Finely dispersed powders are the most characteristic representatives of pyrophoric substances. With decreasing particle size, the surface area of the substance greatly increases, so that oxidation reactions will take place more readily and to a greater extent. Simultaneously, due to the highly dispersed state, dissipation of heat will decrease, the temperature of the substance will rise, and hence surface reactions will be further accelerated, so that finally an explosion, a flame or incandescence will arise. For a more exact discussion of pyrophoric phenomena, the system can be characterized by the relationships between the mass of the sample, specific surface area, specific heat, density and heat of reaction[16,17].

The specific surface area of our catalysts exceeds 10 $m^2 g^{-1}$. This is a particle size where the dissipation of heat is already substantially impaired[16], so that oxidation will be accelerated considerably by increasing temperature. Similarly, heat of reaction being higher due to higher oxidizable nickel content, this will also accelerate the reaction.

Particles of the Ni–Mg catalyst, and even more of the Ni–Si catalyst, due to the high hydroxide content and the gel structure of silica, respectively, will adhere into large, loose lumps in water. Both the hydroxide layer and lump formation may result in greater protection of the surface nickel atoms against oxidation which will take place only at higher temperatures, but then, of course, at a higher rate.

Table 2 also demonstrates that the dry powder prepared of Degussa Raney nickel—although its hydrogen content had been removed—is still more readily oxidizable, and at lower temperatures, than our novel catalysts. Heat treatment may affect the state and particle size of the surface, but under the given conditions (protective liquid layer, argon stream) only a small portion of active surface nickel may be oxidized. The reactivity of unchanged oxidizable active nickel had not been reduced to such•an extent by removal of hydrogen and thermal treatment that oxidation temperature would attain that of the novel catalysts. Since oxidation starts differently at different-type active centres, the process takes place in a broad temperature range and proceeds slowly and calmly.

The results of thermal analysis greatly contributed to the study of the non-pyrophoric behaviour of our novel catalysts. Together with information obtained by other methods, we can now explain the phenomenon in the following way. X-ray diffraction patterns[15] indicated that unchanged intermetallic compounds are also present in the catalysts, and active nickel crystallites represent a smaller share of the substance only[2]. Both specific surface area and hydrogen content of the catalysts are lower than those of Degussa Raney nickel[1]. The main part of hydrogen is bound more weakly than in Raney nickel, the catalysts contain only small amounts of strongly sorbed hydrogen. Weakly bound hydrogen is readily removed from the surface, e.g. at ambient temperature in an inert gas stream, but also when the catalysts are being dried in air. Desorption of hydrogen proceeds practically without any thermal effect, indicating that this sorbed hydrogen is not atomic (presumably it is closer to the molecular state). The thermal effect due to recombination of residual hydrogen desorbed at a higher temperature is also small, since the amount of this hydrogen is small. When this small quantity of heat is released, it is readily dissipated in the less disperse catalyst containing alloy phases and having good thermal conductivity. Hence, desorption of hydrogen is separated in time from oxidation of active nickel (starting at higher temperatures), and is not—at this lower temperature—accompanied by oxidation of desorbed hydrogen. As a result of these two effects, the quantity of heat released simultaneously is substantially smaller, and up to a higher temperature limit, the process is not self-accelerating.

REFERENCES

1 J. Heiszman, S. Békássy and J. Petró, *Acta Chim. (Budapest)*, in press.
2 A. Tungler, S. Békássy and J. Petró, *Acta Chim. (Budapest)*, in press.
3 F. Paulik, J. Paulik and L. Erdey, *Z. Anal. Chem.*, 160 (1958) 241.
4 M. Raney, *U.S.* Pat., No. 1 563 587.
5 M. Raney, *U.S.* Pat., No. 1 628 190.
6 Z. Csűrös, J. Petró, V. Kálmán, L. Erdey and F. Paulik, *Magyar Kém. Foly.*, 70 (1964) 337.
7 Z. Csűrös, J. Dusza, J. Petró, L. Erdey and F. Paulik, *Acta Chim. (Budapest)*, 42 (1964) 131.
8 T. Flóra, H. Szabady, A. Jeges, B. Szeiler and A. Almásy, *Acta Chim. (Budapest)*, 58 (1968) 235.
9 Z. Csűrös, J. Petró, A. Tungler, T. Máthé and S. Békássy, *Hung.* Pat., No. 159 603.
10 Z. Csűrös, J. Petró, A. Tungler, T. Máthé and S. Békássy, *Aust.* Pat., No. 294 781.
11 Z. Csűrös, J. Petró, A. Tungler, T. Máthé and S. Békássy, *Ger. Pat. Offen.*, 2 014 391.
12 Z. Csűrös, J. Petró, A. Tungler, T. Máthé and S. Békássy, *U.S.* Pat., No. 3 691 103.
13 Z. Csűrös, J. Petró, A. Tungler, T. Máthé and S. Békássy, *Brit.* Pat., No. 1 302 563.
14 M. Hansen, *Constitution of Binary Alloys*, McGraw-Hill, New York-Toronto-London, 2nd ed., 1958.
15 S. Békássy, A. Kálmán and J. Petró, under publication.
16 W. Feitknecht, *C.R. Journées Etud. Solides Finement Div.*, (1967) 215.
17 C. R. Schmitt, *J. Fire Flammability*, 2 (1971) 157.