

POSSIBILITIES OF INCREASING THE ACTIVITY OF CATALYSTS OF RANEY-NICKEL TYPE

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The study of the possibilities, both from a theoretical and a practical aspect, of the investigation of catalysts and of their choice for a given chemical process represents a problem of extreme importance. Up to the present, it was not possible to evolve a uniform survey of this field. In addition to the complicated mechanism of heterogeneous catalysis, this is due to the manifold nature of the examined catalysts, together with the fact that in the majority of cases also the catalysts consist of several constituents.

The elucidation of the mechanism of the catalytic process and the problem of choosing the adapted catalyst may be approached by studying, as a main scope, the behaviour of the catalyst and restricting the investigation of substrates to an indispensable extent. In other words, only those changes should be investigated which may occur *with the catalysts themselves*, applying various substrates, under varying conditions (as temperature, pressure, concentration of substrate). The study of this problem at first sight appears to be simpler than approaching it from the field of substrates, at least in the case of hydrogenation catalysts, mainly of Raney-nickel.

In the case of Raney-nickel, the mentioned requirements are met in the first line by the changes in the content of hydrogen of the catalyst during reaction. This catalyst seems to be particularly suitable for investigations of this type as 1. it possesses a content of hydrogen relatively higher than that of other nickel-bearing catalysts, and 2. it consists, at least in principle, only of one constituent (nickel).

It is known since long that Raney-nickel undergoes, during storage, an ageing (reduction of activity) which was interpreted by the decrease of its content of hydrogen [1]. Since 1940, the number of investigations in connection with Raney-nickel increased to a great extent, and several authors (*e. g.* [2—6]) also dealt with the systematic study of its content of hydrogen. All the investigators are of the opinion that two types of hydrogen bond, a stronger and a weaker one, exist in Raney-nickel. Views are, however, different as regards the nature of the bond of hydrogen. Conductance and magnetochemical measurements carried out with nickel films and nickel catalysts [5—6]

indicated that, at room temperature, hydrogen is chemisorbed to various strengths (in the newest interpretation of chemisorption). The ratio of the portion of the strong bond to that of the weaker bond varies according to the nature of the catalyst. It is a common opinion of authors that activity, together with certain physical properties [7,8] of catalysts, are functions of the content of hydrogen. FREUNDLIN and ZIMINOVA [8, 9] (1950) were the first in pointing to the correlation of the various forms of bond (they considered two forms to exist) with the activity of Raney-nickel. They established a sharp quantitative ratio of these two bonds. According to these authors, the majority of hydrogen (about 175 ml/2,3 g of Raney-nickel) are absorbed and the activity of the catalyst depends on this portion. On removing a part of absorbed hydrogen, the activity of the catalyst, together with its capability of taking up further amounts of hydrogen from the gas area decrease, whilst on completely removing absorbed hydrogen, both properties (and also the pyrophoric activity) disappear. The smaller portion of hydrogen, in turn, is present (about 50 ml/2,3 g of Raney-nickel) in an adsorbed form, without any effect on the activity of catalyst. The catalyst is capable of delivering this quantity of hydrogen in a reversible way and replace it from the gas area, without any decrease of activity.

It has been observed [8, 9] that certain substrates are not capable, during hydrogenation, of consuming absorbed hydrogen, even when the hydrogen content of the catalyst is the sole source of hydrogen (as the gas area consists of nitrogen) and the substrate is in excess over the hydrogen of catalyst. On hydrogenating substrates of this type, the activity of catalyst does not decrease during the process, and the catalyst is capable of taking up the quantity of adsorbed hydrogen from the gas area in a reversible way. (FREUNDLIN and his associate denote this group as substrates of type "A", *e. g.* styrene). The other group of substrates (*e. g.* nitrobenzene) vigorously react with both adsorbed and absorbed hydrogen, even when the gas area does contain hydrogen. In this case, the activity of catalyst decreases or completely disappears, depending on the ratio of substrate to catalyst, and the substrate loses its capability of taking up further amounts of hydrogen from the gas area (substrates of type "C"). Besides, there are compounds which are capable of consuming only a portion of absorbed hydrogen and of decreasing activity to a certain degree (compounds of type "B").

The above statements hold for hydrogenations carried out at room temperature as at higher temperatures, *e. g.* over 60°, all substances are capable of taking up the complete amount of hydrogen from the catalyst.

The data of FREUNDLIN and ZIMINOVA were controlled some years later (1954) by SOKOLSKY and BEZVERKOVA [10], complemented by the measurement of the electric potential of catalysts. The results proved that the quantity of adsorbed hydrogen appreciably exceeds that of absorbed hydrogen, the

latter ranging, according to the nature of the medium, 2 to 5-times higher than the adsorbed amount (e.g. the ratios observed in 0,1 N sodium hydroxide, water and ethanol, respectively, were 5 : 1, 3 : 1 and 2 : 1, respectively, indicating that both the solvent and the pH value affect the ratio).

The conductance and magnetochemical measurements carried out by BAKER, JENKINS and RIDEAL [5] in 1955 and by SELWOOD [11] in 1956 with films and catalysts of nickel confirmed the existence of strongly and weakly bound hydrogen at room temperature, although both types should be considered as being chemisorbed.

On the basis of data of literature and of our earlier communications, possibilities of increasing the activity of Raney-nickel are summarized in Table 1.

In connection with Table 1, it must be noted that on plotting the activity values of the catalyst against contents of hydrogen, a sharp maximum is

Table 1

Possibilities of increasing the activity of Raney-nickel

I. During preparation

Scope: to establish the optimum amount of sorbed hydrogen

Method: careful choice of the conditions of preparation

- I.1 Duration
Temperature of extraction
- I.2 Extent
Conditions of washing
- I.3 Quantity
Nature of alkali applied
- I.4 Composition of alloy: Ni/Al
Ni/Co/Al
Ni/Cr/Al
Ni/Cu/Al
Ni/Mn/Al
Ni/Ti/Al

II. On the ready-made catalyst

Scope: to secure the quantity of strongly sorbed hydrogen [(of the activity of catalyst) and to attain hydrogen uptake (from the gas phase) in a reversible way]

Method:

- II.1 To secure the quantity of strongly sorbed hydrogen
 - II.2 To increase the quantity of hydrogen sorbed by the surface
 - II.3 To adjust other factors in a favourable way
- by adding various substances to the reaction mixture
- II.11 with bases
 - II.12 with acids
 - II.13 with salts
 - a) containing metals actively affecting hydrogenations
 - b) other salts
 - II.21 by adjusting pH values
 - II.22 by adequately choosing the medium
 - II.23 by varying the temperature
 - II.32 by adjusting the ratio of adsorption to desorption of the substrate or of the end product
 - II.32 with surface active substances

disclosed, as stated by ABLESOWA and ROGINSKY [12] in conclusion of their experiments conducted earlier (1935) with nickel films. Our observation refers to experiments carried out with only one substrate. Should this phenomenon possess a general validity, it would mean that a maximum content of hydrogen in catalysts is not always of an optimum effect on hydrogenation and on the

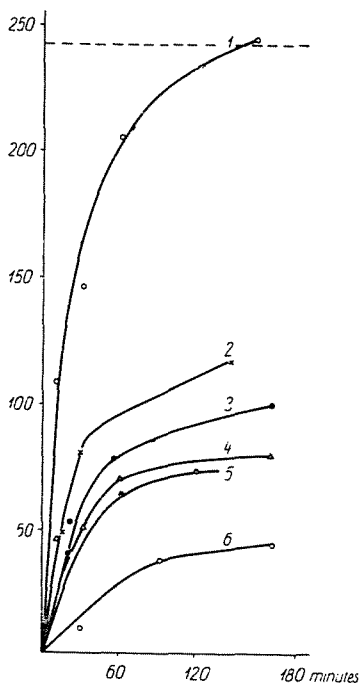


Fig. 1. Quantities of hydrogen taken up from the catalyst by various substrates (0,01 mole of substrate is equivalent to hydrogen in 1 ml of catalyst). 1 : nitrobenzene, 2 : eugenol, 3 : acetophenone, 4 : benzaldehyde, 5 : benzyl cyanide, 6 : benzophenone

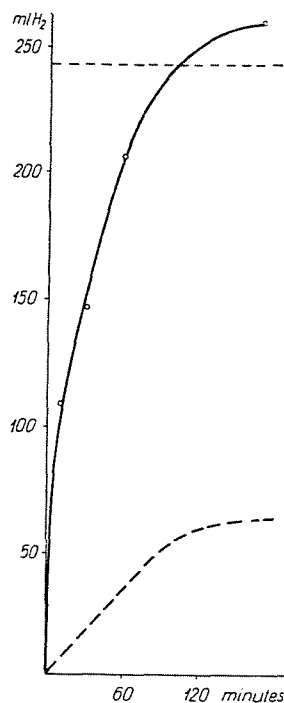


Fig. 2. Quantities of hydrogen taken up by nitrobenzene from the catalyst (continuous line) and those taken up by the catalyst during subsequent hydrogenation (dotted line)

substrate, respectively. Our investigations in this direction are in progress. If the above considerations would generally be valid, then it would be necessary to determine the following main data at the hydrogenation of a given substrate :

1. type of substrate (A, B or C),
2. experimental conditions under which substrates of other type may completely or approximately be converted into those of type A,
3. optimum content of hydrogen of substrate.

The above considerations explain, in our opinion, the phenomenon known from laboratory and industrial practice, namely, that in certain cases of hydrogenations with Raney-nickel, complete hydrogenation only takes place at a given ratio of substrate to catalyst. In these cases, the substrate is presumably of a nature taking up hydrogen more readily (and more rapidly, in general) from the catalyst than from the gas area, and the quantity of hydrogen necessary for hydrogenating the substrate (or an adequate portion of the substrate) is approximately introduced by the amount of catalyst applied. This means that, in an unfavourable case, the total quantity of hydrogen, referring to the substrate, is introduced into the system by the catalyst, whilst in a favourable case the catalyst is capable of taking up the total amount or a portion of the required hydrogen in a reversible way also from the gas area, *i. e.* a much smaller quantity of catalyst is satisfactory. When the quantity of catalyst present ranges below this value, the supply of hydrogen contained by the catalyst

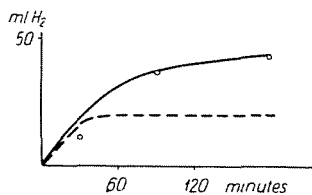


Fig. 3. Quantities of hydrogen taken up by benzophenone from the catalyst (continuous line) and those taken up by the catalyst during subsequent hydrogenation (dotted line)

is quickly consumed by the substrate. In this way, the catalytic activity (*i. e.* the capability of taking up further amounts of hydrogen from the gas area) of the catalyst disappears and the process stops.

In general, we applied 7 model compounds in the present experiments : acetone, acetophenone, benzophenone (carboxyl group), benzaldehyde (aldehyde group), eugenol (aliphatic double bond), benzyl cyanide (nitrile) and nitrobenzene.

At first it seemed necessary to classify our model compounds into the mentioned types A, B and C of substrates [13]. In this series of experiments, 1 ml of Raney-nickel (which contains, according to data of literature, about 250 ml of hydrogen) was shaken in a nitrogen atmosphere with as much substrate as was required to attain, in the presence of excess substrate, a calculated hydrogen uptake of 242 ml (*cf.* Fig. 1). It can be seen in Fig. 1 that of the substrates applied, only nitrobenzene takes up the calculated quantity of hydrogen (which is at the same time also the total content of hydrogen of the catalyst) whilst the uptake in the case of all other substrates ranges lower. The amounts of calculated hydrogen uptake are shown in Fig. 1 by broken

line, whereas continuous line indicates the quantities of total hydrogen uptake of substrates. The greater the difference between both values, the more the compound belongs to type C. These figures disclose that neither of the substrates applied by us belong to type "A" (this type being approximated by benzophenone, see Fig. 3), whilst nitrobenzene proved to be of type "C", quite in accordance with the data of literature (Fig. 5).

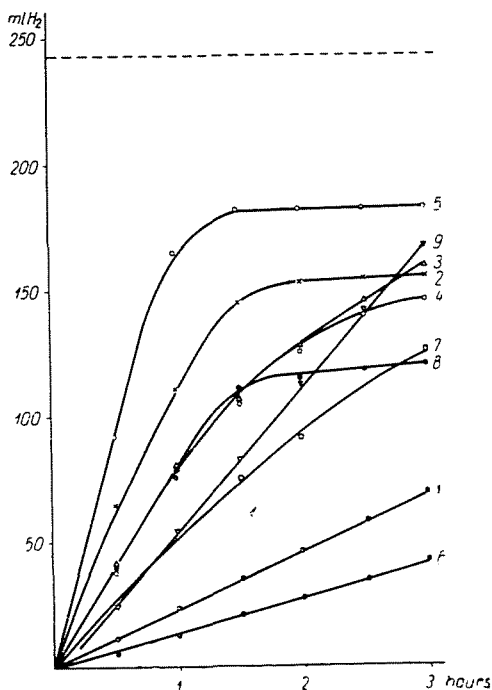


Fig. 4. Hydrogen uptake of acetone with various catalysts. 1 : catalyst extracted at 100° , 2 : catalyst extracted at 50° , 3 : catalyst extracted at 25° for 50 minutes, 4 : catalyst extracted at 25° for 180 minutes, 5 : catalyst extracted at 50° for 150 minutes, 6 : catalyst extracted at 80° for 150 minutes, 7 : catalyst extracted at 0° for 600 minutes, 8 : catalyst extracted at 0° for 1200 minutes and 9 : catalyst W6

The classification of substrates into types on the basis of tests carried out in a nitrogen atmosphere, presumably changes when the atmosphere consists of hydrogen. Namely, in this latter case the catalyst may replace the total quantity or a portion of hydrogen lost (*i. e.* taken up by the substrate) from the gas area. In this way, substrates of type "B" and "C", respectively, may shift into group "A". Our experiments to elucidate this problem are in progress.

On the basis of the data of Table I, possibilities of increasing the activity of catalysts may be summarized as follows.

I. Factors acting on preparation of catalyst

1. Duration and temperature of extraction

Activity is rather sensitive on the above factors [14]. It also varies according to the nature of a given catalyst (type "A", "B" or "C"). Namely, when a substrate is capable of taking up the calculated amount of hydrogen

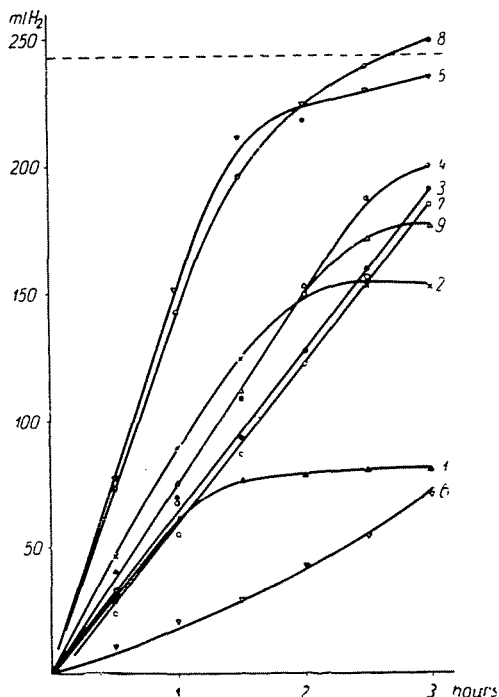


Fig. 5. Hydrogen uptake of benzophenone with various catalysts. 1 : catalyst extracted at 100° , 2 : catalyst extracted at 50° , 3 : catalyst extracted at 25° for 50 minutes, 4 : catalyst extracted at 25° for 180 minutes, 5 : catalyst extracted at 50° for 150 minutes, 6 : catalyst extracted at 80° for 150 minutes, 7 : catalyst extracted at 0° for 600 minutes, 8 : catalyst extracted at 0° for 1200 minutes, 9 : catalyst W6

from the gas area, it belongs to type "A" according to the afore-mentioned and also according to our other investigations. When, however, hydrogenation comes to an end prior to taking up the calculated amount of hydrogen, according to our investigations, hydrogenation may be complete (provided a sufficient quantity of catalyst is present), although the amount of hydrogen is taken up from the catalyst, no decrease of hydrogen content of the gas area being perceptible. It can be seen in Fig. 4 that acetone does not belong to type "A" of substrates with either of the catalysts applied, although it approached type "A" with catalyst 5 whilst it shifted to type "C" with catalyst 8. Fig. 5

discloses that benzophenone pertains to type "A" with catalysts 5 and 8, approximating type "C" with catalyst 1. and meanwhile showing characteristic curves of type "B" as well (*e. g.* with catalysts 2, 3 and 4).

With various model compounds, in general, catalysts prepared at 50° and treated with alkali (sodium hydroxide) for 50 minutes proved to disclose the maximum activity.

2. Nature and quantity of alkali applied

The optimum amount of alkali was the double value of the weight of the alloy, applied as a 20% solution.

We also examined [15] how the properties of catalyst change when, in place of sodium hydroxide, other alkalies (as potassium hydroxide, sodium carbonate, potassium carbonate or a mixture of these alkalies) are used for the extraction of aluminium (Table 2). The optimum temperature of extraction

Table 2
Conditions of preparation and characteristic data of catalysts

Number of catalyst	Alkali applied	Duration (hours)	Temperature (°C)	Duration (hours)	Temperature (°C)	Temperature (°C)	Alkali applied	Content of Ni %
		of addition of alkali		of extraction		of subsequent treatment for 20 mins.		
1	NaOH	1	23—30	1	50	—	—	89,8
2	KOH	1	20—30	1	50	—	—	62,3
3	KOH	1	15—20	1	25	—	—	69,0
4	KOH	1	10—20	3	25	—	—	70,8
5	K ₂ CO ₃	1	15—20	2,5	50	—	—	63,5
6	K ₂ CO ₃	1	50	2,5	80	—	—	59,5
7	K ₂ CO ₃	1	50	2,5	50	50	KOH	71,6
8	K ₂ CO ₃	1	50	2,5	50	80	KOH	80,9
9	K ₂ CO ₃	1	50	2,5	50	80	NaOH	70,8
10	Na ₂ CO ₃	1	100	8	100	100	NaOH	69,5
11	Na ₂ CO ₃	1	100	6	100	100	NaOH 30 mins.	67,0
12	Na ₂ CO ₃	1	100	5	100	100	KOH	62,8
13	NH ₄ OH	at once	—	20	100—150	60	NaOH 30 mins.	36,4
14	NH ₄ OH	at once	—	20	100—150	—	—	60,8

proved to be 50° with sodium hydroxide, 25° with potassium hydroxide, 100° with sodium carbonate and 50° with potassium carbonate, which may be in correlation to the strength of the bases. The duration of extraction also varied :

2,5 hours were required with potassium carbonate against 5—6 hours with sodium carbonate. By an adequate choice of the conditions of preparation, it is possible to produce with potassium hydroxide, and particularly with potassium or sodium carbonate, Raney-nickel preparations of activity exceeding that produced with sodium hydroxide of optimum effect. It can be seen in Fig. 6 that in the case of eugenol; we attained with Raney-nickel (curve 1)

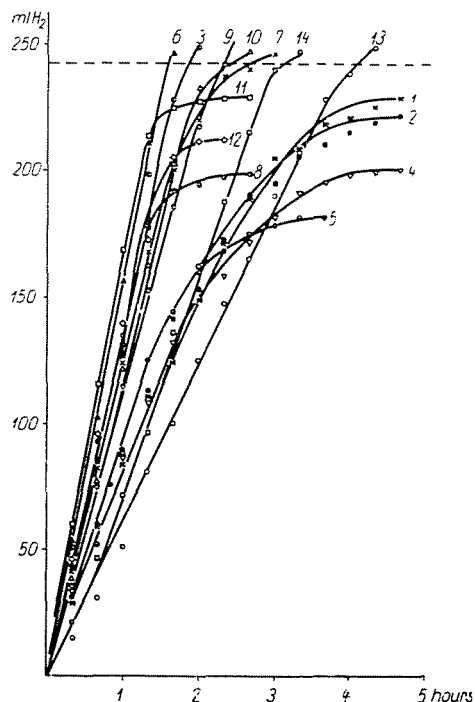


Fig. 6. Hydrogen uptake of eugenol in the presence of catalysts prepared with various alkalis (numbering of catalysts given in Table 2)

an increase of activity nearly identical to that of substrates of type "A" (several catalysts, as 13, 14, 7, 10, 9, 3 and 6 proved to be more active). The curves of hydrogen uptake of nitrobenzene, a substrate completely belonging to type "C" according to the data of Fig. 1 (in a nitrogen atmosphere), with catalysts prepared with various alkalis shown in Fig. 7 indicate that nitrobenzene behaves with catalysts 3 and 8 as a substrate of type "A" whilst with catalyst 4 and with Raney-nickel (curve 1) just so as a substrate of type "B". Further, it can be seen that the substrate disclosing in a nitrogen atmosphere a nature of type "C", behaves in a hydrogen atmosphere as one belonging to type "B" and can be converted into one pertaining to type "A" by choosing an adequate catalyst.

Variations in activity may presumably be due to the fact that, depending on the nature of alkali applied as extracting agent, various residual amounts of aluminium are present in the catalysts as metallic aluminium, oxide or oxide-hydrate (Table 2) and that, in connection with these differences, also the content of hydrogen of the catalysts varies.

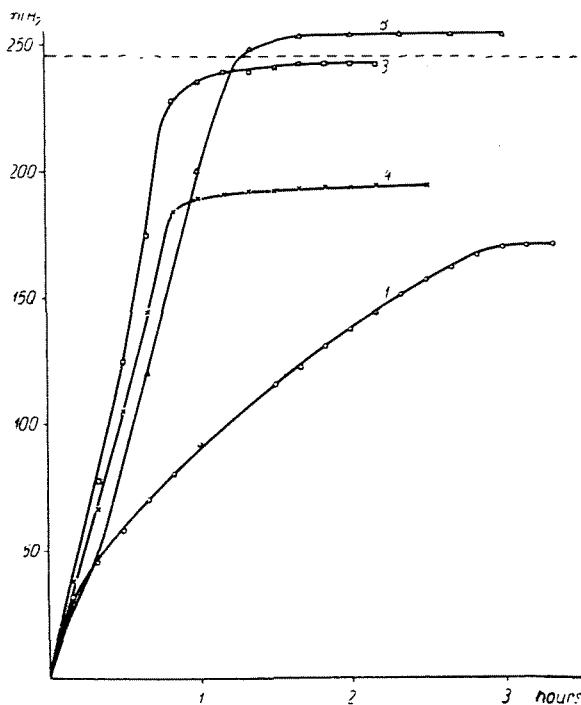


Fig. 7. Hydrogen uptake of nitrobenzene in the presence of catalysts prepared with various alkalies (numbering of catalysts given in Table 2)

3. Composition of alloy

Particularly interesting results were obtained when nickel was alloyed with cobalt and chromium [16]. On increasing the content of cobalt and chromium, respectively, of the alloy, it was easier to remove alkali by washing the catalyst, *i. e.* the quantity of water required, for washing together with the capability of the catalyst of binding alkali appreciably diminished (Table 3).

On investigating the activity of this type of catalysts it was found that catalysts of cobalt content below 50% disclosed, with each of the tested model substances, activities higher than that of Raney-nickel (Fig. 8). The optimum content of cobalt ranged from 3 to 20%, depending on the nature of model substance. In this range, each catalyst possessed an activity over that of

Table 3

Wash-water quantities as function of the cobalt and chromium content (referring to 125 g of catalyst)

Number of catalyst	Content of cobalt %	Quantity of wash-water required l
1	0	50
2	1,14	25,0
3	3,01	17,0
4	16,30	6,0
5	41,70	4,0
6	66,60	4,5
7	93,60	4,0

Number of catalyst	Content of chromium %	Quantity of wash-water required l
1	0,0	50
8	3,80	8,5
9	9,15	4,5
10	46,60	3,0

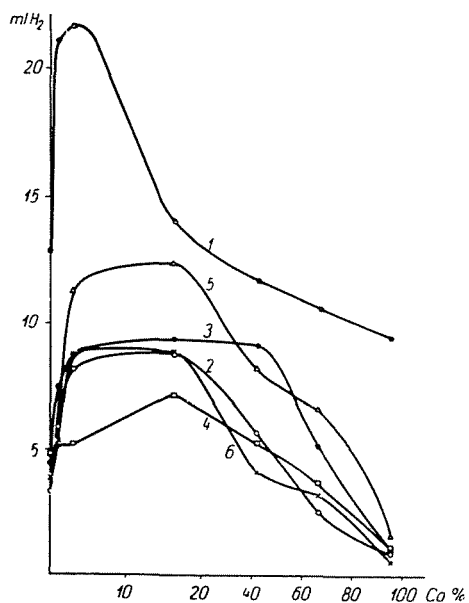


Fig. 8. Activities of catalysts of various cobalt content with various model compounds. 1 : eugenol, 2 : acetone, 3 : acetophenone, 4 : benzophenone, 5 : benzaldehyde and 6 : benzyl cyanide

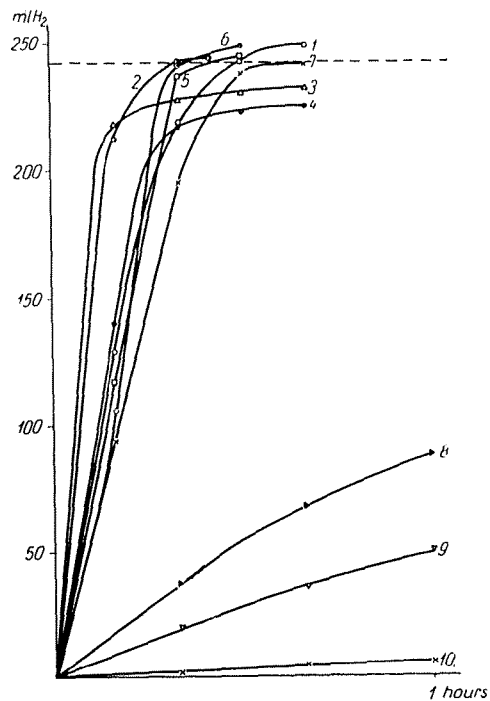


Fig. 9. Hydrogen uptake of eugenol with catalysts of various content of cobalt and chromium (numbering of catalysts given in Table 3)

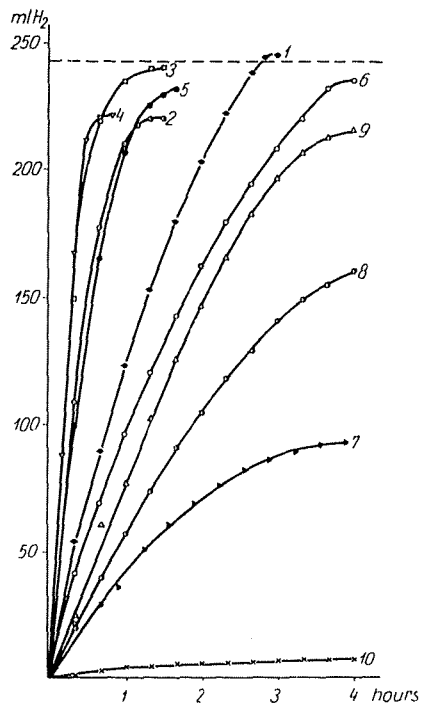


Fig. 10. Hydrogen uptake of acetone with catalysts of various content of cobalt and chromium (numbering of catalysts given in Table 3)

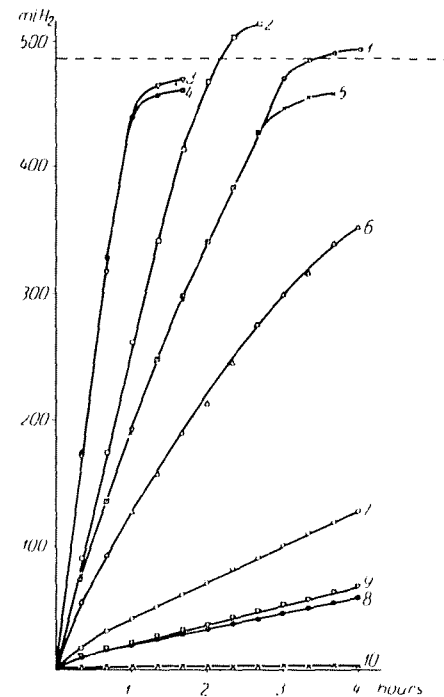


Fig. 11. Hydrogen uptake of benzyl cyanide with catalysts of various content of cobalt and chromium (numbering of catalysts given in Table 3)

Raney-nickel, sometimes showing activities 2,5-times as high as Raney-nickel. Catalyst of 16,3% cobalt content proved to be the most active with the majority of the model substances, with the exception of eugenol where catalyst of 3% cobalt content had optimum activity.

On raising the content of cobalt over 20%, activities diminished. Around a cobalt content of 60%, activities approached that of Raney-nickel, whilst over 60% they decreased to values below those of Raney-nickel. Pure Raney-

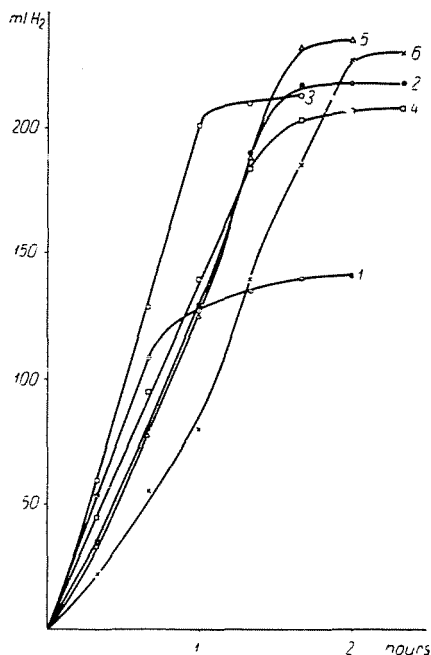


Fig. 12. Hydrogen uptake of nitrobenzene with catalysts of various titanium content; 1: Raney-nickel, 2: 2,4% of titanium, 3: 3,8% of titanium, 4: 5,3% of titanium, 5: 2,4% of titanium + 0,001 mole of dimethylaniline, 6: 3,8% of titanium + 0,001 mole of dimethylaniline

cobalt disclosed minimum activity. It can as well be seen that the optimum activities of catalysts may show broader bands for certain substrates whilst possessing narrower ones for other ones. Figures 9, 10 and 11 disclose the data of hydrogenation for some model substances.

According to the results of investigations not yet published or still in progress, the stability and activity of hydrogen adsorbed by catalysts may appreciably be affected by varying in minute amounts the metals alloyed with Raney-nickel.

The activity of catalysts of Raney-nickel alloyed with chromium ranged, with the examined model compounds, below that of pure Raney-nickel (Figures 1, 9, 10 and 11). The results do not agree with the observations of PAUL [17]

who found that chromium is capable of increasing the activity of Raney-nickel.

On alloying Raney-nickel with some per cents of titanium, similarly to cobalt, favourable effects were observed (Fig. 12). On one hand, the activity and effectiveness of the catalyst rose, and, on the other hand, the behaviour of substrates shifted in the direction of type "A", as shown in Fig. 12 by the example of nitrobenzene.

II. Raising the effectiveness of ready-made catalysts

The behaviour of ready-made catalysts in hydrogenation reactions, as can be seen from column II of Table 1, is affected by various additions.

Effect of added bases

Various basic substances and bases, respectively, are known since long in literature as additions of a favourable effect when hydrogenating

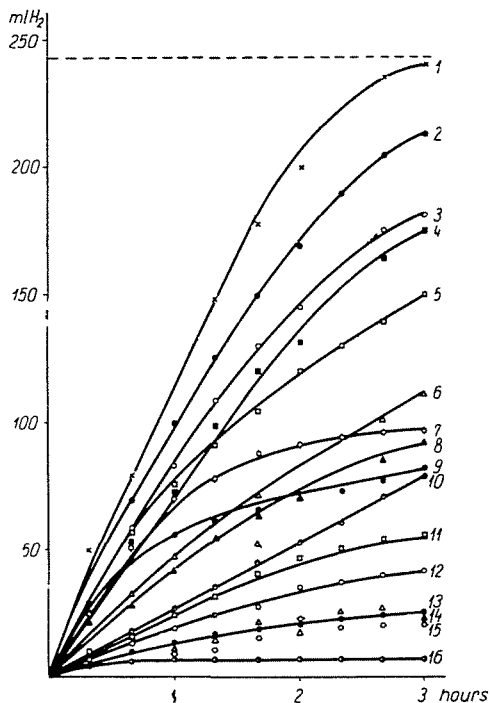


Fig. 13. Hydrogen uptake of acetone in the presence of various organic bases. 1 : dimethylaniline, 2 : triethylamine, 3 : without any additions, 4 : piperidine, 5 : methylaniline, 6 : diphenylamine, 7 : diethylamine, 8 : p-toluidine, 9 : aniline, 10 : quinoline, 11 : o-toluidine, 12 : m-toluidine, 13 : triethanolamine, 14 : diethanolamine, 15 : pyridine and 16 : ethylenediamine

carboxyl groups. Of organic bases, triethylamine was considered to be efficient. In our earlier experiments [18], the effect of a number of aliphatic, cyclic and aromatic amines and inorganic bases were investigated. Under the experimental conditions applied, dimethylaniline proved to possess effects more favourable than those of the mentioned bases. Its optimum concentration was 0,1—0,01 mole, with respect to the substrate. Besides, we found that no correlation exists between the promoter effect and the dissociation constant

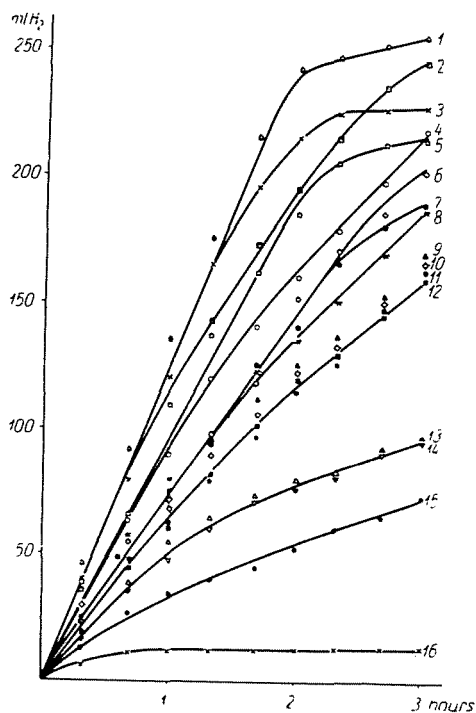


Fig. 14. Hydrogen uptake of benzophenone in the presence of various organic bases. 1: dimethylaniline, 2: methylaniline, 3: triethylamine, 4: diethylamine, 5: without any additions, 6: aniline, 7: diphenylamine, 8: triethanolamine, 9: o-toluidine, 10: ethylenediamine, 11: quinoline, 12: piperidine, 13: p-toluidine, 14: m-toluidine, 15: diethanolamine and 16: pyridine

of the bases. However, certain correlations manifested themselves between the effect and the structure of amines, in that an approximately monotonous increase of effect was observed in the series: primary, secondary, tertiary amines.

The effect of several organic bases on catalysts of various activity was examined as well [18]. According to the experimental results, the organic bases tested disclosed certain buffer effects in that they were more active with weaker catalyst and less active with stronger ones. According to our

recent unpublished investigations, this effect may be attributed to the fact that the activity of hydrogen on the catalyst is affected by these additions. In this way, the type of catalyst changes, being shifted more or less in the direction of type "A".

Effect of added acids

Up to the present, only bases are known in literature as promoters whilst, in the case of Raney-nickel, acids are considered to be catalyst poisons. However, our experiments conducted with oxalic, acetic, chloroacetic, tri-

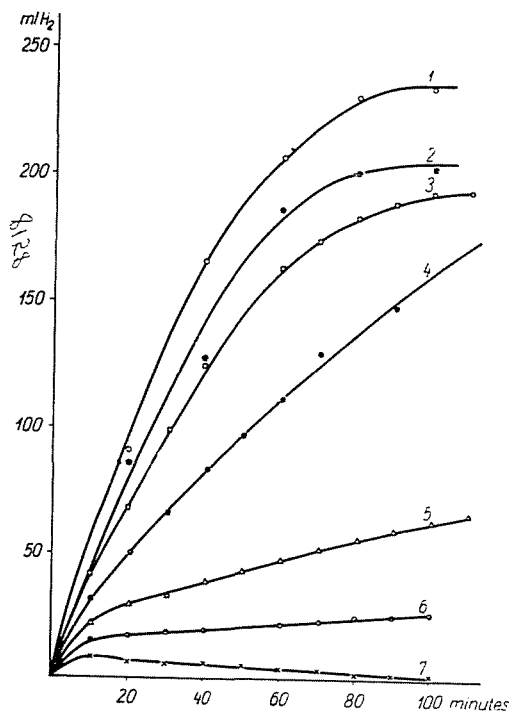


Fig. 15. Hydrogen uptake of acetone in the presence of various quantities of acetic acid. 1: 0,0001 mole, 2: 0,001 mole, 3: without any acetic acid, 4: 0,01 mole, 5: 0,1 mole, 6: 1 mole, 7: 5 moles of acetic acid with respect to the substrate

chloroacetic and hydrochloric acids [19] proved that in low concentrations (10^{-3} to 10^{-5} moles, with respect to the substrate) acids act, in general, as promoters, similarly to bases. Poisoning effects only appear in higher concentrations.

Also in this case two types of effect occur. In certain instances, mainly with catalysts of lower activity, it is possible to raise the activity, whilst in other cases a shift to type "A" is observable (e. g. Fig. 15). This effect was

perceptible with nitrobenzene (Fig. 16), further with benzophenone and acetophenone as substrates. In the case of both latter model compounds, the amount of hydrogen taken up slightly exceeded the calculated value.

In these experiments, already certain correlations could be established between the strength and the effect of acid. Namely, of stronger acids, in general, smaller amounts are required to attain similar effects.

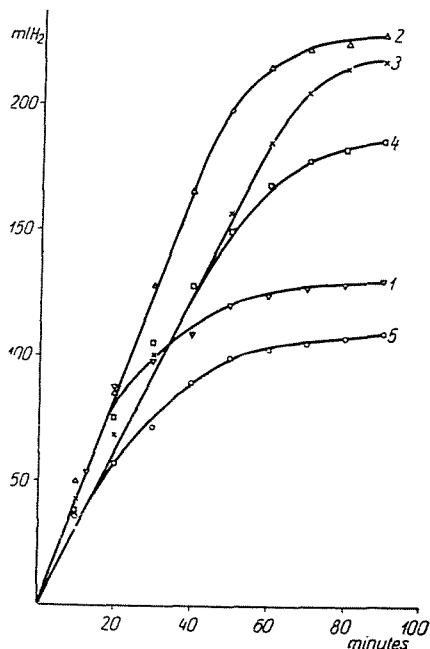
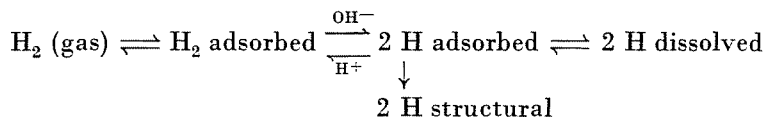


Fig. 16. Hydrogen uptake of nitrobenzene in the presence of monochloro-acetic acid. 1: without any addition, 2: 1,0 mole, 3: 2,0 moles, 4: 0,1 mole and 5: 0,01 mole of monochloroacetic acid with respect to the substrate

The "sensitivity" of substrates on various acids proved to be different, *e. g.* the hydrogen uptake of carboxyl groups was, in general, strongly inhibited by the presence of 0,1 mole of acid, with respect to the substrate, in the case of acetone, whilst the same quantity of acid was nearly inefficient with eugenol and acted as promoter in the case of nitrobenzene or benzyl cyanide. In certain cases this phenomenon points to the possibility of selective hydrogenation. *E. g.* the hydrogenation of eugenol was not perceptibly influenced by the presence of quantities of acid (5,0 moles) which, in a 50-times lower concentration (0,1 mole), markedly poisoned acetone as substrate.

Presumably, the inhibiting effect of acids may be interpreted by the fact that they loosen the bonds of hydrogen on the catalyst or even dissolve the sites of higher activity, become strongly sorbed and thus, when they are

present in appreciable quantities, they may remove hydrogen atoms from the surface of catalyst. This phenomenon was observed by us in some cases when the system only consisted of catalyst, solvent and acid. The effect of bases and acids is explained by SOKOLSKY [20] by presuming that the sorption of hydrogen by the catalyst is promoted by bases and inhibited by acids. Thus, the following equilibria should be considered in the system :



Effect of added salts

The effect on Raney-nickel of various salts of a number of different metals of an active nature (as Ni, Co, etc.) and of an inactive nature (as Na) from the aspect of hydrogenation, was examined, applying common and complex salts, respectively, combined with various anions [21, 22].

The effect of added salts proved to be rather identical to that of acids in that a poisoning action was observed in higher concentrations whilst a pro-

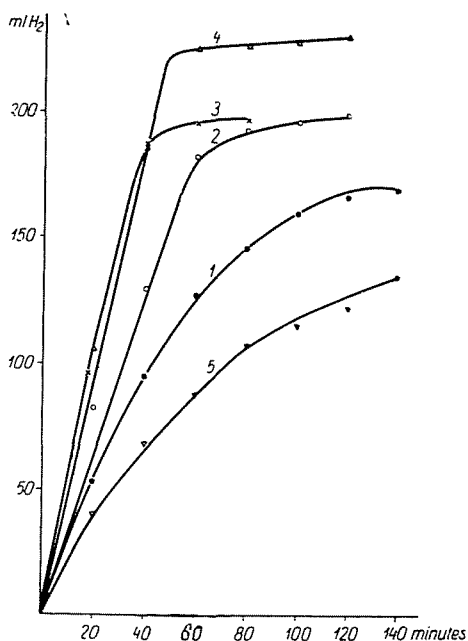


Fig. 17. Hydrogen uptake of benzophenone in the presence of manganese nitrate 1 : without any addition, 2 : 0,0001 mole, 3 : 0,001 mole, 4 : 0,01 mole and 5 : 0,05 mole of manganese nitrate with respect to the substrate

moting effect was disclosed in lower concentrations. No sharp differences were perceptible between the effect of salts of different metals (although manganese salts proved to be more active), or between the action of common salts and complex compounds. However, it was observed that among anions, nitrates showed the optimum effects with all of the metals tested.

The effect of added acids and salts is more easily perceptible when applying catalysts of reduced or low activity, as their influence manifests itself more markedly (Fig. 17). The effect of salts is attributed by SOKOLSKY [20] to the fact that the approach of the substrate by the catalyst is impeded, due to the sorption of salts present.

On the basis of our experiences made with Raney-nickel, our investigations were extended to other nickel catalysts as well, particularly to the mixed catalysts of active nickel and magnesium oxide on nickel and magnesium formate base, the preparation of which was evolved by LANGENBECK [23] and RIENÄCKER [24].

Our previous experiments [25] proved that activities can be raised also in this case by introducing cobalt in that the catalytic activity plotted against quantities of introduced cobalt discloses an optimum. Further marked increases of activity may be attained when, at the preparation of catalyst, the conventional hydrogen current is combined with ammonia. In the latter case, ammonia acts as a promoter. This appears striking since the addition of ammonia was found to be inefficient.

Experiments in this direction are in progress as well.

Summary

The behaviour of Raney-nickel as catalyst was examined in various hydrogenation reactions

- a) by varying the conditions of preparation, and
- b) by applying various additions.

The observed phenomena, *i. e.* the various behaviours of catalyst, were classified and evaluated on the basis of the changes in the content of hydrogen of the catalyst.

In accordance with literature, it was found that the behaviour of various substrates with the hydrogen of catalyst is different. Substrates are capable of taking up more or less hydrogen bound (sorbed) by the catalyst, depending on their affinity to this type of hydrogen. In this way, they may affect (decrease) the activity of catalyst during the hydrogenation process.

Our investigations pointed out that by varying the conditions of preparation of Raney-nickel catalysts or by adding various substances (as salts, bases or acids) to the reaction mixture, the behaviour of substrates with the hydrogen sorbed by the catalyst can be influenced to a certain extent.

Our investigations with mixed catalysts proved that it is possible to further increase the activity of catalysts by introducing, in addition to nickel, also other metals (as cobalt) or by treating the catalysts, during their preparation, with ammonia in an adequate way.

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