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ACTIVE STRUCTURE OF A NICKEL-HYDROGEN CATALYST

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ACTIVE STRUCTURE OF A NICKEL-HYDROGEN CATALYST

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The present investigation reveals the stochiometric ratio between the consumption of poison and the quantity of promoter - in this case, dissolved hydrogen removed from the catalyst - and establishes the linear dependence of the residual activity of the catalyst on the residual quantity of H_{dis} [see below] in it, thus attesting to the uniformity of its elementary active structures.

As N. D. Zelinskiy (1) established for the first time, when nickel is deposited on aluminum oxide its cracking action is decreased while its selectivity in respect to hydrogenation-dehydrogenation reactions is considerably increased. This discovery has made it possible in many cases to employ nickel instead of costly noble metal catalysts. Nickel catalysts will be even more widely used if their activity and stability can be increased. It is therefore necessary to devote further research to the nature of the active structure of a nickel catalyst, particularly its skeleton form, whose activity frequently approaches the activity of Pt and Pd.

Earlier (2) we showed that the skeleton nickel catalyst is a type which is promoted by hydrogen. The removal of this hydrogen brings about the complete deactivation of the catalyst; consequently, there are no other promoting admixtures in it. It was also found possible (3) to distinguish chemically between two forms of hydrogen bonds in the nickel catalyst with the aid of specially selected easily hydrated organic compounds: some of these compounds are capable of removing only surface-adsorbed hydrogen (H_{ads})

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while others remove dissolved hydrogen (H_{dis}) as well. In this way it was possible to establish that H_{dis} alone is the necessary component part of the active structure of the catalyst. The catalyst being investigated can therefore be correctly called nickel-hydrogen (Ni_H, the subscript denoting the nature of the promoter), in order to emphasize the importance of both components of the catalyst which together form its active structures.

In the specimen of catalyst which was investigated (prepared from extremely pure metals, carefully leached out, and well washed), which was obtained by the leaching out of a 50% Ni-Al alloy at 105°C, adsorbed and dissolved hydrogen and nickel were in the following atomic proportions:

$$H_{ads} : H_{dis} : Ni = 1 : 3.5 : 9$$

Since the number of atoms of structural hydrogen in the nickel catalyst was very great, altogether only 2-3 times less than the number of atoms of the metal in which they were dissolved, there was a basis for regarding the solution of hydrogen in metal as a volumetric phenomenon.

The number of atoms of H_{dis} considerably exceeds the number of atoms of H_{ads}. Evidently the simplest active catalytic structure includes several atoms of H_{dis}. We have settled on considering the complex which consists of a certain number of atoms of nickel and N_{dis} as the simplest element of the active structure of the catalyst which is capable of adsorbing one atom of hydrogen and transferring it to the substance to be hydrated. The question arises as to whether all elementary structures of the given specimen of catalyst are identically promoted and equally active.

The quantity H_{ads} (referred to a unit weight of catalyst) characterizes the concentration of active structures in the catalyst, while the ratio $\frac{H_{dis}}{H_{ads}}$ indicates the number of atoms of H_{dis} in each of them under the condition that they are identically promoted. Active structures which are identical in composition must also be uniform with respect to activity. Therefore, if the catalyst is subjected to depromotion by the gradual removal of H_{dis} from it, the number of H_{ads} in it will also be reduced at the same time, while the value of the ratio $\frac{H_{ads}}{H_{dis}}$ will not change. Consequently,

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a linear dependence must be observed between the activity of the catalyst and the residual content of structural hydrogen in it.

In order to test this position we conducted two series of experiments. In the first of these we investigated the variation in the adsorption activity of the catalyst in relation to hydrogen as specific quantities of H_{dis} were progressively removed from the catalyst.

The experimental methods were similar to those described previously (3). The hydrogenation reaction was carried out in a flask fastened to a powerful rocking device. Dissolved hydrogen was removed from the catalyst with the aid of the poison 1-methylcyclopentene-1 (MTsP) in the absence of free hydrogen. The space over the liquid being hydrogenated in the flask was filled with nitrogen.

The poison was introduced into the flask in a quantity corresponding to the volume of H_{dis} to be removed. The more H_{dis} required to be removed, the greater was the quantity of poison used. All experiments were conducted at 20° with the same specimen of freshly prepared skeleton nickel catalyst. One ml of nickel paste (2.33 g) contained 47.4 ml of H_{ads} and 177 ml of H_{dis}. Experiments were 90 min in duration. Preliminary experiments established that this amount of time was completely sufficient for the quantity of poison introduced to be fully hydrogenated under the given conditions at the expense of hydrogen dissolved in the catalyst.

The results obtained in these experiments are cited in Table 1. Along the ordinate axis in Figure 1 are laid out the volumes of hydrogen which the catalyst is capable of adsorbing from the gaseous phase. They characterize its residual activity in dependence on the residual quantities of H_{dis} in the catalyst, which are laid out along the abscissa. It follows from Figure 1 that, the more H_{dis} extracted from a given portion of the catalyst, and the more broken down the active structure, the less is its capability to adsorb hydrogen. Finally, after removal of all H_{dis} the catalyst becomes completely deactivated.

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It may be expected that the activity of a catalyst, as determined by the usual kinetic method, is expressed by an analogous dependence on the number of residual active structures in it; and this has been verified. In the second series of experiments (Table 2) vinylbutyl ether was used as a poison to depromote the active structures of the catalyst. The duration of treatment of the catalyst with ether in the absence of free hydrogen (in the gaseous phase over the liquid in the flask was nitrogen) was 60 min, and the temperature of the experiment was 20°. After removal of a specified quantity of H_{dis} from the portion of catalyst in question, the nitrogen was drawn out of the flask and the catalyst was saturated with hydrogen for 15 min at 20°. Then 0.23 g of allyl alcohol dissolved in benzene was introduced and the agitation continued. Thus each portion of catalyst was subjected twice in the course of the same experiment to treatment with substances capable of being hydrogenated: first vinylbutyl ether for the purpose of breaking down part of the active structures by depromotion, and then allyl alcohol, which, as was shown in our work with K. Rudneva, is incapable of promoting, for determination of the residual activity of the catalyst. The quantity of H_{dis} extracted from the catalyst was determined from the value of the weighed portion of ether used. The degree of hydrogenation of allyl alcohol after 15 min at 20° in this case characterized the residual activity of the catalyst after the breaking down of part of its active structures. From Figures 1 and 2 it is clear that in both series of experiments the linear dependence of residual activity of the catalyst on the quantity of H_{dis} it contained was preserved. If Figures 1 and 2 are superimposed, it will be seen that the straight lines obtained in both series of experiments are mutually parallel. They intersect the abscissa at the same angle, whose tangent has the value of the ratio $\frac{H_{ads}}{H_{dis}} = 0.27$, i.e., $H_{ads} : H_{dis} = 1 : 3.7$. Thus from the kinetic data it is possible to determine the number of atoms of H_{dis} in the simplest structure of the catalyst.

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It is evident from Tables 1 and 2 that both poisons (vinyl ether and cyclopentene) are consumed during the process in equimolecular quantities which bear a stochiometric relation to the quantities of H_{dis} being progressively removed.

Bredig and Allolio (4) remarked that until it was possible to investigate separately the influences of admixtures and of the structure of the crystalline lattice it would be impossible to evaluate each's role in the activity of a nickel catalyst.

Now it is possible to answer this question. If the activity of the catalyst is determined by the presence in it of a promoting admixture and is not connected with the structure of the crystalline lattice, then Ni_H and dehydrogenated nickel must have identical structures. To verify this position we took x-ray photographs of the nickel catalyst before and after its complete dehydrogenation (Figure 3). Vinylbutyl ether was used as the depromoting agent. The depromotion took place at room temperature by the methods described previously.

The x-ray photographs, taken by Professor A. M. Rubinshteyn, to whom we here express our thanks, were exposed with radiation from iron at 30 kv and 10 ma. Specimens were prepared for exposure under conditions which excluded the possibility of contact of the nickel with air. Canadian balsam was added to the nickel, which was dispersed in alcohol; after evaporation of the greater part of the alcohol in the cold, specimens of a cylindrical shape were prepared for exposure from the solidifying paste. In no stage of the preparation of the samples was there heating or contact of the metal with air.

Results of Measurements. The obtained x-ray photographs are shown in Table 3. The number of lines in the photograph is 10. From the character of the distribution of the lines it is evident that both the active specimen, containing H_{dis}, and the completely dehydrogenated, inactive specimen of the nickel catalyst have face-centered lattices.

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Discarding images under small angles, which yield slight deviations, and using images beginning with 022 as the basis, we obtain the parameter a = 3.49 Å, which is characteristic for the cubic structure of nickel.

CONCLUSIONS

1. The results of our investigation show that both active Ni_H and the inactive (dehydrogenated) form possess the same crystalline structure, namely, cubic.

2. We found a stochiometric ratio between the consumption of poison and the quantity of the promoter H_{dis} which was removed from the catalyst. By treating the catalyst with specific quantities of poisons (vinylbutyl ether or 1-methylcyclopentene-1) its activity may be lowered to any predetermined value.

3. We established the linear dependence of the residual activity of the catalyst on the residual quantity of H_{dis} in it. This dependence attests to the uniformity of the active structures in the specimen of skeleton nickel catalyst under investigation; these active structures are at the same time the source and measure of the catalyst's adsorption and catalytic activity.

4. The uniformity of the structures in respect to activity permits the assumption to be made that they are also uniform as to composition. Together with active structures of composition Ni_xH_y, the catalyst probably also contains a certain quantity of dehydrogenated and therefore inactive ballast nickel.

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TABLE 1

Effect of Different Quantities of the Poison 1-Methylcyclopentene-1 (MTsP) on the Change in Activity of a Nickel Catalyst

Amt of MTsP used for removal of H_{dis} (in g)	Amt of H_{dis} removed from catalyst (in ml)	Amt of H_{dis} remaining in catalyst (in ml)	Limit of saturation of catalyst with hydrogen (H_{ads}) (in ml)
0	0	177	47.4
0.131	35	142	38.6
0.319	85	92	25.4 (24.7) *
0.507	135	42	10.2 (11.0)
0.791	177	0	0.2 (0.1)

* In parenthesis are cited results obtained in parallel experiments.

TABLE 2

Effect of Different Quantities of the Poison Vinylbutyl Ether on the Change in Activity of a Nickel Catalyst in the Hydrogenation of Allyl Alcohol

Amt of the ether used for removal of H_{dis} (in g)	Amt of H_{dis} removed from catalyst (in ml)	Amt of H_{dis} remaining in catalyst (in ml)	Degree of hydrogenation of allyl alcohol (in %)
0	0	177	96.6 (97.4) *
0.156	35	142	79.2 (78.1; 80.0)
0.380	85	92	49.4 (51.3; 50.1)
0.603	135	42	22.2 (23.8)
0.735	165	12	8.3 (7.9)
0.791	177	0	0.1 (0.1)

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TABLE 3

Data by Calculation from X-Ray Photographs

Line No.	hkl	For nickel containing H_{dis}		For dehydrogenated nickel	
		$\sin^2 Q$	a	$\sin^2 Q$	a
1	111 β	0.203	3.42	0.204	3.42
2	111 α	0.246	(3.38)	0.246	(3.38)
3	002 β	0.261	3.44	0.262	3.44
4	002 α	0.317	3.44	0.329	3.40
5	022 β	0.524	3.42	0.523	3.43
6	022 α	0.624	3.47	0.624	3.47
7	113 β	0.699	3.48	0.695	3.49
8	222 β	0.760	3.49	0.760	3.49
9	113 α	0.845	3.49	0.844	3.49
10	222 α	0.922	3.50	0.927	3.50

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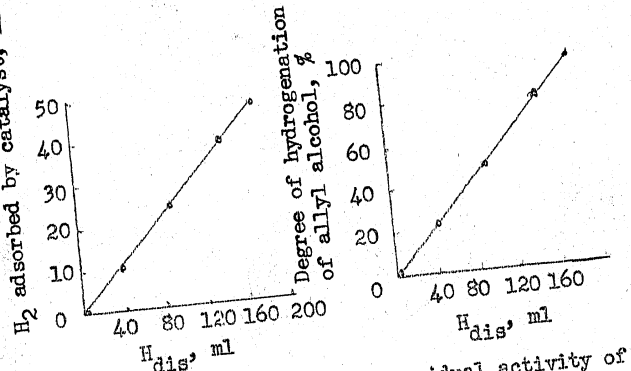

Figures 1-2. Linear dependence of residual activity of nickel catalyst on residual quantity of H_{dis} in it.

Editorial: reproduce photo, opposite p 143, text, if possible.

Figure 3. X-ray photographs of specimens of nickel catalyst: I - active, containing H_{dis}; II - inactive, dehydrogenated; III - obtained by reduction of nickelous oxide.

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