HYDROGENATION OF SUCCINIMIDE TO 2-PYRROLIDONE

II. CATALYSTS FOR THE HYDROGENATION OF SUCCINIMIDE*

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The catalytic hydrogenation of succinimide in isopropanol in the presence of metals on various supports is examined. It is found that the metals have the following order of activity: Pt > Co > Ni > Cu. The nature of the support has a considerable effect on the course of the reaction and it is also found that there is no correlation between the activity of a catalyst and its specific surface area. We found that, in alcoholic solutions of succinimide, an oxidation-reduction process of the Meerwein–Ponndorf type occurs between the substrate and the solvent. Some aspects of the hydrogenation reaction are discussed in the light of these observations.

The catalytic hydrogenation of dicarboxylic imides has not been investigated very much. The contradictory and scanty data in the literature are mainly preparative, and are concerned with the reduction of substituted succinimides and phthalimides [1-4]. The reducing agents usually employed are lithium aluminum hydride, lithium borohydride, or hydrogen over a skeletal nickel catalyst. The patent literature [5] also describes the use of Co, Pt, Pd, and Ru as hydrogenation catalysts.

We have shown previously [6] that hydrogenation of succinimide (I) over skeletal nickel proceeds readily in isopropanol, n-butanol, and isobutanol. This paper reports the results of an investigation into the effects of the type of catalyst on the course of the reaction and on its mechanism. Experiments have been carried out concerning the hydrogenation of I in 2-propanol over nickel oxide, skeletal nickel, Ni, or Co on various supports, aluminum-platinum, and copper chromite catalysts. The methods used in [6] were employed.

Examination of the results (see Table 1) shows that the activity and selectivity of the catalysts depends on the metal and on the nature of the support. The specific activities of the metals, per g-atom (all on alumina) were found to be in the following order: Pt > Co > Ni. The results obtained with nickel and copper chromite hydrogenation catalysts show that nickel is more active than copper.

The effect of the support on the reaction is very apparent in the results. Thus, the catalysts Ni–SiO_2 and Ni–Al_2O_3, or Co–SiO_2 and Co–Al_2O_3, obtained by impregnating supports with the same specific surface and the same metal content, differ considerably in their activity. The hydrogenation of I also occurs differently on nickel-chromium and on nickel-kieselguhr. Among the catalysts investigated on a range of supports, the most acceptable for the hydrogenation of I to 2-pyrrolidone (III) were nickel and cobalt on alumina. Attention is drawn to the lack of correlation between the value of the specific surface and the activity of the catalysts.

Analysis of our present and previous results [6] permits some aspects of the mechanism of the reaction to be discerned. In particular, it is interesting to compare the presence of hydrogenated acetone condensation products (methyl isobutyl carbinol and 2-methylpentane) in the hydrogenation products of I in 2-propanol, with the fact that the rate of uptake of hydrogen in tert-butanol is much lower than in the primary

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*For part I, see [6].

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TABLE 1. Influence of the Nature of the Catalyst on the Hydrogenation of Succinimide

Catalyst	Specific surface*, m^2/g	Active metal content, weight %	Temp of experiment, °C	Amount reacted: H_2, % of theory	Amount reacted: I, % of theory	Yield of III, %	Activity of catalyst, liters of H_2/(g-atom · min)
Skeletal nickel	54	75.9	200	71.8	53.7	38.1	6.0
			230	88.0	62.2	42.8	10.1
Nickel oxide	5† [7]	100	260	—	10.8	4.1	—
Nickel on alumina	78.5 (153)	24.6	240	102.1	100	71.8	12.6
			260	105.1	100	64.1	23.1
Nickel on chromium oxide GOST 12410-66	142	48.3	240	69.1	76.4	48.8	3.9
			260	92.9	100	37.1	8.1
Nickel on kieselguhr	94—100† [8]	51.7	260	45.3	61.8	36.5	10.3
Nickel on silica	(150)	23.7	260	45.5	46.6	26.4	3.2
Aluminum—platinum AP-56	130—150† [9]	0.55	220	59.6	76.6	35.0	595
			240	80.6	100	35.7	758
Cobalt on pumice from the Lisichansk chemical combine	0.4—5† [10]	22.3	260	53.3	78.1	45.8	3.7
Cobalt on alumina	93 (153)	22.4	200	90.6	87.0	63.2	11.7
			240	109.0	100	51.0	29.6
Cobalt on silica	(150)	23.0	260	98.3	100	48.1	11.3
Copper—chromium [14]	52	65.0	260	42.1	50.4	32.7	3.1

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*Specific areas of the supports are given in parentheses.

†Values for the catalyst surfaces are taken from the literature.

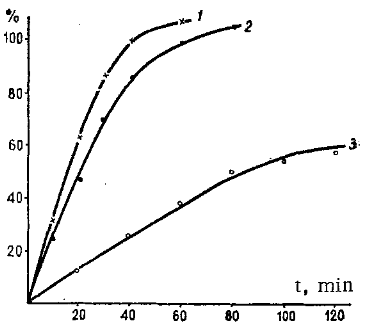
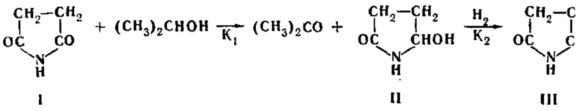


Fig. 1. Relationship between amount of hydrogen absorbed and time, as % of theory, for the hydrogenation of succinimide over skeletal nickel at 230° C and 200 atm: 1) in 2-methylpropanol, 2) in butanol, and 3) in tert-butanol.

butanols (Fig. 1). This indicates that, in the hydrogenation of I in solution in any primary or secondary alcohol, in addition to the reduction of I, oxidation of the alcohol to the aldehyde or ketone, respectively, also occurs, and that these processes are interconnected. It is suggested that one of the reasons for the rate-enhancing properties of alcohols as solvents for the hydrogenation of I is the occurrence of a reversible oxidation-reduction process of the Meerwein-Ponndorf type [11]. The velocity of this reaction is very small, but it is increased substantially by the introduction of metal alkoxides into the system. This reaction probably results in the formation of 5-hydroxy-2-pyrrolidone (II), but the presence of this compound has not been observed. Attempts to synthesize II by reaction of I with 2-propanol at 260° C under a nitrogen pressure of 200 atm in the presence of various catalysts were not successful. Under these conditions, which are similar to the hydrogenation conditions, the reduction of I does not stop at II but, as a result of dehydrogenation of the alcohol, goes to completion. Among the reaction products, acetone and III were isolated and identified. The unsuccessful attempts to synthesize II show that it is highly reactive, and lead to the conclusion that it is of rate-limiting significance in the catalytic hydrogenation of I to III:



$K_1 \angle K_2$

Thus, introduction of substances which catalyze the rate-limiting stage must increase the over-all reaction velocity. Experiments were carried out on the reduction of I in 2-propanol over a nickel-on-kieselguhr catalyst, in the presence of various amounts of aluminum isopropoxide, which is one of the best homogeneous catalysts for the Meerwein-Ponndorf reaction [11]. The results given in Fig. 2 confirm the occurrence of an oxidation-reduction process between I and the alcohol, since addition of the alkoxide increases the initial reaction velocity. The results also explain the increased reaction velocity observed with aluminum-containing catalysts as opposed to the others used in the hydrogenation of I in primary

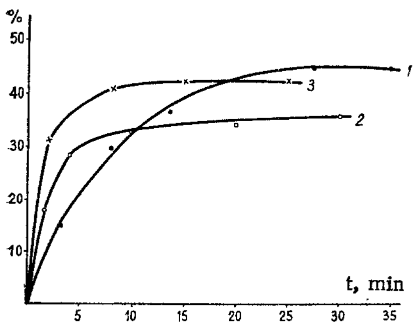


Fig. 2

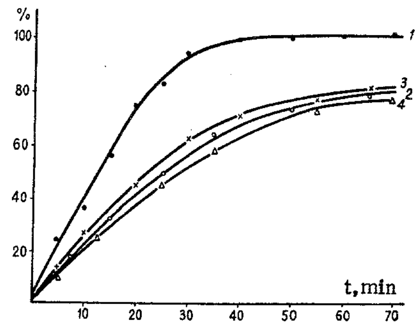


Fig. 3

Fig. 2. Hydrogen absorption curves in the hydrogenation of succinimide (0.25 mole) in 2-propanol over: 1) Ni–kieselguhr, 2) Ni–kieselguhr and 0.14 mole $Al(OR)_3$, and 3) Ni–kieselguhr and 0.28 mole $Al(OR)_3$.

Fig. 3. Hydrogen absorption curves in the hydrogenation of succinimide at 275 atm and 260° C, over: 1) $Ni-Al_2O_3$ in 2-propanol, 2) $Ni-Al_2O_3$ in 2-methyl-2-propanol, 3) $Ni-Cr_2O_3$ in 2-propanol, and 4) $Ni-Cr_2O_3$ in 2-methyl-2-propanol.

and secondary alcohols. Probably, as in the case with alkoxides, use of these catalysts causes the oxidation-reduction process between the substrate and the solvent to proceed at such a rate that it is no longer a rate-limiting process, as it is when other catalysts are used.

In order to show the special properties of aluminum-containing catalysts in relation to the solvent, the hydrogenation rates of I over $Ni-Al_2O_3$ and $Ni-Cr_2O_3$ in 2-propanol and 2-methyl-2-propanol were compared (Fig. 3). As expected, the rate of hydrogen uptake using the first catalyst was dependent on the nature of the alcohol, but for the nickel–chromium catalyst, it was the same in both solvents. Dependence of the hydrogenation rate on the solvent was also demonstrated with skeletal nickel catalysts containing aluminum.

EXPERIMENTAL

An electromagnetically driven autoclave of Vishnevsk construction [12] with a capacity of 0.5 liter was used in the work. The charge for all the experiments (except for those using Raney nickel) was the same: 25 g of succinimide, 150 g of 2-propanol, and 5 g of catalyst. When skeletal nickel was used, the quantity of catalyst was 2.5 g. The hydrogen pressure was held constant at 275 atm during the course of the hydrogenation (80 min). The amount of I and III present in the hydrogenation products was determined chromatographically. The methods used for the preparation of the reagents and for the analysis of the reaction products were similar to those described previously [6].

Skeletal nickel was prepared according to [13], and was washed with isopropanol before use.

Nickel oxide (nickel black) was obtained by the thermal decomposition of nickel nitrate hexahydrate ("pure for analysis, cobalt-free" grade) at 420-440° C. The oxide was reduced with hydrogen at 380-400° C (until no more water was given off) before use. The rate of passage of hydrogen was 60 ml/min per g of catalyst.

Nickel on alumina was prepared by moistening activated alumina (previously calcined at 550° C) with a saturated aqueous solution of nickel nitrate hexahydrate. Then it was calcinated at 420-440° C and reduced over a 4-hr period at 480-490° C and a hydrogen flow rate of 800 vol./vol. of catalyst. The catalysts used were saturated twice. The support used was alumina aluminate of specific surface 153 m^2/g (by thermal desorption of argon).

Nickel on silica was obtained by twice moistening silica gel (ShSM grad), having a specific surface of 150 m^2/g, with a saturated aqueous solution of nickel nitrate hexahydrate. The temperatures of ignition and reduction were 440° and 480° C respectively.

Cobalt on alumina and cobalt on silica were prepared in a manner similar to $Ni-Al_2O_3$ and $Ni-SiO_2$. The metal deposit was obtained by using cobalt nitrate hexahydrate ("pure for analysis" grade).

Samples of industrial catalysts (see Table 1) were reduced before use.

Experiments to determine the effects of aluminum isopropoxide ("pure" grade) were carried out at 260° C, hydrogen pressure 275 atm, and molar ratios of alcohol to succinimide to alkoxide of 2.5 : 0.25 : 0.14, and 2.5 : 0.25 : 0.28.

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