

**Studies on Catalytic Action, X.
A Comparative Study of the Catalytic Activity
of Reduced Copper, Reduced
Nickel and Thoria, I.**

By

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(Received February 22, 1924)

It has already been shown that reduced copper promotes the oxidation and reduction of alcohols, hydration and dehydration of alcohols and acid amides, polymerization and condensation of aldehydes, and molecular transformation of oximes¹. Reduced copper, as a catalyst of oxidizing and reducing action, was regarded as belonging to the same class as reduced nickel, and on the other hand it was compatible with thoria as a dehydrating and condensing agent.

According to one of the authors² (S. K.), reduced nickel acts in promoting dehydration, under certain conditions, as reduced copper does, though its activity being small, it can not compare with that in its oxidizing action.

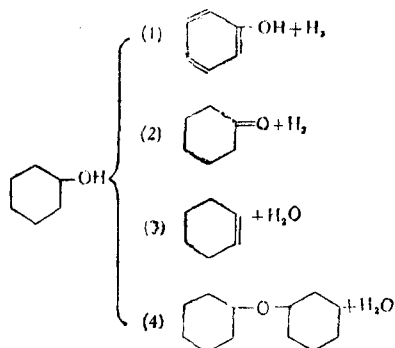
It is, therefore, an interesting problem to study comparatively the activity of these catalysts vis à vis each other, and also the effect of temperature on the individual activity.

For attaining this purpose, the catalytic action of reduced copper, reduced nickel and thoria on hexahydrophenol at 200° and 300° res-

¹ These Memoirs, 7, 85, 147, 151, 157 (1924).

² Ibid., 7, 135 (1924).

pectively, was chosen and their activity compared by determining the yield of reaction products in each case. The following schemes of reactions may be given to represent the possible direct transformation products :



Schemes (1) and (2) represent the oxidation of alcohol, and (3) and (4) the dehydration, and this was the correct method of showing the formation of benzene and other substances such as dodecahydrotriphenylene as the secondary reaction.

The presence of a catalyst which is capable of forming additional compounds with the reactants or resultants may accelerate any set of reactions. The activity of the catalyst will be measured by determining the quantity of the resultants in the reaction system, since the reaction velocity is probably inversely proportional to the chemical resistance, which was generally changed in some way in presence of the catalytic agent.

A Cyclohexanol.

Phenol, purified by distillation, was passed with pure hydrogen over reduced nickel heated at 180° and the reaction product was fractionated under ordinary pressure, and the fraction boiling at 158° was used in this experiment.

B Catalyst.

(a) Nickel.

In experiments (1) and (2), 15 gr. of nickel oxide, prepared from nickel (99.9%) and pure nitric acid, as usual, was spread out in a hard glass tube to a length of 75 cm. and then was reduced with pure hydrogen at 280—300°.

(b) Copper.

To the hot aqueous solution of copper sulphate, purified by recrystallization, the dilute caustic soda solution was added slowly with vigorous stirring and the precipitated copper hydroxide washed by decantation with hot water for many times until not a trace of sulphate could be found in the washing, then filtered and ignited in a crucible. In each experiment, 16 gr. of cupric oxide, thus obtained, was reduced with a slow current of pure hydrogen at 180—200°.

(c) Thoria.

It was obtained by the ignition of pure thorium nitrate and in experiments (5) and (6) 53 gr. were placed in the same reaction tube used in the other experiments.

C Method of Analysis.

The reaction product, which was obtained after passing over the catalysts above mentioned, was subjected to fractional distillation. The fraction boiling to 120°, consisting mainly of water, benzene, hydrobenzene, and some higher boiling substance, the water layer was first separated, weighed, and then the remaining oil was dried over calcium chloride and again fractionated. The fraction B. P. (70—90°) was designated the mixture of tetrahydrobenzene and benzene. The higher fraction combined together with another one which boils above 120° obtained in the first fractional distillation, the mixture was then treated with dilute caustic soda solution (8—5%) to isolate phenol, and the alkaline extract was acidified with sulphuric acid and the phenol was extracted with ether. The insoluble oil in the dilute alkali solution, consisting of unchanged cyclohexanol, dicyclohexyl ether and cyclohexanone, was treated with hydroxylamine to isolate the latter substance as an oxime and extract the oxime with dilute sulphuric acid (Sp. G. 1.17).¹ The acidic solution was made weak alkaline with dilute caustic

¹ E. Beckmann: J. prak. Chem. [2], 55, 17 (1897).

soda solution under cooling with ice, passed carbon dioxide and then the free oxime extracted with ether. The dicyclohexyl ether¹ and cyclohexanol remaining in the residue was separated by fractional distillation. The analytical results of the reaction products in the six experiments are shown in the following tables :

Table I.

No. of expt.	Catalyst.	Reaction temp.	Cyclohexanol used.	Time required for passage.	Reaction product.
(1)	Nickel	200°	25 gr.	5 hours	23 gr.
(2)	Nickel	300°	29 "	5 "	27 "
(3)	Copper	200°	27 "	6.5 "	25 "
(4)	Copper	300°	30 "	7 "	27 "
(5)	Thoria	200°	20 "	5.5 "	18 "
(6)	Thoria	300°	28 "	7 "	24 "

Table II.

No. of expt.	Water.	Benzene & tetrahydrobenzene.	Cyclohexanone.	Dicyclohexyl ether.	Phenol.	Cyclohexanol unchanged.	Dodecahydrotriphenylene.
(1) Ni 200°	tarce	trace	4.9 gr.	0.6 gr.	0.3 gr.	15.1 gr.	trace
(2) Ni 300°	0.2 gr.	0.1 gr.	6.1 "	1.2 "	10.4 "	9 "	—
(3) Cu 200°	0.7 "	3.3 "	7.2 "	0.5 "	0.1 "	9.3 "	—
(4) Cu 300°	1.6 "	6.0 "	8.5 "	0.5 "	2.3 "	6 "	trace
(5) ThO ₂ 200°	0.2 "	0.2 "	1.1 "	0.8 "	—	14 "	—
(6) ThO ₂ 300°	4.5 "	15.5 "	0.7 "	0.6 "	—	—	1.3 gr.

¹ W. Ipatiew u. O. Philipow: Ber. D. Chem. Ges., 41, 1001 (1908).

In the calculation of the yield of the reaction products, shown in the tables, hydrocarbons except dodecahydrotriphenylene were regarded as being formed by dehydration, and the latter substance by oxidation.

Table III.

(Yield in mol%)

No. of expt.	Benzene & tetrahydrobenzene.	Dicyclohexylether.	Cyclohexanone.	Phenol.
(1) Ni 200°	trace	5.8 mol%	88.5 mol%	5.7 mol%
(2) Ni 300°	0.7 mol%	3.7 "	34.4 "	61.2 "
(3) Cu 200°	34.2 "	2.3 "	62.5 "	0.9 "
(4) Cu 300°	39.1 "	1.5 "	46.3 "	13.1 "
(5) ThO ₂ 200°	13.5 "	24.3 "	62.2 "	—
(6) ThO ₂ 300°	87.6 "	1.5 "	10.9 "	—

Table IV.

No. of expt.	Changed cyclohexanol Used cyclohexanol	Ratio 200° : 300°
(1) Ni 200°	34.4%	1 : 2.0
(2) Ni 300°	66.7 "	
(3) Cu 200°	62.8 "	1 : 1.2
(4) Cu 300°	77.8 "	
(5) ThO ₂ 200°	22.2 "	
(6) ThO ₂ 300°	100 "	1 : 4.5

Table V.

No. of expt.	Oxidation.	Dehydration.	Oxidation Dehydration.	Phenol Ketone.	Ether Benzene.
(1) Ni 200°	94.2 mol%	5.8 mol%	16.24	0.06	—
(2) Ni 300°	95.6 "	4.4 "	21.73	1.78	5.7
(3) Cu 200°	63.4 "	36.5 "	1.74	0.01	0.07
(4) Cu 300°	59.4 "	40.6 "	1.46	0.28	0.04
(5) ThO ₂ 200°	62.2 "	37.8 "	1.65	—	1.8
(6) ThO ₂ 300°	10.9 "	89.1 "	0.12	—	0.02

Table VI.

(Ratio of products at 200° and 300°)

Catalyst.	Oxidation.	Dehydration.
Nickel	0.99	1.32
Copper	1.07	0.9
Thoria	5.71	0.42

In experiment (6), it was noticed that white needle crystals were separated when water, benzene and tetrahydrobenzene had been separated from the reaction product. The yield was 1.3 gr. It melted at 224—225°, and with difficulty soluble in ether, alcohol and insoluble in water and showed the following analytical results and molecular weight:

C=90.02, H=10.01; M.W.=240 (by the freezing-point method in benzene solution)

The analytical results and its physical and chemical properties, except melting point, agree quite well with those of dodecahydrotriphenylene obtained by C. Mannich¹ from cyclohexanone, which was denoted by him to melt at 232—233°.

The following conclusions were drawn from the experimental results above mentioned:

1. Reduced nickel acts principally as oxidizing catalyst as noticed by Sabatier, and reduced copper and thoria come next to it in activity (Table V).

2. Thoria promotes mostly the dehydration of alcohol, reduced nickel does this in the least degree, and reduced copper also lies between these two catalysts in this respect. (Table V).

3. The ratio of oxidation products to dehydration products at 200° and 300° is 16.24; 21.73 with nickel, 1.74; 1.46 with copper, and 1.65; 0.12 with thoria respectively (Table V).

4. In the oxidation with pulverulent nickel, hydrogen of hexamethylene ring was split off; while with thoria hydrogen of the hydroxyl group mostly; and with reduced copper both hydrogen atoms were oxidized. Phenol-ketone-ratio at 200° and 300° is 0.06; 1.78; with

¹ Ber. D. Chem. Ges., 40, 153 (1907).

nickel, and 0.01 ; 0.28 with copper, respectively (Table V).

5. The influence of temperature on the activity of these catalysts is greatest with thoria, and reduced copper was affected in the least degree ; the quantity of alcohol transformed at 200° was only 22% with thoria, 34% with reduced nickel, and 67% with reduced copper (Table IV and VI).

6. From the ratio of the total yield of resultants at 200° and 300°, this being $\frac{1}{2}$, 1/1.2 and 1/4.5 with reduced nickel, reduced copper and thoria respectively, it was concluded that the optimum temperature for the catalytic action of reduced copper seemed to be 200°, for thoria 300°, and for reduced nickel it lies between 200° and 300° (Table IV).

7. In the oxidation of alcohol, the yield was increased with the temperature in presence of reduced nickel, while with thoria and reduced copper it was decreased ; in the latter case, however, the rate of decrease was very small compared with that of thoria (Table V).

8. The yield of dehydration products was affected by temperature in opposition to the case of oxidation ; the ratio of oxidation products at 200° and 300°, is 0.99 ; 1.07 and 5.71 in presence of reduced nickel, reduced copper and thoria respectively, while that of dehydration products, 1.32 ; 0.9 and 0.42 for the corresponding cases (Table VI).

9. In reaction (1) reduced nickel serves as the most convenient catalyst at 200°, thoria heated at 300° acts as the convenient catalyst for reaction (3), and at higher temperatures the condensation of ketone began to accelerate. Reduced copper accelerating both sets of reactions (1) and (2), (3) and (4) equally, resembles reduced nickel in facilitating the oxidation of alcohol ; on the other hand it behaves like thoria in the dehydrating (Table III).

10. The specific effect of the catalytic agent is very marked at certain low temperatures, though it becomes negligible at very high temperatures, and reduced copper heated at 200—300° stands as a catalyst between reduced nickel and thoria in every respect.