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THE USE OF MIXED CATALYSTS IN THE HYDROGENATION OF OILS.

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THE USE OF MIXED CATALYSTS IN THE HYDROGENATION OF OILS.

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Numerous instances are known in which the activity of a given catalyst is increased by the addition of a second substance. Ipatieff[1] was the first to discover the accelerating effect of small amounts of iron in the catalytic reduction of amylene to isopentane and of tetrahydrobenzene to the hexahydro-compound by means of oxide of copper. Similarly, an iron-molybdenum catalyst is more efficient than either metal alone in the synthesis of ammonia.[2] In the oxidation of naphthalene to phthalic acid[3] or the complete oxidation of aniline[4] by sulphuric acid, a mixture of the sulphates of copper and mercury is more effective than either sulphate alone. Examples are also encountered in the study of inorganic reactions.[5]

Dewar and Liebmann[6] prepare the catalyst required for the hydrogenation of fixed oils from a mixture of the oxides, hydroxides or carbonates of two or more metals such as nickel, cobalt, copper or iron with or without the addition of silver oxide. Taylor[7] states that the addition of copper to the nickel catalyst increases the ruggedness of the catalyst and renders it less susceptible to poisons, whilst Kahlenberg and Ritter[8] claim that a catalyst containing equal weights of nickel and cobalt is more active than either metal when used alone.

According to Paal and Windisch[9] the addition of copper or iron to platinum or palladium completely inhibits its catalytic activity, whereas the addition of nickel or cobalt produces no appreciable effect.

Armstrong and Hilditch[10] state that nickel-copper catalysts prepared at 180° are not so active as plain nickel catalysts produced at a higher temperature, but nevertheless display appreciable activity.

[1] *Ber.*, 1910, **43**, 3387.
[2] *J. Physical Chem.*, 1921, **24**, 243.
[3] *Z. physikal, Chem.*, 1903, **46**, 502.
[4] *Ibid.*
[5] Cf. Price, *ibid.*, 1893, **27**, 499; Borde, *ibid.*, 1903, **37**, 257; *Ber.*, 1884, **17**, 1062.
[6] Eng. Pat., 12981 and 12982 of 1913.
[7] *Trans. Amer. Electrochem. Soc.*, 1919, **36**, 149.
[8] *J. Physical Chem.*, 1921, **25**, 89.
[9] *Ber.*, 1911, **44**, 1013; 1913, **46**, 4010.
[10] *Proc. Roy. Soc.*, A 1922, **102**, 714.

EXPERIMENTAL.

Oil.—The oil used in all the experiments was a sample of refined olive oil prepared by treating a sample of pale yellow Spanish oil (acid value 1·7) with 10 per cent. sodium hydroxide solution at 60–70°, washing with boiling water and final cleaning with fullers' earth. The refined oil had an acid value 0·15 and a refractive index 1·4548 at 60°.

Hydrogen.—Electrolytic hydrogen was used, prepared and purified as described in an earlier paper.[1]

Method of procedure.—The method also was similar to that already described. So far as possible the rate of stirring was kept the same in each experiment. Thermometers were inserted in the oil and also in the air-bath and during the hydrogenation the temperature registered in the oil was kept as near 180° as possible,[2] or at any other temperature desired. At regular intervals samples of the hardened oil were removed, filtered and the refractive index determined at about 60° and then corrected to 60°.

Catalysts.—All the catalysts used were deposited on kieselguhr. The mixed cobalt-nickel catalysts were prepared as follows. Nickel nitrate and cobalt nitrate were taken in different proportions, but always such that the combined weights of the two metals were 4 grams, and dissolved in water to form a 10 per cent. solution. The solution was heated and mixed with 13 grams of kieselguhr which had passed a 20-mesh sieve. The metallic carbonates were precipitated on the kieselguhr by the addition of a 10 per cent. solution of sodium carbonate with continuous stirring of the heated mixture. After the precipitate had settled, the upper layer of liquid was filtered with the aid of a Buchner funnel and the main precipitate removed to a mortar, triturated six times with hot water and finally transferred to the funnel. After air-drying and a final drying for 4 hours at 110° the precipitate was reduced. In all experiments the weight of metal used was 0·5 gram per 100 grams of oil.

NICKEL AND COBALT.

Effect of reduction-temperature on the activity of the catalyst.

Table I gives the results of a series of experiments made with two catalysts, one a nickel catalyst containing 23·5 per cent. of nickel

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[1] This *Journal*, 1922, 5, 60.

[2] During the reduction of the catalyst the temperature in the flask is lower than the bath-temperature, whereas during hydrogenation the reverse holds good.

and the other 0·25 per cent. of cobalt, 23·25 per cent. of nickel and both 76·5 per cent. of kieselguhr. All the hydrogenations were conducted at 180—185°, but different samples of the two catalysts were reduced at different temperatures, ranging from 260—330°.

The results show that there is practically no difference between the nickel and nickel-cobalt catalyst and that the most active catalysts are obtained by reducing the carbonates at temperatures between 270 and 310°. Below 270° and above 310° the activity of the catalyst is somewhat impaired.

TABLE I.

Effect of reduction-temperature on the activity of nickel and cobalt-nickel catalysts

n_D^{60} original oil = 1·4548 n_D^{60} completely hardened oil = 1·4464

Temperature of reduction in flask	Catalyst	n_D^{60} of the sample after			
		0·25	0·5	0·83	1·25 hours
260—262°	Nickel	1·4530	1·4521	1·4508	1·4493
260—262°	Cobalt-nickel	1·4530	1·4518	1·4507	1·4489
273—278°	Nickel	1·4531	1·4517	1·4501	1·4481
273—278°	Cobalt-nickel	1·4530	1·4517	1·4502	1·4482
286—292°	Nickel	1·4536	1·4524	1·4508	1·4492
286—292°	Cobalt-nickel	1·4530	1·4519	1·4504	1·4488
297—303°	Nickel	1·4530	1·4517	1·4503	1·4489
297—303°	Cobalt-nickel	1·4526	1·4514	1·4499	1·4485
305—310°	Nickel	1·4527	1·4514	1·4496	1·4478
305—310°	Cobalt-nickel	1·4526	1·4513	1·4499	1·4480
330—331°	Nickel	1·4538	1·4529	1·4518	1·4502
330—331°	Cobalt-nickel	1·4532	1·4521	1·4509	1·4497

Effect of hydrogenation-temperature on the rate of reduction.

Two catalysts having the same composition as those used in the experiments given in Table I were prepared and reduced at 298—302°, and samples of the olive oil were hydrogenated with these two catalysts at different temperatures. The results are given in Table II and they show that there is practically no difference between the nickel and the nickel-cobalt catalysts.

TABLE II.

Effect of temperature on the rate of hydrogenation using nickel and cobalt-nickel catalysts.

n_D^{60} original oil = 1·4548[1] n_D^{60} completely hardened oil = 1·4464

Temperature of hydrogenation (in flask)	Catalyst	n_D^{60} of hardened sample after			
		0·25	0·5	0·83	1·25 hours
186—192°	Nickel	1·4532	1·4522	1·4509	1·4493
186—192°	Cobalt-nickel	1·4525	1·4517	1·4499	1·4489
178—180°	Nickel	1·4533	1·4519	1·4506	1·4492
178—180°	Cobalt-nickel	1·4533	1·4524	1·4507	1·4491
170—172°	Nickel	1·4534	1·4523	1·4508	1·4495
170—172°	Cobalt-nickel	1·4531	1·4521	1·4506	1·4492
100—110°	Nickel	...	...	...	1·4530
100—110°	Cobalt-nickel	...	...	...	1·4531

Samples of nickel-kieselguhr catalyst were prepared as before, reduced at 298–302° and then heated to the same temperature for given lengths of time after the reduction was complete as indicated by the black colour of the catalyst. Although the time of this heating was varied from 0·08 to 1·0 hour, no appreciable effect was noticeable on the rate of hydrogenation of olive oil. In all the experiments the values of n_D^{60} for the reduced oil after 1·25 hours lay between 1·4494 and 1·4498.

In Table III are recorded the results of a number of experiments made with catalysts of different composition.

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[1] The oil used in the experiments included in Tables III—VI had the same refractive index and a refractive index 1·4464 at 60° when completely hardened.

TABLE III.

Hydrogenation of olive oil with nickel, nickel-cobalt and cobalt catalysts at 180—185°.

Catalyst	Composition of catalyst. per cent. of			n_D^{60} for samples of hardened oil after					
	nickel	cobalt	kieselguhr	0·25	0·5	0·83	1·25	2·5	5 hours
A	23·50	0	76·5	1·4530	1·4517	1·4503	1·4489	...	...
B1	23·25	0·25	76·5	1·4526	1·4514	1·4499	1·4485	...	...
B2	23·00	0·50	76·5	1·4536	1·4526	1·4513	1·4497	...	...
B3	22·30	1·20	76·5	1·4537	1·4528	1·4516	1·4501	...	...
B4	11·75	11·75	76·5	...	1·4527	...	1·4510	1·4487	...
B5	0	23·50	76·5	...	1·4549	...	...	1·4548	1·4547

The results show that the catalyst containing only small amounts of cobalt (Ni: Co = 23·25:0·25) is as active or even slightly more active than the nickel catalyst, but that increasing the amount of cobalt diminishes the activity and that a cobalt-kieselguhr catalyst is practically inactive.

A few experiments were made with nickel, nickel-cobalt and cobalt catalysts reduced at temperatures from 345–390°. The results are given in Table IV.

TABLE IV.

Nickel, cobalt and nickel-cobalt catalysts reduced at high temperatures.

Catalysts	Temperature of reduction	n_D^{60} for hardened samples after			
		0·5	1·25	2·5	5 hours
A	345–350°	1·4523	1·4497	1·4466	...
B4	345–350°	1·4545	1·4535	1·4520	...
B5	345–350°	...	1·4540	...	1·4532
B5	395°	...	1·4542	...	1·4537

The experiments made with nickel, cobalt and nickel-cobalt catalysts on kieselguhr show that:

1. A nickel catalyst is most active when prepared at a temperature of 300° and reduction at 345–350° tends to impair its activity.

2. A cobalt catalyst prepared at 300° is practically inactive, and when prepared at higher temperatures, e.g., 345° or 390°, has very small catalytic properties.

3. With mixed nickel-cobalt catalysts the activity tends to decrease as the percentage of cobalt increases up to 50 per cent., but a catalyst with nickel to cobalt in the proportion 93 : 1 is as active as a nickel catalyst prepared under similar conditions.

4. A mixed catalyst containing equal weights of nickel and cobalt is more active when reduced at 300° than at 345°, but is always less active than a nickel catalyst prepared under similar conditions.

NICKEL AND SILVER.

The catalysts were prepared from silver nitrate and nickel nitrate in a manner very similar to that described for the preparation of the nickel-cobalt catalyst. The only difference was that the carbonates precipitated on kieselguhr were washed 8 times with cold water by decantation, but trituration in a mortar was not adopted.

The catalyst was finally dried at 110°, powdered to pass a 20-mesh sieve, and reduced at 300°. The hydrogenation of the oil was conducted at 180–185°.

Table V gives the results of experiments made with three catalysts, viz., (A) a nickel catalyst containing 23·5 per cent. of nickel, (C1) a nickel-silver catalyst containing 0·25 per cent. of silver and 23·25 per cent. of nickel and (C2) a similar catalyst containing 1·2 per cent. of silver and 22·3 per cent. of nickel.

The results show that the silver produces a retarding effect.

TABLE V.

Nickel-silver catalysts.

Catalyst	n_D^{60} of hardened sample after			
	0·25	0·50	0·83	1·25 hours
A	1·4533	1·4522	1·4510	1·4498
C1	1·4538	1·4526	1·4518	1·4505
C2	1·4538	1·4531	1·4521	1·4506

NICKEL AND COPPER.

For the preparation of the catalysts the method adopted was exactly similar to that described for the nickel-silver catalysts with the following deviations, (*a*) the metallic sulphates were used and (*b*) the temperature of reduction was 270–275°. The temperature of hydrogenation was 180–185°.

It was subsequently found that copper-nickel-kieselguhr catalysts can be reduced at temperatures even lower than 270°[1], e.g., a catalyst containing 1·2 per cent. of copper and 22·3 per cent. of nickel can be reduced at 200° and one containing only 0·25 per cent. of copper can be reduced at 250°.

Table VI gives the results of experiments made with these catalysts.

TABLE VI.

Copper-nickel catalysts.

Catalyst	Temperature of preparation	Composition of catalyst per cent. of			n_{D}^{60} for reduced samples after			
		nickel	copper	kieselguhr	0·25	0·50	0·83	1·25 hours
A	270	23·5	0	76·5	1·4530	1·4517	1·4505	1·4493
D1	270	23·25	0·25	76·5	1·4530	1·4520	1·4509	1·4500
D2	270	22·3	1·2	76·5	1·4531	1·4523	1·4513	1·4503
D2	200	22·3	1·2	76·5	...	1·4533	...	1·4522
D3	270	16·4	7·1	76·5	1·4540	1·4534	1·4529	1·4521

In the last sample, i.e., with catalyst D3 for 1·25 hours, copper was readily detected.

It is clear that the addition of copper diminishes rather than increases the catalytic activity of nickel.

Although a catalyst containing 1·2 per cent. of copper and 22·3 per cent. of nickel can be prepared at 200°, its activity is less than that of a similar catalyst prepared at 270°.

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[1] Compare Armstrong and Hilditch, *Proc. Roy. Soc.*, A 1922, 102, 714.

SUMMARY.

With nickel-kieselguhr catalysts the presence of metals such as cobalt, silver and copper have an inhibiting effect, the degree of which increases with the amount of foreign metal present. Kahlenberg and Ritter, experimenting with cobalt-nickel catalyst without kieselguhr, state that the presence of cobalt increases the activity of nickel as a catalyst.

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