was made both by the total count under each peak and by spectrographic analysis.

Discussion

The distribution coefficient is defined by the equation

$$K_D = \frac{M_r \times \text{volume of solution}}{M_1 \times \text{mass of resin}}$$

where M_r and M_1 are the fractions of the anion in the resin and the liquid phases, respectively. The dependence of K_D on the concentration of hydrochloric acid for the four elements is shown in Fig. 1, and a good separation of zirconium and hafnium by elution with 9.0 M hydrochloric acid is shown in Fig. 2. The order of elution is the reverse of that shown for the fluo-ions of these elements.[1,2] A small amount of Nb^{95}, which grew in from the Zr^{95} decay, is still on the column at the end of this run.

The curves for the K_D values for niobium and tantalum are quite different from that for protactinium,[5] which they might be expected to resemble. Considerably more data with respect to several variables are needed to show the nature of the exchange in the high and low acid concentration ranges, though it is probable that there is little or no chloride complexing in the low concentrations. Zirconium and hafnium do not show similar behavior in the low acid concentrations.

Although the zirconium and hafnium batch experiments reach equilibrium within four hours and a good column separation can be achieved, the case is quite different for niobium and tantalum. It requires only four hours to reach equilibrium on the high acid side for the latter elements but at least two days on the low acid side of the curves; and neither niobium nor tantalum can be eluted from a column in a normal fashion with low acid concentrations, but are washed off immediately. In addition, tantalum does not behave normally when eluted from a column with 6–9 M hydrochloric acid after it has been adsorbed from 10–11 M acid. The tantalum concentration rises to an immediate peak and then falls off more slowly. It was first thought that the behavior of tantalum was due to the presence of the minute concentration of carrier present. However, a sample of carrier-free Ta^{177} tracer, produced by deuteron bombardment of hafnium, gave the same results. This behavior does allow a good column separation from niobium, which shows a normal elution curve in this region.

The different characteristics of zirconium and niobium have led to a very convenient separation of Zr^{95} from its daughter Nb^{95}. The mixture in 1 ml. of 6–7 M hydrochloric acid is passed through a Dowex-2 column 8 cm. long and 3 mm. i.d. and washed with 3 more ml. of acid. The elutriant and wash contain the zirconium. The niobium is then washed from the column with about 4 ml. of 1.5–4.0 M hydrochloric acid.

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(5) K. A. Kraus and G. E. Moore, THIS JOURNAL, **72**, 4293 (1950).

X-Ray Diffraction Study on the Structure of the Ni–Cu Coprecipitation Catalysts

BY NORIAKI KADOTA AND SADAAKI IKEDA

Both inhibitor and promoter actions are reported as to the influence of Cu on the catalytic activity of Ni catalysts. Copper acts as an inhibitor in Ni catalysts in the Fischer–Tropsch process, whereas in the case of ordinary hydrogenation it is often used as a promoter for Ni catalysts. The study of Ni–Cu coprecipitation by Morris and Selwood[1] suggests the possibility of the existence of a non-equilibrium alloy phase.

The X-ray structure of Ni–Cu catalysts coprecipitated from a mixture of their nitrate solutions on the surface of a kieselguhr carrier has been studied by the authors and a conclusion similar to that of Morris and Selwood obtained directly.

Experimental

Mixtures of nickel and copper nitrate solutions were coprecipitated by addition of K_2CO_3 solution on the kieselguhr surface. The precipitate was washed with hot water (94–96°). Impurities were spectroscopically detected and are as follows: chemicals: $Ni(NO_3)_2$; $Cu(NO_3)_2$; K_2CO_3; impurities: Ag(M), Co(M), Cu(M), Pb(W), Si(M); Na(W), Pb(W), Si(T), Ti(W); no trace of impurities, respectively, where M indicates medium, W weak and T traces, each referring to the intensity of the ultimate spectra lines. The amounts of impurities may be considered to be harmless.

Five kinds of catalysts were prepared, each containing 1.25 times as much kieselguhr by weight as the sum of Ni and Cu. These catalysts were reduced by hydrogen for about 90 hours at 300°. The results of the lattice measurements are shown in Table I, where the ratio of Ni to Cu corresponds to the atomic percentage of the two elements.

TABLE I

Compositions of catalysts Ni:Cu:KG			Lattice distances, Å. expected values	observed values	Additive composition from obsd. lattice dist. Ni	Cu
100	0	125	3.517[a]	3.517	100	0
95	5	125	3.521	3.517	100	0
70	30	125	3.545	3.529	88	12
50	50	125	3.565	3.547	67	33
				3.580	20	80[b]
50	50	125	3.565	3.577	37	63[c]
0	100	125	3.612[a]	3.612	0	100

[a] International Critical Tables. [b] Results after reduction for 10 hours. [c] Results after heat treatment for 90 hours.

A plot of lattice distance *versus* atomic fraction of the two metals is shown in Fig. 1. An S-shaped curve is found in spite of the expectation from the well-known Vegard's relationship in Ni–Cu alloy.[2] In particular, dual structures are observed in the equifractional sample of both metals, and they converge into a single structure after being heated for about 90 hours as shown schematically in Fig. 2. In Fig. 2, the rate constant from the initial structure of 3.547 Å. to the final structure of 3.577 Å. lattice distance is larger than the rate from the structure of 3.580 Å. spacing. This may be attributed to the difference in the rates of the mutual diffusion into each other between Ni and Cu (the rate of diffusion of Cu into Ni is 11 × 10⁻⁷ cm./day and that of Ni into Cu is 5 × 10⁻⁸ cm./day at 1000°).[3] With these results, we reach the con-

(1) H. Morris and P. W. Selwood, THIS JOURNAL, **65**, 2245 (1943).
(2) Sacklowski, Z. Physik, **5**, 21 (1921).
(3) Jenkin, "International Critical Tables," Vol. V, p. 76.
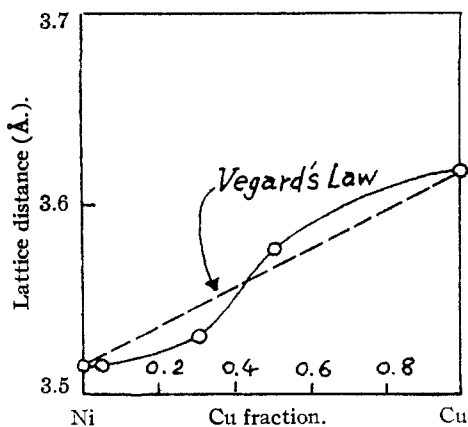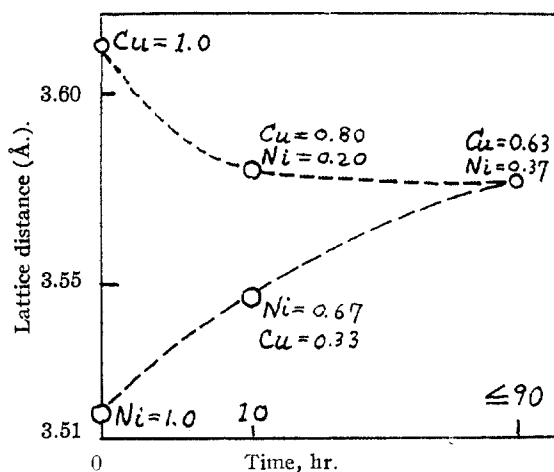
Fig. 1.

Fig. 2.

clusion that a non-equilibrium state of the alloy phase is formed on the catalyst surface, as stated by Morris and Selwood in their paper. It remains unstable on the surface to an extent depending upon the composition of the catalyst. The authors have come to the same conclusion from an adsorption study of these catalysts.[4]

Acknowledgment.—The interest of Prof. S. Kodama and the effective advice of Prof. S. Tawara in this work are gratefully acknowledged.

(4) S. Kodama and N. Kadota, unpublished results, 1949.

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The Dehydrogenation of Coumaran

BY BODO KLARMANN

Coumaran (2,3-dihydrobenzofuran) is readily available by the elegant synthesis of Bennett and Hafez[1] who effected ring closure by treating the diazotized o-amino derivative of β-phenylethyl alcohol with base.

The dehydrogenation of coumaran to coumarone (benzofuran) has not been reported, although the reverse reaction has been accomplished by Alexander[2] by reduction with sodium in absolute

(1) Bennett and Hafez, J. Chem. Soc., 287 (1941).
(2) Alexander, Ber., 25, 2409 (1892).

alcohol and by Weger[3] who employed hydrogenation.

Our experiments have shown that this dehydrogenation can be achieved satisfactorily by the use of sulfur; selenium is less satisfactory. With sulfur, and taking recovered starting material into account, a 45–50% yield was obtained. Since coumarone boils at 169°, and coumaran at 188°, separation by fractional distillation is readily achieved.

Experimental

Three hundred and sixty grams of pure coumaran, m.p. −21.5°, and 96 g. of sulfur are refluxed for 15 hours on an oil-bath (220°) during which time the sulfur dissolves and hydrogen sulfide is evolved. The reaction product was steam distilled, leaving behind a black residue. Addition of sodium chloride to the distillate caused a colorless oil to separate which after drying over calcium chloride was slowly fractionated at 8 mm. through a Widmer column (spiral 70 cm. long). The crude steam distillate (290 g.) yielded as a fore-run approximately 65 g. of pure coumarone boiling constantly at 168–169° (747 mm.), melting at −27°, and resinifying with concd. sulfuric acid in characteristic fashion. Coumarone isolated from high-boiling coal tar fractions by picric acid, purified by recrystallization and regenerated with steam gave an identical melting point.

(3) Weger, Z. angew. Chem., 22, 391 (1909).

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The Preparation of Ethylidene Iodide

BY R. L. LETSINGER AND C. W. KAMMEYER

Reported methods for the preparation of ethylidene iodide either give poor yields or involve reagents such as aluminum iodide which are not readily available. It has been found that ethylidene iodide can conveniently be prepared in reasonable yields (60%) by the action of aluminum chloride on a mixture of ethylidene chloride and ethyl iodide.

Experimental

A mixture of 39.6 g. (0.4 mole) of ethylidene chloride and 187 g. (1.2 moles) of ethyl iodide was heated with 2.0 g. of aluminum chloride on a steam-bath for three hours. During this time ethyl chloride, which was formed in the reaction, bubbled out of the solution. The mixture was then poured into water, washed with a sodium bisulfite solution, and dried over magnesium sulfate. On distillation 67.3 g. (60%) of ethylidene iodide was obtained; b.p. 75–76° (25 mm.); d^{25}_4 2.794.

In a similar reaction where the mole ratio of ethyl iodide to ethylidene chloride was two to one, the yield of the iodide was 42%.

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The Hydrogenolysis of Sulfilimines and its Application to the Purification of Sulfides

BY M. A. McCALL, D. S. TARBELL AND MARY ANN HAVILL

Several types of solid derivatives have been proposed for the characterization of liquid sulfides,[1]

(1) (a) Faragher, Morrell and Comay, THIS JOURNAL, 51, 2774 (1929); (b) Ipatieff, Pines and Friedman, ibid., 60, 2731 (1938); (c) Ipatieff and Friedman, ibid., 61, 684 (1939); (d) Mann and Pope, J. Chem. Soc., 121, 1052 (1922). Other types of derivatives, including sulfonium salts, are discussed by Connor in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1943, pp. 858–861, 867–868.