Engineering
and
Process
development

Phenols by Dehydrogenation

H. C. CHITWOOD, J. T. FITZPATRICK, G. W. FOWLER, AND B. T. FREURE

Research and Development Department, Carbide and Carbon Chemicals Co., South Charleston, W. Va.

IT HAS been known for many years that cyclohexanone and cyclohexanol can be dehydrogenated to phenol (*13–15*). This aromatization is not easy, and the patent literature indicates that it has been the subject of much research by industrial laboratories (*3*, *10*). Difficulty in the separation of phenol from cyclohexanone has hindered attempts to make the dehydrogenation practical, since the two form a maximum boiling azeotrope containing about 75% phenol (*7*). This means that if phenol is to be recovered by simple distillation the reaction must be carried out at temperatures well above 300° C. to attain sufficiently favorable equilibrium. Figure 1, drawn from results obtained in this laboratory together with those of Cubberley and Mueller (*5*) shows the variation in equilibrium concentrations with temperature when the hydrogen pressure is 1 atmosphere. None of the catalysts previously described has withstood the necessary high temperatures long enough to provide a practical process for phenol manufacture. This investigation was started in an attempt to overcome the drawbacks of the older catalysts.

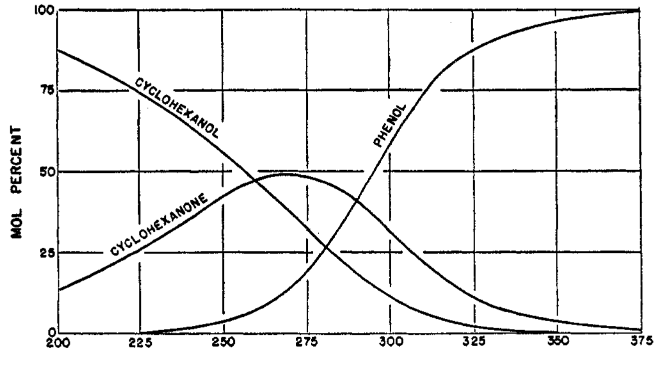

Figure 1. Equilibrium of Cyclohexanol, Cyclohexanone, and Phenol

At 1 atmosphere hydrogen pressure

From previous work nickel catalysts seemed most promising. The usual promoters were tried, and of these copper, chromium, and platinum were found to be beneficial. These were not alternative, but additive, promoters; apparently each acts in a different fashion. Although catalysts made with optimum quantities of these promoters were far superior to unpromoted nickel, they still left much to be desired with respect to yield, reproducibility, and, especially, life.

With these four-component catalysts as a basis, a search was begun for additional promoters. In certain cases sulfate, added either as sulfuric acid or the nickel salt, gave improved performance. However, no correlation could be found between catalyst behavior and the amount of sulfate used; catalysts made in an apparently identical way often had completely different activities. The inconsistency was traced to the presence of small, but variable, quantities of sodium in the reagents and supports. Water extraction of catalysts showed that, regardless of how much sulfate was originally added, only that equivalent to the sodium present could survive the conditions of catalyst preparation. Catalysts which had been washed were uniformly poor, but the original activity was restored by addition of more sodium sulfate. Once the importance of this factor had been established, the way was open for a more rational approach to the problem. The amount of sodium sulfate was varied and the optimum established at about 0.6% of the weight of the nickel. With this catalyst exceptionally high yields of phenol were attained for extended periods of time.

The promoting action is not confined to sodium sulfate; approximately equivalent results were obtained with any of the alkali metal sulfates in the optimum concentration. Nor is the reaction confined to the preparation of phenol itself; dehydrogenation of substituted hydroaromatic ketones and alcohols to the corresponding phenols was equally easy, although in a few cases dehydration reduced the yield of the desired product.

The present catalysts are distinguished by both exceptionally high activity and lack of fouling at the high temperatures employed. Just how the individual promoters contribute to these properties is not certain. Copper seems to affect both the initial activity and the life. Copper is reported to moderate nickel's disruptive effect on rings (*1*, *11*), and probably it functions similarly here. The sodium sulfate increases the catalyst life, perhaps by inhibiting tar-forming centers in the catalyst or support. Although chromium has been used for many years as a promoter for copper and nickel, the various theories which have been advanced to explain its action (*4*, *6*, *8*) have not been proved. It is planned to extend the work on these catalysts in an effort to learn the effect of each of the promoters.

Experimental

CATALYST PREPARATION AND TESTING. The catalysts were prepared by evaporating a solution of soluble salts of the ingredients onto an inert support which had been washed with acid to remove alkali metals. A typical successful preparation was as follows:

Electrolytic nickel (24 grams) was dissolved in nitric acid; to this solution were added 30 grams of copper(II) nitrate trihydrate, 3.5 grams of chromium(III) nitrate nonahydrate, 0.04 gram of platinum chloride, 0.54 gram of nickel(II) sulfate hexahydrate, and 0.080 gram of sodium hydroxide. This solution was added to 200 ml. of 4- to 8-mesh Filtros (a ceramically bonded porous silica, made by Filtros, Inc., of East Rochester, N. Y.), which had previously been digested with nitric acid and washed with water, and the mixture was heated with constant stirring until copious evolution of oxides of nitrogen began. The catalyst was then roasted for 3 hours in an oven preheated to 375° C. Variations in this procedure gave distinctly inferior results.

Catalyst testing was done in 1-inch steel tubes, with thermocouple wells and Dowtherm-heated jackets. All catalysts were reduced in a stream of hydrogen for 8 hours at 375° C. before use.

Since new catalysts showed some tendency to give erratic results, all were run for at least 8 hours or until the initial activity was lost, then were regenerated by air oxidation at 375° C. followed by reduction with hydrogen before comparative activities were measured.

Tests were made at atmospheric pressure with feeds of 150 grams per liter per hour of cyclohexanone or cyclohexanol and 250 liters per liter per hour of hydrogen. The ketone, alcohol, or mixtures of the two could be used with identical results. Omission of the hydrogen reduced the catalyst life very markedly.

Spot samples of condensable product were checked frequently for freezing point and density; the composition was estimated by comparison with known mixtures of phenol and cyclohexanone. The two methods usually give slightly different results, the freezing point indicating a lower percentage of phenol. The difference between the two methods is a rough measure of the amount of dehydration, since the presence of benzene and water has more effect on the freezing point than on the density. In most cases these figures were checked by distillation of larger samples taken over a considerable period of time.

Results

Table I gives the results on a series of catalysts made and tested under the conditions described, but containing varying amounts of sodium sulfate. As can be seen, the proportion is quite critical, with the optimum at about 0.6% by weight on the basis of the nickel. After regeneration by successive treatment with air and hydrogen at 375° C. practically the same results were again obtained. No decline in either maximum conversion or life between regenerations was observed during several months' operation of some of these catalysts.

A catalyst similar to the best in this series except that the platinum was omitted gave results almost identical with those reported. It seems that the platinum serves only to make the catalyst less sensitive to variations in the alkali metal sulfate content. On the other hand, the copper and the chromium are necessary components of the catalyst. The copper content can be varied in the range of 15 to 40% of the nickel without any appreciable effect. The chromium must approximate 2% rather closely for best results, although amounts from 0.5 to 4% show some promoting action; with less than the optimum the activity is low, and with more there is excessive dehydration to give benzene.

The promoting action is common to all of the alkali metal sulfates. As shown in Table II, a series of catalysts made with 0.6% of various alkali metal sulfates in place of sodium sulfate and without platinum gave approximately the same results.

Sodium sulfate was studied much more thoroughly than the others, but a few experiments showed that the concentration is less critical with the higher members of the series. With an increase in the content of rubidium sulfate to 1.2%, no significant change was noted except for a decrease in the catalyst life from 123 to 96 hours. A further increase to 2.25% gave a product having an estimated phenol content of 90.7 to 93.5%, still above that obtained with no alkali sulfate; but the catalyst life at high activity dropped to only 6 hours. The alkaline earth sulfates had a similar but less pronounced beneficial action. Barium sulfate in particular gave a catalyst of exceptionally high activity, but comparatively short life.

Further laboratory experiments showed the catalyst to be of general utility for making phenols from oxygenated cyclohexanes or cyclohexenes. *m*-Cresol, 3-methyl-5-propylphenol, 3,5-xylenol, 1-naphthol, and catechol were made in good yield by passing nonaromatic compounds of corresponding structure over the catalyst at 350° C. in the presence of hydrogen. These results are summarized in Table III.

Development Scale Operation

A cubic foot of catalyst was prepared by a method similar to that described, except that 2- to 4-mesh Filtros was used. Operating at 350° C. in a 3-inch tube 20 feet long, with a feed rate of 7 pounds per hour of cyclohexanone and 116 cubic feet (at standard temperature and pressure) per hour of hydrogen, this catalyst gave a product consisting of over 95% phenol. No loss in activity was observed in 135 hours of operation. The crude product was vacuum distilled through a column of approximately 12 theoretical plates. After removal of a small heads fraction the main phenol fraction came over at 86° C. at 20 mm. of mercury. Sixty per cent of the phenol present was recovered as material having a freezing point above 39° C. Redistillation of the heads and tails fractions brought the recovery of pure phenol up to 80%.

Table I. Effect of Sodium Sulfate Variation

Sodium Sulfate Content, % of Ni by Wt.	Average Purity of Phenol Produced over Successive 20-Hour Periods				
	1st	2nd	3rd	4th	5th
0.296	90.8	89.5	<88.7	..	..
0.444	93.0	95.1	92.3	89.5	..
0.592	94.4	95.8	95.1	95.1	94.4
0.888	90.1	89.0	..	..	..
1.184	90.8	<79.5	..	..	..

Table II. Effect of Different Alkali Sulfates

Alkali Sulfate	Induction Period[a], Hr.	Catalyst Life[b], Hr.	Estimated Phenol Content of Product Based on Physical Properties[c]			
			Freezing pt., ° C.	Per cent	Specific gravity, 40°/15.6° C.	Per cent
Lithium	2	104	34.0	92.5	1.054	96.0
Sodium	11	109	34.5	93.0	1.055	96.5
Potassium	2	128	32.5	91.0	1.052	94.5
Rubidium	0	123	36.0	94.5	1.055	96.5
Cesium	0	100	33.5	92.0	1.051	93.5
None	2	56	28.0	87.5	1.046	90.0

[a] Hours of operation before freezing point of product exceeded 25° C.
[b] Hours of operation after induction period and before freezing point of product fell to 25° C.
[c] Average over active life of catalyst.

Table III. Preparation of Substituted Phenyl

Starting Material	Product	Single Pass Yield, %	Efficiency, %
3-Methyl-2-cyclohexenone (9)	*m*-Cresol	95	96
3-Methyl-5-propyl-2-cyclohexenone (2)	3-Methyl-5-propylphenol	90	95
3,5-Dimethyl-2-cyclohexenone (2)	3,5-Xylenol	90	95
α-Tetralone and α-tetralol mixture[a]	1-Naphthol	74	84
	naphthalene	12	
1,2-Cyclohexanediol[b] (12)	Catechol	65	..
	Phenol	25	..

[a] Obtained by liquid-phase air oxidation of Tetralin.
[b] Fed in a 21% aqueous solution.

The feed to the catalyst was then changed to a mixture of heads fractions and residue from the first distillation, consisting of 87.0% phenol, 1.5% water, a trace of benzene, and the remainder cyclohexanone. The catalyst lost no activity under such conditions. At the end of an additional 45 hours of operation with the changed feed, the crude condensate from the converter effluent contained 97.0% phenol.

Preparation of the catalyst on a larger scale by repeated dipping of the support material into a concentrated solution of the salts of the catalyst ingredients, with intermediate roastings between dippings, resulted in lower activity. Apparently this method did not allow as close control of the ratios of active materials in the finished catalyst as was possible with the single evaporation procedure.

Equilibrium Determination

Cyclohexanone was fed at a very slow rate without added hydrogen to a catalyst maintained at 300° C. The liquid product contained 79% phenol. The feed was then changed to phenol plus two moles of hydrogen; this gave 83% phenol in the product. The average of 81% was used in calculating the equilibrium constant; the remaining 19% was assumed to be cyclohexanol and cyclohexanone (other experiments had shown byproduct formation to be negligible). Application of the data of Cubberley and Mueller (*5*) to determine the alcohol-ketone ratio allowed calculation of a value of 2.0 for

$$K = \frac{P(\text{phenol}) \times P^2(\text{H}_2)}{P(\text{cyclohexanone})}$$

Equilibrium constants at other temperatures were calculated on the assumption of 40,000 calories as the heat of reaction. The curves in Figure 1 are based on these constants, together with those of Cubberley and Mueller.

Literature Cited

(1) Bagnall, W. H., Goodings, E. P., and Wilson, C. L., *J. Am. Chem. Soc.*, 73, 4794 (1951).
(2) Bailey, W. A., and Peterson W. H., Brit. Patent 559,682 (March 1, 1944).
(3) Bartlett, E. P., and Field, E., U. S. Patent 2,291,585 (July 28, 1942).
(4) Berkman, S., Morrell, J. C., and Egloff, G., "Catalysis," New York, Reinhold Publishing Corp., 1940.
(5) Cubberley, A. H., and Mueller, M. B., *J. Am. Chem. Soc.*, 69, 1535 (1947).
(6) Dowden, D. A., *J. Chem. Soc.*, **1950**, 242.
(7) Field, E., U. S. Patent 2,265,939 (Dec. 9, 1941).
(8) Griffith, R. H., "Contact Catalysis," 2nd ed., Oxford, Oxford University Press, 1946.
(9) Knoevenagel, E., and Klages, A., *Ann.*, **281**, 94 (1894).
(10) Loder, D. J., U. S. Patent 2,321,551 (June 8, 1943).
(11) Lukes, R. M., and Wilson, C. L., *J. Am. Chem. Soc.*, 73, 4790 (1951).
(12) Meerwein, H., Schoeller, W., Schwenk, E., and Borgwardt, E., Ger. Patent 574,838 (April 22, 1933).
(13) Sabatier, P., *Ber.*, 44, 1984 (1911).
(14) Sabatier, P., and Gaudion, C., *Compt. rend.*, **168**, 670 (1919).
(15) Skita, A., and Ritter, H., *Ber.*, 44, 668 (1911).

RECEIVED for review November 13, 1951. ACCEPTED March 10, 1952.

Engineering
and
Process
development

Effect of Intraparticle Diffusion

Agitated Nonflow Adsorption Systems

FRED J. EDESKUTY AND NEAL R. AMUNDSON
University of Minnesota, Minneapolis, Minn.

THE problem of adsorption of a solute from a solution onto a solid adsorbent has received such widespread and exhaustive treatment as almost to defy efforts to catalog the work that has been done. Any investigator is soon struck by the fact that of all this mass of research little has been done on the rate of adsorption. Amis (*1*) has given a short review of some rate studies and Harris (*9*) in three review articles covers the recent literature. The many factors which may influence the rate have been discussed by the present writers (*6*). Of all the factors the one which is most amenable to a simple treatment is that of the diffusion of solute inside the particles. It is this aspect of the kinetic process which will be dealt with here although the resistance to mass transfer at the particle surface may be included with little effort. Recently, Foster and Daniels (*7*) have concluded that for adsorption of nitrogen dioxide from air on silica gel the rate-determining step is the diffusion of the solute inside the particles. Eagleton (*5*) has found also that diffusion inside the particles seems to control the adsorption of water vapor on alumina. The general problem will be analyzed first, following which a special case—adsorption on cylindrical-shaped adsorbent particles—will be considered.

Let it be assumed that a vessel containing a volume, V, of solution contains N particles of adsorbent, all of which are the same size and shape. Let α be the fractional void volume of the solid particles and c_0 be the concentration of the solution in the vessel as well as that of the solution in the void volume of the porous adsorbent. At time $t = 0$ additional solute is admitted to the vessel so that the concentration of the solution exterior to the particles is C_0. It is then desired to obtain a formula which will predict the variation of solution concentration with time. The agitation level in the vessel is assumed to be high enough to ensure a uniform concentration throughout the external solution—i.e., there are no concentration gradients in the bulk of the solution. On the other hand, the agitation is not so violent as to reduce to zero the resistance to mass transfer at the particle surface.

If D is the diffusivity, c the concentration of solution in the void volume of a particle, and n the amount adsorbed in the particle per unit of volume of adsorbent, a simple rate balance over an element of volume in the particle gives

$$\alpha \text{ div. } (D \text{ grad. } c) = \alpha \frac{\partial c}{\partial t} + \frac{\partial n}{\partial t} \tag{1}$$

Note that if there is no adsorption, n is zero, and this equation reduces to the ordinary equation for diffusion. The quantities n and c are not independent and are related either by an equilibrium relationship, i.e., isotherm, or more generally by a kinetic relation which describes the adsorption process alone,

$$\frac{\partial n}{\partial t} = f(c,n) \tag{2}$$

where $f(c,n)$ is generally an empirical expression.

The condition at the particle surface may be stated in the form

$$-D \frac{\partial c}{\partial s} = k(c - C), \text{ on } S \tag{3}$$

where S is the surface which bounds the particle, k is the mass transfer coefficient characterizing the mass transfer resistance, and $\partial c/\partial s$ is the normal derivative taken on S.

The initial conditions can be stated as

$$\left.\begin{aligned} c &= c_0 \\ C &= C_0 \\ n &= n_0 \end{aligned}\right\} \text{ when } t = 0 \tag{4}$$

In addition, the relation between the internal and external concentrations must be obtained. The rate at which solute crosses the bounding surface of N particles is

$$-N\alpha \int_S\int (D \text{ grad. } c)\cdot\bar{s}\, dS = -N\alpha \int_S\int D \frac{\partial c}{\partial s}\, dS = V \frac{dC}{dt} \tag{5}$$

where the integrations are to be taken over the surface of a particle and $\bar{s}$ is the unit outward normal to S.