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CATALYTIC HYDROGENATION OF PHENOLS

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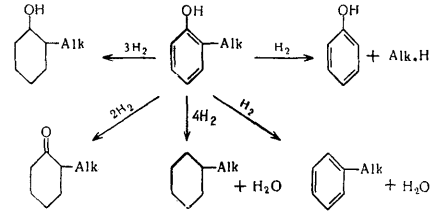
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INTRODUCTION

The primary tar obtained on processing a solid fuel contains a considerable quantity of phenols. Phenol itself and, to some extent, the cresols, are widely employed in industry for the preparation of plastics, synthetic fibres, dyes, chemical insecticides, anti-oxidants, tanning agents, varnish resins, etc. However, xylenols and other higher phenols have so far been insufficiently utilised. Any widespread use of these phenols is prevented by the absence of satisfactory methods for isolating them from the primary tar and for separating them. For this reason, besides the investigation of ways of effectively utilising individual phenols, efforts have been directed towards finding a method of converting the separate fractions of the primary tar into chemical products of value to the economy without isolating the individual components. A hydrogenation treatment is of great importance for exploiting phenols in this way, as it allows either phenol and cresols or hydrocarbons to be obtained from the higher phenols. Hydrogenation has now achieved wide application not only in laboratory practice but also in industry. The hydrogenation of coal, the reductive cracking of petroleum products, and also the refining and stabilisation of crude fuel have been extensively developed.

The hydrogenation of phenols can produce several types of changes: (1) hydrogenation of the benzene ring with retention of the hydroxyl group; (2) hydrogenation to hydroaromatic ketones; (3) conversion of phenols into aromatic and alicyclic hydrocarbons; and (4) reductive dealkylation of higher phenols with the formation of lower phenols:



In a review of published results it is convenient to separate these types of reactions. A description of earlier work on the changes undergone by phenols on hydrogenation has been given by Sabatier[1], Ellis[2], as well as in papers by Tishchenko and Belopol'skii[3], Petrick[4], Moldavskii and Lifshits[5,6] and Rapoport[7], and in the monograph by Lozovoi and D'yakova[8].

The literature on the hydrogenation of phenols is quite extensive. The majority of papers, however, are concerned with the hydrogenation of phenol itself, cresols, and to some extent xylenols. The behaviour of the higher phenols under conditions of hydrogenation has been quite inadequately studied. Investigation of the catalytic changes undergone by the higher fractions of the primary tar, both under conditions of hydrogenation and during processes of alkylation and dealkylation, is necessary for the successful solution of the problem of the effective utilisation of primary tars. It is therefore useful to investigate catalytic changes which occur on hydrogenation, both of the individual phenols in the higher fractions of the primary tars, and of narrow fractions in which one or other component has been concentrated. These fractions can be isolated by fractionation and chromatography. Up to the present, unfortunately, too little attention has been paid to these methods.

I. HYDROGENATION OF PHENOLS TO HYDROAROMATIC ALCOHOLS

The hydrogenation of phenol was first accomplished by Sabatier and Senderens in 1903 by passing phenol vapour together with excess hydrogen over reduced nickel at 215°–230°.[1] The main product was cyclohexanol mixed with cyclohexanone and small quantities of cyclohexene, cyclohexane, and benzene. At highter temperatures (250°–

300°) hydrogenation of the phenol nucleus did not occur at all, but partial reduction of phenol to benzene was observed. The hydrogenation of cresols and xylenols was also investigated. The latter, on hydrogenation by the Sabatier method, behave in various ways: 2,4-xylenol at 190°–200° gives the corresponding alicyclic alcohol in good yield; when 2,5-xylenol is hydrogenated, the hydroaromatic alcohol is accompanied by up to 10% of the cyclic ketone. In contrast, the main product of the hydrogenation of 3,4-xylenol under the same conditions is *o*-xylene (67%), only 25% of dimethylcyclohexanol and 8% of the ketone being obtained.

In 1906 Ipat'ev[9,10] first accomplished the hydrogenation of phenol in the liquid phase, in the presence of nickel oxide under a high pressure of hydrogen in a bomb at elevated temperatures. At 104 atm and 238° for 55.5 h he obtained pure cyclohexanol; lowering the temperature of hydrogenation to 215°–220° led to the formation of a mixture of cyclohexanol and cyclohexanone. These results were later reproduced by Osterberg and Kendall[11]. Orlov et al.[12] showed that the amount of catalyst taken was of great significance in liquid-phase hydrogenation by Ipat'ev's method; thus decreasing the amount of nickel oxide from 8 to 0.4% of the phenol taken trebles the time required for the reaction.

It was subsequently found that higher temperatures and pressures are not necessary to obtain homologues of cyclohexanol by the hydrogenation of phenols. Brochet[13] showed that hydrogenation of the cyclic double bonds in the phenol has already begun at 50°, and is complete between 100° and 120°. He obtained high yields of cyclohexanol, without admixture of the ketone, cyclohexene, or cyclohexane, with three specimens of reduced nickel (nickel vif, nickel carbonique, and nickel formique) at 130°–150° and an initial pressure of 10–15 atm in a copper autoclave. Similar results were obtained by Tishchenko and Belopol'skii, working with analogous conditions[13]. Raising the hydrogen pressure increases the rate of hydrogenation of phenol, but only up to a certain limit[14].

The production of hydroaromatic alcohols from phenols has been investigated in the presence of various hydrogenation catalysts — platinum, palladium, copper, and nickel.

Hydrogenation of phenol in the presence of copper catalysts was unsatisfactory. Thus over reduced copper at 200°–230° and 80 atm only 58% of cyclohexanol was obtained together with 10% of cyclohexane and 3% of dicyclohexyl ether[15]. A mixed copper–nickel catalyst gave somewhat better results, but only with liquid-phase hydrogenation; hydrogenation in the vapour phase was very slow and yielded a mixture of products, containing, apart from cyclohexanol, 9–14% of cyclohexanone and not less than 2–3% of high-boiling products, among which dicyclohexylcyclohexanone could be identified[16]. Catalysts based on copper can be conveniently employed for the selective hydrogenation of arylphenols. Thus, for example, in the presence of a copper–chromium catalyst *p*-phenylphenol yields phenylcyclohexanol, whereas in the presence of a chromium–nickel catalyst cyclohexylcyclohexanol is obtained[17].

Nickel catalysts, thanks to their high activity, comparatively low cost, availability, and simplicity of preparation, have been widely used and have now displaced all other catalysts. They are employed mainly in the form of Raney nickel (predominantly in laboratory practice), as an alloy of nickel with aluminium, and in the form of the finely dispersed metal deposited on different carriers. During recent years Japanese investigators have strongly recommended for the hydrogenation of phenols and other organic compounds the use of a nickel catalyst obtained from nickel formate and distinguished, according to their data, by particularly high activity[18,19].

Palfray[20] found that the ease of hydrogenation of the three isomeric cresols decreased in the order $o > p > m$, the times required for hydrogenation in the presence of Raney nickel at 95° and 120 atm and the yields of the corresponding alicyclic alcohols being 90 min and 90%, 160 min and 81%, and 244 min and 68% respectively. Raising the temperature to 250° favoured the formation of methylcyclohexane, especially in the experiments with *m*-cresol. 2,5-Xylenol and 3,4-xylenol were also hydrogenated comparatively slowly.

In addition to the alicyclic alcohol, hydrocarbons were present among the reaction products. *m*-Cresol was hydrogenated in absolute ethanol or methanol in the presence of Raney nickel at 150° and 140 atm to form 3-methylcyclohexanol in high yield[21]; 2- and 4-methylcyclohexanols were obtained in good yield by the hydrogenation of *o*- and *p*-cresols at 150° and 180 atm in the absence of solvent[22].

Nickel catalysts deposited on carriers, mainly keiselguhr and aluminium oxide, have been widely used for the hydrogenation of phenols because of their high and stable activity, and also the ease with which they can be regenerated, which enables the process to be carried out continuously. The regeneration of catalysts is carried out by oxidation with air at 300°–350° followed by reduction, or by some other suitable method[23,24]. Yukhnovskii and Sorokin[25] hydrogenated *o*-, *m*-, and *p*-cresols at 170°–180° and 15–20 atm in the presence of nickel deposited on kieselguhr and with a mixed cobalt–nickel–copper catalyst, and obtained the corresponding methylcyclohexanols in good yield. In the presence of nickel on kieselguhr at 160° and a maximum pressure of hydrogen of 126 atm, *m*-cresol is quantitatively hydrogenated to 3-methylcyclohexanol[26]; hydrogenation of *m*-cresol at atmospheric pressure, 125°–130°, and a volume flow of 0.1–0.2 h^{-1} in the presence of a 10% nickel–alumina catalyst gives 3-methylcyclohexanol in 86% yield, the catalyst not requiring regeneration for quite a long time[27]. 3,4-Dimethylcyclohexanol was the sole product of the hydrogenation of 3,4-xylenol at 100° and 100 atm pressure of hydrogen in the presence of a 20% nickel–alumina catalyst[28]. The catalyst lost its selective action only at temperatures above 250°.[28,29] Cornubert et al.[30] obtained a mixture of isomeric 3,5-dimethylcyclohexanols in 87% yield on hydrogenating 3,5-xylenol by Skita's method[31] in the presence of nickel deposited on kieselguhr. Nickel catalysts, as well as platinum and palladium, are recommended in several patents on the hydrogenation of mono- and di-t-alkylphenols to the corresponding alcohols, which are of interest as intermediates for organic synthesis, insecticides, and anti-oxidants for mineral oils and petrol[32–35]. Hydrogenation of alkylphenols containing seven or more carbon atoms in the alkyl group[36], and also of t-butylphenols[37,38], is carried out in the presence of nickel on kieselguhr. The hydrogenation of alkylphenols having a side chain containing more than five carbon atoms, and of those with tertiary alkyl groups, is complicated by their hydrogenolysis. This can be prevented by carrying out the hydrogenation in the presence of organic bases (pyridine, triethylamine, etc.). In the presence of pyridine, alkylphenols with a side chain containing 9–12 carbon atoms are readily hydrogenated, over nickel on kieselguhr at 250°, giving good yields of the corresponding alkylcyclohexanols, whereas in the absence of pyridine these alkylphenols are completely reduced to hydrocarbons[39].

Nickel catalysts are successfully employed for the hydrogenation of phenols both in the liquid and in the vapour phase in dynamic systems. For vapour-phase hydrogenation at atmospheric pressure d'Or and Orzéchowski[40-42] and Griffith and Hill[43] recommend the use of a nickel catalyst promoted with cerium. In several patents nickel catalysts are recommended for the hydrogenation of phenols by a continuous process both in the liquid phase with a finely dispersed catalyst[44] and in the vapour phase at atmospheric or a somewhat higher pressure of hydrogen[45,46].

According to results obtained by Ungnade and Nightingale[47], promotion of a nickel catalyst with alkali has a favourable influence on the hydrogenation of phenols. In the presence of small amounts of alkali or the corresponding sodium or potassium phenate, phenol and its alkyl derivatives (cresols, xylenols, trimethylphenols, t-butylphenols) are hydrogenated more rapidly and at lower temperatures. Addition of alkali is particularly necessary for the hydrogenation of sterically hindered phenols, in particular 2,6-disubstituted phenols[48]. This might be explained by the intermediate product, the alicyclic ketone, being more readily enolised in the presence of alkali, and the enol form in turn being considerably more readily reduced by the hydrogen. The promoting effect of alkali on the reduction of aldehydes and ketones has been noted also by other authors[49,50]. Paty[51], however, is inclined to explain the activation of the Raney nickel–aluminium catalyst by alkali in terms of the effect of the latter on a nickel–aluminium alloy, leading to a change in the activity of the catalyst.

Tsutsumi et al.[52] have also shown that cresols are more efficiently hydrogenated in the presence of a Raney nickel catalyst if the amount of alkali used is sufficient to dissolve the whole of the aluminium contained in the catalyst.

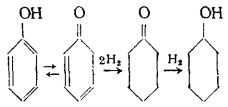
Thus, hydrogenation of the pure individual phenols to hydroaromatic alcohols can be readily achieved at a comparatively low temperature (down to 200°) at high and at ordinary pressures in the presence of nickel or catalysts of the platinum group. Hydrogenation of technical phenolic mixtures is a more difficult problem, owing to the poisoning of the catalyst by sulphur compounds[25,53]. This question has been insufficiently discussed in the literature, and mainly only in relation to the production of cyclohexanol from technical phenol.

Belotzerkovskii[54] noted that a catalyst prepared by heating nickel nitrate to 200° and then reducing it with hydrogen, hydrogenates technical phenol in the vapour phase at 175°–180° provided no thiophenes are present.

Polozov[55] investigated the properties of a series of catalysts not subject to poisoning with sulphur (MoO_3 + + CoS, MoS_3, MoS_3 + S, and $NiMoO_4$) with the aim of obtaining cyclohexanol from technical phenol, and concluded that these catalysts are suitable for hydrogenation only at temperatures of about 220° and above; however, their dehydrating power becomes manifest under these conditions, and diminishes the yield of alcohol.

Rapoport and Sil'chenko[56] achieve a high yield of cyclohexanol (90–95%) from technical phenol in the presence of Raney-type nickel–aluminium and nickel–cobalt–aluminium catalysts at 173°–200° and 50–100 atm pressure of hydrogen. A nickel–aluminium alloy catalyst was first used for the hydrogenation of phenol by Bag et al.[57] Deryabin and Yasnyi[58] obtained 90–95% of cyclohexanol, 3–6% of the ketone, and 0.5–1.0% of cyclohexane by hydrogenating phenol at 130°–140° and 1.5–2.0 atm in the presence of a Bag catalyst. Rapoport and Sil'chenko, by raising the hydrogen pressure during hydrogenation to 50–100 atm, considerably shortened the duration of the process. Supported nickel catalysts, after they have first been specially treated with hydrogen sulphide, may also be useful for the hydrogenation of phenolic tars.

Much research on the hydrogenation of phenols to alicyclic alcohols has been devoted to determining the mechanism of hydrogenation and the configuration of the resulting cyclohexanols. Depending on the experimental conditions, hydrogenation of phenol yields either pure cyclohexanol or a mixture of it with cyclohexanone, cyclohexane, and benzene. Sabatier[1] assumed that cyclohexanone is obtained as a result of the decomposition of cyclohexanol. Ipat'ev[9,10], however, regarded cyclohexanone as the primary product of hydrogenation, subsequent reduction of which yields cyclohexanol. On the basis of these views he suggested the following scheme for the hydrogenation:



He regarded this scheme as confirmed by the fact that at higher temperatures no ketone was obtained, although its formation would be expected from the Sabatier scheme. The same scheme was put forward by Skita and Ritter[59], who, on hydrogenating phenol by the Sabatier method at 100°–120° on nickel, found that hydrogenation of the phenol is accompanied by a partial dehydration of cyclohexanol to cyclohexene with hydrogenation of the latter to cyclohexane, part of which is dehydrogenated to benzene. The formation of cyclohexanone as an intermediate product in the hydrogenation of phenol to cyclohexanol was demonstrated also by the work of Vavon[60-62] and Grignard[63-65]. Ando[66] showed that when reaction is carried out in the absence of hydrogen and at temperatures above 250° the reverse reaction, the formation of the ketone from cyclohexanol, can occur. Under the conditions of the hydrogenation of phenol to cyclohexanol, there is a partial dehydration of cyclohexanol with the formation of cyclohexene and water, the former being hydrogenated to cyclohexane.

The results obtained by Ipat'ev and other investigators on the mechanism of the hydrogenation of phenols were later confirmed by kinetic measurements. The kinetics of the catalytic hydrogenation of phenol in the liquid phase were studied by Jungers and his collaborators[67], who showed that hydrogenation does in fact proceed via the formation of cyclohexanone. The rate of hydrogenation of cyclohexanone to the alcohol was found to be greater than its rate of formation from phenol. The activation energies for the formation of cyclohexanone and for its reduction to cyclohexanol proved to be 8500 and 6500 cal/mole respectively. The order of reaction for the hydrogenation of phenols to hydroaromatic alcohols evidently lies between one and zero[68,69].

The vapour-phase hydrogenation of phenols at normal pressures occurs in the same way as the liquid-phase hydrogenation at high pressures, i.e. via the intermediate formation of the ketone[42].

Published data on the configuration of the geometric isomers of the hydroaromatic alcohols are very contradictory. The production of one or other geometric isomer of the alcohol depends on the conditions of hydrogenation. Patents obtained by Schering–Kahlbaum[70,71] describe the hydrogenation of an aqueous solution of sodium *p*-cresate on

nickel under pressure to form *trans*-4-methylcyclohexanol. Braun and Haensel[72] hydrogenated the symmetrical xylenol in the presence of a nickel catalyst in an autoclave at 230° and obtained a mixture of the *cis*- and *trans*-isomers of the corresponding alcohol and ketone; the content of both *trans*-isomers was increased with decrease in the amount of hydrogen absorbed by the xylenol. Skita[73] found the formation of the *trans*- or *cis*-form of the alcohol to be strongly dependent on the temperature of hydrogenation and the pH of the medium. On hydrogenating *o*-, *m*-, and *p*-cresols in the presence of colloidal platinum in a strongly acid medium (a mixture of acetic and hydrochloric acids) at 2–3 atm and 70°, he obtained all three methylcyclohexanols in the *cis*-form. On hydrogenation in neutral or alkaline medium at room temperature, the *trans*-isomers were obtained; a weakly acid medium yielded a mixture of *cis*- and *trans*-isomers. Similar results were obtained by Vavon[61,62] who hydrogenated *o*-propylphenol and *o*- and *p*-isopropylphenols in the presence of platinum black.

The hydrogenation of *o*- and *p*-cresols in the presence of a nickel catalyst at 150° and high pressures yielded predominantly *trans*-2- and *trans*-4-methylcyclohexanols[22,74,75], as did hydrogenation in the presence of a copper–chromium catalyst[76]. Hydrogenation of *o*- and *p*-cresols at room temperature, both in the presence of platinum oxide by the Adams method[77] and in the presence of Raney nickel[78] in methyl alcohol, yielded the corresponding methylcyclohexanols with the *cis*-forms predominating.

Preferential formation of the *cis*-isomer was also observed in the hydrogenation of *p*-t-butylphenol in the presence of a rhodium catalyst[79].

For a long time mistaken views were held as to the properties of the *cis*- and *trans*-isomers of 3-methylcyclohexanol. It has now been proved[80–82] that the isomer of 3-methylcyclohexanol which Skita[73,83] regarded as the *trans*-isomer, and which was accepted as such in several other papers[21,84], is in actual fact the *cis*-isomer. It has been shown that, in conformity with the concept of axial and equatorial bonds, the *cis*-configuration of 3-methylcyclohexanol is the most stable. This isomer has a lower density and a lower refractive index, in opposition to the Auwers–Skita rule. New data have also been obtained on the stereoisomerism of the 2,5-dimethylcyclohexanols[85].

From a study of the hydrogenation of the cresols and the corresponding alicyclic ketones, Peppiatt and Wicker[86] concluded that hydrogenation at room temperature always leads to the formation of alcohols with a high content of the isomer containing an axial (polar) hydroxyl group, i.e. the *cis*-1,2-, *trans*-1,3-, and *cis*-1,4-isomers; raising the temperature (100°–200°) enriches the mixture in the other isomer. These authors explain the contradictory results in the literature by the possible isomerisation of the isomers obtained initially under the conditions of hydrogenation, since at elevated temperatures nickel and platinum catalysts containing a minute amount of alkali catalyse the interconversion of the *cis*- and *trans*-forms[78,86].

Table 1 gives the properties of *cis*- and *trans*-methylcyclohexanols and the melting points of their derivatives based on results obtained by different workers. The considerable differences in the melting points of several of these derivatives are evidently to be explained by incomplete separation of their isomers, and possibly also by polymorphism, which is particularly characteristic of derivatives of 3-methylcyclohexanol. At the present time, thanks to progress in the stereochemistry of the cycloalkanes[87–89], methods have been worked out for the preferential production of the *cis*- or the *trans*-isomers of alkylcyclohexanols, and more reliable values have been obtained for the properties of their derivatives[22,75,90]. Heats of combustion of the methylcyclohexanols are given in the paper by Eliel and Haber[91].

TABLE 1. Properties of methycyclohexanols and their derivatives.

Methylcyclohexanol	B.P., °C/mm Hg	d_4^{20}	$d_4^{t°}$	n_D^{20}	Melting points of derivatives, °C								reference
					o-nitrobenzoate	*p*-nitrobenzoate	3,5-dinitrobenzoate	acid phthalate	α-naphthylurethane	phenylurethane	*p*-aminobenzoate	acid succinate	*p*-toluenesulphonate	
cis-2-	77–78/20	—	0.9228(25)	—	—	35–36	—	89–90	—	78–80	—	30–31	—	84
	—	0.9337	—	1.4640	—	—	98–99	—	—	90–91	—	—	—	83
	50.5/2.9	—	0.9274(30)	1.4649	oil	56–57	100–101	102–104	112	92–93	—	—	—	22
	60.4/12	0.9360	0.9118(25)	1.4653	—	54.8–55.6	—	103.8–105.0	—	92,6–93,4	—	—	56.7–57.2	75
trans-2-	79/20	—	0.9228(25)	—	—	65	—	124–125	—	105–106	—	44–46	27–28	84
	—	0.9238	—	1.4611	—	—	114–115	—	—	105–106	—	—	—	83
	53.0/3.5	—	0.9174(30)	1.4616	60–60.5	64.5–65	117	124–125	156	105	—	—	—	22
	66.7/12	0.9247	0.9208(25)	1.4616	—	63.7–64.2	—	125,2–125.8	—	105.2–105.5	—	—	27.5–28.4	75
cis-4-	78–79/20	—	0.9180(25)	—	—	94	—	72–73	—	124	—	—	—	84
	—	0.914	—	1.4549	—	—	133–134	—	—	118–119	—	—	—	83
	52.0/2.0	—	0.9173(30)	1.4614	oil	—	106–107	84–85	106–107	103–104	—	—	—	22
trans-4-	78–79/20	—	0.9080(25)	—	—	67	—	119–120	—	124–125	—	—	71–72	84
	—	0.913	—	1.4534	—	—	139–140	—	—	124–125	—	—	—	83
	54.0/3.0	—	0.9040(30)	1.4561	68	64–65	142	120–121	159,5–160	124–124.5	—	—	—	22
cis-3-*	78–79/20	—	0.9104(25)	—	—	58	—	93–94	—	92–94	—	oil	39–40	84
	—	—	0.9072(30)	1.4573	—	48	99	—	130	92	—	—	—	21
	—	0.9155	0.9065(30)	1.4572	—	45.5–46.5	—	—	—	—	141.5–142.5	28.4–29	34–34.4	90
trans-3-*	77–78/20	—	0.9091(25)	—	—	65	—	82–83	—	101–103	—	—	46–47	84
	—	—	0.9137(30)	1.4583	—	63	111	—	118	93–91; 103–?	—	—	—	21
	—	0.9214	0.9138(30)	1.4590	—	83–83.5	—	68–71	—	91	111–112	48.5–49.0	18.6–19.2	90

* In refs. 21 and 84, the *cis*-isomer is denoted as *trans*, and the *trans*-form is regarded as the *cis*-isomer.

II. HYDROGENATION OF PHENOLS TO HYDROAROMATIC KETONES

As has been indicated above, cyclohexanone is an intermediate product in the hydrogenation of phenol to cyclohexanol. Hydrogenation of the ketone takes place more rapidly than its formation from phenol, which makes it difficult to carry out the hydrogenation in such a way that the process can be stopped at the stage of formation of the ketone. The position is still further complicated by the fact that cyclohexanone and similar ketones, even on hydrogenation under mild conditions, yield an appreciable quantity of phenols [92,93], as a result of a dismutation (disproportionation) reaction:

$$3C_6H_{10}O \rightleftharpoons C_6H_5OH + 2C_6H_{11}OH.$$

Nazarov et al. [94] observed that cyclohexanone underwent this reaction in the presence of aluminium oxide at 390°–450°.

According to Zil'berman [95], the dismutation of cyclohexanone is thermodynamically possible over the temperature range 289°–700°K, and may be operative during the catalytic synthesis of this compound. He obtained 35% of the ketone on passing the vapours of phenol and cyclohexanol (at a molar ratio of 1 : 2) over a nickel-containing catalyst heated to 150°–200°.

A review of the literature on the hydrogenation of phenols to hydroaromatic alcohols shows that many investigators have obtained alcohols mixed with the ketone, but in the majority of cases the amount of the latter did not exceed 10–15%. Ando [66], on hydrogenating phenol in the presence of reduced nickel at 260° and 48 atm, obtained 37% of cyclohexanone. Skita [73] obtained 80% of methylcyclohexanone by the controlled absorption of hydrogen by *o*-cresol in the presence of colloidal platinum in a neutral medium at 70°. Barney and Hass [96], by the catalytic hydrogenation of thymol in aqueous alkali at 150°–160° and 42 atm, obtained the corresponding ketone in 80% yield (based on the phenol consumed). In 1958 Joris and Vitrone [97] patented the selective hydrogenation of phenol to cyclohexanone in the presence of palladised charcoal. The hydrogenation products contained 79% of cyclohexanone.

In view of the unavoidability of obtaining a mixture of alcohol and ketone, several workers have recommended that the hydrogenation of phenols should be carried out in two stages: (1) complete hydrogenation in some way to yield a mixture of alcohol and ketone, and (2) dehydrogenation of alcohol to ketone [29,99]. Chinese investigators have prepared cyclohexanone in this way [98]. Cyclohexanol was obtained by hydrogenation of phenol on a nickel–kaolin catalyst at 140° and 80 atm, and then dehydrogenated to the ketone (yield 55%) in a flow system at 250°–300° under reduced pressure (155 mm) in the presence of copper on asbestos. Barney and Hass [96] carried out a direct quantitative dehydrogenation of menthol (crude hydrogenated thymol) by fractionation on an efficient column in a flask filled with Adkins' copper–chromium catalyst.

A partial hydrogenation of phenols cannot always be achieved even in the case of sterically hindered polyalkylphenols. Whitaker [100] showed that the structure of the polyalkylphenol determines the products which can be obtained by its hydrogenation. If one *ortho*-position in the phenol is unoccupied, its partial hydrogenation to the ketone may be impossible, even if the other *ortho*-position is occupied by a strongly shielding group, such as t-butyl. With a methyl and a t-butyl group in the *ortho*-positions, either the alcohol or the ketone may be obtained, depending on the conditions. If, however, both *ortho*-positions are occupied by strongly shielding groups, ketones alone are obtained, and hydrogenation to the alcohol does not occur. These results are in agreement with the data of Whitmore [101] on the effect of steric hindrance on the behaviour of ketones under hydrogenation conditions.

Whitaker [100], by the hydrogenation of polyalkylphenols in the presence of Raney nickel (10%) at 140°–240° and 85–175 atm, obtained the following alcohols and ketones which had not been described previously: 6-t-butyl-3-methyl-, 4,6-di-t-butyl-2-methyl-, 4,6-di-t-butyl-3-methyl-, and 6-t-butyl-2-methylcyclohexanols; 6-t-butyl-2-methyl-, 4,6-di-t-butyl-2-methyl-, 2,4,6-tri-t-butyl-, and 2,6-di-t--butyl-4-methylcyclohexanones; and 2,6-di-t-butyl-4--methylcyclohex-2-enone.

Thus, it is possible in principle to obtain alicyclic ketones by the hydrogenation of the corresponding phenols, but the yield of ketone depends not only on the conditions of hydrogenation, the nature of the catalyst, and the amount of hydrogen absorbed, but also on the structure of the original phenol.

III. REDUCTION OF PHENOLS TO AROMATIC HYDROCARBONS

The reduction of phenols to aromatic hydrocarbons was of interest long ago from the point of view of exploiting the phenols in primary tars. This mode of hydrogenation of phenols has been the most fully studied, and is widely represented in the literature.

Smith [102] in 1890 was the first to direct attention to the formation of benzene and toluene by passing phenol and cresol through a heated tube filled with carbon. However, the yield of hydrocarbons was low [103–105]. Kling and Florentin [106] obtained 35% of hydrocarbons by heating technical cresol at 480° and 80 atm in the presence of aluminium chloride. Ipat'ev and Orlov [107] were able to effect partial conversion of phenol into benzene and of cresol into a mixture of benzene and toluene in the presence of alumina and copper oxide. There are numerous papers on the reduction of phenols to aromatic hydrocarbons published by the school of F. Fischer [108], who showed that the lower phenols (cresols, xylenols, and technical phenolic mixtures) can be reduced by hydrogen to aromatic hydrocarbons by passing them through an iron tube, coated with zinc or sulphur, at 700°–750°. Reduction of phenol homologues is accompanied by a partial elimination of methyl groups. For example, cresol yielded a 5 : 1 mixture of benzene and toluene with a total yield of 65–78%. The formation of aromatic hydrocarbons from phenols, especially cresols, also takes place at such high temperatures in the absence of a catalyst, but the yield is then comparatively low [109].

The work of Fischer gave an impetus to many investigations on these lines. The efforts of research workers were directed towards lowering the reaction temperature and selecting active catalysts which were resistant to poisoning. It was suggested that dehydrating oxide catalysts such as the oxides of aluminium, thorium, and chromium [110–112], which are stable to the action of catalyst poisons, should be used for the reduction of phenols to aromatic hydrocarbons. It was found, however, that dehydrating catalysts are most effective when activated by small amounts of hydrogenation catalysts [113,114] or when these oxides are used as carriers for the latter [115–117].

Hydrogenation catalysts based on metal oxides and sulphides proved to be effective for the reduction of phenols to hydrocarbons. These catalysts were introduced as the result of the work of the IG. Farbenindustrie AG. on the Bergius process for obtaining petrol from coal. They possess several advantages compared with metallic catalysts, for they are resistant to poisoning and are effective at high temperatures. Catalysts based on molybdenum have been most widely used. Molybdenum oxide was found to be effective for the hydrogenation not only of individual phenols but also of their technical mixtures, in particular for the reduction of "tricresol"[118], and also the phenolic oil from low-temperature tar[119-121]. Active molybdenum oxide can be prepared in various ways — from ammonium molybdate, from molybdic acid, or by dissolving the metal in nitric acid and then heating[122] — but technical molybdenum oxide is inactive. Bahr and Petrick[123] noted that the activity of molybdenum oxide diminishes under the conditions of hydrogenation of phenolic tars at atmospheric pressure, and suggested this was the result of the conversion of the active molybdenum trioxide into the less active dioxide. However, a special study of the origin of the molybdenum oxide and X-ray analysis of its structure did not support this hypothesis. It was found that the active hydrogenation catalyst was actually the dioxide, produced by reduction of the molybdenum trioxide in the course of the reaction[124,125]. The essential factor in producing an active catalyst is evidently not the mode of preparation of the molybdenum oxide but its subsequent reduction to the lower oxide. Maslyanskii and Shenderovich[124], studying the preparation of catalysts for the destructive hydrogenation of fuel, found that the greatest catalytic activity is obtained on complete reduction of MoO_3 to MoO_2. The optimum temperature for reduction was determined as about 300° for hydrogen pressures of both 50 and 200 atm. Either raising or lowering the temperature of reduction appreciably diminished the activity of the catalyst. When molybdenum oxide was used on a carrier, its activity varied to a considerably smaller extent with change in the conditions of reduction.

The reduction of phenols in the presence of molybdenum oxide can be carried out at either high or ordinary pressures, a temperature of about 325°–450° being adequate in the latter case. Newall[109] obtained 70% of toluene, 10% of other liquid hydrocarbons, and 14% of water by the hydrogenation of a cresol fraction of a tar from cracking, using atmospheric pressure, 450°, and a volume flow rate of $0.2\ h^{-1}$ and in the presence of molybdenum oxide deposited on activated wood charcoal. However, the rate of hydrogenation of phenols is directly related to the hydrogen concentration. Increase in the pressure of hydrogen greatly shortens the time required for the process and to some extent lessens the formation of coke. It is therefore more economical to carry out the process at high pressure, but this, as will be shown below, limits the yield of the required hydrocarbons.

The activity of molybdenum catalysts is raised by the addition of copper, chromium oxide[122,123,126], and especially sulphur or its compounds. The promoting action of sulphur and its compounds in the reduction of phenols was noted in several papers[127-131]. Tropsch[118] investigated the catalytic effect of a series of sulphur compounds on the hydrogenation of a technical mixture of cresols and found the sulphides of molybdenum, tungsten, and cobalt to be the most active. Moldavskii and Prokopchuk[132] and Prokopets and Eru[133] showed that the most convenient is an MoS_2 catalyst obtained by reduction of MoS_3, since the latter, like MoO_3, is not very stable and gives irreproducible results, being converted during the process into MoS_2.

Moldavskii and Lifshits[5] investigated in detail the influence of physical factors on the hydrogenation of phenol and *o*-cresol in the presence of 5% of MoS_2 in an autoclave. They showed that at 350°–370° and 25–50 atm, phenol and *o*-cresol are readily reduced to a mixture of aromatic hydrocarbons and naphthenes. The results were checked with technical phenolic mixtures (oils from the primary tar of Cheremkhovo coals) containing 50% of phenols[134]. Experiments carried out both in an autoclave and using a continuous plant gave good results in the presence of molybdenum disulphide deposited on clay (1 : 9). Tricresol at 400° and 15–40 atm yielded 72.5% of toluene, 1.5% of unsaturated compounds, and 5–10% of methylcyclohexane; the higher phenols yielded a petrol of the same quality as obtained from individual phenols. Moldavskii and Lifshits showed that hydrogen acts on phenols in two independent ways:

1. Reduction of the phenol with formation of an aromatic hydrocarbon and water:

$$C_6H_5OH \xrightarrow{H_2} C_6H_6 + H_2O.$$

2. Hydrogenation of the ring, via a series of intermediate stages, the result being a hydroaromatic hydrocarbon:

$$C_6H_5OH \xrightarrow{3H_2} C_6H_{11}OH \xrightarrow[-H_2O]{} C_6H_{10} \xrightarrow{H_2} C_6H_{12}.$$

The formation of cyclohexane by the hydrogenation of benzene occurs to a very slight extent, if at all. Special experiments have shown that in the presence of MoS_2 at 350° and 100 atm not more than 3–4% of the benzene and toluene has undergone hydrogenation. In the presence of molybdenum oxide at 400°–450° and 65–100 atm, benzene is not hydrogenated, whereas phenol is converted into cyclohexane to the extent of 10–30%[135]. Further, phenol, as Klimov and Bogdanov[136] have shown, exerts an inhibiting effect on the hydrogenation of aromatic hydrocarbons. The formation of benzene from cyclohexane at high pressures and in the presence of a hydrogenating catalyst is also unlikely. Thus the formation of benzene by the hydrogenation of phenol in the presence of molybdenum catalysts at high temperatures and pressures is a result of the direct reduction of the phenol. The bulk of the cyclohexane is formed by the dehydration of cyclohexanol with subsequent hydrogenation of the cyclohexene formed. This picture of the mechanism of formation of aromatic and hydroaromatic hydrocarbons under these conditions agrees with the views of Roberti[137], Cawley[138], and Ando[139]. Cyclohexene (or methylcyclohexene) has been detected among the reaction products, but it has not yet been possible to detect the alcohols. A series of papers have described the behaviour of cyclohexanol at 340°–470° and 100 atm in the presence of ammonium molybdate[128], wood charcoal impregnated with molybdic acid[138], molybdenum oxide and sulphide[140], and also cobalt sulphide[137]; it was shown that cyclohexanol is completely converted into cyclohexane. Moldavskii and Lifshits[5] found that lowering the hydrogen pressure favours the first reaction, but raising the pressure increases the content of hydroaromatic hydrocarbons. Thus when the pressure of hydrogen was raised from 50 to 150 atm the quantity of aromatic compounds in the petrol fell from 84.7 to 66.4%. Ando[141], by the hydrogenation of the phenolic fraction of low-temperature tar using MoO_3 at 465° and 250 atm, obtained 77% of hydrocarbons consisting of about equal proportions of aromatic

compounds and naphthenes. When the pressure was diminished to 50–100 atm, a hydrocarbon mixture was obtained, containing, depending on the conditions, 14–74% of naphthenic and 23–86% of aromatic compounds[142]. Cawley[138] obtained 37% of C_6H_{12} and 25% of benzene from phenol in the presence of wood charcoal impregnated with ammonium molybdate, at 100 atm and 400°, and, at 450°, 35% of cyclohexane and 44% of benzene. Moldavskii and Lifshits[5] calculated the mean rates of reduction and hydrogenation of phenol and *o*-cresol from experimental results. They found that at pressures above 20 atm the rate of hydrogenation is directly proportional to the pressure of hydrogen. Measurement of the temperature coefficient of the reaction showed that within the range 330°–370° the rate of reaction of phenol over MoS_2 increases considerably with rise in temperature. The temperature coefficients for these reactions with phenol and *o*-cresol were found to be 1.42–1.60. The activation energies amounted to 37 000 for the reduction and for the hydrogenation of phenol, 27 000 for the reduction of *o*-cresol, and 33 000 cal/mole for the hydrogenation of the latter. Bobyshev et al.[143] have determined the temperature coefficient of the hydrogenation of phenol, in the presence of MoS_2 at 200 atm over the range 350°–400°, as 1.36–1.40, and the energy of activation as 24 000–28 000 cal/mole.

Thus experimental and thermodynamic data show that in the hydrogenation of phenols in the presence of molybdenum catalysts a decrease in pressure produces an increase in the amount of aromatic hydrocarbons, but this is accompanied by a retardation of the reaction and an increase in coke formation. At high temperatures phenols tend to undergo various condensation and polymerisation reactions. Among the products which have been detected are diphenyl ether and bicyclohexyl[144], *p*-cyclohexylphenol and cyclohexylbenzene[5], and bicyclohexyl and its isomers[145]. All these products may serve as material for coke formation. In view of this, Rapoport et al.[146] proposed that the conversion of phenols into aromatic hydrocarbons should be carried out in two stages, by (1) obtaining a mixture of aromatic and hydroaromatic hydrocarbons at 370°–430° and 90 atm hydrogen pressure, and (2) dehydrogenating this mixture in the vapour phase at 450°–500° and a lower pressure (20–40 atm) to aromatic hydrocarbons. A 1952 German patent[114] also recommends a stepwise production of aromatic hydrocarbons from high-boiling phenols or oils which are rich in phenols.

In order to obtain from phenols hydrocarbons which are rich in aromatic compounds and contain only a small amount of naphthenes, Bahr[126,147] recommended carrying out the reduction of phenols not with hydrogen itself but with a diluted form of the gas, e.g. water gas. When pure hydrogen was used, he replaced the molybdenum catalyst by a less active iron–copper (1 : 1) catalyst. When phenol was hydrogenated in the presence of such a catalyst at 400°–450° and 30 atm, the content of hydroaromatic hydrocarbons did not exceed 5–9%. Japanese investigators[148] recommend the employment of an iron oxide catalyst on a carrier with added nickel and chromium, and that the hydrogenation of phenols should be carried out at atmospheric pressure.

When phenol is hydrogenated in the presence of an iron oxide catalyst at pressures of the order of 150 atm, the main product is cyclohexane[136]. A high content of aromatic hydrocarbons among the products of the hydrogenation of phenols is characteristic of tungsten sulphide even at high pressures of hydrogen[136,149]. The hydrocarbon portion of the product of the hydrogenation of phenol at 400°–420° and 150 atm in this case consisted of 75–85% of benzene[136]. The hydrogenation of phenols in the presence of either iron or tungsten catalysts, which form the basis of industrial catalysts for the destructive hydrogenation of various forms of fuel, has been insufficiently discussed in the literature. Data exist pointing to the suitability of using a tungsten catalyst together with nickel[111,150], the presence of which diminishes the cracking and isomerising effect of tungsten sulphide[151].

The dependence of the rate of reduction of phenols on their structure has been inadequately studied up to the present. Bobyshev et al.[143] measured the relative rates of reduction of eleven monohydric phenols and thiophenols to aromatic hydrocarbons at 350° and an operating hydrogen pressure of ~ 100 atm in the presence of MoS_2 when the reaction was not more than 30% complete. They observed no great differences in the rates of reduction of phenols with variation in the size, number, and position of alkyl substituents. The majority of phenol homologues are reduced at about 70% of the rate for phenol itself, naphthols are reduced twice as rapidly, and thiophenol 28 times as rapidly, as phenol.

The reduction of alkylphenols to aromatic hydrocarbons can be employed also as a preparative and analytical method to obtain individual aromatic hydrocarbons. For this purpose the corresponding aryl diethyl phosphates or toluene-*p*-sulphonates are first prepared, and they are then reduced to the corresponding hydrocarbons[152–154].

At the present time the reduction of phenols to aromatic hydrocarbons is of no great practical interest, since the phenols themselves and their hydrogenation products — hydroaromatic alcohols — form a valuable raw material for the chemical industry, enjoying a wide application in different branches of the national economy.

IV. PRODUCTION OF HYDROAROMATIC HYDROCARBONS

Hydroaromatic hydrocarbons are obtained in the course of the hydrogenation of phenols mainly as a result of dehydration of hydroaromatic alcohols, as was indicated above. The formation of hydroaromatic hydrocarbons during the hydrogenation of phenols to the corresponding alcohols has been observed by many investigators, but only small amounts were obtained and they were accompanied by the main product of hydrogenation, the hydroaromatic alcohol. For the preferential production of the alicyclic hydrocarbon it is necessary to carry out hydrogenation at a higher temperature to ensure dehydration of the alcohol. Ando[66,155] showed that, whereas at 150°–250° and with high pressures in the presence of reduced nickel cyclohexanol is obtained from phenol, at 250°–350° it is completely dehydrated to cyclohexene, and then converted into cyclohexane, which does not change further on heating to 470°. Ando was able to obtain almost pure cyclohexane from phenol at 470° and an initial hydrogen pressure of 117 atm. Skita[31] obtained a 40% yield of 1,3-dimethylcyclohexane by the hydrogenation of 3,5-xylenol in the presence of colloidal platinum at 250° and 50 atm. Hydroaromatic hydrocarbons can be obtained from phenols at comparatively low temperatures and normal pressures in the presence of a nickel catalyst. Thus Shuikin et al.[27] obtained methylcyclohexane in 71% yield by hydrogenating *o*-cresol in a flow system at 175°, employing as catalyst nickel (20%) deposited on aluminium oxide; 3,4-xylenol at 200° produced 1,2-dimethylcyclohexane with a yield of 62%[28].

When phenols are hydrogenated on oxide catalysts, a mixture of aromatic and hydroaromatic hydrocarbons is usually obtained, the proportion of the latter being greatest in the presence of nickel oxide[156] and less with hydrogenation on a molybdenum and especially a tungsten catalyst[118,141,149]. However, hydrogenolysis with the formation of lower aliphatic hydrocarbons occurs to a greater extent on a nickel catalyst[113].

Alekseeva and Moldavskii[157] obtained mainly naphthenic hydrocarbons in the vapour-phase hydrogenation of phenols in the presence of the industrial catalyst WS_2 + NiS + Al_2O_3. The quantity of aromatic hydrocarbons depended on the structure of the initial phenol. Alkylated phenols gave a greater quantity of aromatic compounds. Thus with phenol, *o*- and *p*-cresol, and n-butylphenol the contents of aromatic hydrocarbons were 4, 5.5, 7, and 15% respectively. The proportions of aromatic hydrocarbons and naphthenes varied also with the conditions of hydrogenation, higher pressures favouring the formation of hydroaromatic hydrocarbons. Cawley[158] gives the following extents of conversion of phenol into hydrocarbons at various temperatures, in the presence of molybdenum disulphide, with a hydrogen pressure of 200 atm and a period of contact of 5 sec: at 250° there is 9.4% conversion, the proportions of benzene and cyclohexane being 0.9 : 1; at 300° conversion reaches 62%, at 350° 98.5%, and at 400° 100%, the ratio $C_6H_6 : C_6H_{12}$ becoming equal to 0.08 : 1. Hydroaromatic hydrocarbons are obtained in high yield by the hydrogenation of phenols in the presence of cobalt sulphide. Roberti[137] obtained predominantly naphthenic hydrocarbons by hydrogenating the phenols in primary tar in the presence of cobalt sulphide at 300° and an operating hydrogen pressure of 100 atm. With the same catalyst at 370° and 50–90 atm, Tropsch[118] obtained methylcyclohexane from a technical mixture of cresols.

Hydroaromatic hydrocarbons obtained from phenols usually contain some cyclopentane hydrocarbons, especially when the isomerising catalysts MoS_2 and WS_2 have been used. When phenol is hydrogenated, more methylcyclopentane is obtained than is usually formed by the isomerisation of cyclohexene under similar conditions[140,159,160].

V. HYDROGENATION OF POLYHYDRIC PHENOLS

Polyhydric phenols are contained in the tars obtained by fractionating and processing various mineral fuels. Their behaviour on hydrogenation has been inadequately studied. Polyhydric phenols are thermally less stable than monohydric phenols, and show an increased tendency to undergo decomposition, condensation, and other reactions[107,128,136,141,158]. Cyclohexanediols can be obtained by the hydrogenation of dihydric phenols in the presence of a nickel catalyst in ethyl alcohol at 130°–140° and 70–80 atm; hydrogenation of 800 g of resorcinol under these conditions yielded 250 g of a mixture of diols and 150 g of cyclohexanol; 800 g of quinol yielded 650 g of diols (84% of the *cis*- and 16% of the *trans*-isomer of cyclohexane-1,4-diol) and 32 g of cyclohexanol[161]. Pure cyclohexane-*trans*-1,4-diol is best prepared by hydrolysis of its diacetate, which can be separated from the products of the acetylation of the mixture of the *cis*- and *trans*-1,4-diols obtained by the hydrogenation of quinol[162].

Fujita[163] obtained cyclohexanediols and cyclohexanetriols by the hydrogenation of the corresponding dihydric and trihydric phenols at 180° and 100 atm in the presence of a nickel catalyst prepared by precipitating a 10% solution of nickel nitrate with 10% alkali and reducing the product at 320°. Hydrogenation of resorcinol yielded 48% of cyclohexane-1,3-diol, 19% of cyclohexanol, and 7% of the monocyclohexyl ether of resorcinol. Catechol under the same conditions gave cyclohexane-1,2-diol in 71% yield; hydrogenation of quinol resulted in a 94% yield of cyclohexane-1,4-diol. The rate of hydrogenation of dihydric phenols in the presence of Raney nickel at 175° and 100 atm is increased by the addition of a small quantity of water; under these conditions the side-reactions which normally diminish the yield of diols are markedly suppressed[164]. According to the patent literature, cyclohexanediols can be obtained also by the hydrogenation of the corresponding phenols in the presence of ruthenium and rhodium catalysts[165,166]. The hydrogenation of polyalkylphenols in the presence of "modified" Raney nickel has been discussed by Anderson[167,168].

This brief summary shows that polyhydric alicyclic alcohols can be obtained by the hydrogenation of the corresponding polyhydric phenols under considerably milder conditions than those required for the hydrogenation of monohydric phenols.

Hydrogenation of polyhydric phenols at high pressures in the presence of molybdenum catalysts results in the formation of hydrocarbon mixtures containing aromatic, hydroaromatic, and various other hydrocarbons; formation of phenol is also observed.

VI. DESTRUCTIVE HYDROGENATION OF HIGHER PHENOLS WITH THE FORMATION OF LOWER PHENOLS

Many investigators have noted an increase in the proportion of lower phenols in the course of the destructive hydrogenation of tars and coals. Thus Tropsch and Ter-Nedden[6], in the hydrogenation of a brown-coal semi-coke at 460° and 200–260 atm, obtained 22% of phenols, two-thirds of which consisted of phenol itself, and the cresols. Rapoport et al.[169], by the destructive hydrogenation of Chelyabinsk tar in a continuous plant at 430° and 150 atm, in the presence of molybdenum trioxide, found that the petrol fraction with b.p. up to 200° contained ~40% of phenols (phenol, cresols, and xylenols). Storch and his collaborators[170] found that the product of the hydrogenation of a coal slurry contained 25% of phenols; when this was hydrogenated further, an additional 25% of lower phenols was obtained. Koshel'[171] observed that, when certain fractions of the primary tar from Ukrainian brown coals were hydrogenated in the presence of nickel sulphide at 100–200 atm in a flow system, the content of lower phenols rose from 9% in the initial raw material to 12% in the product. Lanin et al.[172] found that liquid-phase hydrogenation of Cheremkhovo coal-tar in the presence of an iron catalyst at 460° and 300 atm yielded a product containing 32.2% of phenols, 57% of which were lower phenols. Similar observations have been recorded in several other papers[173–177].

The dealkylation of phenols is thermodynamically possible. Calculations of the equilibrium constants for the demethylation of the cresols show that phenol itself can thus be obtained in good yield[178,179].

Phenols may be dealkylated during the cracking of higher phenols even in the absence of catalysts at high temperatures, but with a low yield of lower phenols[180–184]. In addition, considerable coke formation makes the process impracticable. Dealkylation of phenols under conditions of catalytic hydrogenation considerably diminishes coke formation Such catalysts as the oxides of iron, aluminium, and

tungsten, as well as the sulphides of iron, nickel, cadmium, zinc, tungsten, and other metals, favour the splitting off of alkyl groups from phenols. In practice, however, the process is complicated at high temperatures by condensation and dehydroxylation reactions. Zabavin[185], by passing phenolic fractions together with hydrogen through an iron tube treated with hydrogen sulphide and filled with lumps of ferrous sulphide at 650°–660°, obtained, together with the phenol–cresol fraction, a considerable quantity of hydrocarbons of the benzene series and a compound containing fused benzene nuclei. A great percentage of neutral oil, to the detriment of the yield of lower phenols, was also obtained by Hagemann and Neuhaus[178] in the high-temperature treatment of phenols with hydrogen in the presence of Fe_2O_3. They recommend that condensation and polymerisation reactions should be avoided by carrying out the hydrogenation in an inert solvent, e.g. benzene. However, even in the presence of benzene they were unable to achieve a high yield of lower phenols. Carrying out the reaction in caustic soda solution and in the presence of molybdenum catalysts did not give good results, owing to considerable dehydroxylation[186]. However, according to certain patent claims, the use of alkali is advantageous[187].

Kuznetsov and Belov[188,189] and also Konov[190] have shown that an increased yield of phenol from higher phenols, at the expense of the yield of aromatic hydrocarbons, is favoured by carrying out the reaction in the presence of water vapour.

Rapoport and Masina[191] investigated the hydrogenation of *o*-cresol at 510° in the presence of an iron catalyst, water vapour, and various solvents; using a pressure of 180 atm of steam and 5% Fe_2O_3, they obtained up to 25% of phenol. Benzene as solvent did not give positive results; in the presence of pyridine the yield of phenol was increased. Increasing the pressure of hydrogen and using hydrogenating catalyst additions, e.g. 1% MoS_3, contributed in a marked degree to the suppression of condensation reactions.

Kalechits and Salimgareeva[192] investigated the possibility of dealkylating the phenols of Cheremkhovo tar in the presence of an iron catalyst. They obtained the best yields of lower phenols by hydrogenating the tar at 480°–490° and 300–340 atm. A tar containing initially 12% of lower phenols yielded a product containing 55–75% of phenols boiling below 220° and consisting of phenol itself (21%), cresols (39.8%), and xylenols (19.4%)[193]. It was noted that substituents in the *para*-position to the hydroxyl were most readily eliminated, the *meta*-isomers being the most stable. The great stability of *meta*-isomers has been noted also in the thermal cracking of alkylphenols[194,195].

Research on the hydrogenation of Cheremkhovo tar, both in an autoclave and in a continuous plant carried out in the Institute of Mineral Fuel of the Academy of Sciences of the USSR, has shown[196] that lower phenols boiling below 230° can be conveniently obtained from phenols boiling at 230°–255°. These amount to 30–35% of all the higher phenols in the distillates of Cheremkhovo tar and its liquid-phase hydrogenation product boiling below 320°. The following conditions were used: complete reprocessing, 50–100 atm, 475°, a volume flow rate of 1 litre/h in the presence of Fe_2O_3 (1%) + Al_2O_3, and a 1 : 1 ratio between fresh higher phenols and those returned from the previous cycle. The yield of phenol, and cresols and xylenols was 57.4 and 39.4%, based on the phenols in the tar and in the product of its liquid-phase hydrogenation. The authors recommend a cyclic process of retreating the higher phenols and regeneration of the catalyst by burning out the coke with atmospheric oxygen. The behaviour of all the oxygen-containing compounds of Cheremkhovo tar on hydrogenation in the presence of iron oxide on coal at 420°–460° and 100–290 atm has also been studied by Alekseeva and Moldavskii[197].

For the production of lower phenols boiling below 225° by the destructive hydrogenation of the higher phenols in brown-coal tar, Perna and Pelčik[198] recommend a catalyst consisting of a mixture of tungsten and vanadium sulphides, which proved to be the most effective of all the catalysts which they examined (Al_2O_3, MoO_3, and their mixtures with Fe_2O_3 or Cr_2O_3). In the presence of 0.15–0.75% of this catalyst in aqueous ammonia at 460°–480° and an initial pressure of 30 atm, 55–57% of lower phenols were obtained, of which 19.5–21.5% represents phenol and cresols. Aqueous ammonia can be replaced by water (amount 20%) or pyridine. Under these conditions no polymerisation or condensation was observed, and reduction of the phenols to aromatic hydrocarbons was to a large extent inhibited.

Phenols may be dealkylated also in the absence of hydrogen, but polymerisation then occurs to a considerably greater extent, and a large amount of coke is formed. The hydrogen or other gas containing hydrogen in the dealkylation evidently saturates molecular fragments and unsaturated compounds, and in this way minimises coke formation. When the process is carried out by a flow method with a selective catalyst, the hydrogen can be dispensed with, the catalyst being regenerated periodically. This is particularly useful for the dealkylation of alkylphenols containing not less than four carbon atoms in the alkyl group, which readily lose the alkyl groups at comparatively low temperatures (350°–400°). In this case it is possible to obtain not only the simple phenols but also various unsaturated compounds.

Several recent patents have recommended that degradation of phenols should be carried out in the presence of oxides or sulphides of metals together with cracking catalysts[199–204]. Special researches by Vorozhtsov and Lisitsyn[205,206] and several other workers[207,208] have shown that on an aluminosilicate catalyst phenols undergo disproportionation, isomerisation, dealkylation, and reduction. By selecting appropriate conditions and additions to the catalyst, it is possible to achieve selectivity. Thus Luten and Good[209] patented the dealkylation of alkylphenols, containing not less than four carbon atoms in the alkyl group, by passing their vapours at a flow rate of 0.5–4.0 h^{-1}, 350°–400°, and normal pressure over a mixed synthetic catalyst of the $SiO_2 . Al_2O_3 . MgO$ type with added B_2O_3, ZnO_2, ThO_2, and V_2O_5; methyl and ethyl groups are not eliminated under these conditions. In the presence of water vapour, however, CH_3 groups also can be split off; thus *o*-cresol yielded 14.5% of phenol[210]. Butyl and more complex alkyl groups are readily eliminated as olefins on heating with phosphoric acid[211]. t-Butyl groups are easily split off at 225°–285° even in the absence of a catalyst[212,213].

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This brief review shows that the production of lower phenols from higher analogues has been insufficiently studied. Investigations have been unsystematic and disjointed. Little is known about the dealkylation of phenols in the course of their destructive hydrogenation. Only recently has research started on the changes undergone by

phenols in the presence of various aluminosilicate catalysts. The choice of conditions for the dealkylation of the higher phenols obviously depends on their structure. The dealkylation of alkylphenols containing four or more carbon atoms in the alkyl group can be accomplished comparatively readily at 300°–400° in the presence of various cracking catalysts, as well as in the presence of other oxide or sulphide catalysts. The elimination of alkyl groups containing one, two, or even three carbons atoms, however, requires more severe conditions. Increased demands are also made on the catalyst, especially in relation to its selectivity, since in this case greater importance attaches to competing reactions and in particular to the reduction of phenols to hydrocarbons. The dealkylation of such alkylphenols can be conveniently carried out at high pressures of hydrogen in the presence of nitrogenous bases or water vapour.

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THERMODYNAMICS AND THE STRUCTURE OF METALLIC ALLOYS

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INTRODUCTION

The atomic or molecular structure of solids is determined by the nature of the forces acting between particles. Crystal chemistry is based on the concept that solids acquire a crystal structure corresponding to the chemical bond