

# Hydrogenolysis and Hydrocracking of the Carbon-Oxygen Bond

## I. Hydrocracking of Some Simple Aromatic O-Compounds

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Treatment of phenol, *o*-cresol, anisole, and guaiacol on a Ni-Mo/SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> hydrocracking catalyst is reported. The experiments were carried out in a fixed bed reactor at 250–350°C, 5 MPa hydrogen pressure, and LHSV 0.5–2.5 h<sup>-1</sup>. Phenol and *o*-cresol were found to be relatively stable under the reaction conditions studied. Anisole and guaiacol reacted readily through cleavage of the alkyl-oxygen bond. Phenol, *o*-cresol, and 2,6-dimethylphenol were obtained as the main products from anisole. Guaiacol reacted first to pyrocatechol, which was the main product at 250–275°C. At higher temperatures formation of phenol dominated. *o*- and *m*-cresol were formed in approximately equal amounts. The formation of hydrocarbons was minor in the case of guaiacol but from anisole appreciable amounts of cyclic C<sub>6</sub>-C<sub>7</sub> hydrocarbons were obtained at 325–350°C. The stability of the catalyst is described and tentative reaction mechanisms are discussed.

### INTRODUCTION

The hydrogenative breaking of the carbon-sulfur bond has been extensively studied due to its importance in oil refining technology. The carbon-nitrogen bond has at the same time come under scrutiny for several reasons. Nitrogenous compounds are not wanted in refinery products. Ammonia formed under hydrogenative conditions is a poison for hydrocracking catalysts. The low amount of oxygen-containing compounds in crude oil and the minor influence of the compounds or the products formed from them on catalysts have resulted in an almost complete lack of studies of carbon-oxygen bonds under hydrogenolysis-hydrocracking conditions. Renewed interest in coal as a chemical feedstock has recently raised the interest in hydrodeoxygenation (1). Though a major research effort has been made in methanol transformation and related studies (2–4) there is still a lack of studies in carbon-oxygen bond hydrocracking. This stands in sharp contrast

to the importance of the bond in all renewable organic materials of significance. Cellulose, hemicellulose, and lignin all have a high oxygen content. Of these three materials only lignin has received some attention. Discounting earlier works concentrated on the lignin structure some scattered studies on hydrogenolysis (5–9) and hydrocracking (10) of lignin and lignin model compounds have been published. Quite recently a hydrocracking process for lignin has been announced (11).

The emphasis of the present work is to study the behavior of some simple carbon-oxygen bonds under mild hydrocracking conditions. In order to follow the reaction sequences an aromatic nucleus has been chosen as a marker, i.e., the compounds studied are phenols and phenol ethers.

### EXPERIMENTAL METHODS

*Materials.* All chemicals were pure or analytical grade reagents. Hydrogen was laboratory grade and it was used without further purification.

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**Catalyst.** A commercial hydrocracking catalyst, which contained Ni (4%) and Mo (12%) on an amorphous  $\text{SiO}_2\text{-Al}_2\text{O}_3$  (25 : 75) support, was used. Its pellet size was 1.68–2.00 mm and bulk density 0.66 g/cm<sup>3</sup>. The catalyst was sulfided *in situ* in the reactor at 275°C and 5 MPa hydrogen pressure with a feed containing 0.5 vol%  $\text{CS}_2$  in benzene for 3–4 h, LHSV 2.0 h<sup>-1</sup>. The sulfur content of the sulfided catalyst was ca. 3.5%.

**Equipment and procedure.** A fixed bed continuous flow tubular reactor, made from AISI 316 stainless steel, was used. The internal diameter of the reactor tube was 11 mm and length 160 mm. The reactor was equipped with an electrical resistance heater and a temperature controller ( $\pm 3^\circ\text{C}$ ). The catalyst load was 6 to 9 cm<sup>3</sup>. All runs were made at a constant pressure of 5 MPa. The feedstocks were charged by a micro-feed pump. The reactor effluent passed through two collection traps. The first trap was cooled to between 5 and 15°C with tap water and the second to ca.  $-20^\circ\text{C}$  with an electrical cooling device. The noncondensables, which consisted mainly of hydrogen and a smaller amount of methane formed in the hydrocracking reaction, were recirculated with a gas pump together with fresh hydrogen to the reactor. The accumulation of methane in the gas phase was avoided by lowering the pressure of the system to 1 MPa twice a day and refilling to 5 MPa with pure hydrogen. The gas flow was measured with a mass flow meter. Liquid reaction products were analyzed in a Perkin-Elmer 900 gas chromatograph. Glass columns, length 1.83 m, filled with Carbo-pack C/0.1% SP-1000 and 10% SP-2250 on 100/200 Supelcoport, were used. With the SP-2250 column the samples were usually silylated (12) in order to improve the separation of phenolic components and to obtain a full response for pyrocatechol. With the Carbo-pack C column the silylation technique could not be used because of too long retention times. Gaseous reaction products were analyzed in a Perkin-Elmer 452 gas chro-

matograph using Porapak Q and Porapak S columns.

## RESULTS AND DISCUSSION

One of the main aims of the present work was to study carbon-oxygen bond breaking selectivity. Preliminary runs at temperatures of 350°C and above gave extensive rupture of all oxygen bonds as was to be expected. The emphasis is hence on reactions occurring at temperatures well below 350°C.

### Phenol

The hydrocracking experiments of phenol were run at 300 and 325°C (Table 1). The conversion of phenol was low, 2% at 300°C and 17% at 325°C. The analysis of the reaction products was complicated by the presence of diluent benzene. Separate runs of benzene alone indicated that its reaction was slight, less than 1% at 300°C and 3% at 325°C. In the light of the present results the aromatic carbon-oxygen bond is reacting very slightly at 300°C.

### *o*-Cresol

*o*-Cresol was hydrocracked at 325°C (Table 1). The conversion was higher than for phenol, 26%. The products were phenol

TABLE 1  
Hydrocracking of Phenol and *o*-Cresol<sup>a</sup>

	Phenol		<i>o</i> -Cresol
Temperature (°C)	300	325	325
Conversion (%)	2.2	16.9	25.7
Selectivity (%) <sup>b</sup>			
C <sub>6</sub> hydrocarbons <sup>c</sup>	100	100	—
C <sub>7</sub> hydrocarbons <sup>d</sup>	—	—	50
Phenol	—	—	50

<sup>a</sup> LHSV = 2.0 ml feed/h · ml cat; phenol feed = 34.6 mol% phenol in benzene; *o*-cresol feed = 29.0 mol% *o*-cresol in benzene; H<sub>2</sub>/phenol or *o*-cresol = 140 mol/mol; P = 5 MPa

<sup>b</sup> (Moles formed/moles converted) × 100.

<sup>c</sup> Benzene, cyclohexene, cyclohexane, methylcyclopentane.

<sup>d</sup> Toluene, methylcyclohexane.

(50% of the reacted *o*-cresol), toluene, and methylcyclohexane. Taking the product distribution into account, it is found that the dehydroxylation conversion of *o*-cresol is practically identical to that of phenol. The conversion is only slightly higher than that reported for the reaction of *o*-cresol on active aluminium oxide (13).

#### Anisole and Guaiacol

Extensive runs were made with anisole and guaiacol but only a part is presented in this paper. Major differences were found between these two compounds.

The liquid products from the hydrocracking experiments of anisole were usually obtained as one phase. In some cases when the feed was diluted with benzene and the reaction temperature was above 300°C the product separated into water and an organic phase.

The effects of space velocity and hydrogen/anisole molar ratio on conversion and product distribution were found to be slight in the studied region (0.5–2.5 h<sup>-1</sup>, 35–220 mol/mol). Though some changes could be discerned at the extreme values the signifi-

cance of these was still doubtful. The temperature had a major effect. Typical product distributions are shown in Table 2. The main products (phenol, *o*-cresol, and 2,6-dimethylphenol) are formed with constant selectivities at 250–300°C. The selectivities decrease at temperatures higher than 300°C but the ratio of phenol to *o*-cresol changes very little. *o*-Methylanisole is found in substantial amounts at temperatures below 300°C. Oxygen-free aromatics appear at temperatures above 300°C and at still higher temperatures hydrogenated products (cycloalkanes) are formed. The liquid products from the hydrocracking of guaiacol separated usually into water and an organic phase when the feed was diluted with benzene. Without feed dilution only one phase was obtained. Space velocity (0.5–2.5 h<sup>-1</sup>) and hydrogen/feed molar ratio (20–280 mol/mol) were found to have only a small effect on the conversion and product distribution. The temperature has a strong effect not only on the conversion but also on the product distribution. Typical results at 250–325°C are shown in Table 3. Some striking differences are found when com-

TABLE 2  
Effect of Temperature on Hydrocracking of Anisole<sup>a</sup>

Temperature (°C)	250	275	300	300 <sup>b</sup>	325	350
Conversion (%)	22.8	45.1	85.0	76.4	88.3	99.6
Selectivity (%) <sup>c</sup>						
Methylcyclopentane	<0.1	0.4	2.6	0.7	2.8	10.5
Cyclohexane	<0.1	0.4	1.1	0.5	2.2	1.7
Cyclohexene	<0.1	0.4	0.4	0.4	1.2	0.4
Benzene	<sup>d</sup>	<sup>d</sup>	<sup>d</sup>	4.2	11.2	20.4
Methylcyclohexane	<0.1	<0.1	0.1	0.1	0.9	2.4
Toluene	<0.1	<0.1	<0.1	0.1	1.1	3.3
<i>m</i> -, <i>p</i> -Xylene	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Phenol	64.8	65.5	64.9	60.0	53.1	40.9
<i>o</i> -Cresol	22.1	22.6	25.0	23.8	20.7	16.8
<i>m</i> -Cresol	<0.1	<0.1	<0.1	<0.1	<0.1	0.3
<i>p</i> -Cresol	<0.1	<0.1	<0.1	0.4	0.3	0.2
<i>o</i> -Methylanisole	8.0	5.1	0.9	2.1	0.7	<0.1
2,6-Dimethylphenol	5.0	5.6	4.5	6.7	4.5	0.2

<sup>a</sup> LHSV = 1.5 ml anisole/h · ml cat; feed = 44.9 mol% anisole in benzene; H<sub>2</sub>/anisole = 70 mol/mol; P = 5 MPa.

<sup>b</sup> Feed undiluted anisole.

<sup>c</sup> (Moles formed/moles converted) × 100.

<sup>d</sup> Small amounts of benzene could not be determined accurately because of the benzene dilution of the feed.

TABLE 3

Effect of Temperature on Hydrocracking of Guaiacol<sup>a</sup>

Temperature (°C)	250	275	300	325
Conversion (%)	5.1	14.5	48.4	86.1
Selectivity (%) <sup>b</sup>				
Methylcyclopentane	<0.1	<0.1	0.1	1.1
Cyclohexane	<0.1	<0.1	0.1	0.3
Cyclohexene	<0.1	<0.1	2.0	0.5
Benzene	<0.1	<0.1	0.1	0.5
Toluene	<0.1	<0.1	<0.1	0.6
Phenol	10.5	30.9	45.7	53.5
Anisole	<0.5	1.0	2.6	2.1
<i>o</i> -Cresol	<0.5	3.2	9.0	9.4
<i>m</i> -Cresol	<0.5	2.4	11.5	7.3
<i>p</i> -Cresol	<0.1	0.8	3.8	1.6
Pyrocatechol	68.5	61.4	26.7	8.7

<sup>a</sup> LHSV = 2.0 ml guaiacol/h · ml cat; feed undiluted; H<sub>2</sub>/guaiacol = 65 mol/mol; P = 5 MPa.<sup>b</sup> (Moles formed/moles converted) × 100.

paring these results with those of anisole. The low amount of oxygen-free compounds, ca. 3% at 325°C, can be ascribed to the difficulty of breaking two bonds between oxygen and the aromatic nucleus. The conversion of guaiacol, however, is clearly lower than that of anisole up to a temperature of 325°C. Pyrocatechol is found, as expected, as a primary product formed by the breaking of the bond between oxygen and the methyl carbon. Above 275°C the amount is rapidly decreasing. An interesting result is that phenol is found as a major product also at low temperatures. Already at 250°C roughly 10% of the converted guaiacol is phenol. A major difference from anisole is found in the distribution of cresols since guaiacol gives a mixture of all three isomers, *o*- and *m*-cresol dominating.

The results obtained indicate clearly that the first bond to be broken is the bond between the oxygen and the methyl carbon. This is in accordance with the estimated bond energies for this type of compounds (11, 14). The large difference in anisole and guaiacol reactivity can be explained as follows. A weak coordinative bond can be formed by anisole with the catalyst through the free p-electron pairs at the oxygen atom. The bonding can be through anion vacancies in the metal part of the catalyst (15, 16) whereas aluminium is implicated

on the carrier (17–20). On the metal the alkyl-oxygen bond is homolytically dissociated forming phenoxide and methyl radicals which are hydrogenated to phenol and methane. This is the major reaction route since the loss of methyl groups as methane is 60% or more. If the bond between oxygen and the alkyl carbon is broken on the carrier a heterolytic scission is indicated. The methyl carbonium ion formed then attacks the *ortho*-positions available, as is to be expected. Evidently the aromatic ring is in our case held in a position where the *para*-position is too far away. The formation of *o*-methylanisole further shows that the *o*-position is strongly favored. Our results are in agreement with those of Kannan and Pillai (19) and Klemm *et al.* (17, 18) who found a strong preference for *o*-substitution in the alumina-catalyzed alkylation of phenol and 1- and 2-naphthols, respectively.

Tanabe and Nishizaki (20) found, on the other hand, that SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> produced *o*-, *m*-, and *p*-isomers when anisole and phenol were reacted with methanol. They ascribe this to the acid strength of their catalyst. The metals present in the catalyst used in this work evidently change the behavior of our carrier. The influence of the catalyst acidity on the hydrocracking behavior of the carbon-oxygen bond clearly needs more study.

Guaiacol differs from anisole by its free

phenol group. We ascribe the lower reactivity of guaiacol to the formation of a much stronger bond between the free phenol hydroxy group and basic Al-OH groups on the carrier (21). This reversible chemisorption hinders the reaction until a temperature has been reached where the free guaiacol can react in a way similar to that of anisole. Once this temperature is reached similar reactions occur. The major reaction is demethylation to pyrocatechol. *o*-Methylation of pyrocatechol with subsequent dehydroxylation yields approximately equal amounts of *o*- and *m*-cresol. The slight formation of the *p*-isomer can be ascribed to easier nuclear substitution of pyrocatechol.

A reaction route from guaiacol to phenol which cannot be discarded is the direct elimination of the *o*-methoxy group. This group has been proved to be eliminated in several previous catalytic studies (5, 10). However, these studies have all been made at much higher temperatures and hence are not directly comparable with the present work. The last bond between the aromatic nucleus and oxygen in guaiacol is far more difficult to break, as found already in the case of phenol and *o*-cresol. Complete de-

oxygenation was not of interest in this work and little or no study was thus made of the reaction sequence of the deoxygenation stage onward. It may be noted in passing that neither ring opening nor cracking to lighter hydrocarbons was observed. A general conclusion to be drawn from the present work is that it is advisable to use rather low reaction temperatures, around 300°C, for selective bond breaking of aromatic oxygen-containing materials. The majority of the previous works have been made at substantially higher temperatures (5, 6, 10, 22).

#### The Catalyst

The catalyst chosen for this study was a hydrocracking catalyst used in a process for hydrocracking heavy distillates. The catalyst was of non-noble metal type containing nickel and molybdenum on an amorphous  $\text{SiO}_2\text{-Al}_2\text{O}_3$ . The catalyst is normally run in a sulfided form and this was also used in the present work. In some preliminary experiments it was found that the activity of the catalyst decreased rapidly (in a few hours) when the reactor was fed with pure oxygen-containing compounds at 350-

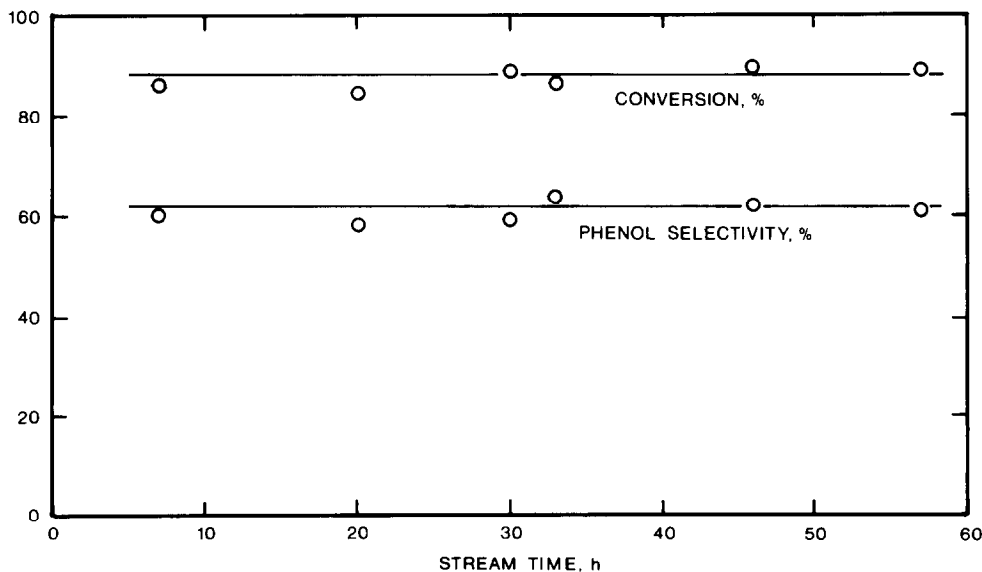


FIG. 1. Performance of the catalyst with anisole-benzene feed.  $T = 300^\circ\text{C}$ ;  $P = 5 \text{ MPa}$ ;  $\text{LHSV} = 0.8 \text{ ml anisole/h} \cdot \text{ml cat}$ ;  $\text{H}_2/\text{anisole} = 130 \text{ mol/mol}$ .

400°C. The deactivation was thought to be caused by breakdown of the catalyst due to formation of large amounts of water, by loss of sulfur from the sulfided catalyst, and by excessive coke deposition at the high temperatures used. In order to avoid a too rapid deactivation of the catalyst, all experiments now reported were performed at temperatures not higher than 350°C.

The sulfur content of the catalyst was kept at a level of about 4% by adding to all feedstocks 0.05 vol% of CS<sub>2</sub>. It should be emphasized in this context that since the reaction studied was carbon-oxygen bond breaking and the temperature was deliberately kept far below usual hydrodesulfurization conditions the common concepts of hydrodesulfurization catalysts and their sulfur level (16, 23, 24) should not be applied as such. This matter is the subject of separate work.

The feedstocks were diluted with benzene in the first part of this work. Later it was found that the dilution of the feed had no (or only a small) effect on the catalyst stability and the dilution with benzene was discontinued.

Figure 1 shows that the activity of the catalyst remains nearly constant for over 50 h when a benzene-anisole mixture is treated. The stability of the catalyst was tested also with undiluted anisole and diluted guaiacol and no substantial loss of activity was observed. The used catalysts contained sulfur 3.5-4.5% and carbon 3.0-9.0%. A substantial amount of the carbon analyzed might have been due to adsorbed feedstocks and products since the catalyst had only been flushed with hydrogen before analysis.

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