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Hydrogenolysis of Differently Substituted Methoxyphenols

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The partial hydrodeoxygenation (HDO) of the three isomeric methoxyphenols was studied in a flow reactor under 5 MPa hydrogen pressure in the temperature range 275–325°C with a sulfided $CoMo/\gamma\text{-}Al_2O_3$ catalyst. The reactivities of the compounds were in the order $p > o > m$, the *p*-compound giving the highest amount of hydrocarbons and the *o*-compound monophenols. Ring substitution by methyl groups was in the order $m \gg o > p$. Increase in sulfidation increased the reactivity. Most reactions were run at a LHSV of 2.2 h^{-1}. An increase of up to tenfold in the space velocity for the *m*-compound gave a decreasing conversion and a lower ring methylation but about the same selectivity of resorcinol and phenol. The differing reactivities are ascribed to the difference in the orientation of the chemisorbed molecules once the methyl group has been split off: there is a planar sorption of the *m*- and *p*-compounds and an inclined sorption by the *o*-compound.

INTRODUCTION

The renewed interest in both coal liquefaction as well as use of biomass, including lignin, has led to an attendant increase in interest in the catalytic behaviour of the carbon–oxygen bond which is present in large numbers in the above-mentioned raw materials. Benzene rings substituted with two oxygen atoms are abundant in lignin as pyrocatechol derivatives. These orthosubstituted compounds are also found in coal pyrolysis products together with substantial amounts of the metasubstituted resorcinols. Parasubstituted hydroquinone derivatives are found in only small amounts.

Catalytic hydrodeoxygenation (HDO) of dihydroxybenzenes has been mainly concentrated on the orthocompound and its substituted forms (*1–4*). Most of the published literature on other phenols is concerned with total HDO or aromatic ring hydrogenation (*5, 6*). in a recent study by Kallury *et al.* (*7*) the three dihydroxybenzenes were compared in a batch autoclave with a $MoO_3\text{-}NiO/Al_2O_3$ catalyst. At the lowest temperature they used (350°C), *o*-dihydroxybenzene was more reactive than phenol and gave predominantly phenol; *m*-dihydroxybenzene was much less reactive than phenol, and *p*-dihydroxybenzene was more reactive than phenol and gave primarily products of ring saturation. Their work was published at about the time the present work was preliminarily communicated (*8*).

In the present work we have compared the monomethyl ethers of the three isomers under rather mild conditions. The reason for using a monomethylether was that the methyl group could function as a marker for the corresponding reactivities of free hydroxyls and aromatic rings.

EXPERIMENTAL

All chemicals were pure or analytical grade reagents. The catalysts used was a commercial grade HDS-type catalyst (Harshaw CoMo 0402 T, $\frac{1}{8}$ in.). It was crushed and sieved to a particle dimension of 0.84–2.00 mm. The catalyst was sulfided *in situ* at 275°C and 5 MPa hydrogen pressure with benzene containing 0.5 vol% (low S) or 5.0 vol% carbon disulfide (high S) at a LHSV of 2 h^{-1} for 5–6 h.

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The small laboratory integral reactor and its use has been described earlier (*1*). In the present work the undiluted feedstocks contained 0.1 vol% of CS_2 in the low-sulfidation runs and 1.0 vol% CS_2 in the high-sulfidation runs. All runs were made under a hydrogen pressure of 5 MPa. The space velocity was 2.2 h^{-1} except for one series of runs where space velocity was varied at constant temperature (300°C). The molar hydrogen/methoxyphenol feed ratio was about 60.

The separate runs with different feedstocks were continued for at least 3 h by which time a pseudo-stationary state had been reached. A sample of the cooled liquid products was withdrawn and analysed by gas chromatography using both silylated and unsilylated compounds (*4*). Practically all the monoaromatic and alicyclic compounds were identified with known, authentic compounds. Though no specific attempt was made to identify heavier products, they consisted mainly of dimers like biphenyl and cyclohexylphenols. Relative GC response factors of the identified products were evaluated and used in the quantitative calculations. The gas phase was not analysed.

The sulfur content of the catalyst after a run time of about 40 h was at a level of 2% (low S) or 4% (high S).

RESULTS

The results at the same LHSV for different isomers are summed up in Tables 1–3. Repeat runs under the same conditions normally gave satisfactory reproducibility. The

TABLE I

Hydrogenolysis of *o*-Methoxyphenol[a]

Sulfidation level	Low S			High S		
Reaction temperature (°C)	275	300	325	275	300	325
Conversion (%)	23.4	52.2	93.2	40.1	73.9	99.0
Selectivity (%)[b]						
Two oxygen atom products	45.9	31.4	8.3	44.9	33.7	2.7
Pyrocatechol	31.7	21.5	5.9	32.2	26.2	2.1
Veratrole	2.6	1.2	+			
Monomethylated ring	11.1	8.0	1.8	12.4	7.0	0.5
Polymethylated ring	0.5	0.7	0.6	0.3	0.4	0.1
One oxygen atom products	32.8	53.2	77.1	45.1	54.3	77.5
Phenol	20.8	32.6	47.0	20.5	32.2	52.5
Anisole	0.9	2.0	2.2	0.7	1.1	0.4
o-Cresol	4.8	6.7	11.4	6.6	6.4	10.0
m-Cresol	2.8	4.8	6.9	7.2	6.3	7.1
p-Cresol	0.6	0.7	1.1	3.8	2.6	2.4
Polymethylated ring	2.9	6.3	8.4	6.3	5.7	5.1
Hydrocarbons	12.4	10.4	8.7	6.6	7.6	14.4
Benzene	2.7	4.2	2.3	0.5	1.2	3.1
Other aromatics	0.1	0.1	0.6	0.1	0.4	3.8
C_6-alicyclics	8.7	5.3	4.8	5.2	4.9	5.9
Other alicyclics	0.9	0.8	1.0	0.8	1.1	1.6
Dicyclics and unknown	8.9	5.0	5.9	3.4	4.4	5.4

[a] Pressure, 5 MPa; LHSV, 2.2 h^{-1}.
[b] Selectivity normalised to sum 100%.

TABLE 2

Hydrogenolysis of *m*-Methoxyphenol[a]

Sulfidation level	Low S			High S		
Reaction temperature (°C)	275	300	325	275	300	325
Conversion (%)	27.2	41.3	70.2	37.0	66.6	95.8
Selectivity (%)						
Two oxygen atom products	72.5	71.3	63.6	65.7	63.3	32.9
Resorcinol	27.3	25.5	20.6	31.8	28.4	12.0
1,3-Dimethoxybenzene	8.9	5.6	3.4	1.5	1.1	—
Monomethylated ring	31.9	31.9	27.5	28.6	25.6	13.8
Polymethylated ring	4.4	8.3	12.1	3.8	8.2	7.1
One oxygen atom products	11.3	15.8	22.0	17.32	22.3	36.9
Phenol	7.4	9.4	14.4	11.4	14.2	22.3
Anisole	1.8	2.7	1.3	1.8	2.0	0.4
o-Cresol	2.1	2.0	3.9	1.7	3.2	7.3
m-Cresol	+	0.1	0.1	+	0.1	0.2
p-Cresol	+	0.7	0.3	2.1	1.6	2.1
Polymethylated ring	+	0.7	1.9	0.3	1.2	4.5
Hydrocarbons	15.9	11.8	12.3	11.5	11.6	27.6
Benzene	8.5	3.9	1.8	1.7	1.3	1.5
Other aromatics	0.9	0.5	0.3	+	0.6	1.5
C_6-alicyclics	4.4	5.6	6.3	9.0	8.6	16.0
Other alicyclics	2.1	1.8	3.9	0.8	1.1	8.6
Dicyclics and unknown	0.3	1.1	2.1	5.5	2.8	2.6

[a] Pressure, 5 MPa; LHSV, 2.2 h^{-1}.

catalyst did undergo slow deactivation but the selectivities did not change. Normally over 90% of the feedstock was accounted for in the products and no systematic error seemed to prevail. The products are grouped into four categories:

(a) Compounds containing two oxygen atoms. Only aromatics having the same ring structure as those of the feedstock were found, e.g., only pyrocatechol and methyl-substituted pyrocatechols from *o*-methoxyphenol. Compounds having no methyl substituents or only one could be identified by authentic samples. More highly methylated compounds could be identified only to a limited extent. The *meta*-compounds formed a particularly difficult group due to the large amounts of di- and tri-methyl-substituted compounds.

(b) Compounds containing one oxygen atom. This group consisted of phenol and its methyl derivatives with varying degrees of substitution, all identified. Cyclohexanol was occasionally found in very small amounts.

(c) Hydrocarbons. Only cyclic compounds were found. The aromatics consisted mainly of benzene. The alicyclics were identified only according to their extent of ring methylation and amount of double bonds.

(d) Other compounds. This group consisted of several ill-defined compounds boiling in the range of dicyclic compounds.

The gross conversion of the methoxyphenols follows the order $p > o > m$. The gross conversion is only a crude way to express the relative reactivities since the

TABLE 3

Hydrogenolysis of *p*-Methoxyphenol[a]

Sulfidation level	Low S			High S		
Reaction temperature (°C)	275	300	325	275	300	325
Conversion (%)	31.8	75.8	97.6	32.59	5.3	99.8
Selectivity (%)						
Two oxygen atom products	54.6	22.6	2.8	40.2	2.9	0.2
Hydroquinone	19.2	6.3	1.1	20.0	1.8	0.2
1,4-Dimethoxybenzene	19.6	6.8	0.5	11.3	0.3	—
Monomethylated ring	15.4	8.4	1.0	8.9	0.7	—
Polymethylated ring	0.4	1.1	0.2	+	0.1	—
One oxygen atom products	10.5	13.7	22.1	14.9	14.7	20.8
Phenol	6.3	6.6	10.5	8.0	8.2	12.3
Anisole	1.0	1.2	0.7	1.2	0.3	+
o-Cresol	0.9	2.4	4.0	1.6	2.7	4.3
m-Cresol	0.6	0.9	1.8	1.2	1.0	1.3
p-Cresol	0.5	0.1	0.6	1.8	0.2	0.2
Polymethylated ring	1.2	2.5	4.3	1.1	2.2	2.7
Hydrocarbons	27.8	50.5	62.0	32.7	72.0	72.2
Benzene	4.0	3.5	3.0	1.8	3.0	6.9
Other aromatics	0.7	0.6	2.5	0.3	1.3	4.0
C_6-alicyclics	19.8	38.4	46.2	26.9	59.3	52.6
Other alicyclics	3.3	8.0	10.3	3.7	8.4	8.7
Dicyclics and unknown	7.1	13.2	13.1	12.2	10.4	6.8

[a] Pressure, 5 MPa; LHSV, 2.2 h^{-1}.

methyl–oxygen ether bond is broken relatively easily in all cases. A striking difference in the behaviour of the reactants can be noted when account is taken of the amount of removed oxygen atoms. The selectivity of formation for monophenols is $o \gg m \sim p$ but for formation of hydrocarbons it is $p \gg m \sim o$. This is in agreement with the results of Kallury *et al.* (*7*) obtained at much higher temperatures.

Both HDO and ring hydrogenation are affected by the sulfidation level in the same way: higher sulfidation increases both processes. The effect is most pronounced in the *p*-compound whereas the smallest change in hydrocarbon formation is noted for the *o*-compound. The increase in temperature increases the conversion, as expected, but there is a difference between the isomers. The *p*-isomer reacts already at the lower temperature range whereas both the *meta* and *ortho* isomers require a higher temperature for larger changes. Complete HDO is strongly resisted by the *ortho* isomer.

The methyl group split off from the reactant can be found as (i) the diether, (ii) a ring substituent, or (iii) methane (the latter compound was not routinely and quantitatively measured). The diether formation follows the order $p > m > o$ but is very sensitive to increases in temperature and sulfidation level. The ring substitution behaves differently. The lowest substitution occurs for the *p*-compound (about 20% of the methyl groups) followed by the *o*-compound (about 30%). Only a slight temperature effect can be discerned in either case. The S level has an effect only on the *p*-compound where a slight decrease can be

seen. For the *m*-compound there is a clear increase in ring methylation with temperature: at 275°C, 40% (low S) and 37% (high S) and at 325°C, correspondingly, 50% and 44%. The extent of multiple methylation is quite clear. Only the *m*-isomer gives appreciable amounts of triply methylated compounds. The methylation stays mainly at the monosubstitution level for the *o*- and *p*-isomers.

The order of formation of hydrocarbons has already been mentioned. In addition, it should be pointed out that any increase in hydrocarbon formation is in the group of C_6-alicyclics, viz., cyclohexane, cyclohexene, and, to a small extent, cyclohexadienes.

The runs at different space velocities (Table 4) show that the conversion is most strongly affected. The selectivities do not change much, although a decrease in HDO and ring hydrogenation can be noted. The selectivity of formation of resorcinol does not change at all.

TABLE 4

Influence of Space Velocity on Hydrogenolysis of *m*-Methoxyphenol[a]

Space velocity LHSV (h^{-1})	5.6	11.0	21.7
Conversion (%)	49.7	35.1	21.8
Selectivity (%)			
Two oxygen atom products	71.2	81.5	84.9
Resorcinol	25.9	31.5	32.7
1,3-Dimethoxybenzene	3.1	3.3	4.1
Monomethylated ring	30.6	35.3	38.8
Polymethylated ring	11.6	11.4	9.3
One oxygen atom products	12.4	8.2	6.5
Phenol	7.8	5.2	3.6
Anisole	0.8	+	+
o-Cresol	2.0	1.2	0.8
m-Cresol	0.1	+	+
p-Cresol	0.4	1.5	2.0
Polymethylated ring	1.1	0.3	+
Cyclohexanol	0.2	—	—
Hydrocarbons	10.0	8.8	7.4
Benzene	1.3	1.1	0.9
Other aromatics	0.2	0.2	0.2
C_6-alicyclics	6.6	6.0	5.0
Other alicyclics	1.9	1.5	1.3
Dicyclics and unknown	6.4	1.5	1.2

[a] Pressure, 5.0 MPa; reaction temperature, 300°C; low sulfidation.

DISCUSSION

The differences in behaviour of the three isomers can partly be explained by electronic effects. In the *ortho* and *para* compounds the electronic effect is more strengthened for hydrodeoxygenation and ring hydrogenation than the *meta* compound. Methyl group substitution follows the order dihydroxybenzenes > monohydroxybenzenes > pure aromatics > pure alicyclics. Thus, the ring methyl substitution follows the order $m \gg o > p$, i.e., the opposite for HDO and ring hydrogenation. Electronic effects alone do not explain the great difference between the *ortho* and *para* compounds. The *para* compound is much more active for total HDO and for ring hydrogenation whereas the *ortho* compound produces a high amount of monophenols. We presume that the mode of adsorption plays a central role in this behaviour. Hence, we propose a flat mode of adsorption for the *para* compound (as well as for the *meta* compound) and an inclined mode due to steric hindrance for the *ortho* compound. Recent FTIR work by Bredenberg and Sarbak (*9*) shows that chemisorption is strong on alumina but is also seen on MoS_2 and a HDS catalyst. The mode of adsorption advanced for the ring is flat for the *meta* and *para* compounds and inclined for the *ortho* compound. The results presented here strongly support this hypothesis. It can further be assumed that there is an interaction between the free *p*-electrons of the ether oxygen and the surface since the first reaction which occurs is clearly demethylation. The methyl group which is freed has a cationic character (*10, 11*) and stays sorbed on the catalyst surface, presumably on the alumina (*11*). Once the demethylation has taken place, the planar

mode of chemisorption is enforced on the *meta* and *para* isomers by covalent bonding of the freed oxygen bond. For HDO, which is a hydrogenolysis reaction, and ring hydrogenation to take place, the primary location of the rings is near the anion vacancies (*12*) or above Mo cations (*13*). The *ortho* isomer stays inclined due to steric forcing by the *ortho*-located oxygen bonds.

Once the methyl group is freed it can react rapidly in one of the following ways:

(1) The hydroxyl groups can be reversibly methylated. This occurs preferentially at low temperature and a low sulfidation level. The order of reactivity is $p > m > o$. The low reactivity of the *ortho* form is probably due to steric hindrance whereas the order $p > m$ follows the general rules of isomer reactivity.

(2) Irreversible methylation of the aromatic ring under formation of methyl derivatives can occur. The major compounds so formed are monomethyl compounds but dimethyl compounds are also formed to some extent. Higher methylation can be observed, but in rapidly decreasing amounts. Only the *meta* isomer forms triply methylated compounds in substantial amounts. The nuclear methylation clearly follows the order $m \gg o > p$, which is the order to be expected from the mechanisms described in this paper. One special case is noted for the *p*-compound where a small amount of *p*-cresol shows that the oxygen can be substituted. (The possibility of the route oxirane → benzyl alcohol → cresol (*14*) cannot be excluded.)

(3) Irreversible reaction to methane with hydrogen chemisorbed on the catalyst can occur. The amount of methane formed is based on how favoured the competing reaction of aromatic substitution is and an "inverse" order is thus formed: $p > o \gg m$.

The mechanisms are described schematically in Figs. 1–3. For the *ortho* isomer (Fig. 1) the inclined form favours monodeoxygenation. In addition to the dominant phenol, *o*-cresol is the favoured form. Once the monophenol stage is reached most of the adsorbed compounds are released.

The *meta* isomer (Fig. 2) is bound in the flat form. In this form the sorbate is prone to strong ring methylation, hence the large amount of highly methylated compounds. *Meta*-cresol is formed only in trace amounts. The ring is not activated for hydrogenation by its *meta*-located substituents and the hydrocarbon formation stays on the same level as in the *ortho* isomer. Phenol is again the dominant monohydroxycompound but the amount is much less.

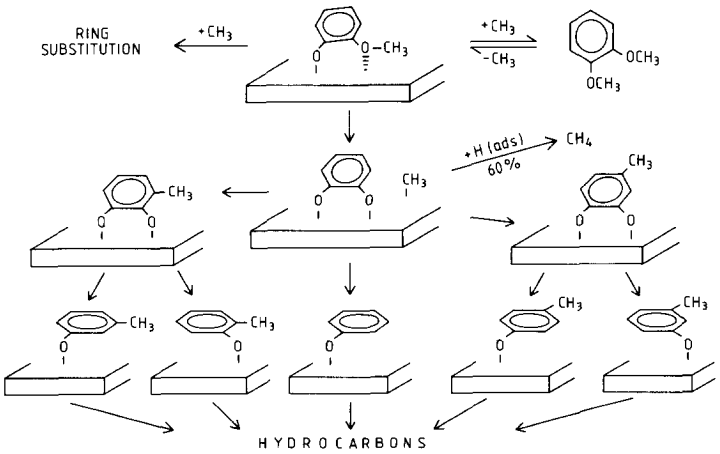

FIG. 1. Major routes for the reaction of *o*-methoxyphenol.

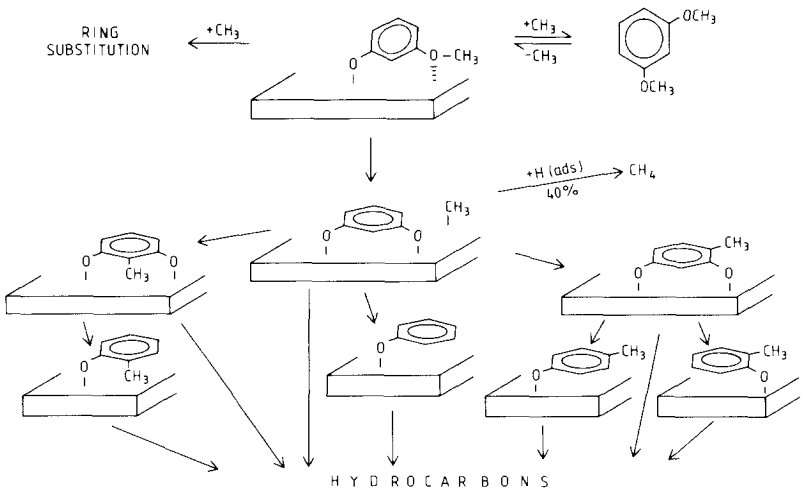

FIG. 2. Major routes for the reaction of *m*-methoxyphenol.

The *para* isomer (Fig. 3) is also bound in the flat form but, differing from that of the *meta* isomer, this is a form which is strongly activated for ring hydrogenation.

For the *p*- and *m*-compounds total HDO is thus envisaged to take place prevalently during the time the ring is planarly adsorbed. The higher activation of the *p*-compound gives more hydrocarbons. The nonplanarity of the *o*-compound makes the ring hydrogenation relatively slow. HDO takes place stepwise and total deoxygenation occurs only through a monophenolic stage.

The results of HDO and ring hydrogenation are the same as those obtained at higher temperature by Kallury *et al.* (*7*). The increase in hydrogenation at a higher sulfidation level is a well known, though not necessarily well explained, effect (*5, 15*). In the case of HDO there is a further complication of the competition of oxygen with sulfur on anion vacancies. One group of workers even claims better HDO for a nonsulfided catalyst (*16*). We are presently studying the different sulfur and oxygen levels on the catalyst. Several different

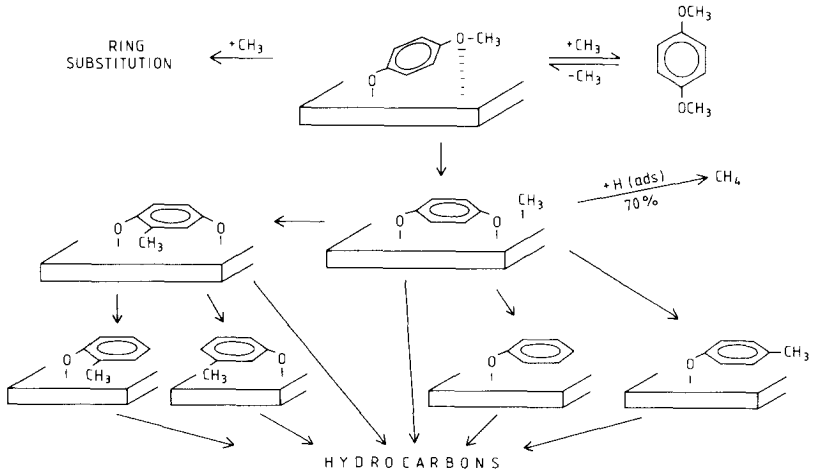

FIG. 3. Major routes for the reaction of *p*-methoxyphenol.

sites are probably needed to explain the different reactions, as noted recently by Gevert *et al.* (*6*).

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