Catalytic Hydrodeoxygenation

I. Conversions of o-, p-, and m-Cresols

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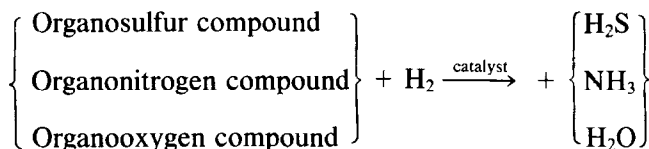*Department of Chemical Engineering, University of California, Davis, California 95616*

The hydrodeoxygenation (HDO) of o-, m-, and p-cresols on HDS catalysts (sulfided CoO–MoO$_3$/γ-Al$_2$O$_3$) at 225–400°C and 68 atm hydrogen gives toluene and methylcyclohexane as the major products on both fresh and aged HDS catalyst. The relative reactivities of the cresols are found to be *meta > para > ortho*. HDO activity is slowly lost with time, but hydrogenation activity drops more rapidly and is less recoverable with reductive/sulfiding regeneration. As a consequence, the hydrogen consumption per atom of oxygen removed in cresol hydrodeoxygenation *declines* nearly 50% as the catalyst ages. The fresh catalyst operating at lower temperatures (225–275°C) gives primarily a consecutive conversion pattern (cresol → toluene → methylcyclohexane), while the less active aged catalyst used at higher temperatures (350–400°C) appears to exhibit a parallel path behavior to toluene and methylcyclohexane from a common surface intermediate. Ring saturation prior to hydrodeoxygenation does not appear to be necessary.

INTRODUCTION

Hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) are important hydroprocessing applications which involve reactions leading to the removal of sulfur and nitrogen, respectively, from petroleum compounds, shale oil, and coal-derived liquids. Removal of these heteroatoms results primarily in their well-established conversion to hydrogen sulfide (H$_2$S) and ammonia (NH$_3$). Much less studied, but important in determining both hydrogen consumption in HDS and HDN operations and liquid viscosity properties, is hydrodeoxygenation (HDO). In general these three reaction classes can be represented by:

$$\left\{ \begin{array}{l} \text{Organosulfur compound} \\ \text{Organonitrogen compound} \\ \text{Organooxygen compound} \end{array} \right\} + H_2 \xrightarrow{\text{catalyst}} + \left\{ \begin{array}{l} H_2S \\ NH_3 \\ H_2O \end{array} \right\}$$

It is necessary to remove these elements from the petroleum, oil shale, and coal liquids so as to reduce the downstream poisoning of hydrotreating catalysts, to reduce the eventual emission of N and S as SO$_x$, NO$_x$ in fuel consumption, and to improve the quality and stability of finished liquid products (*1–3*).
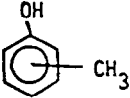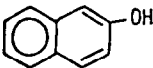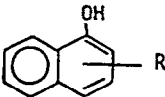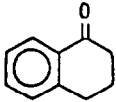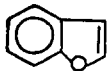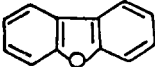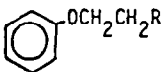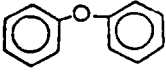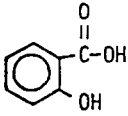
In this and a subsequent small group of papers, we present the intrinsic HDO kinetics of particular oxygenates and establish clearly the existence and importance of HDO interactions with HDS and HDN heterogeneously catalyzed conversion.

Table 1 lists the representative oxygen compounds in coal liquids, oil shale, and

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TABLE 1

Representative Oxygen Compounds in Coal Liquids,
Oil Shale, and Petroleum Crude

1. Phenols

Phenol · · · · · · · · · · · · Cresols (*o-*, *m-*, *p-*) · · · · · · · · · · · · Polyhydric phenols

2. Naphthols

· α-Tetraldne

3. Furans

Furan · · · · · · · · · · · · Benzofuran · · · · · · · · · · · · Dibenzofuran

4. Ethers · 5. Acids

Phenolic ethers · · · · · · · · · · · · Benzylic ethers

petroleum crude. The structural similarity of the compounds in Table 1 to many S and N compounds of importance in HDS and HDN, and the related electronegativities of these heteroatoms, suggests rather strongly that appreciable kinetic interactions may attend simultaneous HDS/HDO and/or HDN/HDO, as has already been clearly shown for simultaneous HDS/HDN (*4*). A survey of the literature of hydrodeoxygenation (*5*) reveals that of all the different oxygen functionalities in coal, only the single-ring phenols, aromatic ethers (heteroaromatics), and a few mixed ethers are stable under liquefacton conditions. The other compounds (ethers, polyhydric phenols, polyaromatic phenols, carbonyls,

etc.) decompose at lower temperatures, some in the absence of a catalyst and others by the catalytic action of mineral matter in coal (*6, 7*). Moreover, in catalytic treatment of coal and coal liquids the products are more likely to contain mostly single-ring phenols and aromatic ethers (*8*). This is because whereas very little hydrogenation activity is required for conversion of polyhydric and multiring phenols, more activity is required for the conversion of other compounds. Indeed, Whitehurst *et al.* (*8*) found an excellent correlation between the hydrodeoxygenation of phenols and hydrogenation of phenanthrene.

Thus knowledge of HDO conversions may be important for three primary reasons

in HDS and HDN processing:

(a) HDO increases hydrogen consumption rates;

(b) oxygenate product content influences liquid viscosity;

(c) HDO competition with HDS and HDN may strongly affect the relative rates of simultaneous HDS/HDO and HDS/HDN.

Although phenols are the most studied of the oxygen-containing species in coal, the HDO of alkyl phenols has been studied by only a few investigators (8–12). In some of these studies, toluene and methylcyclohexane are products commonly observed; in others, cyclohexanols and cyclohexanes form (the latter via the intermediate cyclohexenes). The HDO of phenols, which has been studied under different reaction conditions using different catalysts, is known to proceed by the following two reaction pathways:

$$(1a)$$

$$(1b)$$
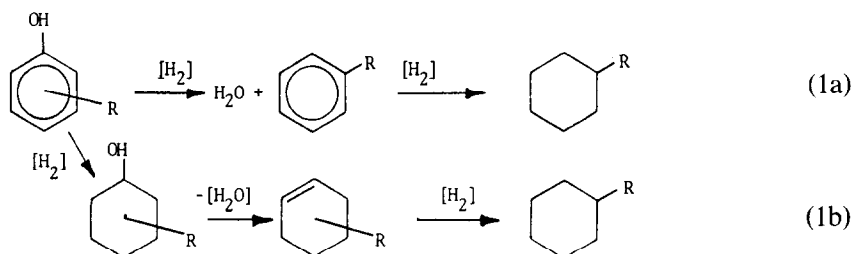
In these equations R can be hydrogen or an allkyl group (e.g., R = CH_3 for cresols). The old data of Moldavskii and co-workers (11) suggest the two reaction pathways given in Eq. (3), the more recent studies of Rollmann (10) and Whitehurst et al. (8) support the first pathway [Eq. (1a)], while those of Roberti (27) and Polozov (28), involving phenol hydrogenation on sulfide catalysts (CoS, MoS_2) at pressures over 100 atm, find the second reaction pathway [Eq. (1b)] to be important. The hydrodeoxygenation reaction, as with HDS and HDN, has been reported to be pseudo-first order in the heteroatom compound (10).

A subsequent pair of papers (16, 17) examines interactions during simultaneous benzothiophene HDS and cresol HDO (16) and indole HDN and cresol HDO (17). HDO of the aromatic ether, benzofuran, and interactions of (di)benzothiophene HDS and benzofuran HDO are examined in a subsequent pair of papers (19, 20). Thus this series of papers initiates study of HDO/HDS/HDN interactions arising from HDO of the most stable oxygenates under coal liquefaction conditions: single-ring phenols and aromatic ethers (heteroaromatics).

EXPERIMENTAL METHODS

Figure 1 presents a schematic diagram of the high-pressure microreactor experimental apparatus.

(a) The *reactor* is a smooth-bore ¼-in. 316 stainless-steel tubing with a 3.2-mm internal diameter and a length of 25 cm. The reactor volume (2 cm^3) is divided into three sections. The flow distribution and preheater zone contains inert calcined Vycor quartz chips (30 to 40 μm) in a length of approximately 5 cm preceding the active zone (catalyst bed). This arrangement allows for saturation of the liquid phase with hydrogen, and it ensures achievement of a uniform liquid temperature. The catalyst bed itself is 15 cm of 30 to 40 presulfided $CoO–MoO_3/\gamma$-Al_2O_3 catalyst particles diluted with Vycor quartz chips. Another 5-cm length of inert quartz chips sits below the catalyst bed. Full details of design and operation are given elsewhere (5).

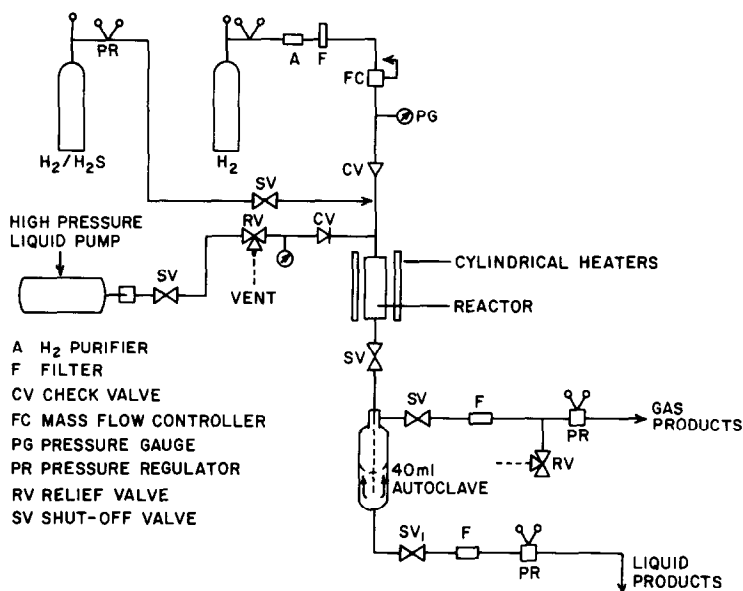The catalyst used for all the HDO runs

FIG. 1. Schematic diagram of high-pressure microreactor.

was a commercial $CoO-MoO_3Al_2O_3$ (American Cyanamid HDS-2A: 15.4% MoO_3, 3.2% CoO; 310 m^2/g). Experimental data were obtained at two temperature ranges, using two different catalyst charges. The high-temperature (350–400°C) data were collected using a catalyst charge containing 0.085 g of Co–Mo diluted with 1.301 g of inert quartz chips, and 0.090 g of Co–Mo mixed with 1.001 g of quartz chips provided the low-temperature (225–275°C) data. The catalysts used for the high-temperature (350–400°C) experiments are aged because they had been used in prior HDO experimental runs, and they will henceforth be referred to as Co–Mo catalysts I. The catalysts for the low-temperature runs (225–275°C), hereafter referred to as Co–Mo catalysts II, were fresh.

Both catalyst charges were pretreated *in situ* before use. The pretreatment involved reduction with hydrogen at 400°C for 3 to 5 hr (CoMoI) or 11 hr (CoMoII) followed by sulfidation with 11 vol% H_2S in H_2 at 400°C for 2 and 3 hr, respectively, for Co–Mo catalysts I and II.

The hydrodeoxygenation experiments were carried out with a liquid feed rate of 3.0 to 12.5 cm^3/hr, and a co-current gas flow rate of approximately 120 cm^3/min (STP). The reactor (hydrogen) pressure was varied between 34 and 100 atm for hydrogen order determinations; a standard pressure of 68–69 atm was used for most runs.

High-grade *n*-hexadecane, *o*-cresol, *m*-cresol, and *p*-cresol, all of 99+% purity, were used as received from Aldrich Chemicals Company. Ultrahigh-purity hydrogen (99.999%) obtained from Matheson Co. was first dried and purified with Deoxo oxygen removal purifier and 5A zeolite filter before use. The gases used for the analytical work (hydrogen, helium, and compressed air) were also of high purity, and were dried before use.

Each reactant feed solution contained *n*-hexadecane solvent, to which was added 0.15 moles/liter of the cresol and 0.0075 mole/liter of heptane thiol (*n*-heptyl mercaptan); the latter was added to ensure that the catalyst would remain sulfided throughout the run.

Liquid samples collected from the exit of the high-pressure flow microreactor (Fig. 1) were analyzed on a Perkin–Elmer Sigma 1 gas chromatographic system equipped with

a flame ionization detector (FID) and a microprocessor. The packed columns which contained 3% OV-101 (methyl silicone) on 100/120 gas chrom Q (Applied Science Laboratories, Inc.) effectively separated all the components, the identities of which were established by both GC-MS (Finnegan 3200) and use of authentic standards.

In operation, reactant conversions of 0.1 to 5–7% were typical. As none of the reaction products appeared to indicate appreciable product inhibition, these data are near differential conversion. Cresol conversions were calculated by dividing the total concentrations of the major products formed (toluene and methyl cyclohexane) by the original cresol level.

Appreciable loss of catalyst activity was noted over long-term operation (3 months) using catalyst I. Following rereduction and sulfiding after the experiments reported here, all but 10% of the original HDO activity was regained. Catalyst II was regularly rereduced and resulfided between sets of experiments, typically regaining nearly 100% of its original HDO activity.

Preliminary tests established that the quartz chips were totally inactive, even at the most severe conditions examined (400°C and 100 atm), in agreement with prior studies (6, 8). To maintain the catalyst in a sulfided state, n-heptyl mercaptan was present in the feed liquid at a constant level of 0.0075 M; its conversion to H_2S and n-C_7 was 90–100% under all conditions examined.

RESULTS

Hydrogen pressure dependence appeared to be approximately first order as shown by a plot of $\ln(1 -$ cresol conversion $(X_c))$ vs P_{H_2} for both catalysts I and II (Fig. 2). The apparent first-order rate constant for catalyst I (400°C, dotted line in Fig. 2) is 6.2 × 10^{-5} liter hr^{-1} (g cat)$^{-1}$.

The cresol conversions at fixed hydrogen pressures are all adequately represented by pseudo-first-order behavior as shown by linearity of plots of $\ln(1 - X_{cresol})$ vs recipro-

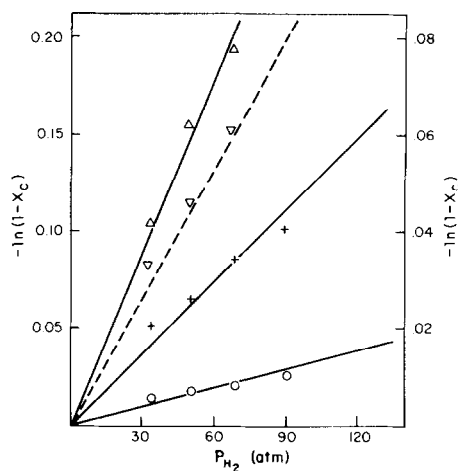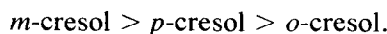FIG. 2. Hydrogen pressure dependence: $-\ln(1 -$ HDO conversion) vs P_{H_2}. Catalyst I: ($\triangledown$) 400°C, right vertical axis; catalyst II: ($\bigcirc$) 225°C, (+) 250°C, ($\triangle$) 275°C left vertical axis.

cal space velocity, W/F_{co}, as exemplified in Fig. 3 for catalyst I. At all three temperatures, the relative reactivity was found to be

$$m\text{-cresol} > p\text{-cresol} > o\text{-cresol}.$$

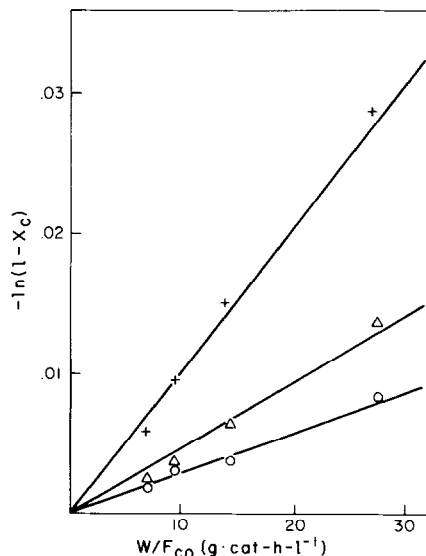The corresponding activation energies and frequency factors calculated from the

FIG. 3. Cresol HDO conversion vs reciprocal space velocity (W/F_{co}): $T = 350°C$, catalyst I, (+) m-cresol, ($\triangle$) p-cresol, ($\bigcirc$) o-cresol.
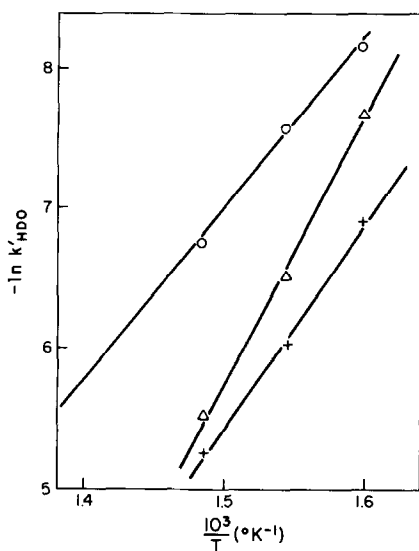
FIG. 4. Arrhenius plot: $-\ln(k_{HDO})$ vs $1/T$, catalyst I, (O) o-cresol, (△) p-cresol, (+) m-cresol.

Arrhenius plots (Fig. 4) for the apparent first-order rate constants for catalyst I (68 atm H_2, H_2 flow = 120 cm³/min) are as follows:

	E_a (kcal/mol)	ln A (liter-hr⁻¹ (g cat)⁻¹)
o-cresol	23	11.1
m-cresol	27	15.0
p-cresol	37	21.9

Fresh catalyst (II) provided a much higher activity for cresol hydrodeoxygenation, the data again indicating apparent first-order behavior at the lower-temperature range of 225–275°C. The corresponding Arrhenius parameter values for m-cresol hydrodeoxygenation were E_A = 27 kcal/mole and ln A = 15 liter-hr⁻¹ (g cat)⁻¹.

The distribution of the major products toluene (TOL) and methylcyclohexane (MCH) were markedly different on fresh (II) vs aged catalysts (I). Figure 5 indicates that at higher temperatures on an aged catalyst the ratio of (MCH)/(TOL) remained essentially unchanged with percentage m-cresol conversion. On fresh catalyst (II), however, this ratio increased monotonically with m-cresol conversion at all three temperatures studied.

Variation of hydrogen pressure had little effect on the (MCH/TOL) ratio over catalyst I (aged), while this ratio increased continuously with increased hydrogen pressure (Fig. 6) over catalyst II (fresh).

Water is a product of hydrodeoxygenation. Experiments performed with catalyst I under conditions of 0.15 M cresol and 0.0075 M n-heptyl mercaptan were run with no water and with 0.045 M water in the entering feed. The results in Fig. 7 indicate that water does not have an inhibitory role of any importance in high-temperature (400°C) cresol conversion, since the results are independent of the presence of water added in the feed.

DISCUSSION

The order of reactivity of the cresols with respect to HDO is indicated from our results on aged (I) or fresh (II) catalysts to be meta > para > ortho. Data by other authors on a similar catalyst (10) or on NiS_2–WS_2/Al_2O_3 (11) are consistent with these results, while some older autoclave data of Bobyshev et al. (12) find para > meta. The o-cresol low reactivity appears to be associated with an entropic (steric)
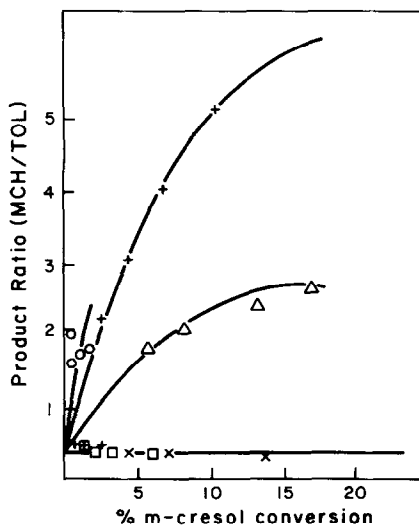

FIG. 5. Product ratio (methylcyclohexane (MCH)/toluene (TOL)) vs % m-cresol conversion (100 × X_c). Catalyst I (aged): (+) 350°C, (□) 375°C, (×) 400°C; catalyst II (fresh): (O) 225°C, (+) 250°C, (△) 275°C.
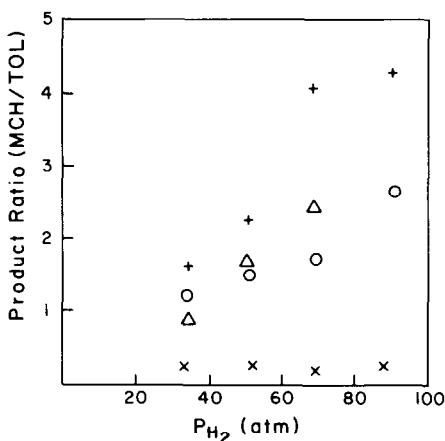
FIG. 6. Product ratio (MCH/TOL) vs hydrogen pressure P_{H_2} (atm), m-cresol. Catalyst I (aged): ($\times$) 400°C; catalyst II (fresh): ($\bigcirc$) 225°C, (+) 250°C, ($\triangle$) 275°C.

influence, although the results suggest a compensation effect for which we have no rationale.

Our observed order of cresol reactivity is similar to findings from analogous HDS and HDN studies. Givens and Venuto (13) reported that methyl substitution of benzothiophene resulted in a decrease in the reactivity to HDS. Gates et al. (14) observed that methyl substitution at positions *ortho* to the sulfur atom resulted in reduction of the rate of HDS of dibenzothiophene, whereas ring substitution at positions *meta* and *para* to the heterocyclic sulfur did not appear to have any significant effect. Enhancement of HDS by methyl substitution on the parent compound at other than *ortho* positions has been noted for thiophene by Desikan and Amberg (21) and Houalla et al. (22). Although the effect of alkyl substitution on the ring on the rate of HDN has not been reported, the reactivity of N-containing species to HDN is believed (1, 8) to decrease in the order

pyridine > indole > quinoline > acridine.

Rollmann (10) and Gates et al. (14) rationalized the observed low reactivity of alkyl *ortho*-substituted O- and S-heteroaromatics as due to increased steric hindrance at these positions.

The conversion of m-cresol on the freshly sulfided catalyst II is higher than on the aged Co–Mo catalyst I. Extrapolation of our low-temperature (225–275°C) data on the Co–Mo catalyst II to the higher temperatures (350–400°C) at which Co–Mo catalyst I was used shows that the cresol deoxygenation (HDO) conversion at the same temperature would be at least an order of magnitude higher than on the aged Co–Mo catalyst I. Whitehurst and co-workers (8) similarly found that fresh catalysts (Co–Mo, Ni–Mo, etc.) were more active than the aged catalysts (Co–Mo, Ni–Mo, etc.) for the HDS of benzothiophene, HDN of indole and picoline, HDO of p-cresol and dibenzofuran, and the hydrogenation of phenanthrene.

The variation of major products with m-cresol conversion (Fig. 5) and hydrogen pressure (Fig. 6) offers major mechanistic differences between the high-temperature conversion on an aged catalyst (I) and the lower temperature conversion on a fresh
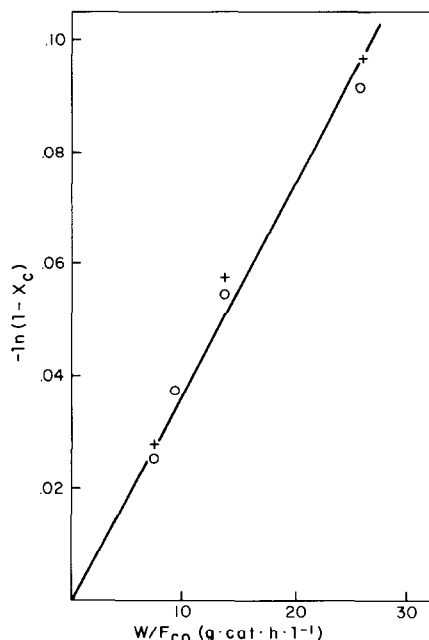

FIG. 7. Influence of water. $\ln(1 - \text{HDO conversion})$ vs reciprocal space velocity (W/F_{co}), m-cresol, $T = 400$°C, catalyst I, ($\bigcirc$) conventional feed (0.15 M cresol), (+) 0.045 M water +0.15 M cresol.

catalyst (II). With catalyst I, the insensitivity of the (MCH/TOL) ratio to either hydrogen pressure or cresol conversion is consistent with a series-parallel network (A) in which lack of hydrogenation activity results in (MCH/TOL) determined by the kinetic selectivity of an adsorbed early intermediate:

$$m\text{-cresol} \xrightarrow{\text{slow}} (\text{intermediate})_1 \rightarrow$$

(A)
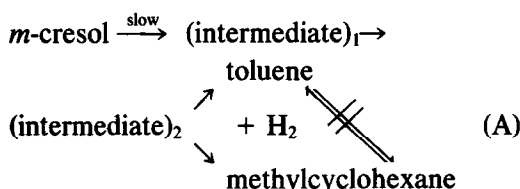
The contrasting behavior of catalyst II suggests that the primary mass flow at lower temperature on this more active catalyst is through a strictly serial pathway:

$$m\text{-cresol} \rightarrow (\text{intermediate}) \rightarrow$$
$$\text{toluene} \rightarrow \text{methylcyclohexane}. \quad (B)$$
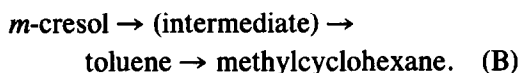
The data in Fig. 5 do not rule out a small contribution from pathway (A) for fresh catalyst as well.

The essentially constant value of the (MCH)/(TOL) ratio on an aged catalyst (Fig. 5) suggested the possibility of an equilibrium MCH $\rightleftarrows$ TOL + 3H$_2$. This hypothesis was ruled out by the insensitivity of the MCH/TOL ratio to hydrogen pressure on the aged catalyst (Fig. 6). In contrast, the increased value of MCH/TOL ratio for fresh catalyst (Fig. 5) and its strong dependence on P_{H_2} (Fig. 6) are consistent with the presence of major hydrogenation activity on catalyst II, relative to HDO activity.

Deactivation of hydrogenation activity was observed with catalyst II. At 250°C and essentially constant cresol conversion, the MCH/TOL ratio declined from 69% to 43% (after 1 month) to 27% (after 3 months). Similar declines were noted at 275°C. This unregenerable hydrogen activity loss vs HDO activity is reminiscent of similar findings for hydrogenation vs HDS activity (23–26). (No analysis for coke deposits was made.) To date no reaction mechanism has

admitted of an equilibrium in any of the steps. Also, hydrogenolysis of the cyclohexane ring to give straight- and branched-chain hydrocarbons has not been reported.

Our low-temperature and high-temperature data on the two catalyst systems indicate that the HDO of phenols is more complicated than the above simple consecutive process. A general reaction pathway consistent with these results is shown in Fig. 8. The pathway using k_1 is contrary to Rollman's suggestion (10) that HDO proceeds analogously to HDN, i.e., that oxygen removal from a phenol requires ring saturation prior to HDO.

The loss of hydrogenation activity, relative to hydrodeoxygenation activity, has a clear beneficial effect. At 5% conversion, for example, the data of Fig. 5 indicate that the molecules of H$_2$ consumed per O atom removed declined from a fresh catalyst value of 3.3 (250°C) to an aged catalyst value of 2.2 at the same temperature (and to a yet lower value of 1.9 at 350–400°C).

The duality of pathways noted in Fig. 8 for our fresh vs aged HDO catalysts is reminiscent of the two-site model of Desiken and Amberg (18) involving HDS sites of differing kinetic selectivities, as well as differing susceptibilities to deactivation. This model has been cited by Satterfield et al. (4)
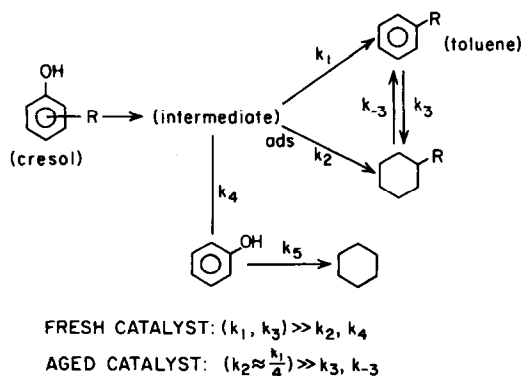
FRESH CATALYST: $(k_1, k_3) \gg k_2, k_4$

AGED CATALYST: $(k_2 \approx \frac{k_1}{4}) \gg k_3, k_{-3}$

FIG. 8. General pathways for cresol HDO conversions. Fresh catalyst (II) behavior is dominated by relatively large k_1 and k_3 values. Aged catalyst (I) behavior is dominated by k_1 (reduced vs fresh catalyst) and k_2, with k_3 being essentially zero, and k_4 giving a small contribution at the highest temperature.

for HDS/HDN results. In a recent report Broderick and Gates (15) made a similar note of competing reaction pathways in the hydrodesulfurization of dibenzothiophene by sulfided $Co-O-MoO_3/\gamma-Al_2O_3$ catalysts. The first route involves hydrogenolysis of the C–S bonds to give H_2S and biphenyl (hydrogenolysis pathway). The second route that involves hydrogenation of one of the benzenoid rings followed by rapid hydrogenolysis of the C–S bonds gives cyclohexylbenzene (hydrogenation pathway). They noted further that the differences in the kinetics of the two reactions resulted in a selectivity (rate of hydrogenolysis/rate of hydrogenation) which is a strong function of temperature (and H_2S (inhibitor)) concentration.

We show in the following paper (II), using mixed-feed experiments, that a Langmuir–Hinshelwood form is needed to describe the true *fractional*-order HDO kinetics and to account for the very clear mutual inhibitions of oxygenate and sulfur heterocycle on simultaneous HDO/HDS. The same conclusion is demonstrated in paper III for simultaneous HDO/HDN.

CONCLUSIONS

The hydrodeoxygenation of cresols on sulfided $CoO-MoO/\gamma-Al_2O_3$ at 225–400°C and 68 atm hydrogen pressure gives toluene and methylcyclohexane as major products. At low temperatures on freshly sulfided Co–Mo catalsts the HDO proceeds primarily by a simple oxygen extrusion to give toluene, which is subsequently hydrogenated to methylcyclohexane. At higher temperatures (350–400°C) on aged catalysts, subsequent hydrogenation of toluene disappears, and the simple linear-consecutive process is replaced by a competing branched reaction which appears to yield methylcyclohexane directly from the cresol complex adsorbed on the catalyst surface. The HDO reaction is first-order in hydrogen pressure. The reactivity of the cresols to deoxygenation decreases in the order
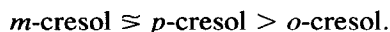
m-cresol $\gtrsim$ p-cresol $>$ o-cresol.

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