JOURNAL OF CATALYSIS 96, 535–543 (1985)

Hydrodeoxygenation of Hydroxy, Methoxy, and Methyl Phenols with Molybdenum Oxide/Nickel Oxide/Alumina Catalyst

R. K. M. R. KALLURY,* WANDA M. RESTIVO,* THOMAS T. TIDWELL,*
D. G. B. BOOCOCK,† A. CRIMI,† AND J. DOUGLAS†

*Department of Chemistry, University of Toronto, Toronto, Ontario M5S 1A1; and †Department of Chemical Engineering, University of Toronto, Toronto, Ontario M5S 1A4, Canada

Received December 31, 1984; revised June 21, 1985

Hydrodeoxygenation (HDO) with MoO_3–NiO–Al_2O_3 catalyst gives markedly different results for the isomeric dihydroxybenzenes, in contrast to previous studies with molybdenum or other catalysts which suggested similar behavior for these substrates. Thus, at 350°C *o*-dihydroxybenzene is more reactive than phenol and gives 60% of phenol, *m*-dihydroxybenzene is much less reactive and gives primarily ring saturation, and *p*-dihydroxybenzene is more reactive than phenol and gives primarily products of ring saturation. At 500°C total conversion of all three isomers is achieved. Other substrates studied are *o*-methoxyphenol, 2,6-dimethoxyphenol, and various methyl- and dimethylphenols. Reaction variables examined include temperature, the effects of added H_2O and MeOH, and repeated use of the same catalyst batch for successive runs. The results are interpreted in terms of the geometries of the substrates and their ability to adsorb on the catalyst surface, the blocking of active sites on the catalyst by H_2O and MeOH either generated during HDO or added directly, and the different electronic properties of the substrates.

INTRODUCTION

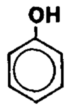
During recent years much attention has been devoted to the utility of synthetic liquids from biomass as sources of fuels and chemical feedstocks (*1*). As pointed out in a recent review (*2*), oils obtained from sources such as coal, shale, or tar sands are characterized by a high oxygen content (0.4–4%), mostly in the form of phenolic and ether groups. For oils derived by the liquefaction of wood these figures are even higher (5–50%) (*3*).

In particular it has been found that liquefaction of whole wood (*4*), or of individual constituents of wood such as lignin (*5*) or cellulose (*6*), produces oils that contain large amounts of phenolic materials. However, the presence of such compounds is not desirable in oils to be used as fuels because they have a tendency to polymerize thereby increasing the viscosity of the oils to unacceptable levels (*2*). In addition, the fuel value of such oxygenated materials are not as high as for hydrocarbons.

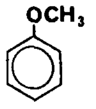
In order to devise methods to reduce the oxygen content of such oils there has been a great deal of effort devoted to the study of catalytic hydrodeoxygenation (HDO) (*2*). We have recently reported a study of the hydrogenation of phenol (**1**) and anisole (**2**) using a BASF MoO_3–NiO–Al_2O_3 catalyst as a model study for this process (*7*). Other recent investigations have dealt with **1**, **2**, *o*-cresol (**3**), and *o*-methoxyphenol (guaiacol, **4**) with a Ni–Mo–SiO_2–Al_2O_3 catalyst (*8*); 4-*n*-propyl-2-methoxyphenol with Al_2O_3 (with or without Co–Mo) (*9*); **2** and **4** with a MoO_3–CoO–Al_2O_3 catalyst (*10*); dibenzofuran with a Ni–Mo–Al_2O_3 catalyst (*11*); **3**, *m*-cresol, and *p*-cresol (**5**) with CoO–MoO_3–Al_2O_3 catalyst (*12*); and benzofuran and *o*-ethylphenol with CoO–MoO_3–Al_2O_3 catalyst (*13*).

Because lignin is composed principally of functionalized phenols in its polymeric structure (*14*) and on liquefaction gives oils with a high content of phenolic materials, we have now extended our study using MoO_3–NiO–Al_2O_3 catalyst to **3–5**, *o*-di-

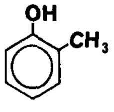
0021-9517/85 $3.00



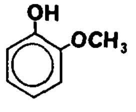
1



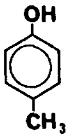
2



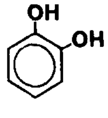
3



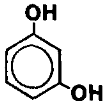
4



5

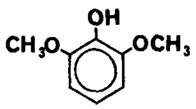


6

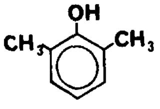


7

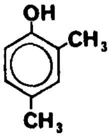
8



9



10



11

hydroxybenzene (catechol, **6**), *m*-dihydroxybenzene (resorcinol, **7**), *p*-dihydroxybenzene (hydroquinone, **8**), 2,6-dimethoxyphenol (syringol, **9**), 2,6-dimethylphenol (**10**), and 2,4-dimethylphenol (**11**). By studying all of these compounds with a single catalyst under comparable conditions we hoped to attain a systematic understanding of the interconversion pathways of these model compounds for lignin. The prevalence of hydroxy, methoxy, and alkyl phenols in lignin and wood pyrolytic oils (*4*) dictated our choice of substrates. The clear advantages of molybdenum-containing catalysts for HDO are well established (*8–13, 15*) and Mitchell (*16*) found Mo–Ni to be superior to Mo–Co catalysts for deoxygenation of mixed phenols.

The effects of added H_2O and MeOH on the HDO of phenol (**1**) have also been included in the current investigation, as well as the use of a single batch of catalyst for repetitive runs on phenol.

EXPERIMENTAL

The substrates were commercial samples whose purity was checked by gas chromatography. The commercial samples of guaiacol (**4**) were contaminated with cresols and xylenols, so were purified by distillation. Methanol used as a substrate and ether used for extraction were reagent grade samples purified by distillation. The catalyst used was BASF M 8-21 (15% MoO_3, 3% NiO on activated alumina).

The experimental procedure for the HDO utilized 10 g of each phenol with 1.5 g of the catalyst as reported earlier (*7*). In all the runs there was an initial (cold) hydrogen pressure of 2.8 MPa and a heating rate of 5.5°C/min was used for bringing the reactants to the desired temperature. Heat-up times were thus 1 h for reactions at 350°C and 1.5 h for 500°C and the reactions were all kept at the final temperature for 1 h. At 450°C the final observed pressure was 6.4 MPa. In the workups whenever aqueous layers were encountered in the products these were extracted with ether and the extractable material analyzed by GC. The results are reported in Tables 1 and 2.

To test the catalytic activity of MoO_3

TABLE 1

Hydrodeoxygenation of Hydroxy- and Methoxyphenols

Substrate	T (°C)	Percentage conversion[a]	MeCyclo-pentane	Cyclo-hexane	C_6H_6	PhOH	Cyclo-hexanone	PhMe	Me_2-C_6H_4	Me_3-C_6H_3	Me-phenol	Me_2-phenol	Cyclohexyl-phenols	Other
1	350	36		11	12	64							9	
1	450	100	7	16	60			2	2	2				*d*
1 + H_2O[b]	450	14			1	86								*d*
1 + H_2O[b]	500	100	2	4	75			2	1					*d*
4	350	60				14		1			13	14		*e*
4	400	98	2	2	7	31		8	2	2	24	18		*f*
4	450	98	3	7	23	3		27	7	4	6	10		*g*
4	500	100	4	5	32	1		30	8	4	1	2		*h*
4 + MeOH[c]	400	95		1	5	14		6	6	5	17	26		*i*
4 + MeOH[c]	450	99	1	2	8	14		10	8	4	19	15		*j*
6	350	70				60	4							
6	400	98				83	8	3						
6	450	98	5	15	37	12	3	1	1		10		4	
6	500	100	2	6	52	7		1	1		18	4		
6 + MeOH[c]	450	92	1	2	8	38		5	2		15	8		*f*
6 + MeOH[c]	500	99	2	4	27	11		16	7	2	20	8		*f*
7	350	15		1		1	3				2			*k*
7	400	30		1		8	3				5	5		*l*
7	450	94	4	6	5	14		3	3	2	6	8	8	*m*
7	500	100	2	3	30	3		13	11	4	1	1		*n*
8	350	80		6	1	17	11						21	*o*
8	400	91	2	5	14	17	10	1	0.5		5		9	*p*
8	450	94	5	13	18	22	7	3	3	2	2		5	*q*
8	500	100	5	17	42			9	6					*r*
9	400	98	1	5	7	2		11	9	3	6	24		*s*
9	500	100	3	5	23	2		28	14	4	4	6		*t*

[a] C_{12} products assumed derived from two substrate molecules.

[b] 1/1 (wt/wt).

[c] 2/1 (wt/wt).

[d] Bicyclohexyl (2), cyclohexylbenzene (3).

[e] **6** (4), $MeC_6H_3(OH)_2$ (8), **2** (1).

[f] MeCyclohexane (2).

[g] Me_2Cyclohexanes (5).

[h] MeCyclohexane (2), cyclopentane (1).

[i] **6** (4), $MeC_6H_3(OH)_2$ (13), Me_2Cyclohexanes (2).

[j] $Me_3C_6H_2OH$ (7), $Me_4C_6H_2$ (4), Me_2Cyclohexanes (2), MeCyclohexane (3).

[k] Hydroxycyclohexanone (3), cyclohexanedione (3), bicyclohexyl (2).

[l] Cyclohexanedione (3), bicyclohexyl (1).

[m] *n*-Pentane (2), cyclopentane (2), MeCyclohexane (4), bicyclohexyl (4), naphthalene (2), methylbiphenyls (2), methylbicyclohexyls (2).

[n] MeCyclohexane (2), bicyclohexyl (4), naphthalene (8), methylbiphenyls (3).

[o] Cyclohexanedione (11), cyclohexene (6).

[p] Cyclohexanedione (4), cyclohexene (6), naphthalene (4), diphenyl ether (5).

[q] Cyclohexanedione (4), cyclohexene (10).

[r] Naphthalene (8), diphenylmethane (2).

[s] **6** (5), $MeC_6H_3(OH)_2$ (7), **2** (1), MeCyclohexane (1), Me_2Cyclohexane (6).

[t] MeCyclohexane (3).

TABLE 2

Hydrodeoxygenation of Alkylphenols

Substrate	T (°C)	Percentage conversion	Cyclohexane	C_6H_6	PhOH	MePh	Me_2-C_6H_4	Me_3-C_6H_3	Me-phenol	Me_2-phenol	MeCyclohexane	Me_2Cyclohexane	Me-PhPh	Other
3	400	60	2		2	18	3		40	14	17		2	
3	450	99	7			36	10	2		2	18	12	3	[a]
5	400	55	1	3	1	19	2	1	45	13	10		5	
5	450	100	6			61		3		2	19	7		
10	400	70		5		6	22	8	5	35	2	5		
10	450	97	2		1	11	37	10	1	3	5	15		[b]
11	450	98	3	4	2	4	49	4	2	1	8	12	6	
3 and 5	400	66	2	6	1	28	4	1	34	10	11		2	
3 and 5	450	99	10	2		37	8	3			10	20		
3–5, 9–11	450	99	5	11		37	22	4	1	5	10		2	

[a] Methylbicyclohexyl (5).

[b] Trimethylphenols (11).

with hydroquinone (**8**) 10 g of **8** was reacted with 1.5 g of MoO_3 (Fisher reagent grade) for 1 h at 2.8 MPa and 355°C. The recovery of **8** was 40% and phenol (**1**, 18%), cyclohexanone (13%), cyclohexanedione (5%), cyclohexane (3%), benzene (2%), and cyclohexylphenol (3%) were the principal products detected.

The products were analyzed by a combination of ^{1}H NMR, GC (analytical and preparative), and GC–MS. The instrumentation used has been described previously (*4a*). The relative GC response factors of authentic samples of some of the major components of the product mixtures were evaluated by a CDS-111 computer attached to the F.I. detector of the gas chromatograph (Varian 2700) with a 2 m × 33 mm 5% QF-1 column used in these studies and were benzene (1.00), cyclohexane (1.00), toluene (1.03), *p*-xylene (1.04), mesitylene (1.07), biphenyl (1.01), cyclohexylbenzene (1.01), bicyclohexyl (1.25), phenol (0.60), cyclohexanone (0.63), 2,6-xylenol (0.64), catechol (0.59), *p*-cyclohexylphenol (0.66), hydroquinone (0.60). Peak areas on the gas chromatograms were converted to relative molar yields using these factors.

For repetitive runs the catalyst after the initial run was washed with ether and air-dried prior to use in a subsequent run. In each new run an additional 10 g of phenol was reacted with the washed and dried catalyst, with the results shown in Table 3.

RESULTS AND DISCUSSION

Catechol (***6***)

This substrate is somewhat more reactive than phenol itself, undergoing 70% conversion at 350°C as compared to 36% for phenol. At 400°C, **6** is 98% consumed whereas with phenol as the substrate there is only 73% conversion at this temperature even after 2 h and somewhat higher pressures (*7*). The major HDO pathway of **6** at these reaction temperatures is the cleavage of one hydroxyl group to give phenol.

TABLE 3

HDO of Phenol in Repeated Runs with Recycling of Catalyst[a]

Run	Methylcyclopentane	Cyclohexane	Benzene	Cyclohexylbenzenes
1	10	20	60	3
2	12	17	58	5
3	10	40	40	4
4	13	21	58	2
5	12	37	42	4

[a] 450°C, 100% conversion, and approximately 1% each of toluene, xylenes, and trimethylbenzenes, and 2% biphenyl, observed in each case.

After the initial formation of phenol from catechol the system becomes less reactive. Thus at 350°C beginning with **6** there is no more than 10% of product formed which could have come from phenol, whereas with phenol as the initial reactant there is 36% conversion at this temperature, and even at 400°C there was 83% phenol present from **6**. At 450 and 500°C the deoxygenation is, however, more thorough, with only 12 and 7% residual phenol, respectively. Deactivation of the catalyst, quite possibly by the water formed in removal of the first hydroxyl, is the likely cause of the reduced activity, but this effect is overcome at higher temperatures.

The deactivation of HDO catalysts by water was considered by Furimsky (*2*) who reasoned that even though this effect had not been thoroughly elucidated, the hypothesis could be made that the water occupied and blocked the active site of the catalyst, evidently by coordination of oxygen to the metal. Our experiments using phenol and an equimolar amount of water (Table 1) confirm there is decreased activity at 450°C, but total conversion occurs at 500°C. Thus there is a marked similarity in the product composition from phenol at 450°C (benzene 60%, cyclohexane 16%, and methylcyclopentane 7%), and catechol at 500°C (benzene 52%, cyclohexane 6%, and methylcyclopentane 2%).

In the presence of methanol there are significant amounts of ring methylated products formed from catechol, just as was found from phenol (*7*). No methylcatechols were detected but these probably would not have survived in these reactions which were conducted at 450 and 500°C. In experiments with guaiacol (**4**, vide infra) at 350 and 400°C methylcatechols were observed but not at 450 and 500°C. Since phenol is known (*7*) to be efficiently methylated at 450°C in the presence of methanol it appears likely that under these conditions catechol is both methylated to methylcatechols and deoxygenated to phenol and both of these primary products react to give cresols and other products. The extent of ring deoxygenation with catechol is reduced in the presence of methanol, especially at 450°C. This evident deactivation of the catalyst in the presence of methanol resembles the effect already noted with water in the reduction of phenol and suggests that methanol can also act to occupy and block the active sites of the catalyst by oxygen coordination to the metal.

Our results on **6** are in agreement with the qualitative studies of Bahr and Petrick of 50 years ago, who studied all three of the isomeric dihydroxybenzenes and reported that each gave phenol, benzene, and a small amount of biphenyl (*17*). Interestingly, it was found that in hydrogenation of the dihydroxybezenes with Pt or Rh catalyst resulting in ring saturation that **6** was less reactive than phenol, in contrast to the situation here (*18*).

Resorcinol (*7*)

This substrate is for the most part unreactive at 350 and 400°C with only 15 and 30% conversion, respectively, at these temperatures, and so is not only less reactive than **6** but also is less reactive than phenol itself. At 450–500°C there is effective conversion of **7** but a large number of products are formed, without high selectivity for any single material.

The complex product formed is in contrast to the report of Bahr and Petrick that **7** gave mainly phenol and benzene (*17*), and the low reactivity is also in contrast with the results of the ring hydrogenation studies, where **7** was more reactive than **6** but less reactive than phenol (*18*).

Hydroquinone (**8**)

The behavior of **8** under HDO conditions is quite different from both **6** and **7**. Thus, whereas **6** gives a rather clean conversion to 83% phenol at 400°C, there is only 17% of this product from **8** at 350 or 400°C, with much more of the product from **8** resulting from ring saturation. At 350°C, **8** gives significant amounts of cyclohexanone, cyclohexanedione, cyclohexene, and cyclohexylbenzenes, but at higher temperatures the yields of these products diminish and at 500°C none are detected and 17% cyclohexane and 42% of benzene were formed (Table 1). Ring saturation of hydroquinone with Pt and Rh catalysts has been observed before (*18*), but the preference for this mode of behavior with an HDO promoting catalyst is surprising and **8** is unique in this regard among the substrates we have examined.

Our results are in apparent disagreement with the only previous study of hydroquinone hydrogenation with a molybdenum catalyst, as reported by Bahr and Petrick (*17*). These authors used a MoO_3 catalyst obtained by calcination of $Mo(NO_3)_6$ and a hydrogenation temperature of 360°C, and reported the formation of phenol, benzene, and a small amount of biphenyl. Quantitative ratios of these materials and the presence or absence of the other products we detected (cyclohexane, cyclohexanone, cyclohexanedione, cyclohexene, cyclohexylphenols, and cyclohexylbenzene) were not reported and indeed would have been difficult to determine with the methodology available to these authors.

For comparative purposes we carried out the hydrogenation of **8** with reagent grade MoO_3 at 355°C and obtained rather similar results to those with the BASF catalyst under comparable conditions (pure MoO_3 results given first): conversion, 60 and 80%; phenol, 18 and 17%; cyclohexanone, 13 and 11%; 1,4-cyclohexanedione, 5 and 11%; cyclohexane, 3 and 6%; benzene, 2 and 1%; and cyclohexylphenols, 3 and 21%.

For the pure MoO_3 catalyst 39% of the C_6 ring products actually formed are saturated, whereas with the BASF catalyst there is not only a greater conversion but 57% of the C_6 rings formed are saturated. The greater tendency of the NiO-containing BASF catalyst for ring saturation is not surprising, in view of the known tendency of Ni catalyst to promote this process (*7*). With reference to the report of Bahr and Petrick (*17*) it appears reasonable to assume that while phenol and benzene are formed, just as they reported, that there were probably also products of ring saturation present which were not detected by their methods of product identification (titration of the phenol and distillation).

Several factors may be responsible for the difference in reactivity between the three isomeric dihydroxybenzenes **6**, **7**, and **8**. One of these is the differing pK_a values, which are 9.25, 9.20, and 9.91 for the *o*, *m*, and *p* isomers, respectively (*19*). The efficiency of adsorption of the phenols on the catalyst and their subsequent HDO and hydrogenation could well be affected by this property, but the influence of pK_a on reactivity in this process has not been systematically studied.

The distance of the OH groups from one another could also be important, particularly if adsorption at both groups occurred. The detailed structure of the catalyst we have used has evidently not been reported, but it has been argued that the Mo–Mo distance in MoO_3–Al_2O_3 catalysts should be about 2.8 Å (*20*), and this agrees with the experimental distances found in a variety of dimolybdenum complexes (*21*). The O–O distance in the dihydroxybenzenes is 2.72 (*22*), 4.78 (*23*), and 5.54 Å (*24*) for the *o*, *m*, and *p* isomers, respectively, and so it would appear that the *o* isomer could simultaneously coordinate to two neighboring Mo atoms, while the *p* compound could interact with the first and third Mo atoms in the lattice. However, because of the uncertainty in the molecular structure of our catalyst and of the geometry of the catalyst–phenol interaction this analysis cannot be carried further.

Still other factors that might influence the relative reactivities are the known greater reactivity of the *m* isomer in electrophilic aromatic substitution (*25*), and the possibility of a cooperative effect of the adjacent oxygens in the reaction of the *o* isomer. The results show a facile reaction of the latter compound to form phenol at lower temperatures, whereas the former is the least reactive of the three at 350°C, but at 450°C gives a large number of different ring-substituted products.

The noncatalyzed thermal decomposition of *o*-, *m*-, and *p*-dihydroxybenzene (**6**, **7**, and **8**, respectively) has been studied (*26*) and provides an interesting comparison to the catalytic HDO. At 500 and 600°C each of these compounds reacted primarily through decarbonylation and also through deoxygenation to phenol which underwent further reaction to give benzene. The deoxygenation was enhanced by the presence of H_2. The order of reactivity for both decarbonylation and deoxygenation was reported as $o > p > m$, and for catechol there was already 36% conversion of the reactant after 20 min at 500°C.

In our system phenol undergoes 53% conversion in 20 min at 450°C (*7*), so it appears that while the catalyzed reactions are certainly more effective than the uncatalyzed ones, the latter may also make some contribution in the higher temperature runs, particularly in the enhanced formation of benzene and the decreased yield of phenols at 500°C. The effectiveness of the catalyst in promoting HDO is shown by the fact that in the presence of H_2 phenol is reported to be 40% converted after 1 h at 600°C, giving 34% benzene (*26*), whereas the catalyzed reaction gives 100% conversion, and a 60% yield of benzene, after 1 h at 450°C.

o-Methoxyphenol (*Guaiacol*, ***4***)

Reaction of this substrate gives product mixtures that resemble those from catechol (**6**) (Table 1). For example, reaction of catechol with 0.5 equivalent of MeOH at 500°C gives benzene, toluene, and xylenes in 27, 16, and 7% yields, respectively, as opposed to 32, 30, and 8%, respectively, from **4** without added methanol. The primary difference between the two systems is an evident lower reactivity for HDO with catechol–MeOH which, for example, gave 38% phenol and 23% of substituted phenols at 450°C, whereas the total yield of phenolic products identified from **4** under these conditions was 19%. In our previous work with phenol (*7*) we concluded that methyl groups cleaved from methyl phenyl ethers and those from methanol are both capable of alkylating electron-rich aromatics and the same situation arises here, but it is not certain that the active methylating agent is the same for the two systems. It is known from the observations of Hurff and Klein (*10*), who isolated as much as 40% of catechol from **4** at 250°C with a $CoO-MoO_3-Al_2O_3$ catalyst, that cleavage of the methyl from aryl methyl ethers is a facile process.

Evidently, under our conditions demethylation of **4** is still the major initial step as both catechol and methylcatechols are observed, especially at lower reaction temperatures, along with other products derivable from these catechols.

In the reaction of **4** and methanol at 400°C there is a lower yield of phenol and cresols compared to **4** alone but somewhat more xylenols and methylcatechols. Catechol (6%) is observed and evidently demethylation of **4** to catechol is still the first step. The decreased HDO activity of the system with added methanol is evident with the **4**–methanol binary substrate which at 450°C gives 14% phenol and 43% methylated phenols as compared to 3 and 16%, respectively, from **4** alone.

As already noted, the deactivating effect of methanol for HDO is similar to that of water and may well arise from a similar cause involving blocking of active catalytic sites.

2,6-Dimethyoxyphenol (*Syringol*, ***9***)

In spite of the additional methoxy group which could cause some steric hindrance **9** undergoes equally high conversions compared to **4** and **6**. The resemblance of the product yields from these three suggests that initial demethylation and dehydroxylation of **9** are rather efficient and that methylcatechols and **4** are significant intermediates along the reaction path from **9**.

The products from **4** and **9** at 500°C are quite similar with a modest amount more of methylated and phenolic products in the latter case, which is not unreasonable considering the extra methoxyl group in the substrate.

Cresols and Xylenols

The products from *o*- (**3**) and *p*-cresols (**5**) were rather similar with the primary difference being a lower yield of toluene from the former at 450°C and a concomitantly higher yield of xylenes and dimethylcyclohexane. Disproportionation is also observed with the xylenols, and rather more toluene and trimethylbenzene were formed from the 2,6-dimethyl isomer. Whatever the mechanism of the disproportionation step it appears more prevalent with the 1,2-isomer in the case of the cresols and the 1,2,3-isomer in the case of the xylenols. Rather similar results were reported for reduction of isomeric cresols with a sulfided $CoO–MoO_3–Al_2O_3$ catalyst (*27*).

Mixtures of the cresols, and of all the substrates, when treated with the HDO catalyst at 450°C gave essentially complete conversions to hydrocarbons. These reactant mixtures simulate many of chemical features of lignin and illustrate the value of the HDO process for upgrading lignin and lignin-derived oils as fuels (Table 2).

Catalyst Recycling

In order to test the reusability of the catalyst for repeated batch runs the catalyst from HDO of phenol was recycled in a series of subsequent runs without any catalyst regeneration. As shown in Table 3 after five successive runs there was still total conversion of the phenol and high yields of hydrocarbons were observed. There was, however, an interesting variation observed in the relative amounts of benzene and cyclohexane produced in different runs. In the initial runs the benzene/cyclohexane ratio was 3/1, but in the third run this ratio was 1/1 as more cyclohexane was formed at the expense of benzene, but then the ratio rose only to fall again.

Evidently, after two runs the deoxygenating ability of the catalyst was reduced, probably due to the water formed. This effect was also noticed both in experiments where H_2O or MeOH was added initially, and when catechol, which can produce two equivalents of water, was utilized. The specific role of the water or methanol in hindering deoxygenation is not certain, but competition between solvent, product, and phenolic hydroxyl groups for active sites on the catalyst appears plausible. Presuambly, this would occur at the molybdenum atoms which appear responsible for the HDO properties of the catalyst. The hydrogenation properties are evidently due to the nickel and are not affected, so that ring saturation increases at the expense of deoxygenation to benzene. The cyclohexanol formed by ring saturation then undergoes deoxygenation in a nonmetal-catalyzed process resulting in cyclohexane and methyl cyclopentane as we have discussed previously (*7*).

The reappearance of the HDO activity of the catalyst in run 4 is perhaps surprising, but presumably indicates that there is a gradual regeneration of active sites on the catalyst so that deoxygenation is more competitive with hydrogenation. The high activity of the catalyst for HDO at 500°C even in the presence of added water suggests that catalyst reactivation is much faster at higher temperature and that benzene formation will be favored relative to cyclohexane at higher temperatures, even with recycled catalyst. Indeed our previous work indicated the benzene/cyclohexane product ratio at 350 and 400°C was significantly lower than at 450°C (*7*).

CONCLUSION

The above results show that models of lignin and its thermolysis products can be deoxygenated to more fuel-efficient hydrocarbon mixtures with the BASF $MoO_3–NiO–Al_2O_3$ catalyst, even in the presence of moisture. The activity of the catalyst is diminished at lower temperatures with added water or methanol, but could be restored at higher temperatures (450–500°C). The role of methanol in these HDO reactions may be considered favorable from the fuel-efficiency point of view, since the active phenolic nuclei can be methylated and deoxygenated to arenes which increase the fuel value of oils. In this event the presence of methoxyl groups is useful since their cleavage liberates an active methylating species at lower temperatures without affecting the activity of the catalyst.

ACKNOWLEDGMENTS

Financial support by a Strategic Grant from the Natural Sciences and Engineering Research Council of Canada and by Imperial Oil, Limited, is gratefully acknowledged.

REFERENCES

1. (a) Grohmann, K., and Viffet, R., *in* "Bioconversion Systems," (D. L. Wise, Ed.), pp. 1–16. CRC Press, Boca Raton, Fla., 1984; (b) Klass, D. L., and Emert, G. H., Eds., "Fuels from Biomass and Wastes." Ann Arbor Science Pub., Ann Arbor, Mich., 1981; (c) Overend, R. P., Milne, T. A., and Mudge, L. K. Eds., "Fundamentals of Thermochemical Biomass Conversion." Elsevier, London, 1984; (d) Bridgewater, A. V., Ed., "Thermochemical Processing of Biomass." Butterworths, Kent, 1984.
2. Furimsky, F., *Catal. Rev.—Sci. Eng.* **25,** 421 (1983).
3. (a) Elliott, D. C., "Analysis and Upgrading of Biomass Liquefaction Products," Final Report, Vol. 4, IEA Co-operative Project D1 (BLTF Project—Dec. 1983); (b) Elliott, D. C., *in* "Fundamentals of Thermochemical Biomass Conversion" (R. P. Overend, T. A. Milne, and L. K. Mudge, Eds.), pp. 1003–1018. Butterworths, Kent, 1984; (c) Eager, R. L., Mathews, J. F., and Pepper, J. M., *in* "Fundamentals of Thermochemical Biomass Conversion" (R. P. Overend, T. A. Milne, and L. K. Mudge, Eds.), pp. 1051–1071. Butterworths, Kent, 1984.
4. (a) Boocock, D. G. B., Kallury, R. K. M. R., and Tidwell, T. T., *Anal. Chem.* **55,** 1689 (1983); (b) Eager, R. L., Pepper, J. M., Roy, J. C., and Mathews, J. F., *Canad. J. Chem.* **61,** 2010 (1983); (c) Barrows, R. D., and Elliott, D. C., *Fuel* **63,** 4 (1984).
5. (a) Goldstein, I. S., *Appl. Polym. Symp.* **28,** 259 (1975); (b) Bobleter, O., and Concin, B., *Cell. Chem. Technol.* **13,** 583 (1979); (c) Coughlin, R. W., Sundstrom, D. W., Klei, H. E., and Avni, E., *in* "Bioconversion Systems" (D. L. Wise, Ed.), p. 41. CRC Press, Boca Raton, Fla., 1984.
6. (a) Nelson, D. A., Molton, P. M., Russel, J. A., and Hallen, R. T., *Ind. Eng. Chem. Prod. Res. Dev.* **23,** 471 (1984); (b) Richards, G. N., Shafizadeh, F., and Stevenson, T. T., *Carbohydr. Res.* **117,** 322 (1983).
7. Kallury, R. K. M. R., Tidwell, T. T., Boocock, D. G. B., and Chow, D. H. L., *Canad. J. Chem.* **62,** 2540 (1984).
8. Bredenberg, J. B-son, Huuska, M., Raty, J., and Karpio, M., *J. Catal.* **77,** 242 (1982).
9. Vuori, A., and Bredenberg, J. B-son, *Holzforschung* **38,** 133 (1984).
10. Hurff, S. J., and Klein, M. T., *Ind. Eng. Chem. Fundam.* **22,** 426 (1983).
11. Krishnamurthy, S., Panvelkar, S., and Shah, Y. T., *AIChE J.* **27,** 994 (1981).
12. Oldebunmi, E. O., and Ollis, D. F., *J. Catal.* **80,** 56 (1983).
13. Lee, C., and Ollis, D. F., *J. Catal.* **87,** 325 (1984).
14. Freudenberg, K., and Neish, A. C., "Constitution and Biosynthesis of Lignin." Springer-Verlag, Berlin, 1968.
15. Shuikin, N. J., and Erivanskaya, L. A., *Usp. Khim.* **29,** 648 (1960); *Russ. Chem. Rev.* **29,** 309 (1960).
16. Mitchell, T. O., *Coal Process. Technol.* **6,** 28 (1980).
17. Bahr, Von Th., and Petrick, A. J., *Brennst.-Chem.* **14,** 161 (1933).
18. Smith, H. A., and Stump, B. L., *J. Amer. Chem. Soc.* **83,** 2739 (1961).
19. Coffey, S., Ed., "Rodd's Chemistry of Carbon Compounds," Vol. IIIA, pp. 380–381. Elsevier, Amsterdam, 1971.
20. Weigold, H., *J. Catal.* **83,** 85 (1983).
21. Spivak, B., and Dori, H., *in* "Chemistry and Uses of Molybdenum" (P. C. H. Mitchell, Ed.), p. 131. Climax Molybdenum Co., London, 1974.
22. Brown, C. J., *Acta Crystallogr.* **21,** 170 (1966).
23. Bacon, G. E., and Jude, R., *Kristallogr.* **138,** 19 (1973).
24. Maartmann-Moe, K., *Acta Crystallogr.* **21,** 979 (1966).
25. Patinkin, S. H., and Friedman, B. S., *in* "Friedel-Crafts and Related Reactions" (G. A. Olah, Ed.), Vol. 2, Part 1, Chap. 1, p. 75. Wiley, New York, 1964.
26. Sakai, T., and Hattori, M., *Chem. Lett.*, 1153 (1976).
27. Rollmann, L. D., *J. Catal.* **46,** 243 (1977).