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CATALYST DEVELOPMENT FOR HYDRODEOXYGENATION AND DEALKYLATION OF LIGNINS FOR FUELS

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ABSTRACT

The addition of phosphate, even in small amounts, has a significant effect on the properties of the support material of heterogeneous catalysts. The surface area passes through a maximum at a P/Al ratio of 0.1 before decreasing continuously with an increase in the P/Al ratio. The supports have unimodal pore distributions with the median pore size increasing with increasing P/Al ratio. An increase in the P/Al ratio results in material with a decreasing order of crystallinity, as evidenced by x-ray diffraction. The absence of alumina or aluminum phosphate crystals indicates that the supports are randomly arranged composite material rather than intimately mixed domains of alumina and aluminum phosphate.

The addition of phosphate to catalysts prepared by this method has a marked affect on the catalyst activity and selectivity. The catalyst screening with 4-propylguaiacol (4PG), a lignin model compound, has shown that the formation of phenolic compounds suitable for conversion to methyl aryl ethers for fuels is possible. A Ni-Mo catalyst having a phosphated alumina support (P:Al = 0.5) gave the highest yields of these compounds with hydrocarbons as the major side products. Initial tests with Mo catalysts suggest that the side product hydrocarbons can be biased in favor of aromatic hydrocarbons, which are more desirable as high-octane-fuel components and because they will consume less hydrogen in a lignin-to-liquid fuels process than the formation of cycloparaffins would. The Mo catalysts with phosphated alumina supports P:Al = 0.5 and 0.8 will be tested next to determine if higher selectivities to phenols, cresols, ethylphenols, etc., are possible while suppressing aromatic ring saturation as the results at P:Al = 0.2 suggest. The best catalysts will then be synthesized in larger quantities and tested with pretreated lignins in our parallel reactor engineering task.

CATALYST DEVELOPMENT FOR HYDRODEOXYGENATION AND DEALKYLATION OF LIGNINS FOR FUELS

INTRODUCTION

The conversion of lignin into liquid fuels has been the goal of our research for the past two years. Depolymerization of lignin, followed by deoxygenation and dealkylation of the phenolic monomers, by heterogeneous catalysts, produces a mixture of phenols and aromatic hydrocarbons. Singerman (1980) demonstrated that a mixture of phenols obtained from coal liquids could be converted to methyl-aryl ethers (MAE) and blended with commercial gasolines. The resultant fuel was tested in several automobiles and found to be completely compatible with the engines and fuel systems of those vehicles. The MAE could be used to either replace or supplement the aromatic fraction of gasoline while simultaneously adding oxygen to the fuel, which has the added benefit of reducing carbon monoxide emissions from internal combustion engines and reducing vapor emissions of the gasoline.

The research began in 1985 with a thorough review of the literature, including that from Eastern European countries. A report, "Lignin Hydrotreatment to Low-Molecular-Weight Compounds" (Chum et. al.) encompassing that review is in press. On the basis of that review and discussions with researchers at the Colorado School of Mines (CSM), it was decided to pursue our goal by borrowing from the petrochemical hydrotreating and coal liquefaction technologies hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) and early work in the field of hydrodeoxygenation (HDO). The processes are similar in practice and sometimes occur concurrently in hydrotreating. More specifically, we wanted to develop catalysts that would simultaneously deoxygenate and dealkylate monomeric and oligomeric lignins.

Since it was our goal to not only deoxygenate (partially) the phenolics but to partially dealkylate them as well (dealkylation is necessary to bring the MAE into the gasoline boiling range and to increase the octane number) it seemed unlikely that commercially available catalysts would be suitable. In commercial hydrotreating, dealkylation is generally done in a separate operation with different catalysts. We envisioned performing the HDO and dealkylation simultaneously on the same catalyst. Researchers at CSM were already investigating such catalysts for the HDO of coal liquids so a collaborative effort was initiated. Two parallel series of catalysts were prepared at CSM for screening with the model compounds: Mo and Ni-Mo impregnated on γ -alumina supports whose acidity was varied during synthesis by coprecipitation with phosphoric acid. The catalysts were then tested at SERI for their HDO and dealkylation abilities using the model compound 4-propylguaiacol (2-methoxy,4-propylphenol) which is representative of the types of compounds expected from lignin depolymerization.

EXPERIMENTAL METHODOLOGY

Catalyst Preparation

All catalysts were synthesized in the laboratory at CSM with the exception of the commercial reference catalysts (American Cyanamid Aero HDN-30 and Strem Chemicals Mo/ γ -alumina). Unless otherwise specified, the chemicals were used as received without further purification. The method used to incorporate phosphate into the catalyst support was primarily by the alumina-aluminum phosphate coprecipitation method. For example, in order to prepare a support with a P/Al atomic ratio of 0.5 the following procedure was used. First, an acidic solution was prepared by adding 200 grams of aluminum nitrate to 2 liters of 18 M ohm deionized water, followed by 31 grams of an 85% (w/w) solution of ortho-phosphoric acid. Second, a basic solution was prepared by diluting 250 mL of concentrated (28 wt.%) ammonium hydroxide with 250 mL of deionized water. The acidic and basic solutions were added simultaneously to a 4-liter stirred reaction vessel which contained 1000 mL of deionized water. The acidic solution was added at a rate of 100 mL per minute, while the basic solution was added at a rate sufficient to maintain a pH of 9.0 in the reaction vessel. After the addition was complete, the reaction mixture was stirred for 30 minutes. The resulting hydrogel was filtered, washed, dried at 120°C for 24 hours, calcined at 500°C for 16 hours, crushed and sieved to 14/20 mesh particles, and stored in an airtight desiccator containing no desiccant.

The support was then impregnated with salt solutions of para ammonium molybdate and/or nickel nitrate using conventional impregnation techniques (Maholland 1987). The impregnated catalyst was dried at 120°C for 12 hours, calcined at 500°C for 16 hours, and stored in a desiccator.

Initial Catalyst Testing

Approximately 0.2 grams of the catalysts were reduced and presulfided in a plug-flow reactor using a multi-step procedure. The hydrodeoxygenation and dealkylation activity of the catalyst was evaluated by using benzofuran in heptane as a model feedstock. The tests were conducted at 350°C and 500 psi. The reaction products were analyzed by a 5840 Hewlett-Packard gas chromatograph using a 10-ft glass column packed with 80/100 mesh 10% SP-1000. Details of the catalyst pretreatment and testing conditions have been described elsewhere (Kehl 1980).

Catalyst Characterization

The surface area of all catalysts and supports were measured on a Micromeritics Accusorb 2100E surface area analyzer. Nitrogen was used as the adsorbate. Multipoint measurements were made and sample surface areas were replicated 2 to 4 times and the results averaged.

The pore-size distribution, pore volume, total surface area, median pore diameter, and bulk and skeletal densities were determined using a micromeritics Auto-Pore 9200 mercury porosimeter. An interfacial contact angle of 130° was assumed and the surface tension of mercury was taken as 473 dynes/cm.

The x-ray diffraction patterns of selected catalysts and supports were obtained on a Rigaku powder diffractometer. A copper target with a current of 100 mA and an accelerating potential of 40 KV was used.

The apparatus for the ammonia temperature programmed desorption (TPD) experiments has been described elsewhere (Maholland 1987). Approximately 0.33 grams of catalyst were placed into the quartz sample tube. The catalyst was dried for 3 hours in an oxygen-free helium flow at 500°C. Ammonia was adsorbed onto the catalyst at 175°C for 30 minutes. The temperature of the sample tube was increased at a rate of 20°C/min in a helium flow until a final temperature of 500°C was reached. The amount of ammonia desorption profile was obtained by a thermal conductivity detector. Acid scrubbers were used to collect the desorbed ammonia. The amount of ammonia desorbed was determined by titrating the acid in the scrubbers with a standard sodium hydroxide solution.

Catalyst Screening with 4-Propylguaiacol

The catalysts were tested in a trickle-bed reactor constructed from 316 stainless steel suspended in a tube furnace described in the 1986 Contractors Report. The catalyst bed was built up as follows: (1) a stainless steel frit served as the bed support on top of which was placed a plug of glass wool, (2) 1.0 g of α -alumina was poured over the glass wool to serve as a particle guard bed, (3) 1.0 g of catalyst was mixed with 1.0 g of α -alumina and poured over the guard bed, (4) 12.0 g of α -alumina was poured on top of the catalyst to serve as a liquid distribution bed. At the temperatures and pressures employed the 4-propylguaiacol remains in the liquid state, making this a true trickle-bed reactor not a vapor phase reactor. The catalysts were presulfided using 10% H_2S/H_2 by first heating the reactor to 175°C under a H_2 atmosphere and holding at that temperature for one hour. The atmosphere was then changed over to 10% H_2S/H_2 (125 psig) and the temperature raised to 200°C and held there for one hour. The temperature was then raised to 400°C over a period of one hour and held at 400°C for two hours. The reactor was cooled under the sulfiding atmosphere and stored under 100 psig H_2S/H_2 .

The activity of a catalyst was stabilized by performing a hydrodeoxygenation experiment at 500 psig H_2 , 350°C and $WHSV = 1h^{-1}$, using a feed solution of 10 vol. % benzofuran and 2 vol. % methylsulfide in heptane for a period of at least 12 hours. During this time, liquid samples were collected periodically and analyzed by gas chromatography to determine that the conversion had become constant.

After the benzofuran test, the catalysts were tested using 4-propylguaiacol in a 70.0 vol % solution with 2 vol. % dimethylsulfide, dissolved in hexane. All experiments were performed at 500 psig H_2 , using $WHSV = 1.16 h^{-1}$ and $2.80 h^{-1}$ and temperatures of 350°C and 400°C. Liquid samples were collected and diluted to 50 mL in acetonitrile before being analyzed by either a Varian 3700 GC equipped with a SPB5 wide bore capillary column (30 m x 0.75 mm ID, 1 μ m film), or more recently a Hewlett-Packard GC/MSD equipped with an Ultra 1 capillary column (25 m x 0.2 mm ID, methyl silicone gum, 100% dimethyl polysiloxane).

RESULTS

Catalyst Characterization

The effect of phosphate on the total surface area of the support was measured using the Brunauer, Emmett, and Teller (BET) method. The relationship between composition and surface area for the various aluminophosphate supports is shown in Figure 1. The total surface areas were found to be reproducible within $\pm 5 \text{ m}^2/\text{g}$. The results indicate that even a small amount of phosphate has a great effect on the structure of the support. The surface area passes through a maximum at a P/Al ratio of 0.1 before decreasing continuously with increasing P/Al. This observation is in agreement with that found by other researchers using a slightly different washing procedure from that used in this work (Vogel and Marcelin 1983).

Nitrogen adsorption-desorption isotherms for supports with P/Al ratios of 0.0 and 1.0 are shown in Figure 2. The 0.0 P/Al support corresponds to a Type IV isotherm with a Type E hysteresis loop. This indicates that the support is a solid with open or closed-end pores of variable radii (i.e., ink bottle pores). Based on the profile of the desorption isotherm, the pores also appear to have a narrow size distribution. The 1.0 P/Al adsorption-desorption isotherm is also of Type IV; however, the hysteresis loop is classified as Type A. In this case, condensation of nitrogen does not occur inside the pore until the gas pressure approaches its vapor pressure. The desorption isotherm closely mirrors the adsorption isotherm with only a slight offset. These results indicate that this has large diameter cylindrical pores, again with a narrow size distribution.

Additional information on modal pore diameters and on the pore size distribution was obtained from the results of mercury porosimetry. Two peaks were observed in each of the P/Al = 0.0 and 1.0 plots. The first, at a diameter of approximately $144 \mu\text{m}$ (corresponding to an applied pressure of 1.2 psia), represents mercury filling the interstitial void volume between the support particles. Both supports are seen to exhibit a unimodal pore distribution with a narrow distribution around the maximum pore diameter. The 0.0 P/Al support has a median pore diameter of 48 \AA while the 1.0 P/Al support has a median pore diameter of 253 \AA . The pore diameter was observed to increase smoothly as the P/Al ratio increased. High P/Al ratios yielded supports of large porosity, with pore size distributions consisting of pores with median diameters greater than 200 \AA .

X-ray diffraction (XRD) patterns of the supports are shown in Figure 3. The XRD patterns are similar to those reported by previous workers using other preparation methods (Kehl 1980; Vogel and Marcelin 1983; Cheung, et al. 1986). In the absence of phosphate (P/Al = 0.0), a γ -alumina support with a low order of crystallinity is obtained. Addition of phosphate changes this spectrum, giving no XRD pattern at all for the 0.1 P/Al sample. Further additions of phosphate show a new peak emerging at $24^\circ 2\theta$. This peak is characteristic of the tetrahedral structure of AlPO_4 . At P/Al = 1.0, the peak at $24^\circ 2\theta$ is greater in magnitude but still very broad in its shape. This suggests that the support is mostly in an amorphous state rather than the crystalline tridymite form of AlPO_4 .

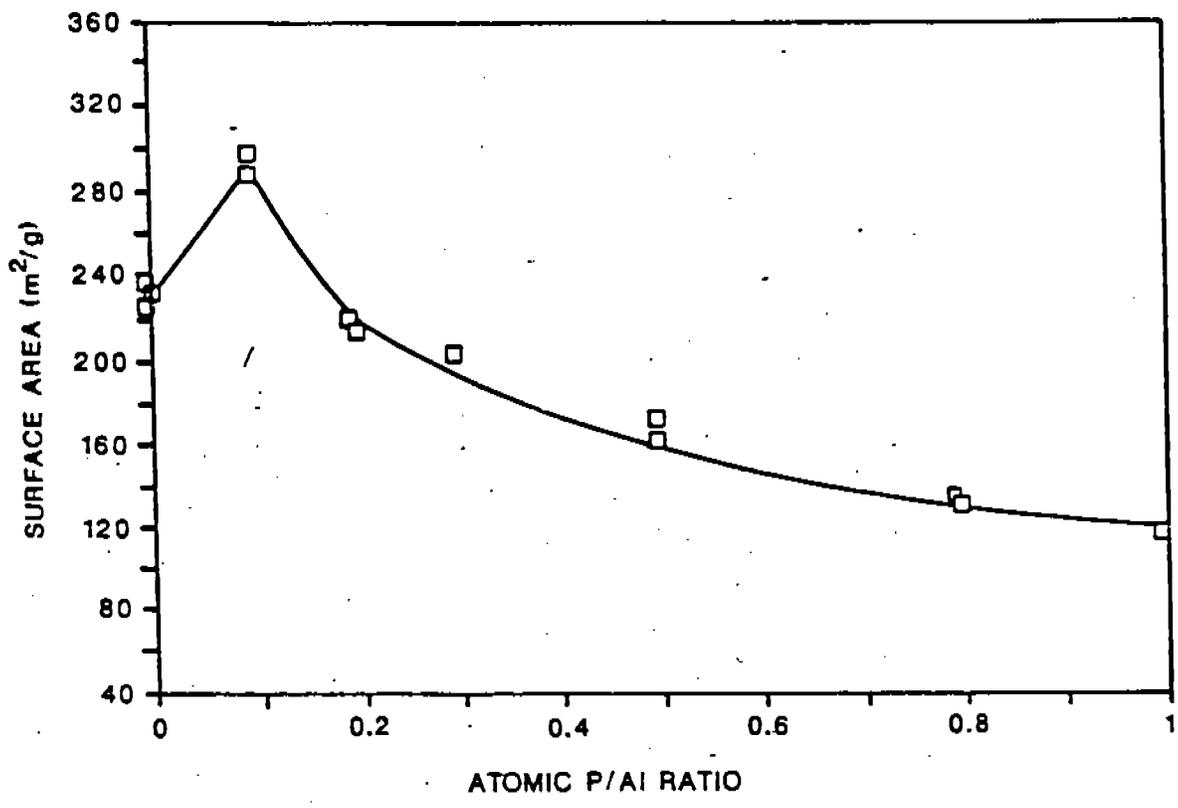


Figure 1. Support Total Surface Area vs. Atomic P/Al Ratio

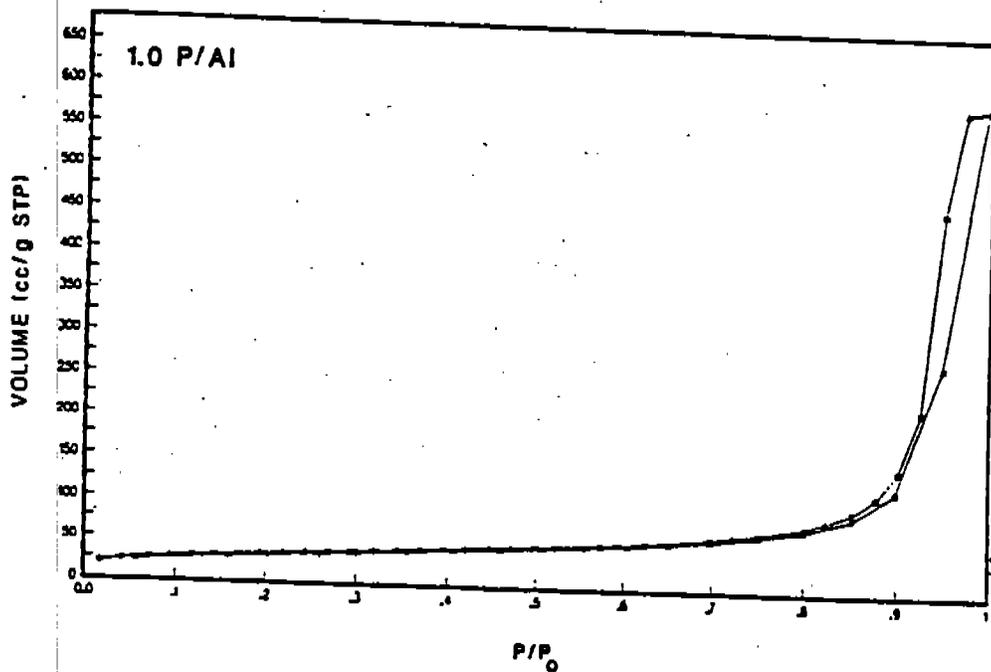
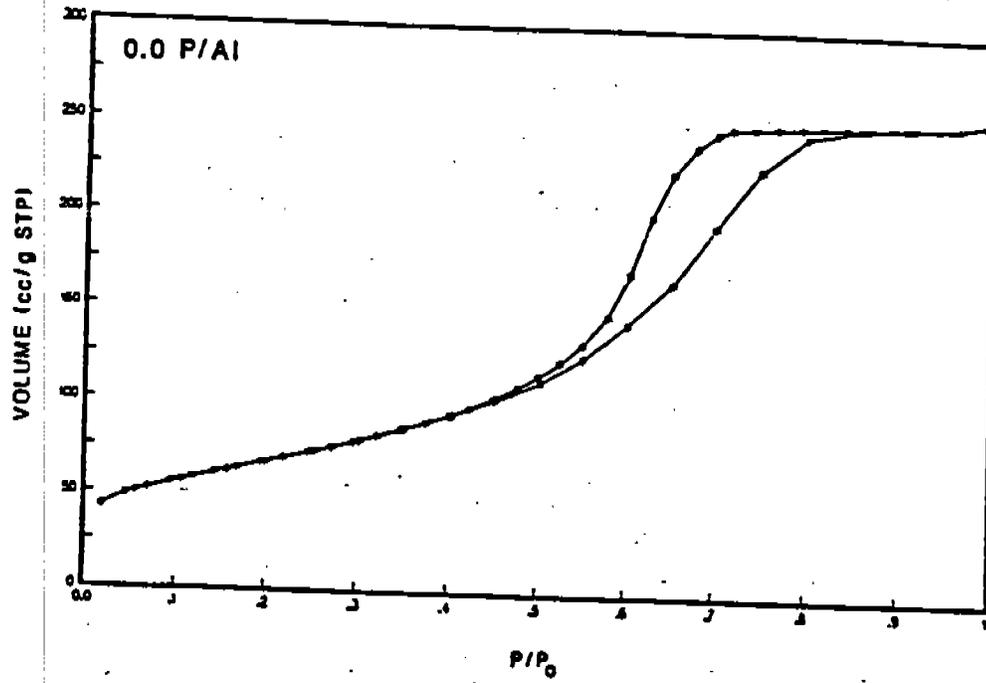


Figure 2. Nitrogen Adsorption-Desorption Isotherms of Aluminophosphate Supports

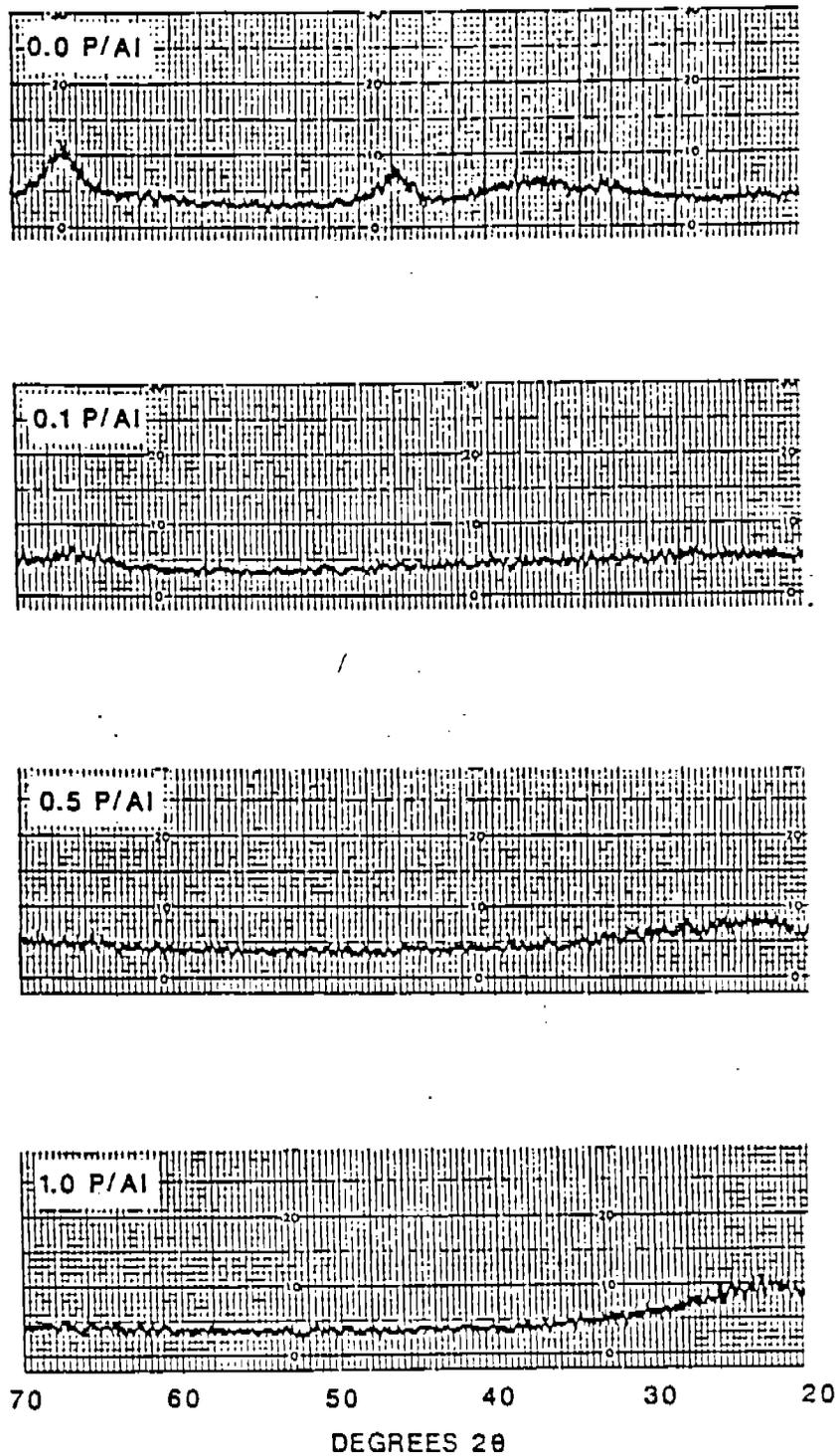


Figure 3. X-ray Diffraction Patterns of Aluminophosphate Supports

Ammonia temperature-programmed desorption profiles of three supports are shown Figure 4. In order to eliminate the contribution of the very weak acid sites to the profiles, a starting temperature of 175°C was used. The weak acid sites are believed to be of little importance to catalytic reactions. The desorbed ammonia was reacted with an acid solution which was subsequently titrated with a standard solution of sodium hydroxide. The titration results are in excellent agreement with desorption profiles shown in Figure 4. The P/Al = 0.0, 0.5, and 1.0 desorbed 6.8, 10.4, and 16.3 scc of ammonia/g-catalyst respectively. These results show the acidity of the catalyst increases as the P/Al ratio increases.

Initial Catalyst Testing

The active form of the catalyst was produced by impregnating the supports discussed above with the salts of molybdenum and/or nickel. Benzofuran was selected as a model oxygenated compound to study the hydrodeoxygenation and dealkylation activity of the prepared catalysts. The hydrodeoxygenation kinetics of benzofuran over a commercial catalyst (American Cyanamid HDN-30) were found to be pseudo-first order in benzofuran concentration (Edelman et al. in press). The testing results of the prepared catalysts were compared to those for the commercial catalyst and the results for all these screening tests are given in Table 1. One result that becomes immediately apparent from the screening tests of the Mo and Ni-Mo impregnated aluminophosphate catalysts is the decrease in conversion with increasing P/Al ratio. An increase in the P/Al ratio also results in the gradual loss of the promoting activity of nickel, until the catalyst behaves exactly like those catalysts without any promoter present. Conversions of both the Mo and Ni-Mo catalysts decrease to a level of roughly 31% and remain constant with further increase in P/Al. Product selectivity also changes significantly as the P/Al ratio is varied. Hydrocarbons, present at low phosphate loadings, are absent at P/Al ratios greater than 0.5. The extent to which changes in conversion and product distribution can be solely attributed to the changing P/Al ratio is, however, unclear.

4-Propylguaiacol Results

The total conversion of 4-propylguaiacol (4PG) to products ranged from 90%-100% with all the catalysts tested under all reaction conditions explored. Blank experiments with an empty reactor or filled with α -alumina gave conversions of <6%. The total high 4PG conversion can be misleading, however, because there are dramatic effects on the types of products depending on the temperature and space velocity employed. The most labile functional group in 4PG is the methoxyl group which cleaves at the methyl carbon-oxygen bond to produce propylcatechol, methane and methyl-propylcatechols even at 300°C and weight hourly space velocity (WHSV in g of 4PG/g catalysts x h) = 4.2 h⁻¹ in the presence of a catalyst. In general, low temperatures (<300°C) and high space velocities (>2.8h⁻¹) yield primarily catechols; high temperatures (>400°C) and low space velocities (<1 h⁻¹) yield primarily hydrocarbons. Similar trends were observed by Vuori and Bredenberg (1984) in the temperature range of 250-350°C with Co/Mo on γ -alumina (Ketjenfine 124-3E). It is interesting to note that with all the catalysts tested, the optimal operating condition for the formation of phenols (dealkylated or not) has always been 400°C and

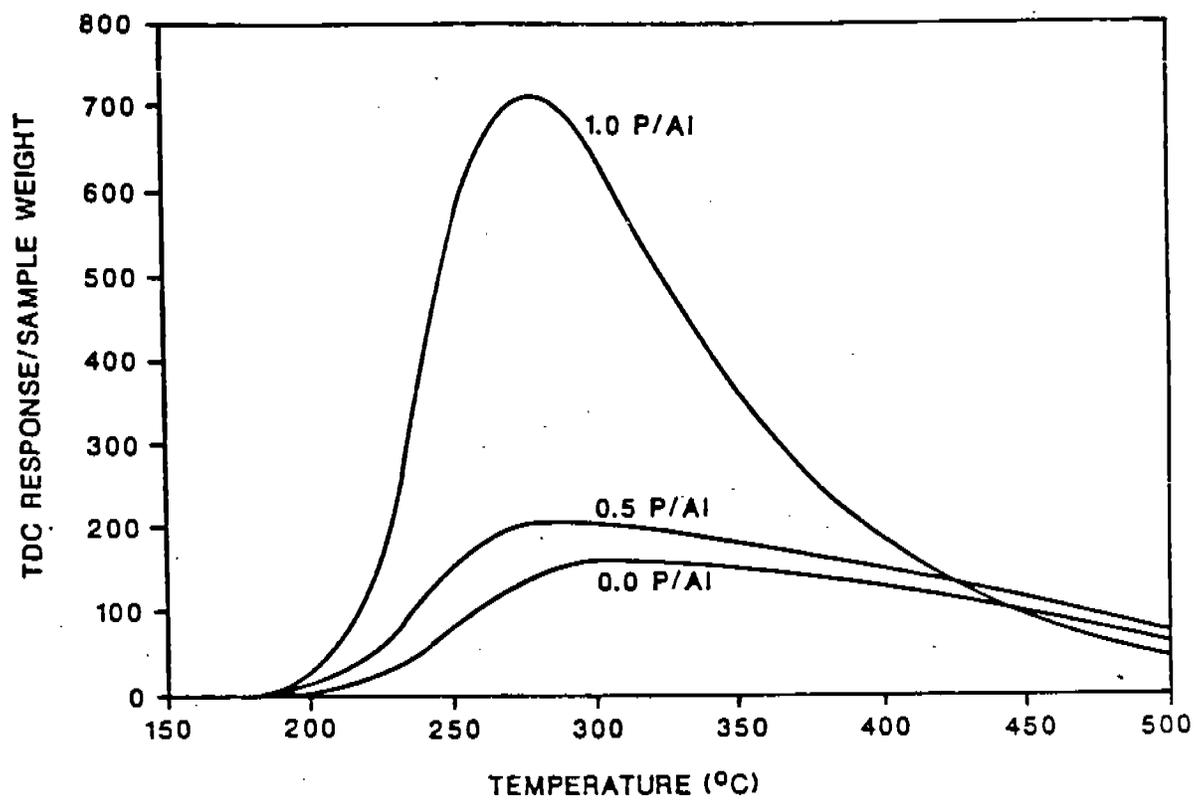


Figure 4. Ammonia Temperature Programmed Desorption Profiles of Aluminophosphate Supports

Table 1

Product Distribution Comparison of Laboratory-Prepared Ni-Mo Catalysts to Commercial HDN-30 Catalyst

Run Number:	IC12	IC22	IC5	IC1-B	IC13	IC10	HDN-30
Metals Loaded:	Ni-Mo						
P/Al Ratio:	0.0	0.1	0.2	0.5	0.8	1.0	0.1
Surface Area:	208.2	169.7	111.4	88.2	69.1	64.26	140.45
Compound (Mole %)							
Cyclohexane	13.65	3.65	2.13	0.00	0.00	0.00	2.11
Cyclohexene	0.63	0.47	0.68	0.00	0.00	0.00	0.64
Ethylcyclohexane	21.91	10.88	3.76	0.24	0.00	0.00	3.13
Benzene	1.81	0.00	0.00	0.00	0.00	0.00	0.00
Ethylcyclohexene	1.40	0.89	0.81	0.00	0.00	0.00	0.53
1-Ethylcyclohexene	2.54	3.19	2.66	0.00	0.00	0.00	1.57
Toluene	0.00	0.00	0.42	0.00	0.00	0.00	0.00
Diethylcyclohexane	3.81	0.52	0.00	0.00	0.00	0.00	0.13
Ethylbenzene	4.14	4.08	2.17	0.34	0.00	0.00	2.04
Diethylbenzene	0.93	0.44	0.06	0.00	0.00	0.00	0.22
Benzofuran	25.26	28.58	42.41	63.93	69.38	68.82	48.63
Dihydrobenzofuran	0.40	1.00	2.04	2.64	2.82	2.45	2.18
2,6-Diethylphenol	3.47	2.48	1.11	0.00	0.00	0.00	0.73
Phenol	3.49	5.09	6.35	14.16	12.50	13.22	7.35
2-Ethylphenol	13.91	36.29	31.73	12.64	9.71	9.52	25.69
Ethylphenol	0.66	0.54	0.84	0.57	0.47	0.47	0.85
Diethylphenol	2.01	1.91	2.82	5.50	5.12	5.52	4.12
% Conversion	74.74	71.42	57.59	36.07	30.62	31.19	51.37
% Deoxygenation	50.82	24.12	12.69	0.57	0.00	0.00	10.45

WHSV = 2.8 h⁻¹ (see Table 2). The preferred phenols show the least sensitivity to space velocity changes at 400°C (Figures 5-7). The remainder of the products were mostly other phenols and some hydrocarbons. Few catechols survive at 400°C, even at WHSV = 4.4 h⁻¹.

Table 2. Major Phenolic Product Selectivities (%) at 400°C and Weight Hourly Space Velocity of 2.8 g of 4PG/g Catalysts x Hour as a Function of the Type of Catalyst

Products	Catalysts				
	Mo/γ Al ₂ O ₃ P/Al = 0.0 ^a	Mo/P:Al ₂ O ₃ P/Al = 0.2	NiMo/P:Al ₂ O ₃ P/Al = 0.2	NiMo/P:Al ₂ O ₃ P/Al = 0.5	NiMo/P:Al ₂ O ₃ P/Al = 0.8
	Selectivity ^b %				
Phenol	0.0	3.6	3.2	7.5	6.0
Cresols	0.0	4.6	4.4	15.7	12.4
Ethyl-phenols	0.8	0.5	0.9	8.6	1.4
Propyl-phenols	36.9	11.2	13.3	7.0	9.0
Sum of above products	37.7	19.9	21.8	38.8	28.8

^aWeight hourly space velocity of 1.0 h⁻¹.

^bSelectivity % = [mmole product/(mmole 4PG injected - mmole 4PG unreacted)] x 100.

The effect of nickel is that of a promoter towards hydrogenation. While this effect has not been thoroughly investigated with 4PG, the results from catalysts with P/Al = 0.2 phosphated-alumina supports confirm this role. Figure 8 compares the selectivities of phenolic, aromatic, and cycloparaffin-type compounds as a function of nickel promotion. The operating conditions were 400°C and WHSV = 2.8 h⁻¹. The selectivity to propylphenol and cresols was not very sensitive to the presence of nickel with this support, however the effect on aromatic and cycloparaffin selectivities was more dramatic. The selectivity ratios of toluene:methylcyclohexane were 0.64 and 2.80 for the Ni-Mo and Mo catalysts, respectively. The selectivity ratios of propylbenzene:propylcyclohexane were 0.64 and 6.5 for the Ni-Mo and Mo catalysts, respectively. The loss of the promoting activity of nickel observed in the benzofuran tests needs to be confirmed with the 0.5 and 0.8 P/Al catalysts.

The amount of phosphorous in the support has a marked influence on the ability to dealkylate 4PG as was previously demonstrated with benzofuran (see phenol in Table 1). Figure 9 compares the selectivities of the major phenolic products as a function of support acidity using Ni-Mo catalysts at 400°C and WHSV = 2.8 h⁻¹. The formation of phenol, cresols, and ethylphenols increases to a maximum of 31.8% combined selectivity with a

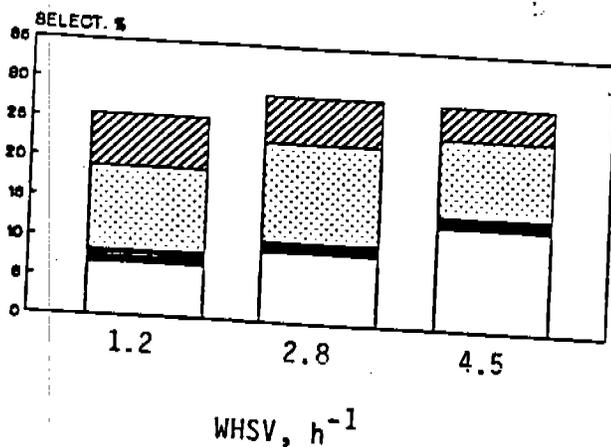


Figure 5. Phenolics Selectivity as a Function of 4PG Space Velocity with Ni-Mo Aluminophosphate Catalyst (P:Al = 0.8) at 400°C

- Propylphenols
- Ethylphenols
- ▤ Cresols
- ▨ Phenol

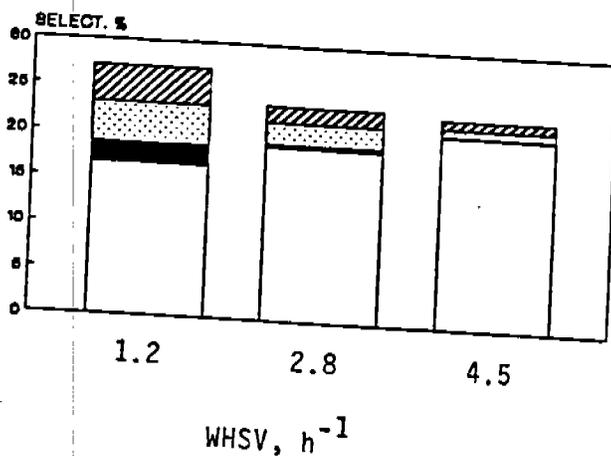


Figure 6. Phenolics Selectivity as a Function of 4PG Space Velocity with Ni-Mo Aluminophosphate Catalyst (P:Al = 0.8) at 350°C

For compounds' definitions, see above.

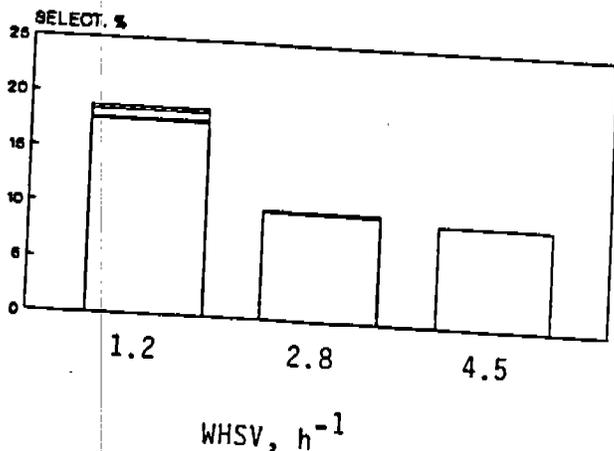


Figure 7. Phenolics Selectivity as a Function of 4PG Space Velocity with Ni-Mo Aluminophosphate Catalyst (P:Al = 0.8) at 300°C

For compounds' definitions, see above.

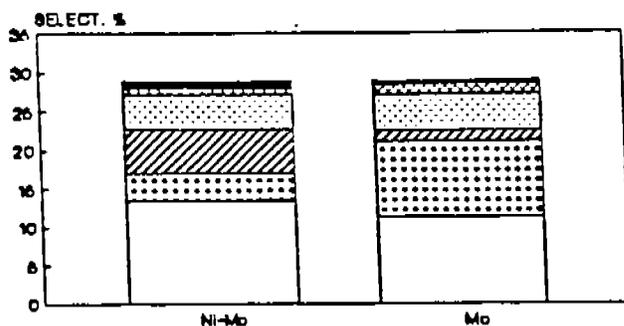


Figure 8. Effect of Nickel Promotion on Product Selectivities from 4PG with Aluminophosphate Supports (P:Al = 0.2) at 400°C, WHSV = 2.8 h⁻¹

- Propylphenols; ▨ Propylbenzenes; ▩ Propylcyclohexanes;
- ▤ Cresols; ▥ Toluene; ■ Methylcyclohexane

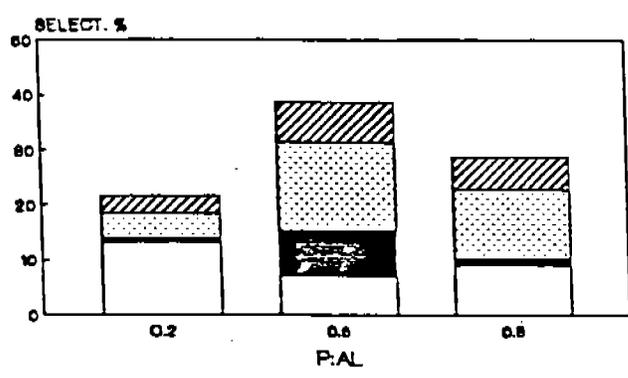


Figure 9. Effect of Phosphorus Loading on Dealkylation of Pheno}s from 4PG at 400°C, WHSV = 2.8 h⁻¹

- Propylphenols
- Ethylphenols
- ▤ Cresols
- ▩ Phenol

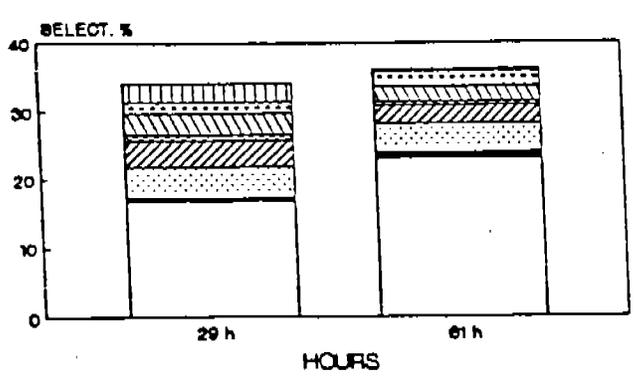


Figure 10. Change in Ni-Mo Aluminophosphate (P:Al = 0.8) Catalyst Activity at 350°C, WHSV = 1.2 h⁻¹

- Propphenol; ■ Ethphenols; ▤ Cresols;
- ▩ Phenol; ▨ Probenzene; ▩ Propylcyclohexanes;
- ▥ Xylene; ▨ Cyclohexanes

catalyst support composed of P/Al = 0.5. Recall that conversions to products at these conditions were >98%, and the balance of the products were other phenolics and hydrocarbons. The Ni-Mo/aluminophosphate (P/Al = 0.8) catalyst gave a lower combined selectivity of 19.8% and the 0.2 P/Al Ni-Mo catalyst was lower still at 8.5% combined selectivity to phenol, cresols, and ethylphenols. These results are consistent with the trends of phenol formation from benzofuran using these same catalysts.

The stability of the Ni-Mo/aluminophosphate (P:Al = 0.8) catalyst was tested over a period of 61 h of operation (see Figure 10, benzofuran was the feed for the first 25 h). It can be seen that the overall activity has not changed significantly (conversions based on the disappearance of 4PG were 98.8% and 98.6%), however, the selectivity to propylphenols increased from 16.5% to 22.9%. An obvious explanation for this decrease in dealkylation activity is that the catalyst support acidity is decreasing with time, possibly due to coking. This hypothesis will be tested by detection of carbon through surface analysis.

DISCUSSIONS

It has been demonstrated that the amount of phosphorus in the catalyst support affects the surface area inversely proportional to the phosphorus loading and that the support acidity is proportional to the phosphorus loading. An apparent contradiction in the activities of the catalysts tested with benzofuran and 4PG needs an explanation. In the benzofuran results, supports with P/Al ratios higher than 0.1 showed decreasing conversion, whereas with 4PG, the conversions remained high (>90%) up to P/Al = 0.8 in the case of Ni-Mo catalyst at 350°-400°C. The answer to this contradiction could lie in the fact that the methoxyl oxygen in 4PG is much easier to remove than the phenolic oxygen. The phenolic OH group in 4PG is likely to be dissociatively adsorbed onto the catalyst at anion vacancies. The methyl-oxygen bond in the methoxy group is then homolytically cleaved, forming propylcatechol and methane. Propylcatechol is then dehydroxylated to form propylphenols (in our results, primarily 4-propylphenol). It appears that the remaining hydroxyl group is not removed until the ring is first saturated. These observations are consistent with those reported by Vuori and Bredenberg (1984) using lower temperatures and a Co/Mo on alumina catalyst and Bredenberg et al. (1982) using a more acidic support Ni-Mo/SiO₂-Al₂O₃ in the 250°-350°C range. In benzofuran, the oxygen is stabilized by resonance and probably requires reduction to 2,3-dihydrobenzofuran before the ring can be opened to form 2-ethylphenol. Then the aromatic ring can be saturated and dehydroxylation can take place. This additional requirement of ring saturation makes benzofuran more difficult to convert.

Because we are interested in forming lightly substituted phenols (and some aromatic hydrocarbons) and the conversions remain high for 4PG with high phosphorus loadings, the higher phosphorus content supports are of greatest interest to us.

The comparison of Ni-Mo and Mo catalysts on P/Al = 0.2 support suggests that ring saturation of the phenols can be suppressed by not including Ni in the catalyst. This would decrease hydrogen consumption and could improve the selectivity to phenols. Additionally, any hydrocarbons

formed would be primarily aromatic which are more suitable for fuels than cycloparaffins.

FURTHER WORK

The investigation of the series of Mo catalysts on aluminophosphates with P:Al ratios of 0.5 and 0.8 will be completed to assess the effect of increased support acidity on the hydrodeoxygenation and dealkylation of 4-propylguaiacol. It appears that the hydrodeoxygenation ability depends upon the hydrogenation activity of the catalyst. The alkylation/dealkylation activity and selectivity of the catalyst is a marked function of the P/Al ratio of the support. A simpler model system, 4-propylphenol, will be employed in the future studies to assess catalyst alkylation/dealkylation capabilities.

The best catalyst from these studies will be prepared in larger scale and tested in the 300 mL autoclave (see Johnson et al., this Proceedings) with pretreated lignins.

An exploratory-level synthesis effort of new catalysts that do not require presulfidization is underway. The new catalysts may simplify operating conditions and lead to the desired product distribution.

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