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Hydroprocessing of Organo-Oxygen Compounds in Coal Liquids Catalyzed by Sulfided Ni–Mo/γ-Al_2O_3

Coal liquids and shale oil contain high concentrations of organo-oxygen compounds. The reactivities of these compounds under practical catalytic hydroprocessing conditions are poorly known. Our goal was to determine reactivities of organo-oxygen compounds in a liquid prepared from Powhatan No. 5 coal in the SRC-II coal hydroliquefaction process (*1*). This coal liquid was separated by preparative liquid chromatography into acidic, basic, and neutral fractions (*2*), each consisting of chemically similar compounds (*3*). The fractions are so much simpler in composition than the whole coal liquid that a number of the individual compounds can be identified by gas chromatography/mass spectrometry. Most of the organo-oxygen compounds in the acidic fractions are substituted phenols and substituted and partially hydrogenated naphthols. The organo-oxygen compounds in the basic fractions are largely hydroxypyridines or hydroxyindoles. The neutral oils fraction contains dibenzofuran as the predominant oxygen-containing compound. The oxygen contents (determined by elemental analysis) of the weak acids, weak bases, and neutral oils were 9.79, 8.42, and 0.72 wt%, respectively.

Here we summarize the reactivities of the organo-oxygen compounds in these coal-liquid fractions under hydroprocessing conditions representative of potential industrial practice. Most of the results were obtained with a high-pressure flow microreactor; some were determined with a batch reactor. The catalyst was presulfided Ni–Mo/γ-Al_2O_3 (American Cyanamid HDS 9A), the properties of which are given elsewhere (*4*).

In the flow microreactor (*5–7*), the catalyst particles (0.025 to 0.20 g) were mixed with inert alundum particles (0.4 g) to give a bed height of about 4 cm. The catalyst was sulfided *in situ* for 2 h with a flow of 0.5 to 0.7 cm^3/s of 10 vol% H_2S in H_2 at atmospheric pressure and 400°C. Hydrogen was initially dissolved in the feed solution in an autoclave at 86 atm. The feed contained 0.25 wt% of the coal-liquid fraction (or, in one experiment, 2-hydroxyphenylbenzene) in cyclohexane; it also contained 0.1 wt% CS_2 to keep the catalyst sulfided and 0.01 wt% *n*-decane, an internal standard for the product analysis. The liquid feed was then pumped at a constant rate to the high-pressure reactor; all the reactants were maintained in the liquid phase. The molar concentration of hydrogen was at least 22 times the atomic concentration of oxygen to assure that the hydrogen concentration could be assumed to be virtually constant throughout the reactor. Liquid products were analyzed by capillary-column gas chromatography and gas chromatography/mass spectrometry.

In the batch-reactor experiment (*7, 8*), the catalyst was first sulfided outside the reactor under the conditions mentioned above and then transferred to a loader with 20 to 30 cm^3 of the neutral oils. After the neutral oils (without solvent, saturated with hydrogen) had been brought to the reaction temperature, the catalyst was injected into the autoclave. The reaction was carried out at 355°C and 36 atm for 25 h. The reactor initially contained 281 g of neutral oils, 1.04 g of CS_2, and 5 g of catalyst. Samples of liquid were drawn periodically and analyzed as stated above.

Conversion data for the oxygen in pheno-

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lic compounds in the weak-acid fraction and in the basic fractions were determined by elemental analyses and by infrared spectroscopic determination of the —OH group concentration; some results are shown in Fig. 1. Data were also obtained by gas chromatography/mass spectrometry for individual compounds in the weak-acid fraction (Fig. 2); details are given elsewhere (*6*).

Conversion data for dibenzothiophene and dibenzofuran, determined in the autoclave experiment, are plotted in Fig. 3. The rate constants calculated for dibenzothiophene and dibenzofuran, respectively, are 2.3×10^{-6} and 3.0×10^{-7} liter/(g of catalyst · s). The ratio of these rate constants (7.8) is in good agreement with the results reported by Rollmann (*9*) (who observed a ratio of 9 with a Co–Mo/γ-Al_2O_3 catalyst at 344°C and 49 atm) and with those of Krishnamurthy *et al.* (*10*) (who observed a ratio of 10 with a Ni–Mo/γ-Al_2O_3 catalyst at 365°C and 106 atm).

The conversion of dibenzothiophene in

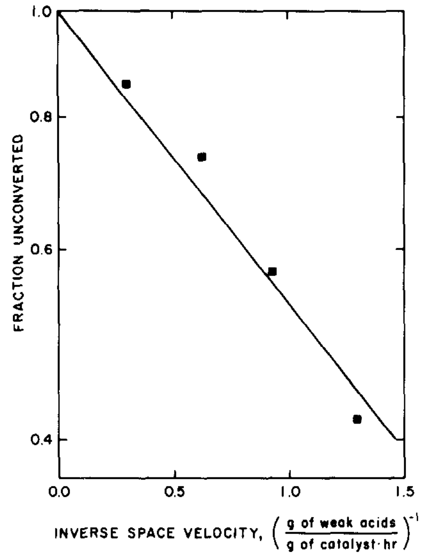

FIG. 1. Conversion of phenolic oxygen in the weak-acid fraction of SRC-II coal liquid catalyzed in a flow reactor by sulfided Ni–Mo/γ-Al_2O_3 at 350°C and 120 atm.

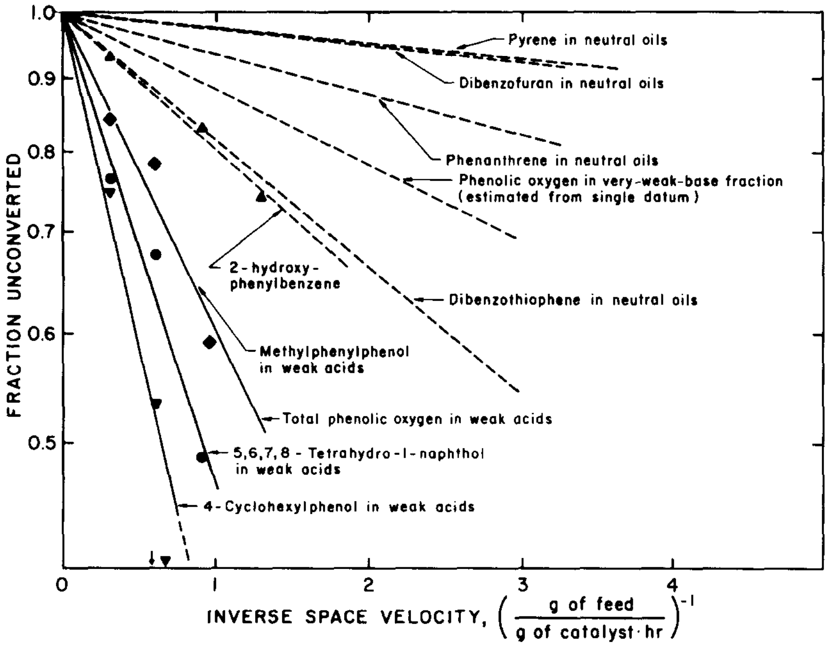

FIG. 2. Reactivities of phenolic oxygen in coal-liquid fractions and of individual compounds in the weak-acid and neutral oils fractions. The reactions were catalyzed in a flow reactor by sulfided Ni–Mo/γ-Al_2O_3 at 350°C and 120 atm.

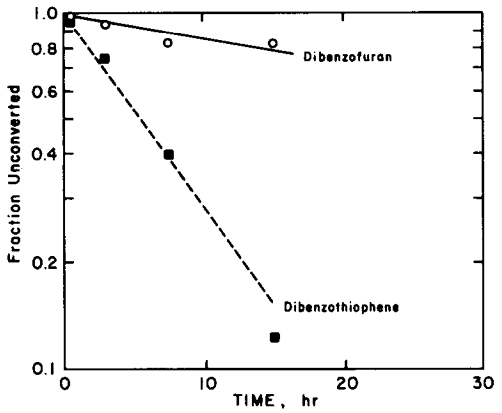

FIG. 3. Conversion of dibenzothiophene and of dibenzofuran in the neutral oils fraction. Data were obtained in a batch reactor in the absence of solvent at 355°C and 36 atm.

the neutral oils fraction has been determined with the flow microreactor at 355°C and 120 atm (*7*) (Fig. 2). These data were used with the ratio stated above (determined with the autoclave reactor and a higher concentration of the neutral oils) to estimate the line for dibenzofuran shown in Fig. 2. Rate constants for the hydrogenation of pyrene and phenanthrene were also determined with this method: The values obtained in the autoclave experiment are 2.2×10^{-7} and 7.9×10^{-7} liter/(g of catalyst · s), respectively. The calculated lines, each determined by the ratio of the rate constant to that measured for dibenzothiophene in the same experiment, are also shown in Fig. 2.

It has been shown (*11*) that the reactivity for hydrodesulfurization of individual compounds decreases in the following order: mercaptans $\gg$ thiophene $>$ benzothiophene $\gg$ dibenzothiophene $\approx$ benzonaphthothiophene. The pattern emerging for hydrodeoxygenation of oxygen-containing compounds in coal liquids (Fig. 2) indicates that the compounds similarly fall into several categories of reactivity. Nonpolar oxygen-containing compounds, typified by dibenzofuran, have low reactivities. Phenolic compounds in the acidic fraction are more than an order of magnitude more reactive. The phenolic compounds in the basic fraction are apparently intermediate in reactivity, but the literature indicates sig-

TABLE 1

Reactivities of Oxygen-Containing Compounds with Hydrogen in the Presence of Sulfided Ni–Mo/γ-Al_2O_3 at 350°C and 120 atm

Reactant	Pseudo-first order rate constant for disappearance of the reactant liter/(g of catalyst · s)
Pure compound in cyclohexane solvent	
2-Hydroxyphenylbenzene	1.5×10^{-4}
Compounds in the weak-acid fraction in cyclohexane solvent	
2-Hydroxyphenylbenzene	0.83×10^{-4}
5,6,7,8-Tetrahydro-1-naphthol	1.91×10^{-4}
Methylphenylphenol	1.52×10^{-4}
4-Cyclohexylphenol	4.46×10^{-4}
Compounds in the neutral oils fraction	
Dibenzofuran	7.4×10^{-6}[a]
Dibenzothiophene	5.8×10^{-5}
Total organo-oxygen in the weak-acid fraction	1.56×10^{-4}
Total organo-oxygen in the weak-base fraction	2.01×10^{-4}[b]

[a] Estimated from data obtained in a batch reactor at 350°C and 34 atm.

[b] Rate constant at 400°C.

nificant inhibition by the basic nitrogen-containing compounds (*12*), and we speculate that the intrinsic reactivity of the phenolic —OH groups is about the same in all the fractions.

The rate constant for 2-hydroxyphenylbenzene in the acidic fractions is only about half that observed for pure 2-hydroxyphenylbenzene (0.25 wt% in cyclohexane) (Table 1). We therefore suggest that self inhibition among phenolic oxygen compounds was significant.

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C.-L. LI[1]
S. S. KATTI
B. C. GATES[2]

Center for Catalytic Science
and Technology
Department of Chemical Engineering
University of Delaware
Newark, Delaware 19711

L. PETRAKIS

Gulf Research and
Development Company
Pittsburgh, Pennsylvania 15230

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[1] Present address: East China Institute of Chemical Technology, Shanghai, China.

[2] To whom correspondence should be addressed.