

EFFECTS OF PORE STRUCTURE AND SUPPORT TYPE OF CATALYSTS IN HYDROPROCESSING OF HEAVY COAL LIQUIDS

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INTRODUCTION

Catalyst pore structure determines how easily the reactants can access the interior surface of the catalyst. The pore structure parameters include pore sizes and their distribution, pore volume and surface area. Various classification of pore sizes can be found in literature, but the International Union of Pure and Applied Chemistry (IUPAC) classifies pores of different sizes in the following manner: micropores, < 20 Å; mesopores, 20-500 Å; and macropores, > 500 Å in diameter. The IUPAC classification will be used in this paper. In general, hydrotreating catalysts are prepared by impregnation methods and the catalyst pore structure is determined mainly by the support. Earlier reports by Ho and Weller [1981], Bertolacini et al. [1978], and Shimada et al. [1984] have shown that pore diffusional limitation of reaction rates can be serious in hydroliquefaction of coals over supported catalysts. The catalyst pore structure is also very important for hydroprocessing of heavy coal liquids due to diffusional limitations [Tischer et al., 1985; Yoshimura et al., 1986; Song et al., 1988a, 1989a, 1991a]. However, systematic knowledge of pore size effects is still very limited for hydroprocessing of heavy coal-derived liquids. Reviews of previous work in this area may be found elsewhere [Derbyshire, 1988; Onuma, 1988; Song et al., 1991b].

The present work involves the upgrading of several solvent refined coals (SRC) derived from thermal liquefaction of coals, which contain both asphaltene and preasphaltene. This work attempts to provide a better understanding of the relationship of catalyst pore structure and support type to the conversion of asphaltene and preasphaltene, which in turn could lead to the development of more effective catalyst. This paper will describe 1) the effects of pore size of Ni-Mo/Al₂O₃ catalysts on their performance in hydroprocessing of two different SRCs in terms of oil yields and conversions of heavy fractions, and the interactive chemistry involved in the pore-size dependence for simultaneous conversion of asphaltene and preasphaltene on catalyst surface, 2) the differences in reactivity of heavy fractions in several SRCs and their convertibility in catalytic runs, and 3) comparative examination of alumina- and silica-supported catalysts as well as carbon-coated catalysts.

EXPERIMENTAL

Catalyst Preparation. The four gamma-Al₂O₃ cylindrical extrudates are the same supports that have been in a previous work [Song, 1991a]. The SiO₂ supports were two spherical Cariact-50 and Cariact-10 beads from Fuji-Davison Chemical Company. Table 1 gives their properties provided by the manufacturers. Four Ni-Mo/Al₂O₃ catalysts (NiO: 2.9, MoO₃: 15.8 wt%) were prepared by co-impregnation of (NH₄)₆Mo₇O₂₄·4H₂O and Ni(NO₃)₂·6H₂O from their aqueous solution, followed by calcination and sulfidation [Song et al., 1991a, 1991b]. Two Mo/SiO₂ catalysts containing 15.8 wt% MoO₃ (Cat-SA, Cat-SB) were prepared by using the same procedure. Figure 1 shows the pore size distribution of the prepared Ni-Mo/Al₂O₃ catalysts measured by using a Shimadzu AutoPore-9200 mercury porosimeter. The maximum intrusion pressure was 60,000 psi, which corresponds to pore radius of 18 Å as dictated by Washburn equation with contact angle and surface tension of mercury taken as 140° and 480 dyn/cm, respectively. A commercial catalyst, Akzo Ketjenfine 153S sulfided Ni-Mo/Al₂O₃ [Song et al., 1988, 1991c] was also used in some experiments.

SRC Upgrading. Solvent refined coals (Table 2) derived from Wandoan subbituminous coal (Wan-SRC) and Akabira bituminous coal (Aka-SRC) were used as feedstocks. Aka-SRC was produced from Run 5511 at 420 °C for 34 minutes, and Wan-SRC from Run 5512 at 440 °C for 34 minutes in a 3 ton/day coal liquefaction plant at Sumitomo Coal Mining Co. [Hanaoka et al., 1988]. In some experiments we also used a SCT-SRC sample produced from short contact time pyrolytic liquefaction (SCT-PL) of Wandoan coal at 440-465 °C for 5 minutes in H-donor solvent under N₂ atmosphere [Song et al., 1989b]. The hydroprocessing was carried out in a 60 ml SUS-316 stainless steel rocking

autoclave at 425 °C for 1 h with 4.9 MPa H₂ (5 g SRC : 0.5 g catalyst : 5 g tetralin). The runs of SCT-SRC were carried out under the same conditions, but using 2.5 g SRC, 5 g tetralin, and 1 g catalyst.

Product Separation and Analysis The volume of gaseous products was measured by a continuous flow-type gas volume meter, through which the gases were introduced from the reactor into a plastic gas bag. The gases were analyzed by GC (Shimadzu GC-8A). The liquid and solid products were separated into oil (hexane soluble), asphaltene (hexane-insoluble but benzene-soluble) and BI or preasphaltene (benzene-insoluble). The concentrated oil plus the reaction solvent were analyzed by GC to determine the tetralin/naphthalene ratio. After the solvent has been removed by vacuum distillation (up to 115°C, 8 mmHg), the oil products were subjected to elemental and ¹H NMR analyses [Song et al., 1988c]. The catalysts that have been used once in SRC hydroprocessing were also analyzed (after benzene extraction and drying) by using scanning electron micrograph (SEM, Hitachi S-450) combined with electron probe microanalysis (EPMA, Horiba EMAX-1800E).

RESULTS AND DISCUSSION

Property and Reactivity of SRC. As shown in Table 2, Wan-SRC and Aka-SRC have similar carbon and hydrogen contents, although Wandoan and Akabira coals differ significantly in elemental composition. Both SRCs contain a high proportion of heavy fractions such as asphaltene and preasphaltene. Wan-SRC contains less benzene-insolubles and more asphaltene and oil, as compared to Aka-SRC. Analysis of the fractions from both SRCs showed that the H content and atomic H/C ratio decrease, but N and O contents and the average molecular weights (MW) increase in the order of oil, asphaltene, and BI. The average MW values determined by vapor pressure osmometry are about 590-600 and 270-320 for asphaltene and oil fractions, respectively [Song et al., 1988a]. In addition, relative to the SRCs from long residence time runs in pilot plant, the SCT-SRC from laboratory SCT-PL has higher oil content and H/C ratio, and lower preasphaltene content.

Table 3 gives the data on the thermal runs and some catalytic runs at 425°C. The oil yields from Wan-SRC are generally higher than those from Aka-SRC. Relative to the raw SRCs, thermal runs increased oil yields by 16-18 % and produced 4-5 % gas. The use of a catalyst promoted the production of oil. It appears that the BI fraction of Aka-SRC is more reactive than that of Wan-SRC, and this trend becomes more remarkable when a catalyst was used. Probably this is due in part to the lower severity of conditions used for producing Aka-SRC than that for Wan-SRC. In addition, SCT-SRC of Wandoan coal (see below) appears to be much more reactive than both Wan-SRC and Aka-SRC in terms of higher BI and asphaltene conversions. These results demonstrated that the liquefaction conditions affects the reactivity of the products; the SRC derived from a lower-severity run exhibits a higher reactivity.

Comparison of SiO₂- and Al₂O₃-Supported Catalysts. We examined two Mo/SiO₂ and a number of Ni-Mo/Al₂O₃ catalysts. Since a SiO₂-supported catalyst is less active as compared to a Al₂O₃-supported one for hydrotreating, and since a Ni- or Co-promoted Mo catalyst is more active than a unpromoted catalyst, one would expect a higher activity of Ni-Mo/Al₂O₃ catalyst. As shown in Table 3, KF-153S and Cat-1 did afford higher asphaltene conversion than the SiO₂-supported Cat-SB. However, it is very interesting to note that Cat-SB exhibited considerably higher effectiveness for converting BI fractions of both Wan-SRC and Aka-SRC. It is known that the acidity increases in the order of SiO₂ < Al₂O₃ < SiO₂-Al₂O₃ [Satterfield, 1991]. Because Cariact-50 has much lower surface area than the Al₂O₃ support (78 vs. 203 m²/g) and Cat-SB contains no Ni promoter, the observed superiority of Mo/SiO₂ catalyst over Ni-Mo/Al₂O₃ in BI conversion can be attributed to the large pore diameter (507 Å) and/or lower surface acidity of the silica support.

Table 4 compares the results for runs of Wan-SRC at 400 °C using 20-32 mesh particles of two Mo/SiO₂ and KF-153S Ni-Mo/Al₂O₃ catalysts. The data for Cat-SA and Cat-SB show that a large pore silica (Cariact-50) is better than a small pore silica (Cariact-10) in terms of higher BI conversion. Relative to the two Mo/SiO₂, KF-153S Ni-Mo/Al₂O₃ afforded higher oil yield and higher asphaltene conversion. However, the conversion of BI was substantially higher with Mo/SiO₂ than with KF 153S. Combination of data in Tables 3 and 4 reveals that using silica support is more effective for converting preasphaltene, the BI fraction, while the use of alumina gives higher conversion of asphaltene and in most cases, higher oil yields.

Effect of Particle Size of Ni-Mo/Al₂O₃. Table 5 shows the effects of crushing KF-153S Ni-Mo to <100 mesh particles for hydroprocessing of SCT-SRC. The higher oil yield and conversion with crushed catalyst provide another indication of the intraparticle diffusional limitations occurring during SRC hydroprocessing. In fact, relative to the thermal runs, the cylindrical KF-153S Ni-Mo and its 20-32 mesh (0.84-0.50 mm) particles promoted asphaltene conversion but did not improve BI conversion both for Wan-SRC (Tables 3 and 4) and for SCT-SRC (Table 5). However, the use of <100 mesh (<0.15 mm) KF-153S resulted in significant increase in BI conversion (Table 5).

These results indicate that improving mass transfer has greater impact on conversion of preasphaltene. The superiority of the fine catalyst particles can be attributed to greatly increased external surface area and decreased length of diffusional path, as compared to the 1.5 mm extrudate. In practice, the lowest catalyst sizes permitted in industrial fixed-bed operations are 0.8-1.6 mm. Described in the subsequent sections is SRC conversion using 0.8-1.5 mm cylindrical extrudate Ni-Mo/Al₂O₃.

Effects of Pore Size of Ni-Mo/Al₂O₃ on Product Distribution. In order to examine the pore size effects on a unified basis, one should prepare the catalysts having unimodal and narrow pore size distribution, different median pore diameters, and similar chemical composition. As can be seen from Figure 1, the unimodal pore structure and the significantly different pore sizes of Cat-1 through Cat-4 prepared by using the same procedure, enabled us to evaluate the pore size effects.

Figure 2 presents the results for Wan-SRC hydroprocessing over a series of cylindrical Ni-Mo/Al₂O₃ catalysts with different MPD. Also shown in Figure 2 are the data from the run with KF-153S sulfided Ni-Mo, which has a MPD value (90 Å) similar to that (100 Å) of the well known Shell 324M Ni-Mo [Baker et al., 1987, Lee et al., 1991]. All of these catalysts were used in the form of cylindrical extrudate. It should be noted that Cat-1 though Cat-4 is alumina-supported catalyst, while KF-153S contains 4.5 wt% SiO₂. Relative to thermal run, each of the four prepared catalysts enhanced the production of oil. Figure 3 shows the results for Aka-SRC which originally contained more BI and less asphaltene and oil as compared to Wan-SRC. As can be seen from Figures 2 and 3, both for Wan-SRC and Aka-SRC, the conversion of SRC into benzene soluble products increased in the order of Cat-1 < Cat-2 < Cat-3 ≤ Cat-4. This order is contrary to that of catalyst surface area. The yields of asphaltene, however, decreased with increasing MPD in the small pore size region, but rose with further increase in MPD in the large pore range. The oil yields from catalytic runs of both SRCs with the four prepared Ni-Mo did not vary considerably, but the oil yield from Wan-SRC with KF-153S was lower. The gas yields were nearly constant in the runs of both SRCs.

Pore-Size Effects on Conversion of Heavy Fractions and Interactive Chemistry. Table 6 compares the product distribution and hydrogen consumption for typical runs of Aka-SRC in this work and its isolated asphaltene fraction Aka-Asp reported in previous paper [Song 1991]. The oil yields from thermal runs of Aka-SRC and Aka-Asp are relatively similar to each other, but the catalytic run of Aka-Asp with Cat-1 gave 11% higher, and that with Cat-3 afforded 17% higher oil yield than the corresponding values for runs of Aka-SRC. This is surprising because Aka-SRC originally contained about 32% oil but Aka-Asp contained no oil. The conversions of asphaltene as well as the consumption of gas phase H₂ are considerably higher in the runs of the isolated asphaltene than for the whole SRC. This comparison indicates that catalytic conversion of asphaltene into oil is suppressed during the runs of whole SRC. Probably the presence of preasphaltene inhibits the catalytic reaction of asphaltene.

Table 7 compares the results for hydroprocessing of Wan-SRC and its BI fraction Wan-BI. Apparently, the runs of whole SRC gave better product spectra than those of its BI fraction. This is because Wan-BI is composed of about 85% preasphaltene and about 15% quinoline insolubles (Table 2), which are the heaviest fractions in coal liquids. Taking into account the oil content of original Wan-SRC, the oil yields produced from Wan-BI with Cat-3 and Cat-4 are only 2-3% lower, and that with Cat-1 is about 6% lower than the corresponding values for net oil production from Wan-SRC. The net conversion of BI fraction appears to be higher for the runs of isolated Wan-BI than for the whole Wan-SRC. However, such a difference is much smaller as compared to that between the runs of whole SRC and asphaltene. Therefore, the negative impact of asphaltene on preasphaltene conversion is very limited, but preasphaltene materials appear to inhibit the catalytic conversion of asphaltene.

Carbon-Coated Catalysts. Analysis of the benzene-extracted spent catalysts that have been used once in runs of Wan-SRC by using SEM-EPMA showed that the deposition of carbonaceous materials and metal species such as Ca, Fe and Ti took place in the 1 h reaction, being consistent with the findings of Stiegel et al. [1983] and Stohl and Stephens [1987]. These catalysts are denoted as carbon-coated catalysts, in which the amounts of benzene-insoluble materials are estimated to be around 10 wt%. We also conducted the runs of Wan-SRC using the carbon-coated Ni-Mo/Al₂O₃ catalysts. The consumption of gas-phase H₂ decreased and the oxygen content of oil and asphaltene products increased slightly, as compared to the runs with fresh Ni-Mo, which suggest a small decrease in catalytic activity. However, the conversion of BI fraction was substantially higher with the carbon-coated Ni-Mo than with the fresh Ni-Mo, while oil yields with each pair of fresh and carbon-coated Ni-Mo were similar to each other.

Figure 4 shows the relationship between MPD and conversions of BI and asphaltene for runs of Wan-SRC and Aka-SRC over fresh and carbon-coated Ni-Mo catalysts. Increasing catalyst MPD up to about 150 Å increased the conversion of both asphaltene and preasphaltene. Within this range, the BI has relatively less inhibiting effect on asphaltene conversion. Further increasing MPD leads to further increase in conversion of preasphaltene, but this results in decrease in asphaltene conversion. The decrease in the apparent asphaltene conversion is considered to be due

to two different effects: 1) increasing MPD increased conversion of preasphaltene, producing more asphaltene, as suggested by data in Table 7, and 2) diffusion and preferential adsorption of highly polar and polyaromatic BI materials on surface inside pores of large-pore catalysts, which inhibits the adsorption and conversion of asphaltene on catalyst surface, as revealed by the data in Table 6.

It is interesting to note that carbon-coated catalysts gave substantially higher conversion of BI than the fresh catalysts, but the fresh Ni-Mo gave higher asphaltene conversion. We also observed that pure SiO₂-supported catalysts gave higher BI conversion. The KF-153S, which contains 4.5 wt% SiO₂ and is more acidic than pure alumina-supported Ni-Mo, did not improve BI conversion, as compared to the thermal runs. All of these results point to the conclusion that less acidic hydrogenation catalysts are more effective for conversion of BI materials into asphaltene. These observations are consistent with the findings of Derbyshire et al. [1988] and Masuyama et al. [1990] who reported the improved performance of carbon-coated alumina supported Mo catalysts or carbon-supported Mo catalysts and Ca-modified Ni-Mo, respectively, for hydrotreating of coal liquids. Ca addition serves to neutralize or passivate, and carbon coating covers the surface acidic sites. These results, however, are in distinct contrast with those of McCormick et al. [1989] who reported that relative to the other catalysts a Co-Mo/Al₂O₃ catalyst containing 5% SiO₂ exhibits an extremely low coking tendency because of the Bronsted acid sites on the silicated alumina.

A New Concept for Catalyst Design. In industrial practice, a compromise between the need for high activity and for extended life can be achieved by using a bimodal pore size distribution. Some recently developed catalysts such as Shell 317, Amocat 1C and Amocat 1A are Ni-Mo or Co-Mo supported on bimodal Al₂O₃ supports [Lee et al, 1991; McCormick et al., 1989]. Al₂O₃-supported bimodal catalysts have been shown to exhibit better apparent activity for coal liquids upgrading [Tischer, 1985]. However, the present results point to the conclusion that less acidic and larger-pore hydrogenation catalysts are more effective for preasphaltene conversion, but efficient conversion of asphaltene requires mild hydrocracking catalysts. These results suggest a new concept for design of coal liquids upgrading catalyst: two component-bimodal catalyst consisting of a moderately acidic mild hydrocracking component having mostly mesopores and a less acidic hydrogenating component with large mesopores or mostly macropores. This concept needs to be verified by further investigation.

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Table 1. Properties of Al₂O₃ and SiO₂ Supports Used for Preparing the Supported Mo Catalyst

	SiO ₂ Support		Al ₂ O ₃ Support				
	Cariact-10	Cariact-50	S-1	S-2	S-3	S-4	S-C ^a
Median pore diam, Å	90	507	115	120	280	750	90 ^b
Surface area, m ² /g	267	78	203	174			255 ^b
Pore volume, mL/g	1.00	1.05	0.79	0.65	1.05	1.49	0.56 ^b

a) The Kejefine 153S catalyst contains 4.5 wt% SiO₂. b) The values measured for the KF 153S catalyst.

Table 2. Representative Analyses of Samples

Sample	Elemental (wt%, daf)					Atomic H/C	Fractional (wt%, daf)				Ash (wt%)
	C	H	N	S	O ^a		Oil	Asp.	Preasp. ^b	QI or Pyl ^c	
Solvent Refined Coals											
Wan-SRC	85.7	6.1	1.5	0	6.7	0.85	35.7	33.1	26.4	4.8	0.9
Aka-SRC	84.9	6.2	1.8	0.3	6.8	0.87	31.5	27.0	39.9	1.6	0.5
SCT-SRC	86.3	6.7	1.2	0	5.8	0.93	46.0	34.1	19.9	0	—
Raw Coals											
Wandoan	78.3	5.9	1.0	0.1	14.7	0.90	0.9	4.7	1.7	92.7	7.3
Akabira	83.2	6.2	2.1	0.6	7.9	0.89	0.8	0.9	19.5	78.8	8.4

a) By difference; b) Quinoline or pyridine soluble; c) quinoline or pyridine insoluble.

Table 3. Results of Thermal and Catalytic Hydroprocessing of SRC at 425°C

Catalyst		Products (wt%)				Conv (wt%)		H Consum (wt%)	
Name	Composition	Gas	Oil	Asp	BI	Asp	BI	H ₂	Tetralin
Original Wan-SRC		—	35.7	33.1	31.2	0	0	—	—
None	None	4.6	54.4	22.9	18.1	30.8	42.0	0.7	0.6 ^a
KF-153S	Ni-Mo/Al ₂ O ₃	6.2	58.7	14.6	20.6	55.9	34.0	1.4	0.3
Cat-1	Ni-Mo/Al ₂ O ₃	3.6	65.2	15.4	15.8	53.5	49.4	1.6	0.8
Cat-SB	Mo/SiO ₂	3.9	61.5	23.0	11.6	30.5	62.8	1.6	0.3
Original Aka-SRC		—	31.5	27.0	41.5	0	0	—	—
None	None	5.0	48.2	23.7	23.1	12.2	44.3	0.7	0.9
Cat-1	Ni-Mo/Al ₂ O ₃	4.3	59.2	20.7	15.8	23.0	61.9	1.4	0.4
Cat-SB	Mo/SiO ₂	5.4	58.7	25.4	10.5	5.9	74.7	1.3	0.3

a) This value seems to be lower than real value, as compared to the data in Table 4.

Table 4. Hydroprocessing of Wan-SRC over 20-32 mesh SiO₂- and Al₂O₃-Supported Catalysts at 400°C

Catalyst		MPD (Å)	Yields (wt%)		Conv (wt%)		H consum (wt%)	
Name	Composition		Gas	Oil	Asp	BI	H ₂	Tetralin
None	None		1.9	45.9	16.9	20.8	0.7	1.0
Cat-SA	Mo/SiO ₂	90 ^a	1.8	49.7	21.2	28.2	0.9	0.4
Cat-SB	Mo/SiO ₂	507 ^a	1.9	51.3	19.0	35.9	1.1	0.4
KF-153S	Ni-Mo/Al ₂ O ₃	90	1.9	55.5	44.4	22.4	ND	0.3

a) Median pore diameter of SiO₂ supports Cariact-10 and Cariact-50, respectively.

Table 5. Hydroprocessing of SCT-SRC over Cylindrical Extrudate and Finely Crushed KF-153S Ni-Mo/Al₂O₃ Catalysts at 425°C

Catalyst		Gas + Oil (wt%)	Conv (wt%)	
Composition	Size		Asp	BI
Orig. SCT-SRC	—	46.0	0	0
None	—	70.9	40.5	55.8
Ni-Mo/Al ₂ O ₃	1.5 mm cylinder	81.5	72.4	54.8
Ni-Mo/Al ₂ O ₃	<100 mesh powder	87.8	80.6	71.9

Table 6. Comparison of Hydroprocessing of SRC and Its Asphaltene Fraction

Sulfided Ni-Mo/Al ₂ O ₃ MPD (Å)	Aka-SRC			Aka-Asp ^a		
	None	Cat-1 120	Cat-3 290	None	Cat-1 120	Cat-3 290
Products (wt%)						
Gas	5.0	4.3	4.3	5.7	5.2	5.1
Oil	48.2	59.2	62.5	50.7	69.8	80.3
Asphaltene	23.7	20.7	21.7	32.3	22.4	12.8
BI	23.1	15.8	11.5	12.2	2.6	1.8
H Consumed (wt%)						
H ₂	0.7	1.4	1.5	0.5	2.1	2.3
Tetralin	0.8	0.5	0.3	0.4	0.3	0.2

a) Hexane-insoluble but benzene soluble fraction of Aka-SRC.

Table 7. Comparison of Hydroprocessing of SRC and Its Preasphaltene (BI) Fraction

Sulfided Ni-Mo/Al ₂ O ₃ MPD (Å)	Wan-SRC			Wan-BI ^a		
	Cat-1 120	Cat-3 290	Cat-4 730	Cat-1 120	Cat-3 290	Cat-4 730
Products (wt%)						
Gas	3.6	3.7	3.6	10.5	7.6	10.3
Oil	65.2	66.8	66.0	23.5	27.9	27.1
Asphaltene	15.4	18.2	19.6	24.8	30.1	33.1
BI	15.8	11.3	10.8	41.2	34.4	29.5
H Consumed (wt%)						
H ₂	1.6	1.7	1.7	1.7	1.7	1.9
Tetralin	0.8	0.5	0.4	ND	ND	ND

a) Benzene insoluble fraction of Wan-SRC.

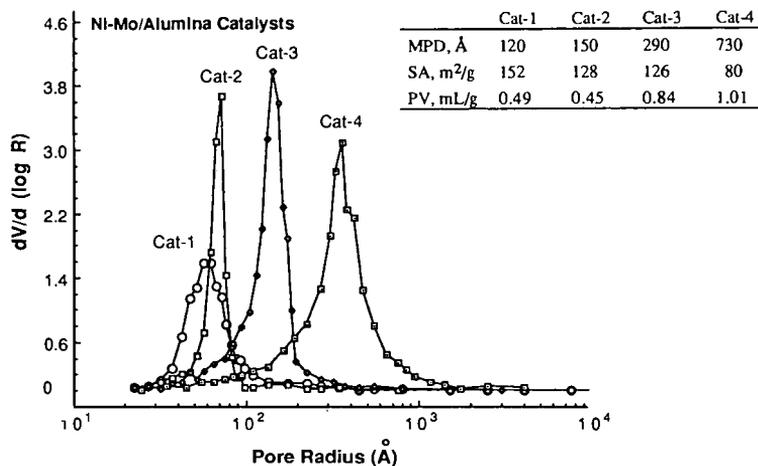


Figure 1. Pore size distribution of prepared Ni-Mo/Al₂O₃ catalysts.

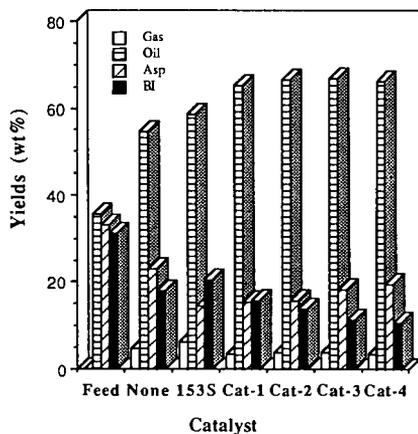


Figure 2. Hydroprocessing of Wan-SRC over unimodal Ni-Mo/Al₂O₃ catalysts with different median pore diameter. See Figure 1 for MPD values.

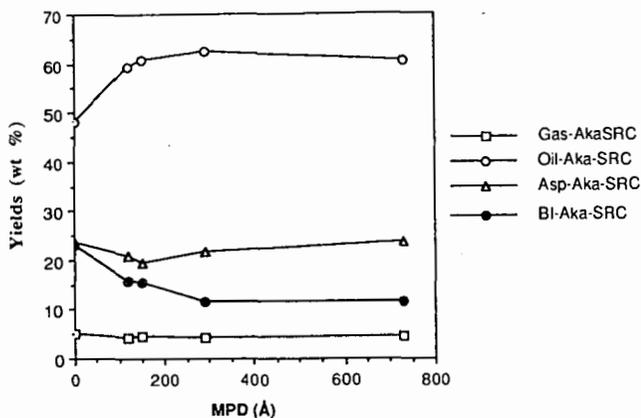


Figure 3. Effects of pore size of Ni-Mo/Al₂O₃ catalysts on product distribution for hydroprocessing of a solvent refined coal (Aka-SRC).

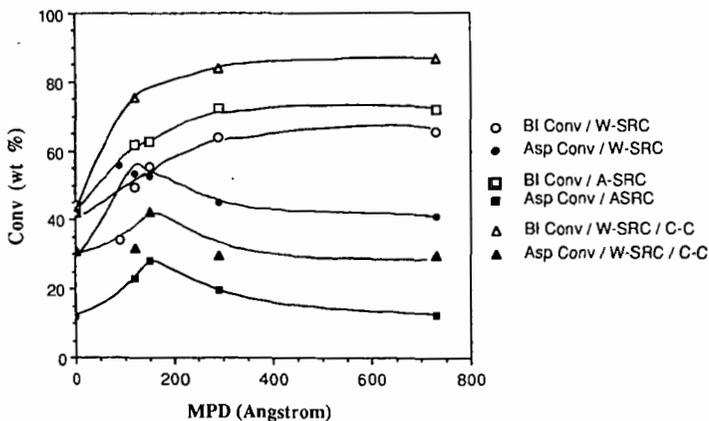


Figure 4. Relation between median pore diameter and conversion of BI and asphaltene with fresh and carbon-coated (C-C) Ni-Mo/Al₂O₃ catalysts for hydroprocessing of Wan-SRC and Aka-SRC. Note that incorporation of the data with KF-153S Ni-Mo containing 4.5 % SiO₂ resulted in some deviation at MPD of 90 Å.