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Large-Pore Ni–Mo/Al_2O_3 Catalysts for Coal–Liquids Upgrading[1]

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A novel method that can produce large-pore unimodal or bimodal alumina extrudates was developed. Since the method used to produce the larger-diameter pores does not involve a steaming or sintering process, the resultant supports have high surface areas, ~350 m^2/g. Also, the technique allows catalysts with widely varying pore structures to be prepared while holding all preparation variables constant except for the extent of mixing used during preparation of the extrusion batch. These experimental supports were used to prepare Ni–Mo catalysts for upgrading coal liquids. The results of an initial batch-screening test suggest that the resulting bimodal catalysts are more effective for upgrading coal liquids than the corresponding unimodal catalysts.

INTRODUCTION

New catalysts are needed for the processing of coal and coal liquids that contain high concentrations of fairly large aromatic molecules, relatively high quantities of heteroatoms, and significant quantities of mineral matter. For heavy feedstocks, pore structure can have a large effect on catalyst activity. Indeed, previous work at Amoco Oil Company shows that large-pore bimodal catalysts are necessary for single-stage coal-liquefaction processes where the catalyst is in contact with coal (*1–3*). Pore size affects the initial activity of the catalyst, where a broad maximum in activity exists for those catalysts having pores in the range of 10–20 nm. Similar results were obtained for desulfurization, with a more pronounced maximum around 12 nm. Of greater significance, unimodal catalysts show much larger deactivation rates than bimodal catalysts (*4*).

In current liquefaction work, emphasis has shifted from single-stage processes, where the catalyst is directly in contact with coal, to two-stage processes involving a thermal dissolution step followed by a coal-liquid upgrading step. In the second scheme, the hydroprocessing catalyst is used to upgrade the primary liquefaction products to provide a high-quality solvent for coal dissolution. This work on two-stage processing has shown that the severity (i.e., reaction temperature, pressure, residence time) in the liquefaction reactor could be reduced because the removal of heteroatoms can be performed more efficiently in a catalytic hydroprocessing reactor. The products produced in the liquefaction reactor under the lower severity conditions were more reactive in the catalytic hydroprocessing reactor than products produced at higher severities (*5*). Catalysts being used currently in the two-stage processes are unimodal and proprietary in nature.

The work reported by researchers at Amoco on the use of catalysts in single-stage coal liquefaction suggests that bimodal catalysts might be more effective than unimodal catalysts for hydroprocessing coal liquids (*4*). Techniques were previously developed at the Pittsburgh Energy Technology Center (PETC) for preparing

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[1] Reference in this report to any specific commercial facility, product, process, or service is to facilitate understanding and does not necessarily imply its endorsement or favoring by the United States Department of Energy.

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large-pore bimodal supports (*6*). However, the previous techniques involved the use of sintering to increase the average mesopore diameter, which is undesirable because it reduces surface area. A new technique that involves mixing a fumed alumina with the boehmite precursors during preparation of the extrusion batch was discovered. This new technique produces large-pore catalysts that also have a high surface area. In addition, the pore structure can be controlled merely by changing the extent of mixing. The work in this paper describes the preparation procedure for these catalysts and the results obtained on the catalytic activity of these catalysts for upgrading coal liquids.

METHODS

(*A*) *Preparation of Supports*

Previous work (*6*) showed that the pore diameter of alumina extrudates prepared from boehmite depends primarily on the characteristics of the boehmite powder used to prepare the extrudates. In this work, the supports were prepared from a mixture of Kaiser SA boehmite gel and Degussa aluminum oxide-C, which produces a system whose physical characteristics are much more dependent on processing conditions. The Kaiser boehmite on calcination yields a γ-alumina having a surface area of 375 m^2/g, a pore volume of 0.939 cm^3/g, and an average pore diameter of 7 nm. The Degussa aluminum oxide-C is a fumed alumina consisting of 20-nm particles of γ-alumina, which has an intermediate surface area of 100 m^2/g. A mixture of the two aluminas produces large-pore unimodal supports. Supports with a bimodal pore structure were prepared by adding combustible microcrystalline cellulose (FMC's Avicel-pH-101) to the mixture.

The extrusion batches were prepared to contain 300 ml of material. The batches for the unimodal support contained 185.0 g of Kaiser SA, 79.2 g of Degussa aluminum oxide-C, and 216.3 g of 5 vol% acetic acid solution. The batches for the bimodal supports contained 100.0 g of Kaiser SA, 42.9 g of Degussa aluminum oxide-C, 35.7 g of Avicel-pH-101, and 227.3 g of 5 vol% acetic acid solution. The batches for the bimodal supports contained 55 wt% acetic acid, compared to 45 wt% for the unimodal support. The additional solution required for the bimodal-support batches was necessary to reduce the stiffness of these batches and obtain acceptable extrusion characteristics.

The batches were mixed in a Haake Rheocord torque rheometer equipped with a Model 410 Rheomix mixer. The degree of mixing was determined by the total energy input to the mixer rather than mixing time, since this is a more accurate measurement of the amount of mixing. The mixed batch was then extruded using a Hydromet Model HEB-50 hydraulic extrusion press equipped with a 1.59- or 1.19-mm die. The extrudates were then dried overnight at 120°C, broken into small random lengths, and calcined at 500°C for 16 h.

(*B*) *Catalyst Preparation*

The nominal concentration of the metals in the catalysts was 3.0 wt% NiO and 15.0 wt% MoO$_3$. The active components were impregnated onto the supports using the incipient wetness technique. A double impregnation technique was used, with drying and calcination steps between impregnations. The molybdenum impregnation step was always performed before the nickel impregnation step. Reagent-grade ammonium heptamolybdate and nickel nitrate hexahydrate were used in the impregnations. After impregnation, the extrudates were tumble-dried in a rotary evaporator at 90°C. The dried extrudates were calcined to 400°C in a tube furnace with a 5 (STP)-liter/min air purge, which ensured rapid removal of water vapor during the calcination step. This prevents the loss of overall surface area that occurs if the calcination step is carried out in a stagnant environment. The final catalysts were then calcined at 500°C for 16 h.

The calcined catalysts were presulfided before being run in the screening test. The presulfiding was carried out in a 10 mol%

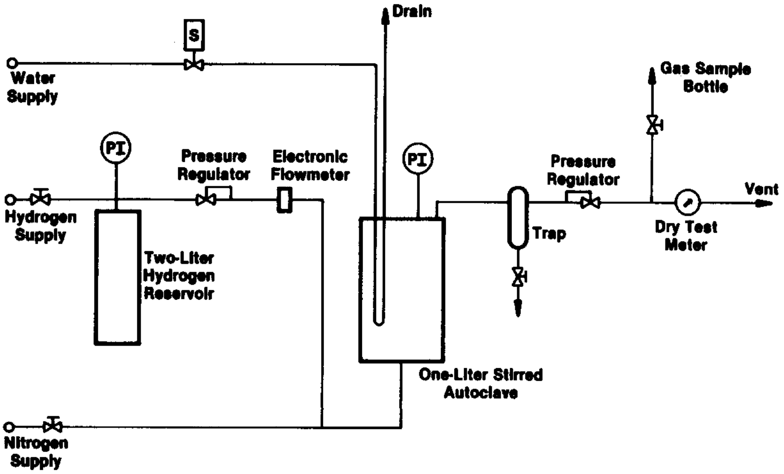

FIG. 1. Simplified schematic diagram for the batch autoclave reactor.

mixture of hydrogen sulfide in hydrogen. The catalysts were heated to 200°C at ambient pressure in a nitrogen flow to remove adsorbed water. The flow rate of the hydrogen sulfide mixture was set at 165 cm^3/min, and sulfiding was allowed to proceed until breakthrough occurred. The temperature was then raised to 350°C, and sulfiding was continued for an additional 4 h. At the end of this period, the furnace was purged with nitrogen for 1 h to remove adsorbed hydrogen sulfide, then cooled to room temperature. The sulfided catalysts were stored in sealed containers under a nitrogen atmosphere until used.

(*C*) *Activity Measurements*

The activity of the catalysts for upgrading a coal-liquid residuum was measured in a batch autoclave. A simplified schematic diagram of the batch reactor is shown in Fig. 1. The reactor consists of an Autoclave Engineer's 1-liter Magnadrive autoclave equipped with a 4-liter hydrogen reservoir. A combination of a forward and backward pressure regulator was used to maintain a constant hydrogen pressure of 2000 psig in the reactor, while the selected hydrogen flow was maintained using a Brook's electronic mass flow controller. The unit is operated in a batch mode with respect to the coal-liquid feed, while a continuous feed of hydrogen is used to purge water, ammonia, and hydrogen sulfide from the unit during the test. The batch-screening test has been described in detail elsewhere (*7*). The extrudates are contained in a wire basket, where liquid flow through the basket is maintained by the design of the impeller and internal baffles. The reactor internals are identical to those used in our continuous hydroprocessing reactor (*8*, *9*). Similar catalyst baskets are available commercially through Autoclave Engineers.

The composition of the feedstocks used in the batch test and the reactor conditions are given in Table 1. The performance of the catalysts is determined by their hydrogenation activity (increase in H/C ratio of the product versus the feed), their heteroatom removal activity (both HDS and HDN), and their ability to convert the feed into products soluble in ethyl acetate and cyclohexane. The hydrogenation and heteroatom removal activities were determined from standard ultimate elemental analyses of the feed and products, while the conversions to products soluble in ethyl acetate and cyclohexane were determined using a microfiltration procedure (*1*, *2*).

RESULTS AND DISCUSSION

(*A*) *Catalyst Characterization*

Previous work showed that the pore structure of alumina supports prepared from boehmite precursors (such as Con-

TABLE 1

Batch Reactor Test Conditions

Material (wt%)	Coal-liquid residuum (CLR)	Hydrogenated creosote oil (HCO)
A. Feed stock composition		
Carbon	87.0	92.0
Hydrogen	6.0	7.9
Nitrogen	2.2	0.42
Sulfur	0.72	0.06
Oxygen (by diff.)	4.0	—
Ash	0.1	0.01
B. Reaction conditions		
Coal-liquid residuum	150 g	
Hydrogenated creosote oil	150 g	
Catalyst	40 cm^3	
Temperature	415°C	
Pressure	2000 psi	
Time	60 min	
H_2 flow rate	8 scfh	
Agitator speed	1200 rpm	

oco's Catapal SB and Kaiser's SA medium) is only slightly affected by fabricating conditions (*6*). However, for the mixture of Kaiser SA and Degussa aluminum oxide-C used in this work, the pore structure is dependent on conditions used during fabrication. Thus, it was possible to prepare supports with drastically different pore structures merely by changing the extent of mixing of the extrusion batch while all other factors were held constant. Also, the resulting pore structure of the composite catalyst is very different from what one would expect from a mere physical mixture of the two aluminas. This is shown in Fig. 2 for a composite catalyst having a total energy input of 975 kcal during the mixing step. Also, increasing the degree of mixing shifts the pore distribution to smaller pore sizes. With this procedure, it is possible to prepare high-surface-area supports having a significant fraction of their pore volume in the range 8–10 nm. Also, the technique has been found to be quite reproducible provided the energy input (*E*) during mixing is used to control the mixing process rather than the total mixing time.

The addition of a microcrystalline cellulose, such as Avicel, to the mixture not only introduces bimodal character to the supports but also causes a general increase in the size of the pores. The amount of increase depends on the extent of mixing during preparation of the extrusion batch. Increased mixing has two different effects, as shown in Fig. 3. With increasing extent of mixing, as characterized by the total energy input (*E*) during mixing, the microcrystalline cellulose fibers are broken down into their component fibrils, which causes the macropore distribution to shift to smaller diameters. At the same time, the mesopore distribution also shifts to smaller diameters. Apparently, increasing the amount of mixing causes the alumina crystallites to pack more tightly, so the resulting pore structure shifts to smaller average-pore diameters. The physical characteristics, as determined by mercury porosimetry, of the supports prepared by this technique are given in Table 2. All the catalysts except F were extruded through a 1.59-mm die. Notice that the Avicel-containing extrudates experience much larger shrinkage during drying than the extrudates that do not contain Avicel. Catalyst F was extruded through a

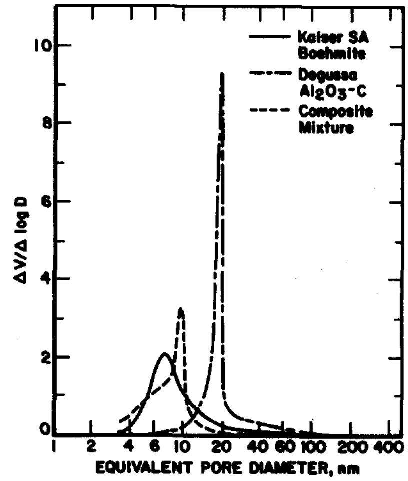

FIG. 2. Pore structure of a composite support and component aluminas.

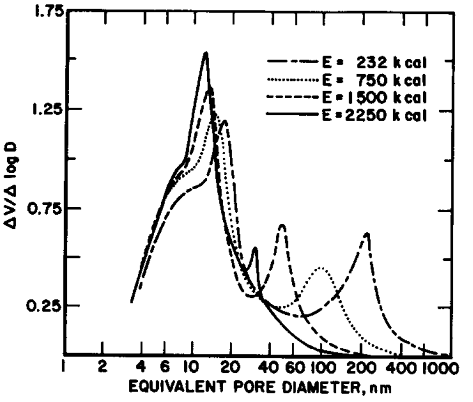

FIG. 3. The effect of mixing on the pore structure of the resultant catalysts.

1.19-mm die and experienced the same amount of shrinkage as the other bimodal extrudates.

The chemical composition and physical characteristics of the finished catalysts in both the oxidic and sulfidic forms are given in Table 3. The analyzed compositions were very close to the target composition. The surface areas given in Table 3 were measured using the standard BET gas adsorption technique and agree to within 2% of values calculated from the mercury porosimetry data. They are also in good agreement with values calculated from the support surface areas using a monolayer model, so it appears that surface area is not lost during the impregnation process. However, there is a very significant shift in the pore distribution to larger pore sizes during the impregnation and calcination steps.

(*B*) *Activity Characterization*

The batch autoclave test is used to measure the initial activity of potential coal-liquid hydroprocessing catalysts. For residuum/recycle-solvent feed used in this study, very little reaction occurs during a thermal run in the absence of a catalyst. Also, work in our laboratory shows that activities measured in the batch-testing unit correlate well with initial activities measured in our continuous hydroprocessing reactor. Likewise, the amount of carbonaceous material deposited on the catalyst during the batch test is very close to the amount of such material observed in the line-out catalyst owing to the very rapid buildup of these carbonaceous deposits in catalysts processing coal or coal liquids. Therefore, these test results should give a good indication of the catalysts' activities under steady-state conditions for this sytem where intraparticle diffusional effects are important.

The activity data for the Ni–Mo catalysts are given in Table 4. The data given in Table 4 are the results for single runs. Based on the results obtained for other types of

TABLE 2

Physical Characteristics of Alumina Supports[a]

	Support					
	A	B	C	D	E	F
Energy input during batch preparation (kcal)	975	2250	1500	750	232	395
Pellet density (g/cm^3)	1.04	0.83	0.80	0.75	0.71	0.73
Pore volume (cm^3/g)	0.67	0.85	0.89	0.99	1.04	0.99
Average mesopore diam. (nm)	9.8	12.2	13.0	14.8	16.8	16.5
Average macropore diam. (nm)	—	30	55	105	200	120
Surface area (m^2/g)	367	348	333	366	311	307
Extrudate diam. (mm)	1.44	1.19	1.19	1.19	1.21	0.97

[a] Unimodal support A was prepared from a batch containing only the mixed aluminas. The bimodal supports B–F were prepared from batches that also contain Avicel.

TABLE 3

Physical Characteristics of Ni–Mo/Al$_2$/Al$_2$O$_3$ Catalysts

	Catalyst					
	A[a]	B	C	D	E	F
Wt% of NiO	3.0	3.1	2.9	2.9	3.0	3.0
Wt% of MoO$_3$	14.9	15.0	15.0	14.9	15.0	14.7
g(NiO + MoO$_3$)/cm^3 of reactor	0.112	0.096	0.089	0.088	0.087	0.083
A. Oxidic form						
Pellet density (g/cm^3)	1.25	1.04	0.95	0.92	0.88	0.89
Pore volume (cm^3/g)	0.523	0.675	0.739	0.807	0.853	0.862
Average mesopore diam. (nm)	11.0	13.0	14.0	17.0	18.8	18.8
Average macropore diam. (nm)	—	30	56	108	200	130
Surface area (m^2/g)	274	275	274	267	287	252
Surface area (m^2/g Al$_2$O$_3$)	334	335	334	325	350	306
B. Sulfidic form						
Pellet density (g/cm^3)	1.26	1.10	0.99	0.96	0.95	0.91
Pore volume (cm^3/g)	0.537	0.675	0.732	0.820	0.850	0.881
Average mesopore diam. (nm)	11.2	13.0	15.0	17.0	20.0	20.4
Average macropore diam. (nm)	0	35	64	140	210	128
Surface area (m^2/g)	259	266	259	260	249	239
Surface area (m^2/g Al$_2$O$_3$)[b]	324	334	324	325	312	299

[a] Unimodal catalyst that does not contain macropores.

[b] Calculated assuming NiO → NiS and MoO$_3$ → MoS$_2$.

catalysts run in this feed, the expected reproducibility of the measurements is ±0.5% for the percentage change in H/C ratio, ±1% for the denitrogenation results, ±2% for the ethyl acetate conversion values, and ±2.5% for the cyclohexane conversion and sulfur removal data. In view of this expected reproducibility, the results in Table 4 show that introducing bimodality into the catalyst does improve its performance. The hydrogenation activity is measured by the percentage increase in the atomic H/C ratio of the product with respect to the feed. The catalysts containing the larger macropores, except for catalyst B, have better hydrogenation activity than the unimodal catalyst. A similar trend is seen in the ability of the catalysts to convert heavy coal liquids into products soluble in ethyl acetate and cyclohexane. The ethyl acetate conversion data measure the conversion of the heavy coal liquids into asphaltene and oils, while the cyclohexane data measure their conversion to oils only. These changes in solubility are mainly due to reduction in intermolecular interactions caused by hydrogenation and heteroatom removal, since little cracking or change in total 650°F+ distillate fraction occurs under the testing conditions used. The somewhat better heteroatom removal ability of the bimodal catalysts is seen in the HDS activity data. However, there appears to be very little difference in HDN activity. Appreciable oxygen removal from the coal liquid occurs during the test. However, because of the difficulty of obtaining reliable elemental-oxygen analyses, the results are too scattered to interpret. Overall, the bimodal catalysts exhibit better activity than the unimodal catalysts, but the differences are not large.

Comparison of catalysts D and F shows that changing the extrudate diameter from 1.21 to 0.97 mm has no significant effect on the activity of these catalysts that contain large macropores. If intraparticle diffusion was affecting the observed overall reaction

TABLE 4

Spent Catalyst Characterization and Activity Data for Bimodal Ni–Mo/Al_2O_3 Catalysts

	Catalyst						Thermal data
	A	B	C	D	E	F[a]	
Average mesopore diam. (nm)	11.2	13.0	15.0	17.0	20.0	20.4	
Average macropore diam. (nm)	—	35	64	140	210	128	
Activity data							
% Change in H/C ratio[b]	6.6	5.6	8.7	7.4	8.4	7.1	−1.5
Ethyl acetate conv. (%)	49	52	58	58	64	64	28
Cyclohexane conv. (%)	39	42	46	45	55	49	17
Heteroatom removal							
Sulfur (%)	56	62	69	64	69	72	15
Nitrogen (%)	15	11	14	11	14	14	0.8
Spent catalyst characterization							
% Reduction in pore volume	42	40	36	38	40	41	
% Reduction in surface area	29	40	37	43	44	37	
Reduction in average mesopore diameter (%)	36	17	29	19	22	29	
Loss on ignition at 450°C (%)	18	19	18	20	20	21	

Note. The percentage heteroatom removal is based on the total feed composition, consisting of a 50/50 mixture of coal-liquid residuum/hydrogenated creosote oil.

[a] Catalyst F had an extrudate diameter of 0.97 mm, while all the other bimodal catalysts had an extrudate diameter of 1.19 mm.

[b] Percentage change in the H/C ratio is defined as the increase of the H/C ratio of the hydrotreated product with respect to the H/C ratio of the feed mixture of coal-liquid residuum and hydrogenated creosote oil.

rate in these catalysts, the smaller-diameter catalyst should be the more active of the two. However, the data show no significant difference in activity. This suggests that in these large-pore bimodal catalysts, the pore structure is open enough that configurational diffusion effects are not important. This would probably not be true for the unimodal catalyst, since changes were seen in activity when the intraparticle diffusional resistance was reduced by introducing macropores with the catalyst.

One of the difficulties in interpreting the activity data is that both the mesopore and macropore diameters varied in the prepared catalysts. This was not intentional but was caused by the inability of the preparative technique to allow each to be changed independently. Work is currently in progress to determine the effect of varying the mesopore diameter in unimodal catalysts and then to reexamine the effect of introducing bimodality into the catalyst.

Differences in pore structure induced in the catalysts due to carbon deposition were observed between the unimodal and bimodal catalysts. The amount of carbonaceous material, and the resultant pore volume reductions were identical in both types of catalysts. However, the bimodal catalysts suffered a larger reduction in surface area but smaller reductions in average mesopore diameters than the monomodal catalyst. There was no detectable change in the average macropore diameters.

The experiments were performed at a constant hydrogen pressure of 2000 psig. Changing the hydrogen pressure should have some effect on the amount of coke deposited in the pores of the catalyst and possibly on the dependence of reactivity on pore structure, but this was not determined in this study. Such studies should be carried out using unimodal catalysts where the pore structure can be more closely controlled.

CONCLUSIONS

A technique to produce large-pore alumina extrudates without resorting to a steaming or sintering process was developed. As a result, high-surface-area supports with mesopores in the range 10–20 nm can be produced. By adding combustible fibers to the extrusion mixture, large-pore catalysts with a bimodal structure can also be produced. In addition, the technique allows one to make supports with widely varying pore structures while keeping all preparation variables constant except for the extent of mixing used to prepare the extrusion batches. One should therefore expect the chemical characteristics of the resulting supports to be identical. Such supports should be ideal for studying those catalytic systems where intraparticle diffusional effects are important.

The results of upgrading coal liquids using a series of Ni–Mo catalysts prepared from these supports showed that opening up the pore structure by introducing bimodality into the catalyst produced increases in the activity of the catalyst, but the effect is not large. Unfortunately, changes in the distribution of both mesopore and macropore diameters occur simultaneously during preparation, which makes interpretation of the data difficult. Therefore, work needs to be done to determine the effect of increasing average mesopore diameters in unimodal catalysts before one can sort out the relative contributions of the two changes.

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