Effects of Pore Size Distribution on the Catalytic Performance for Coal Liquefaction. I.   The Activity and Selectivity of the Catalyst

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Coal liquefaction experiments were carried out by using seven catalysts with different pore structures. As for the unimodal catalysts, the total conversion increased with the pore radius of the catalyst because of the lesser pore-diffusional limitation. However, the ratio of oil to oil-plus-asphaltene decreased with the pore radius. In the case of a large-pore catalyst, heavy components with a large molecular size and a low reactivity can approach the intra-particle active sites and occupy them to prevent the hydrocracking of asphaltene to oil. Bimodal catalysts with micropores (r<10 nm) and macropores (r>300 nm) gave higher values of both the coal liquefaction and the oil yields than did the unimodal catalysts. The presence of macropores seems to enhance the pore diffusion and increase the efficiency of the micropore use, while mesopores with radii between 10 nm and 300 nm did not make such a high contribution to the pore diffusion as was shown for the macropores. For the removal of heteroatoms, there was little difference in the performance among the catalysts with different pore structures. It is suggested that the active sites for the heteroatom removal are deactivated easily by the heavy components.

Molybdenum alumina catalysts have long been used for the hydrodesulfurization (HDS) of gas oil and the refining of the petroleum residue. Recently serious attention has been paied to the use of these catalysts for the direct liquefaction of coal in a fixed bed or an ebullated bed. However, since there are many differences in properties between coal (or coal derived liquids) and petroleum, MoO_3/Al_2O_3 catalysts designed for petroleum refining cannot show a high activity or favorable selectivity for the direct liquefaction of coal. Further, the catalytic activity, especially the hydrogenation activity, declines rapidly during the hydrotreatment of coal because of coke build-up and metal deposition on the surface of the catalyst.[1,2]

During the course of the development of molybdenum catalysts for coal liquefaction, a deliberate designing of the catalyst is absolutely necessary. For this purpose, it is necessary to clarify the effects of the properties of the catalyst on its activity, selectivity, and life. The present paper will describe the effects of the pore size distribution (PSD) on the activity and selectivity of the supported catalyst.

Recently, in the petroleum hydrotreating process the feedstocks have become heavier, and many kinds of functions besides HDS and hydrocracking activity, such as asphaltene conversion and demetallation, have come to be required for the catalyst. Furthermore, large amounts of poisoning materials contained in heavy feedstocaks deactivate the conventional HDS catalysts rapidly. One of the solutions to these problems can be found in designing the proper pore structure of catalyst support. Numerous catalysts with different pore structures have been tested and reported in many patents[3-10] and papers.[11-13] As a result of these investigations, some effects of the PSD on the catalytic activity and life have become obvious. They are;

1. The pore-diffusional limitation of the reaction rates is serious in the hydrotreating of heavy feedstocks than in the light gas oil.
2. The optimal pore structure may not be the same for every hydrotreating reaction, desulfurization, denitrogenation, asphaltene conversion, and demetallation.
3. Carbonaceous and metal deposition from the feedstocks on the catalysts varies as a function of the pore structure.

On the contrary, a few fundamental studies have been undertaken on the effects of the PSD of the catalyst used for coal liquefaction. Weller and his co-workers[14-16], by using several kinds of supports which have different average pore diameters, demonstrated that the catalysts with large pores showed a higher performance than those with small pores. Bertolacini et al.[17,18] indicated that a bimodal PSD is required for high performance, especially in terms of aging. As has been shown above, it has become somewhat clear that the PSD of the catalyst support plays an important role in the performance of the catalyst for coal liquefaction. However, the proper PSD of the catalyst for coal liquefaction will differ with the starting materials and with the products aimed at. Process conditions, such as the type of reactor, will also change the most favorable PSD. Accordingly, further practical studies have to be undertaken on the effects of the PSD on the catalytic activity, selectivity, and life in order to develop practical catalysts with high performance.

In the present study, the effects of the PSD on the activity and selectivity of the catalyst will be investigated by using both unimodal and bimodal catalysts. Moreover, the roles of micro-, meso-, and macropores in the catalytic activity will also be clarified. Seven catalysts with different PSD values, with the same weight loading of molybdenum, were prepared and screened for coal liquefaction in a batch autoclave. From the results of the product distribution and the removal of nitrogen and sulfur, the proper pore structure for each reaction will be discussed.

Experimental

Equipment.   A 500-cm³ autoclave with a magnedrive stirrer was used for all runs of coal liquefaction. The auto-

clave was equipped with a wire basket to prevent the catalysts from being crushed. The hydrogenation of 1-methylnaphthalene (1-MN) was carried out using a 50-cm³ autoclave in order to examine the activity of the catalysts.

Catalysts.   Seven kinds of Al₂O₃ (sphere with a diameter of 1.6 mm) with different PSD values were chosen as catalyst supports (prepared by Sumitomo Aluminum Smelting Co., Ltd.). Figures 1—3 show the PSD curves of the catalyst supports (before impregnation with active components) as measured by using a mercury porosimeter (AMINCO

Fig. 1. Pore size distributions of catalysts.
●: Catalyst A, ▲: catalyst B, ■: catalyst C

60,000 psi).   The MoO₃/Al₂O₃ catalysts were prepared by impregnating the Al₂O₃ supports with an ammoniacal solution of ammonium heptamolybdate, and the NiO–MoO₃/Al₂O₃ catalysts with an ammoniacal solution of ammonium heptamolybdate and nickel nitrate. All the operations of the impregnation procedure were performed at pH values over 9.0 for 42 h (at 27 °C) using the equilibrium adsorption method.[19] The samples were subsequently dried (at 110 °C, 16 h) and calcined (at 300 °C, 50 min; subsequently at 500 °C, 3 h).

The loading of molybdenum was determined by chemical analysis, and that of nickel, by the use of an X-ray fluorescence analyzer (Rigaku, Ultra Trace System). The specific surface areas and pore volumes of all the catalysts were measured by using the mercury porosimeter. The properties and the chemical components of the catalysts are summarized in Tables 1 and 2. Reductive sulfiding was carried out in a stream of 10 vol% of H₂S (balance H₂) at 350 °C for 2 h before liquefaction.

Procedures.   *Coal Liquefaction*:   The coal used was a subbituminous Taiheiyo coal containing 16.1% ash (dry base). The rersults of the elemental analysis of the coal were: C, 74.9; H, 6.2; N, 1.3; S, 0.4; O, 17.2% (moisture and ash free base).   The powdered coal with a diameter smaller than 150 µm was dried at 110 °C in a nitrogen atmosphere before use.   The solvent used was hydrogenated anthracene oil (HAO), which contained: C, 91.8; H, 7.0; N, 0.6; S, 0.1; O, 0.5%.

The autoclave was charged with coal (60 g), a solvent (140 g), and a catalyst (5 g), and then pressurized with H₂ to an initial pressure of 100 kg cm⁻² at room temperature. The temperature of the unit was increased to 400 °C over a period of 2 h and then held at this temperature for 1 h. The stirring rate was 900 min⁻¹ for all runs.
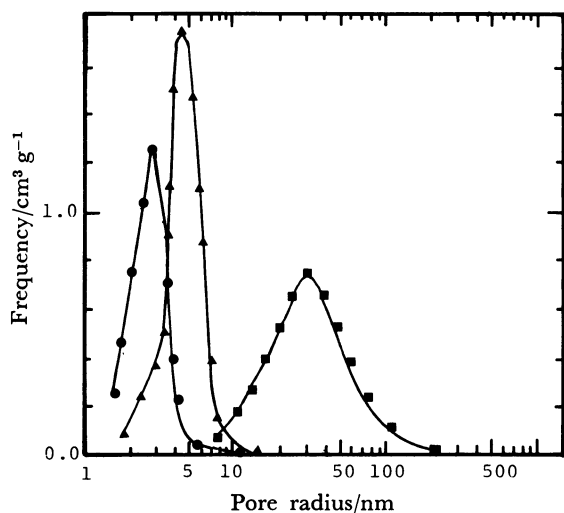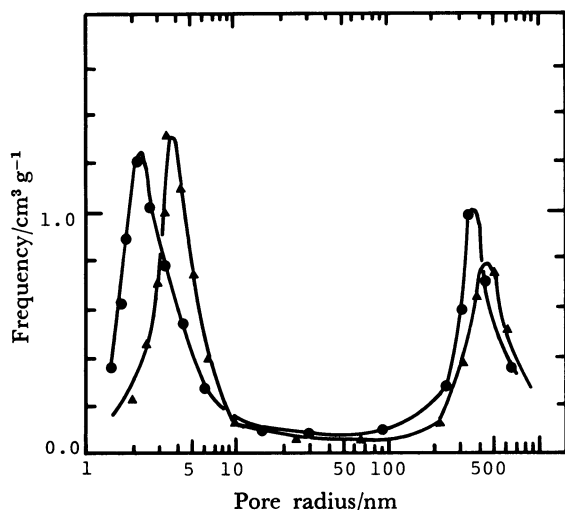

Fig. 2. Pore size distributions of catalysts.
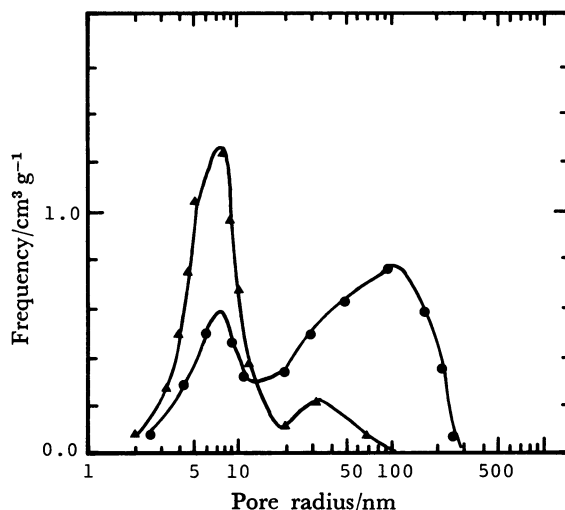●: Catalyst D, ▲: catalyst E

Fig. 3. Pore size distributions of catalysts.
▲: Catalyst F, ●: catalyst G

TABLE 1. PROPERTIES OF MOLYBDENUM CATALYSSTS

Catalyst	A	B	C	D	E	F	G
Phase of Al₂O₃[a]	γ	γ	α	γ	γ	γ	γ
S. A.[b]/m² g⁻¹	276	211	39	316	261	175	120
P. V.[c]/cm³ g⁻¹	0.37	0.48	0.55	0.76	0.84	0.63	1.25
MoO₃/wt%	3.4	3.2	2.8	3.5	2.9	2.8	3.4
SiO₂/wt%	tr.[d]	tr.	3.8	tr.	tr.	4.0	tr.

a) Decided by using X-ray diffraction.   b) Surface area.   c) Pore volume.   d) Less than 0.5.

Table 2. Properties of nickel molybdenum catalysts

Catalyst	P[a]	Q[b]	R[c]
S.A.[d]/m^2 g^{-1}	252	34	188
P.V.[e]/cm^3 g^{-1}	0.36	0.50	0.74
MoO$_3$/wt%	11.7	11.0	15.3
NiO/wt%	3.3	3.3	3.6
SiO$_2$/wt%	tr.[f]	3.8	tr.

a) The same support was used as for the catalyst A.
b) The same support was used as for the catalyst B.
c) The same support was used as for the catalyst C.
d) Surface area. e) Pore volume. f) Less than 0.5.

After cooling to room temperature, the gas was slowly discharged through a wet gas meter. During this letdown, a sample of the gas was collected in a syringe in order to determine the gas composition. The liquid and solid products were separated into "toluene insolubles," "asphaltene (toluene soluble and hexane insoluble)," and "oil (hexane soluble)" portions using a Soxhlet extractor. The nitrogen and sulfur contents in the liquid products were determined by means of a nitrogen and sulfur analyzer (Mitsubishi Kasei, MCI-TN-02).

Hydrogenation of 1-Methylnaphthalene (1-MN): The hydrogenation activity of the catalysts was examined using 1-MN as a reactant. The autoclave was charged with 10 cm^3 of 1-MN and 0.5 g of a catalyst, and then pressurized with H$_2$ to an initial pressure of 70 kg cm^{-2}. The unit was then heated to 375 °C over a 10-min period and then held at this temperature for 90 min. The analysis of the liquid product was done using a gas chromatograph equipped with a FFAP fused silica capillary column (25 m).

Results and Discussion

Conversion and Oil Yields.   The results of the coal liquefaction and hydrogenation of 1-MN on molybdenum catalysts are summarized in Table 3. In the liquefaction of coal, the total conversion (oil-plus-asphaltene yields) and the oil yields for a blank run were much lower than those for runs with a catalyst. 1-MN did not react without a catalyst. These results made it clear that the catalysts accelerated the reaction rates.

In the liquefaction test, the gas composition for the blank run was: CO$_2$, 5.9; CO, 1.3; CH$_4$, 4.0; C$_2$H$_6$, 1.1% (in addition, trace amounts of H$_2$S and NH$_3$ were detected), whereas that for the runs with a catalyst was: CO$_2$, 6.0—6.4; CO, 1.5—1.6; CH$_4$, 4.0—4.2; C$_2$H$_6$, 1.5%.

There was little difference in gas composition among runs with a catalyst. A small difference in the gas composition was found between runs with and without a catalyst. In catalytic runs the concentrations of CH$_4$ and C$_2$H$_6$ (hydrocarbons) were a little higher than those in the run without a catalyst. The hydrocracking activity of the catalyst seems to result in this difference.

Unimodal Catalysts: The total conversion increased with the pore size of the catalyst (A<B<C) despite the smaller surface area of the large-pore catalysts. In the case of the catalyst C, which has an eminently small surface area, the loading of MoO$_3$ exceeded the monolayer coverage. Therefore, the catalyst C showed a much lower activity for the hydrogenation of 1-MN. However, a higher total conversion was given for coal liquefaction by the catalyst C than by the catalysts A and B. This tendency shows that the production of asphaltene from coal was greatly affected by the pore structure of the catalyst because the pore diffusion limited the reaction rates seriously. On the other hand, with an increase in the pore diameter of the catalyst, the production of oil remained constant, or even decreased, the ratio of oil to oil-plus-asphaltene decreasing obviously.

Ho et al.[16] also reported that the total coal liquefaction was seriously limited by the pore diffusion, and that the ratio of oil to oil-plus-asphaltene decreased with an increase in the diameter of the catalyst pore. They explained that this phenomenon was due to the low reaction temperature (400 °C) when the oil production rate was small. In the present study, however, a high oil yield was given by some catalysts (D and E) in spite of a low reaction temperature. This result suggests that the pore structure of the catalyst also affected the production rate of oil from asphaltene.

It has been known that the molecular weight of the asphaltene derived from coal, although always much lower than that from petroleum, ranges from 400 to 800.[20—22] Considering the fact that the coal-derived asphaltene has a polyaromatic ring structure, its molecular size might be larger than 1 nm. In addition, large molecules with polyaromatic rings are known to have a tendency to aggregate with each other and to give a micell-like structure. It may thus be assumed that there exists a pore-diffusional limitation in the production of oil from asphaltene.

Mass-transfer theory for porous catalysts indicates that, in a series reaction, poor yields of intermediate

Table 3. Activity tests of molybdenum catalysts

Catalyst	None	A	B	C	D	E	F	G
Most probable pore radius/nm	—	2.5	4.5	30	2.5, 350	4.5, 450	7, 35	7, 100
Coal liquefaction								
Total conversion/wt%[a]	83.3	89.9	93.2	94.4	94.7	95.7	92.8	93.4
Oil yields/wt%	52.7	65.7	65.6	64.2	71.9	70.0	64.5	66.7
Oil/(oil+asp.)[b]	0.63	0.73	0.70	0.68	0.76	0.73	0.70	0.71
Hydrogenation of 1-methylnaphthalene								
Conversion/%[c]	0.0	13.5	14.8	7.2	12.2	16.4	15.2	12.2

a) Oil plus asphaltene yields (toluene solubles). b) Oil yields/Total conversion. c) (1-MT*+5-MT)/(1-MT+ 5-MT+1-Methylnaphthalene). *MT: Methyltetralin.

products are obtained for a catalyst with a low effectiveness factor.[23] In the case of coal liquefaction, asphaltene is an intermediate product, when coal is the starting material and oil is the final product of a series reaction, indicating that a small-pore catalyst with a low effectiveness factor gives a higher ratio of oil to asphaltene than dose a large-pore catalyst.

On the other hand, it is considered that heavy components with a low reactivity (heavier than preasphaltene) can reach the intra-particle active sites of large-pore catalysts and occupy them easily, thus preventing the hydrocracking of asphaltene to oil. In fact, the analysis of the aged catalyst showed that the carbonaceous materials deposited on the catalyst were heavy components with a lower H/C ratio than asphaltene.[24]

The contribution of the catalyst to coal liquefaction is considered to be smaller than that of the hydrogen-donor solvent at the first stage of liquefaction.[25,26] The effects of catalysts on the product distribution are reflected in the increase in light components, such as the oil or distillate fraction, especially in the case of molybdenum catalysts.[27,28] In the present study, all of the catalysts gave a higher ratio of oil to oil-plus-asphaltene than was observed in the blank run. This result shows that the production of oil was more accelerated by the catalysts than that of asphaltene. However, as has been shown above, the product distribution changes with the pore size distribution of the catalyst. This result suggests that an elaborate designing of the proper pore size distribution of the catalyst is required to get a desirable product distribution.

Bimodal Catalysts: Bimodal catalysts with micropores with radii smaller than 10 nm and macropores with radii larger than 300 nm (D and E) gave a much higher value in both total conversion and oil yields than did the unimodal catalysts (Table 3). When the physical properties of bimodal catalysts were compared with those of unimodal catalysts, the pore volume of the former was found to be approximately twice as large as that of the latter in spite of the small difference in surface area between them (Table 1). This fact suggests that the macropores did not increase the number of the active sites, but enhanced the diffusion rates of the molecules inside the catalyst particle. In fact, in the case of the hydrogenation of 1-MN, which has a small molecular size, no effect of the macroporosity was observed.

A higher total conversion and lower oil yields were given in the catalyst E, with large micropores, than in the catalyst D, with small micropores. Micropores with small radii were favorable for the production of light components, even in the case of the bimodal catalysts, this result being in keeping with that obtained for the unimodal catalysts.

The catalysts with large micropores (r~7 nm) and mesopores (10 nm<r<300 nm) (F and G) gave lower values both in total conversion and oil yields than the catalysts D and E. The catalyst G, with a large volume of mesopores with a large diameter, gave a higher total conversion and higher oil yields than the catalyst F. However, even in the case of the catalyst G, mesoporosity did not enhance the catalytic activity as compared with the macroporosity.

TABLE 4. COAL LIQUEFACTION WITH NICKEL MOLYBDENUM CATALYSTS

Catalyst	P	Q	R
Pore radius[a]/nm	2.5	30	4.5, 450
Total conversion/wt%[b]	87.9	95.9	95.1
Oil yields/wt%	59.5	71.8	78.1
Oil/(oil+asp.)[c]	0.68	0.75	0.81

a) Most probable pore radius.   b) Oil plus asphaltene yields (toluene solubles).   c) Oil yields/total conversion.

Nickel Molybdenum Catalysts: The results of coal liquefaction with nickel molybdenum catalysts are shown in Table 4. Higher oil yields were given for the catalysts Q and R as compared with the catalysts C and E. This result is due to the high loading of molybdenum and the additional loading of nickel. However, the catalyst P, with only microporosity, gave a lower total conversion and lower oil yields than the catalyst A. This result indicates that the high loading of the active components decreased the effective pore size of the catalyst if the catalyst has only microporosity.

The effects of the pore structure observed for NiO–MoO$_3$/Al$_2$O$_3$ catalysts were similar to those obtained for MoO$_3$/Al$_2$O$_3$ catalysts; a high total conversion was given by the large-pore or bimodal catalysts, and high oil yields, by the bimodal catalyst. These results support our previous discussion and show that, in the case of industrial catalysts, the pore size distribution of the support also affects the activity and selectivity of the catalyst. It may also be suggested that a high loading of active metal components cannot enhance the performance of the small-pore catalyst because of the pore-diffusional limitation.

Heteroatom Removals.   The contents of nitrogen and sulfur in each fraction of the products are given in Table 5. Excepet for the catalysts F and G, higher contents of nitrogen were given in the runs with a catalyst than in the run without a catalyst. In most cases, the hexane-soluble fraction gave a higher concentration of nitrogen compounds than the toluene-soluble fraction. These results suggest that the catalysts do not very much accelerate the hydrodenitrogenation (HDN) of light components during the hydrogenation of coal. One reason for this phenomenon is that the strong adsorption of heavy components on the catalyst reduced the catalytic activity for HDN. As has been mentioned above, coal derived oil obtained by the catalytic hydrogenation of coal contains fairly large amounts of heteroatoms. However, it may be useful as a liquefaction solvent because of its polar interaction with coal molecules.[29,30]

In the runs with catalysts having meso- or macropores, lower nitrogen contents were given in spite of the high total conversion and oil yields, as compared with the runs with micropore catalysts or without a catalyst. This suggests that large pores are preferable to small pores for nitrogen-removal reaction from coal molecules.

In terms of HDS, although the sulfur contents in the products of the runs with catalysts were smaller than those without a catalyst, there was little difference

TABLE 5. CONTENTS OF NITROGEN AND SURFUR IN LIQUEFACTION PRODUCTS

Catalyst	None	A	B	C	D	E	F	G
Most probable pore radius/nm	—	2.5	4.5	30	2.5, 350	4.5, 450	7, 35	7, 100
Nitrogen								
Hexane solubles/wt%	0.62	0.76	0.78	0.64	0.63	0.62	0.57	0.53
Toluene solubles/wt%	0.64	0.73	0.70	0.64	0.62	0.62	0.47	0.50
Sulfur								
Hexane solubles/wt. ppm.	1210	750	850	760	730	620	830	820
Toluene solubles/wt. ppm.	1200	810	710	790	720	820	740	730

among catalysts. Plumail et al.[13] reported that smaller pores were more favorable for HDS than asphaltene conversion in the case of petroleum refining, while Ho et al.[16] indicated that in the case of coal liquefaction the bimodal PSD, which was most favorable for a total conversion, also gave the highest HDS performance. In the present study, the concentration of sulfur in the starting material was extremely low. Therefore, it may be difficult to discuss the HDS activity of the catalyst.

As has been described above, the pore size distribution has great effects on the activity and the selectivity of the catalyst, because the pore diffusion limits the reaction rates seriously. Large pores are more advantageous in the production of asphaltene than small pores. On the other hand, small pores are required for the production of light components. In fact, mesopores are superior to micropores in terms of total conversion, while inferior in the production of oil. Bimodal catalysts with macroporosity (r>300 nm) and microporosity (r<10 nm) performed excellently in terms of both total conversion and oil yields. Macropores enhance the efficiency of the catalyst, while micropores are useful for the production of oil. Mesopores, as compared with macropores, have no great effect on the increase in the pore-diffusional limitation.

Finally, these results show that the design of the pore structure is very important in getting a favorable product distribution. On the other hand, the pore structure of the catalyst support is also known to have great effects on the life of the catalyst. The effects of the pore size distribution of the support on the aging behavior of the catalyst during coal liquefaction will be discussed in the following work.

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