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MoO_3-SILICATE SLUDGE CATALYST FOR COAL LIQUEFACTION

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Silicate sludge obtained from a geothermal power generation plant was applied to prepare the catalyst for coal liquefaction. The sludge has a very high surface area, a large pore volume, and a wide-range pore size distribution. It was found that the activity of the catalyst prepared by supporting MoO_3 on the sludge is superior to commercially available Ni-Mo/Al_2O_3 catalyst.

The effort for the research and development of geothermal energy has been made to establish the technology of new energy resouces as Sunshine Project (Governmental project) in Japan. Geothermal hot water contains 600 - 1500 ppm of silicate including small amounts of aluminium and sodium. These inorganic materials have to be removed as sludge in order to prevent pipes of a geothermal power generation plant from plugging or clogging by the deposition of silicates. Accordingly, a large amount of inorganic materials enriched in silicates are produced in the geothermal power generation plant. The sludge produced is required to be used for some purpose. In this work, the application of the sludge for the catalyst of coal liquefaction was investigated by preparing supported catalysts and measuring the activity and the property of the catalyst.

Three types of the sludge obtained from the geothermal power generation plant at Ohtake in Kyushu were used for the preparation of coal liquefaction catalyst. In some cases, the pore size distribution of the sludge was changed by heating at temperatures

Table 1. Chemical composition of sludge

	SiO_2	Al_2O_3	Na_2O	Fe_2O_3	CaO	TiO_2	K_2O
S 1	92.3	3.7	3.7	0.08	0.09	0.03	0.18
S 2	93.6	3.3	2.5	0.08	0.07	0.03	0.16
S 3	85.3	12.7	0.05	0.89	0.15	0.78	0.10

These analyses were made by using an atomic absorption spectrometer.

over 500 °C or treating under hydrothermal conditions in order to get a suitable pore size distribution. The sludge was impregnated in an aqueous solution of ammonium molybdate. After drying at 110 °C for 10 h, the catalyst was calcined at 500 °C for 4 h. In some cases, catalysts were presulfided in a 4 vol% H_2S/H_2 mixture at 380 °C for 4 h before liquefaction.

Coal liquefaction tests were carried out by using batch type reactors.[1)] The batch reactor and it's conditions were chosen to give a sensitive screening test to measure the activity of coal liquefaction catalyst. The batch tests were run in two modes, a normal heat-up or a rapid heat-up mode. In the normal heat-up mode, 60 g of coal cruched below 100 mesh, 5 g of catalyst and 140 g of hydrogenated anthracene oil were mixed, and were then charged into the stirred autoclave (500 ml, stainless steel). The unit was pressurized with hydrogen to 10 MPa and was subsequently heated to 400 °C, while the pressure increased to approximately 20 MPa. After 60 min of reaction the autoclave was cooled to room temperature. In the rapid heat-up mode, four microautoclaves (50 ml) pressurized to 100 kg/cm^2 were injected into an oven heated at 400 °C. Fractions of the reaction product were based on the solubility in toluene and hexane. By measuring these fractions, Asphaltene (toluene soluble, hexane insoluble) and Oil (hexane soluble) are defined.

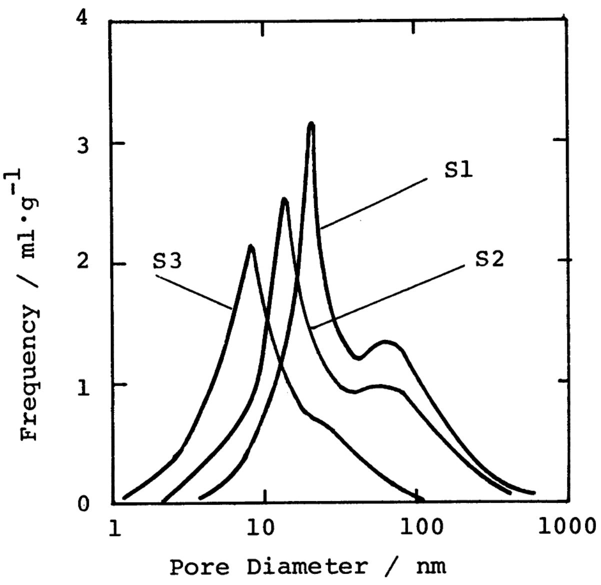

Fig. 1. Pore size distribution of sludge.

Measurements of surface area, pore volume and pore size distribution were carried out by the BET method (CARLO ERBA, Sorptometic 1800) and with a porosimeter (AMINCO 60000 psi). The amount and intensity of acidic groups on the catalyst was examined by

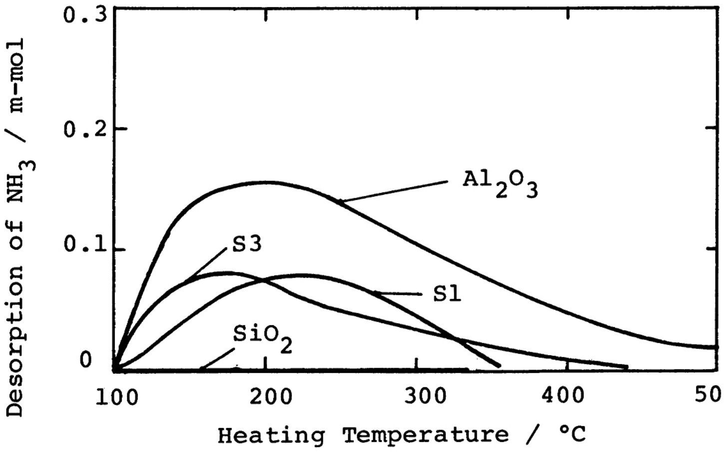

Fig. 2. Desorption of NH_3 versus heating temperature.

measuring the amount of ammonia desorbed from the catalyst with increasing temperature. Before measurement of acidity, the catalyst was heated under vacuum at 500 °C for 24 h and then exposed in ammonia at room temperature.

The composition of the sludge varies from each other by the procedure of removing silicates in hot water (Table 1). Surface areas and pore volumes of these sludge are 270 - 320 m^2/g and 0.87 - 2.62 ml/g, respectively. Figure 1 shows pore size distributions of the sludge. Average pore diameters of Sludge 1 and 2 are larger then that of Sludge 3. A wide-range pore size distribution of the sludge (3 - 600 nm) seems to be suitable for the catalyst of coal liquefaction. The amount of acidic groups of the sludge are much less than that of γ-Al_2O_3, the intensity of acidic groups being also smaller than that of γ-Al_2O_3 (Fig. 2). However, the sludge has some amounts of acidic groups as compared with those of SiO_2, while there is a little difference in acidity between Sludge 1 and 3. These properties will be effective for decreasing the carbonaceous deposition on the catalyst comparing with the case of alumina supported catalysts.

Figure 3 shows changes in the pore size distribution of Sludge 1 after heating. Hydrothermal treatments also changed pore size distributions of the sludge. These data indicate that the pore size distribution as well as the surface area can be controlled by heating or hydrotreating of the sludge. The pore size distribution of the catalyst effective for coal liquefaction is different in each process. For example, smaller pore sizes will be required for the catalyst for a secondary hydrogenation of coal liquid comparing with the one for the first stage liquefaction. Accordingly, the techniques to control the pore size of the sludge is useful to develop highly active catalysts.

Results of coal liquefaction tests are summarized in Table 2. The sludge was found to be active by itself for coal

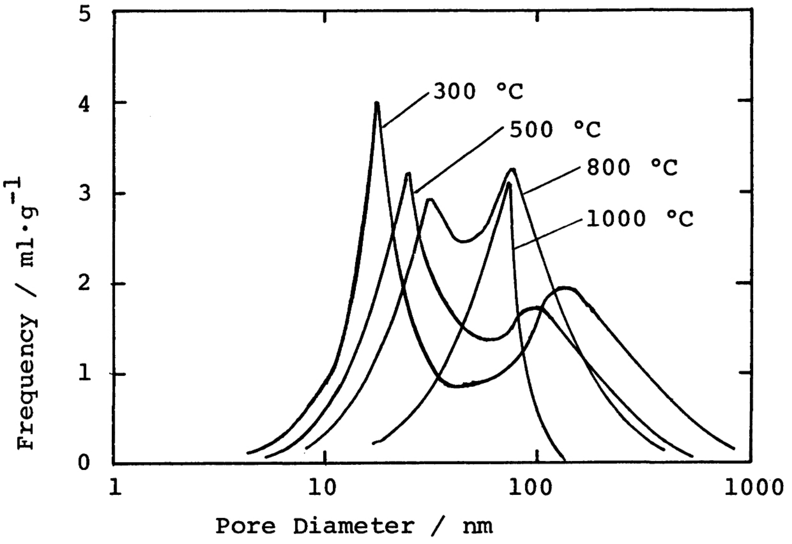

Fig. 3. Change in pore size distribution after heating.

Table 2. Catalytic activity of sludge catalyst

	None	S 1	S 3	MoO_3/S1	MoO_3/S3	Cat.1[a)]	Cat.2[b)]
Oil+Asp.(wt%)	56.6	63.5	64.5	89.6	87.6	85.4	85.8
Oil (wt%)	36.5	38.2	38.7	56.0	59.1	47.9	54.0
Oil/Oil+Asp.	0.65	0.60	0.60	0.63	0.68	0.56	0.63

10wt% of MoO_3 was supported on sludge. Sulfur was added into the reactor.
a) : $CoO-MoO_3/Al_2O_3$. b) : $NiO-MoO_3/Al_2O_3$.

liquefaction catalyst. After supporting 10 wt% of MoO_3 on the sludge, the activity of the supported catalyst was superior to commercially available $NiO-MoO_3/Al_2O_3$ or $CoO-MoO_3/Al_2O_3$ catalyst which is considered to be the most active for coal liquefaction. As shown in Table 2 high conversion of coal was obtained on the supported catalyst having larger pore sizes (Sludge 1). On the contrary, the supported catalyst having smaller pore sizes (Sludge 3) was effective in increasing oil yield. These results were in good agreement with our other study in which the effect of the pore size on the catalytic activity of the catalyst was studied.[2)]

In this research, the application of the sludge for the catalyst of coal liquefaction was investigated. The sludge was found to have suitable properties required for the catalyst of coal liquefaction. In fact the catalysts prepared by supporting MoO_3 on the sludge showed higher activities comparing with commercially available catalysts using alumina supports. The pore sizes and the surface areas can be changed by heating or hydrotreating. Moreover, the sludge is inexpensive and readily available. Therefore, it is considered that this new type of coal liquefaction catalyst will be an alternative one for coal liquefaction. This catalyst will be also useful for the catalyst in the field of hydroprocessing of heavy oil.

References

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