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METAL DEPOSITS ON Ni-Mo CATALYST USED FOR COAL LIQUEFACTION

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The characterization of Nio-MoO_3-Al_2O_3 catalyst used for coal liquefaction was performed using some spectrometers. Behaviors of metal elements deposited on the catalyst, such as Fe, Ti, Ca, and Na, were clarified in this work.

Molybdena catalysts supported on γ-Al_2O_3, which contain cobalt or nickel as promoter have long been used for hydrodesulfurization of the petroleum fractions containing sulfur$^{1,2)}$. Recently Co-Mo or Ni-Mo supported catalysts have also been used for direct coal liquefaction$^{3-8)}$. However, the catalysts used for hydrogenation of coal are more rapidly deactivated by the deposition of metal elements and by the formation of coke on the catalysts than catalysts used for petroleum purification. It is possible to regenerate the catalysts, which have been deactivated by the formation of coke, by calcining them in air$^{8)}$. But it is difficult to remove the metal deposits from catalysts effectively. Therefore the establishment of practical methods and engineering processes both for the lessining of catalyst poisoning from the metal deposits and for catalyst regeneration is needed. During the course of development of these methods and processes, it will be most important to understand fully the interaction of metal elements with catalysts. From this point of view, the behavior of metal elements during coal liquefaction was studied for this paper.

A Ni-Mo catalyst was prepared by an impregnation method. The γ-Al_2O_3 support (1mmø) having bimodal pore size distribution (average pore diameter : 10nm and 300nm) was impregnated at 30°C with the solutions of ammonium molybdate and nickel nitrate. The catalyst was dried at 110°C for 10h, and calcined in air at 500°C

Table 1 Composition of Ash in Taiheiyo Coal

Ash	SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	TiO_2	K_2O	MgO	V_2O_5
wt%	65.1	20.0	5.6	5.2	1.6	0.86	0.63	0.63	0.33

The amount of each element was measured by AAS.
Taiheiyo coal used in this work contains 16.1wt% of ash in it.

for 4h. The catalyst prepared contains NiO (3.6wt%) and MoO_3 (15.2wt%), which were measured by an atomic absorption spectrometer (AAS, Seiko SAS-722) and an absorptiometry (Shimazu UB 360), respectively. Taiheiyo coal containing high-ash content (Table 1) was chosen in this study to clarify the depth profile of metal deposits on the catalyst.

The catalyst was presulfided in a gas mixture containing H_2 and H_2S (4 vol%) at 380°C for 4h. The catalyst (5g) was placed in a steel wire basket in a stirred autoclave (500ml) to prevent the catalyst from crushing during reaction. Coal (60g) and hydrogenated anthracene oil (140g) were charged into the autoclave. The unit was pressurized with hydrogen to 100 kg/cm^2, and was subsequently heated to 410°C. After 60 minutes of reaction the unit was cooled to room temperature and the catalyst was washed by tetrahydrofuran using a soxhlet extractor for 16h, followed by vacuum drying (110°C, 10^{-1}Pa).

Amounts of Fe, Ti, and Ca deposited on the catalyst were determined by an X-ray fluorescence analyzer (XFA, Rigaku, Ultra Trace System) with glass bead method. Flame emission spectrometer (FES) was used for the measurement of Na and was AAS for that of Mg. Surface chemical composition and property were investigated by using an X-ray photoelectron spectrometer (XPS, Shimazu ASIX 1000) and Al anode (300w). Both an X-ray microanalyzer (XMA, Shimazu EMX-7) and an ion microanalyzer (Hitachi IMA-2) were used to clarify the depth profiles of metal elements deposited on the aged catalyst.

XFA, FES, and AAS analyses showed that main metal elements deposited on the catalyst are Fe, Ca, Ti, Na, and Mg. The XPS study on fresh and aged catalysts showed that carbonaceous materials and some metal elements such as Fe, Ca, Ti, Na, Mg, and Si, which were originated from coal, increased with reaction time on outer surface layers of the catalyst, while intensities of spectra from the catalyst components were relatively weakened. Quantitative analysis of the aged catalyst is shown in Table 2. The results from XFA, FES, and AAS show the chemical composition of the whole catalyst particle. On the other hand, an XPS result shows

Table 2 Difference in Concentration of Metal Deposit between Surface and Bulk for Aged Catalyst

	Analyzer	Fe_2O_3	CaO	TiO_2	Na_2O	MgO
Bulk	XFA, FES, AAS	0.0034	0.0033	0.0025	0.0087^{*1}	0.0010^{*2}
Surface	XPS	0.22	0.29	0.22	0.09	0.39

Figures show the ratio for Al_2O_3 concentration. XPS analysis was performed using measured areas of spectra as demonstrated in the recent paper (9).

*1 : Flame emission, *2 : Atomic absorption.

the concentration of metal deposits on the external surface of the catalyst particle. Accordingly, the difference between them shows that the amounts of deposited metals decrease with the depth from external surface to the center of the catalyst particle. Further confirmations for the distribution of metal foulants came from the XMA and the IMA measurements. The XMA measurement (Fig. 1) showed that the inorganic materials except carbon and sulfur deposited on the external surface layers (< a few hundred micrometers) of the catalyst particle. The analysis by IMA showed that there was a large difference in the depth profile among metals near outer surface layers (< a few micrometers) as shown in Fig. 2. Concentrations of Fe and Si decreased rapidly with the depth from external surface to the center of the catalyst particle, while those of Ca, Na, and Mg decreased gradually. On the other hand, amount of Ti increased at the inner part of the particle surface.

These phenomena seem to be attributed to the difference in the particle size and the chemical state of ash components in coal, and/or the interactions of metal elements in ash with the catalyst particle. It is also considered that there is a difference in the degree of the deactivation for the catalytic activity among each element deposited. These metal elements deposited on the outer surface will decrease the effective active sites of the catalyst by plugging or narrowing pores on the

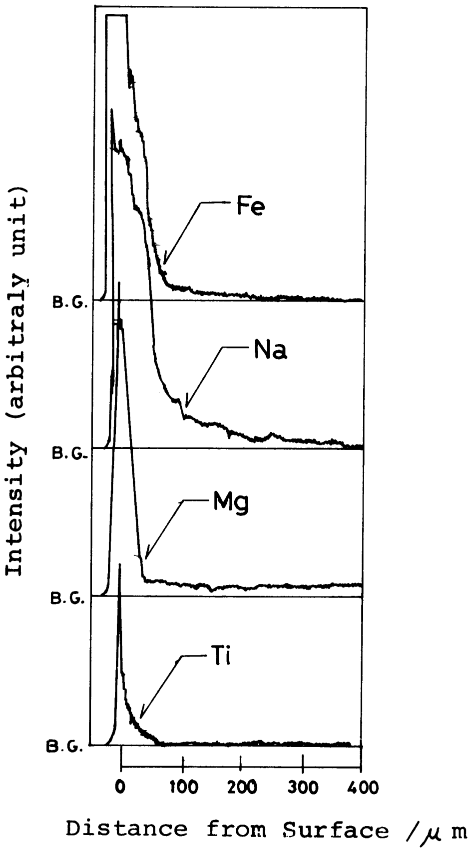

Fig. 1 Depth Profile of Metal Deposition on the Catalyst Measured by XMA

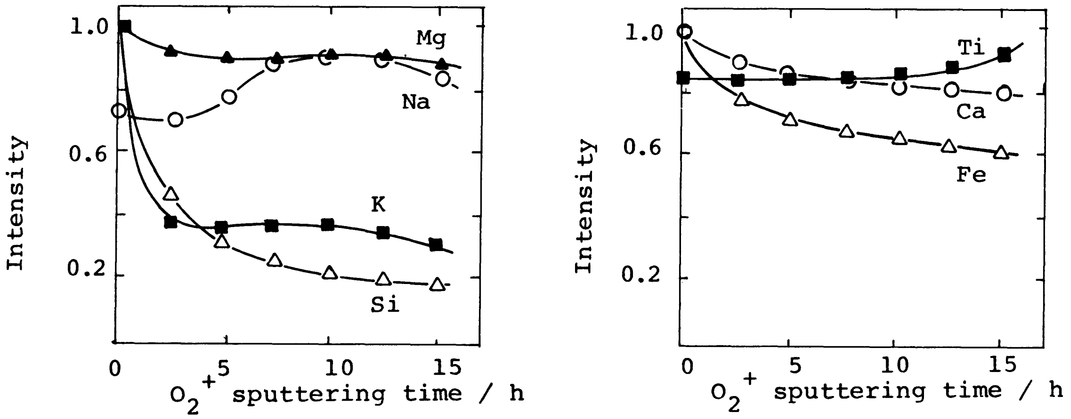

Fig. 2 Depth Profile of Metal Deposit on the Catalyst measured by IMA Intensities of metals were normalyzed using the intensity of Al.

catalyst surface. Moreover there will be a change in the chemical state of active species of the catalyst by forming complexes with some metal elements orginated from coal. As mentioned above, the characterization of the catalyst surface is more important than that of bulk if one wants to know the effect of metal deposits on the activity and the life of the catalyst used for coal liquefaction. More information, such as chemical state of the catalyst and ash components, can be obtained by surface analysis. More research is now needed on such alumina-molybdena catalysts to understand fully the behavior of metal elements on catalysts and to clarify the mechanism of catalyst deactivation.

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