

New Type of Crystalline Support for HDS Catalyst

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Molybdenum sulfide catalysts supported on crystalline $\text{CoO} \cdot \text{Al}_2\text{O}_3$ spinel showed much higher hydrocracking activity of C-C bonds and lower hydrogenation activity of aromatic rings than those other supports. Superior HDS activity of the catalyst was obtained on this new type of crystalline supports.

Molybdenum sulfide catalyst containing nickel or cobalt promoter has long been used for hydrodesulfurization (HDS) in the petroleum industry. In these catalysts, alumina supports such as $\gamma\text{-Al}_2\text{O}_3$ have been employed. However, improvement in the selectivity of the molybdenum catalyst for HDS reaction is now required to develop highly selective catalysts and to minimize the consumption of hydrogen. During the course of development of these catalysts,¹⁾ preparation of new type supports will be most important. The present authors have been trying to find better catalysts by applying new type of supports. The supports employed in this work were synthesized from magnesium, cobalt and aluminium nitrates solution by a spray pyrolysis method.²⁾ The specific surface areas of the supports prepared are 50 -150 m^2/g . 10wt% MoO_3 and 2wt% NiO -7wt% MoO_3 were then loaded on the supports by using an impregnation method. After sulfiding at 400 °C for 1 h, each function of the catalyst such as HYC (hydrocracking) activity of C-C bonds or HYG (hydrogenation) activity of aromatic rings was examined by using model test reactions.¹⁾

Table 1 shows the composition and surface area of the spinel type support synthesized by changing the atomic ratio of Co/Mg. X-Ray diffraction measurement shows that support A is stoichiometric MgAl_2O_4 spinel. Support G was also found to be a spinel type crystal. HYC and HYG activities of Mo catalysts on various supports evaluated by the model test reactions are shown in Fig.1. The HYC activity increased with the increase of Co/Mg ratio, though surface area decreased with increasing CoO content. On the contrary, HYG activity decreased with the increase of Co/Mg ratio.

XPS measurement showed that cobalt in the support exists as an oxide after presulfiding. This result suggests that these crystalline supports are stable and that no exchange between cobalt and nickel or molybdenum occurs during presulfiding. Ni-Mo catalyst supported on CoAl_2O_4 also showed higher HYC activity and lower HYG activity. The ratio of activity index (HYC/HYG) for the Mo catalysts increased

from 0.1 to 1.0 with the increase of CoO content. On the other hand, the ratio values obtained from commercially available catalysts are from 0.2 to 0.5, showing that the catalysts prepared in this work have a qualitatively different catalytic function.

These works showed that spinel types of CoAl_2O_4 supports give relatively higher HYC activity and rather lower HYG activity. These supported catalysts will be suitable for HDS reaction of petroleum distillate. In fact, higher HDS activities were obtained over these supports. On the other hand, MgAl_2O_4 spinel gave lower HYC activity and relatively higher HYG activity. The reason for this behavior is not yet clear. Crystalline supports will increase the concentration of active ions on catalyst surface. EXAFS results for γ -alumina supported Ni-Mo sulfide catalyst showed only Ni-O species, though Ni-S species were observed by XPS. On the other hand, Ni-S species were observed on the spinel supported catalysts by EXAFS measurement. These results indicate that the formation of aluminate with nickel promoter does not occur, resulting in enrichment of promoter ions on the catalyst surface. Chemical properties of crystalline supports will also affect catalytic functions of the catalyst. However, no correlation was found between acidic property and HYC activity when reaction was performed under high pressure of H_2 . The surface area of CoAl_2O_4 support is much less than that of MgAl_2O_4 . Therefore, there is more growth of MoS_2 like crystals on CoAl_2O_4 support than that on MgAl_2O_4 support. This may be one of the reasons for these phenomena. The new support developed in this work has a novel function which has never been found in past supports. Accumulating basic knowledge about this new support, especially about HYC active sites, will lead to developing a new generation of HDS catalyst.

References

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Table 1. Properties of supports

Support	Composition			Surface area $\text{m}^2 \text{g}^{-1}$
	CoO	MgO	Al_2O_3	
A	0	1.0	1.0	142
B	0.2	0.8	1.0	109
C	0.4	0.6	1.0	95
D	0.5	0.5	1.0	84
E	0.6	0.4	1.0	77
F	0.8	0.2	1.0	65
G	1.0	0	1.0	57

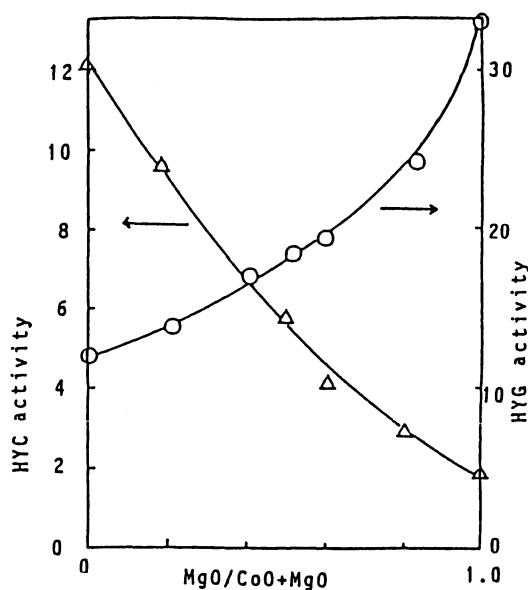


Fig. 1. HYC and HYG activities of Catalyst.

HYC of diphenylmethane and HYG of 1-methylnaphthalene were performed for testing catalyst functions.

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