

SELECTIVE HYDRODESULFURIZATION OF 4,6-DIMETHYL-
DIBENZOTHIOPHENE IN THE DOMINANT PRESENCE OF
NAPHTHALENE OVER HYBRID CoMo / Al₂O₃
AND Ru / Al₂O₃ CATALYSTS

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INTRODUCTION

It has been revealed that significant desulfurization of refractory 4-methyldibenzothiophene and 4,6-dimethyldibenzothiophene (4,6-DMDBT) is very essential to achieve the low sulfur level of gas oil requested by the current regulation (1). Their direct desulfurization through the interaction of their sulfur atom with the catalyst surface is sterically hindered by its neighbouring methyl groups. The substrate is found kinetically to be hydrogenated at one of its phenyl rings prior to the desulfurization in order to reduce the steric hindrance through non-planar configuration (2-4). NiMo / Al₂O₃ was reported to be superior to CoMo / Al₂O₃ in the deep desulfurization, because of its higher hydrogenation activity (2). However, such a hydrogenation route suffers severe inhibition by aromatic species in their dominant presence (3), because 4,6-DMDBT must compete with the aromatic species to the hydrogenation sites on the catalysts. The aromatic species up to 30 wt % in the gas oil was that completely stop the desulfurization of the particular substrate (3). The catalyst for the selective hydrogenation of 4,6-DMDBT in the dominant aromatic partners is most wanted to achieve its extensive desulfurization in the gas oil, although there have been reported activities of various transition metal sulfides for HDS of dibenzothiophene (5), and hydrogenation of aromatic hydrocarbons (6).

The present authors have reported that different hydrogenation selectivity for 4,6-DMDBT and naphthalene over mixed sulfides of molybdenum and other transition metals (7). Ru-CoMo / Al₂O₃ catalyst which was impregnated from aqueous HCl of Co, Mo and Ru salts showed four times higher hydrogenation selectivity for 4,6-DMDBT than NiMo / Al₂O₃ catalyst (8). In the present study, HDS of 4,6-DMDBT in decane containing a significant amount of naphthalene was examined over a hybrid of CoMo / Al₂O₃ and Ru / Al₂O₃ to design the selective hydrogenation and successive desulfurization of 4,6-DMDBT in an aromatic moiety. Its activity was compared to those of CoMo / Al₂O₃, NiMo / Al₂O₃ and Ru / Al₂O₃ in their single use.

EXPERIMENTALS

Chemicals and Catalysts ; 4,6-DMDBT was synthesized according to the reference (9). Commercially available (NH₄)₂MoO₄, Co(NO₃)₂·6H₂O, and RuCl₃·3H₂O were used as catalyst precursor salts. Al₂O₃ as the catalyst support was commercially available.

The precursor salt was impregnated onto Al₂O₃ according to an incipient wetness impregnation procedure. Content weight of metal oxide on each catalyst as follows ; Co(0.25 wt%)-Mo(15 wt%) / Al₂O₃, Ni(1 wt%)-Mo(15 wt%) / Al₂O₃ and Ru(6 wt%) / Al₂O₃, respectively. After the impregnation, the catalyst was dried at 160°C, calcined at 420°C under air flow, and presulfurized at 360°C for 2h by flowing H₂S (5 vol %) in H₂ under atmospheric pressure just before its use.

Reaction ; HDS of 4,6-DMDBT in decane with naphthalene was performed in a 50ml batch-autoclave at 300°C under 2.5MPa H₂ pressure for 1.0 - 2.5h, using 1.5g catalyst and 10g substrate including solvent. The concentrations of 4,6-DMDBT and naphthalene were 0.1 and 10 wt %, respectively. After the reaction, products were qualitatively and quantitatively analyzed by GC-MS, GC-FID (Yanaco G-3800 and G-100) and GC-FPD (Yanaco G-3800 and 50ml OV-101).

RESULTS

HDS Activity of 4,6-DMDBT

Fig. 1(A) and (B) illustrates the conversion of 4,6-DMDBT and naphthalene versus reaction time, respectively, over CoMo / Al₂O₃, NiMo / Al₂O₃, Ru / Al₂O₃ and a hybrid of CoMo / Al₂O₃ and Ru / Al₂O₃ at 300°C. CoMo / Al₂O₃ exhibited an excellent activity for HDS of 4,6-DMDBT, giving conversions of 46% by 1h and 74% by 2h as shown in Fig. 1(A). The particular NiMo / Al₂O₃ was inferior to CoMo / Al₂O₃, giving conversions of 24% by 1h and 47% by 2h. Ru / Al₂O₃ was very inactive for HDS, giving conversions of 6% by 1h and 8% by 2h. The hybrid showed the highest activity for HDS of 4,6-DMDBT among the catalyst examined, giving conversions of 71% by 1h, 87% by 2h and 90% by 2.5h, when 20 wt% of Ru / Al₂O₃ and 15 wt% CoMo / Al₂O₃ were used. NiMo / Al₂O₃ showed high activity for the hydrogenation of naphthalene, giving conversion of 90% by 1h. Tetralin and decalin were the products, their yields of the latter produced being 6% by 1h and 18% by 2h, respectively. CoMo / Al₂O₃ and its hybrid with Ru / Al₂O₃ exhibited similar activities, being much inferior to NiMo / Al₂O₃ to give conversion of 61 and 77% by 1h, respectively. Decalin of 80% produced by 1h over CoMo / Al₂O₃, 5% by 1h over the hybrids. Ru / Al₂O₃ was very inactive, giving a conversion of 10% by 1h and 23% by 2h.

Products from 4,6-DMDBT

Fig. 2(A) and (B) illustrates the product yields from 4,6-DMDBT over the CoMo / Al₂O₃, NiMo / Al₂O₃, Ru / Al₂O₃ and a hybrid of CoMo / Al₂O₃ and Ru / Al₂O₃ at 300 °C. The major products were hydrodesulfurization products B_{4,6} and A_{4,6}, respectively. B_{4,6} and A_{4,6} were produced through the hydrogenation of one or both phenyl ring in 4,6-DMDBT. In addition, hydrogenation products of H and desulfurized product C_{4,6} were also found in minor yields, being produced through the hydrogenation of one phenyl ring and successive direct sulfur elimination, respectively, by the yields over CoMo / Al₂O₃, NiMo / Al₂O₃, Ru / Al₂O₃ and hybrids with 10 and 20 wt% Ru / Al₂O₃, respectively, as summarized in Table 1. CoMo / Al₂O₃ and the hybrid provided B_{4,6} by the yields of 24 and 35%, respectively, by 1h, while the yields of H were 3 and 10% by 1h, respectively. The yield of H decreased beyond 1h over CoMo / Al₂O₃ and hybrids, indicating its consecutive reaction pathway. Large yield of A_{4,6} over the hybrid was noted, being produced of A_{4,6} 43% and 45% by 2h over hybrid with Ru / Al₂O₃ 10 wt% and 20 wt%, respectively, while giving conversions of 29% and 11% by 2h over CoMo / Al₂O₃ and NiMo / Al₂O₃, respectively. Yield of C_{4,6} were 0 to 2%, respectively over these catalysts, indicating very minor contribution of direct elimination of sulfur from 4,6-DMDBT as reported previously (2).

The particular Ru / Al₂O₃ was inferior in the desulfurization to CoMo / Al₂O₃ and the hybrid, however it produced more H, giving its yield of 6% by 1h, and 8% by 2h. Longer reaction time beyond 1h increased the yield, although no definite product of desulfurization was found.

DISCUSSION

Fig. 3 illustrates the hydrodesulfurization scheme of 4,6-DMDBT carries two methyl groups on 4 and 6 carbons neighbouring sulfur atom. Because two methyl groups on the sulfur atom, sterically hinder the interaction of sulfur through its Pz orbital with the sulfur vacancy of sulfide catalyst, the direct elimination of sulfur atom is strongly hindered. The hydrogenation of one of two phenyl rings breaks the co-planarity of the dibenzothiophene skeleton, moderating the steric hindrance of the methyl groups in the neighbors of the sulfur atom. Furthermore the hydrogenation of the neighboring phenyl ring increases electron density of the sulfur atom enhance its elimination through electron density interaction with the active site. Thus, it is very essential to hydrogenate the phenyl ring of 4,6-DMDBT for the accelerate of its desulfurization.

The hydrogenation of 4,6-DMDBT at one of its phenyl ring certainly competes the hydrogenation active site with aromatic partners of dominant presence in the diesel oil as observed in the present study. The selective hydrogenation of 4,6-DMDBT is very essential to accelerate its desulfurization. NiMo / Al₂O₃ exhibited preferable hydrogenation of naphthalene on the conversion-base to that of 4,6-DMDBT in the dominant presence of the former substrate. While CoMo / Al₂O₃ and the hybrid of CoMo / Al₂O₃ and Ru / Al₂O₃ did similar or slightly preferable selectivity to 4,6-DMDBT, respectively. Thus, the latter catalyst promoted the largest desulfurization activity of 4,6-DMDBT with the smallest hydrogenation of naphthalene.

The products for 4,6-DMDBT are classified into three categories, hydrogenation, direct-desulfurization and desulfurization through the hydrogenation. Ru / Al₂O₃ produce more hydrogenation product of 4,6-DMDBT than CoMo / Al₂O₃ and the hybrid catalyst, because of its insecutive desulfurization reactivity, while the hybrid catalyst gave the largest yield of bicyclohexyl which is the desulfurized product of both rings hydrogenated. Based on the above discussion, the hybrid catalyst performed the selective desulfurization of 4,6-DMDBT in the dominant presence of naphthalene through the selective hydrogenation of substrate over Ru / Al₂O₃ and the desulfurization of hydrogenated products over CoMo / Al₂O₃. High activity of NiMo / Al₂O₃ for the non-selective hydrogenation rules out the efficiency of its hybrid with Ru / Al₂O₃.

The origin of selectivity for 4,6-DMDBT may be worthwhile for speculation, although no sufficient evidence is available at moment. π orbital localized on the sulfur atom in 4,6-DMDBT may interact preferable to d orbital of the sulfide catalyst to that of the naphthalene ring, being free from the steric hindrance of its methyl groups. Such a Sr - Md interaction may be expected more strongly with Ru than Ni, Co or Mo because of the higher polarizability of noble Ru, allowing the higher selectivity of Ru / Al₂O₃ to 4,6-DMDBT than naphthalene.

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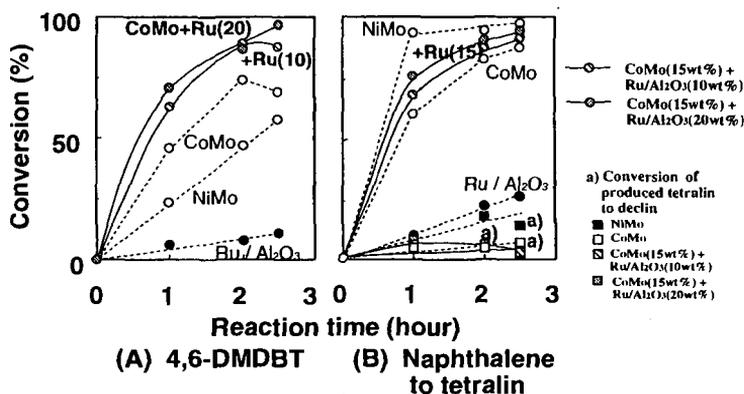


Fig.1 Conversions of 4,6-DMDBT and naphthalene over a hybrids of CoMo / Al₂O₃ and Ru / Al₂O₃. (300°C-2.5MPa, 4,6-DMDBT 0.1wt% + Nap 10wt% in decane, Catalyst content; 15 wt%, (CoMo / Al₂O₃) / (Ru / Al₂O₃) = 1.0 and 2.0)

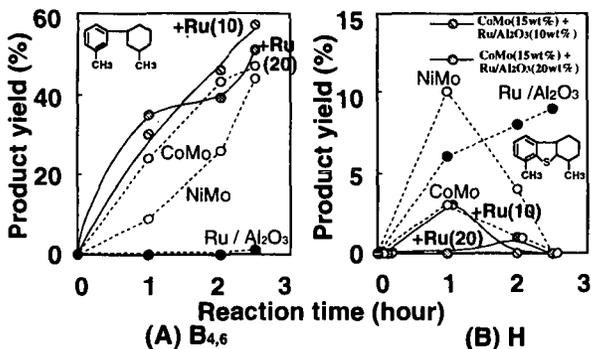


Fig.2 Products from 4,6-DMDBT over a hybrids of CoMo / Al₂O₃ and Ru / Al₂O₃.

Table1 Product distribution of 4,6-Dimethylbenzothiophene over NiMo, CoMo, Ru / Al₂O₃ and a hybrid of CoMo / Al₂O₃ and Ru / Al₂O₃.

Catalyst	Conversion ^{a)} of 4,6-DMDBT to A _{4,6} (%) ^{b)}	Conversion ^{a)} of 4,6-DMDBT to C _{4,6} (%) ^{c)}
Co-Mo / Al ₂ O ₃	29	1
Ni-Mo / Al ₂ O ₃	12	5
Ru / Al ₂ O ₃	0	0
Co-Mo / Al ₂ O ₃ + Ru / Al ₂ O ₃ (10wt%)	43	0
Co-Mo / Al ₂ O ₃ + Ru / Al ₂ O ₃ (20wt%)	45	2

a) reaction condition: 300°C-2.5MPa-2h, 4,6-DMDBT 0.1wt% and Nap 10wt%

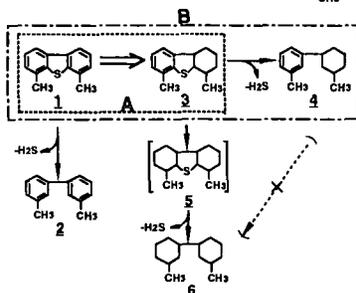
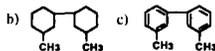


Fig.3 Reaction Pathway of 4,6-Dimethylbenzothiophene over Mo Sulfide Based on Catalyst. (300°C-2.5MPa)