

Preparation and Modification of Recoverable Particle Catalysts for Coal Liquefaction

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INTRODUCTION

Highly active catalyst of higher activity is still a key to design the more efficient coal liquefaction process, which will increase the oil yield, minimize its cost, and environmental impact due to catalyst disposal.

The authors assumed that the recovery and recycle of the catalyst from the residue are an approach to improve the economy of coal liquefaction and to reduce the solid waste.^{1,2} The organic residue has been recycled with the catalyst and minerals to the primary liquefaction stage as the bottom recycle. Its favorable results have been reported, although the accumulation of the inorganic solid requires a fixed rate of purging the catalyst as well as minerals.

The authors have examined Fe_3Al , strong ferromagnetic particles, as one of the potentially recoverable catalysts^{1,2}, in order to prepare an active catalyst with the recovery function through magnetic separation.

Ketjen Black(KB) particles have hollow spheric structure which carries their extremely high surface area and for high dispersion of catalytic species and low specific gravity for catalyst recovery through the gravimetric separation. The activity of carbon particles and their supporting NiMo catalysts have been reported,^{3,5} to exhibit the high activity for the hydrogen transferring cracking, hydrodesulfurization and hydrocracking. KB-supported NiMo catalyst is expected to be one of the most promising catalysts to exhibit a large activity for hydrogenation and liquefaction at its least catalyst amount. To achieve the successful reuse of recovered catalyst, the deactivation, contamination, and adhesion of the catalyst should be avoided by designing the liquefaction and distillation schemes. The pretreatment and hydrogen transferring liquefaction prior to the catalytic steps are responsible to define the forms of minerals and to reduce the coke precursors⁶⁻⁸. Separation of the catalyst should assure its dispersed state.

In the present study, two types of recoverable catalysts were examined in terms of catalytic activities for the liquefactions of Wyoming coal (USA) and Tanitohalm coal (Indonesia). Optimization of reaction conditions and design of recovery procedures were studied in order to practice recovery and recycle of the catalysts in the liquefaction of both coals as well as to increase the oil yield with the least yield of organic residue.

EXPERIMENTAL

Some properties of Ketjen Black(KB) EC and JD, and Fe₃Al examined in the present study are summarized in Table 1. Ni, Mo-supported KB catalysts (NiMo/KB) were prepared by impregnation method from Ni(NO₃)₂ or Ni(OAc)₂ and (NH₄)₆Mo₇O₂₄ or Mo dioxyacetylacetonate (MoO₂-AA) in their water or methanol solutions, respectively. The catalyst precursors were dried at 120°C for 12 h in vacuo and presulfided in 5% H₂S/H₂ flow at 360°C for 2 or 3 h prior to the reactions. KB was pretreated in conc. nitric acid at 80°C for 1 h followed by filtration, repeated washing with water, and drying at 120°C in vacuo. The nitric acid-treated KB JD was abbreviated as KB JD-O.

Synthetic pyrite powder and KF842 (NiMo/Al₂O₃, pellet or its powder (<60 mesh)) provided by NEDO and Nippon Ketjen Co., respectively were also used as the reference catalysts for the comparison. These catalysts and Fe₃Al particles were also presulfided under the same conditions as KB-based catalysts.

The elemental analyses of Wyoming and Tanitohalm coals are summarized in Table 2. Tetralin (TL) of commercial guaranteed grade was used as a liquefaction (hydrogen donating) solvent. The liquefaction was carried out in an autoclave of 50-ml capacity (11 or 20°C/min) at the prescribed temperatures(380 - 460°C). The coal (3.0 g), the solvent (4.5 g) and catalyst (0.09 - 0.10 g) were charged into the autoclave, which was then pressurized with hydrogen to 6~9.3 MPa at room temperature after replacing the air with nitrogen gas. After the reaction, the product remaining in the autoclave was recovered with THF, and extracted in sequence with hexane, acetone and THF after evaporating THF. The hexane soluble (HS), hexane insoluble-acetone soluble (HI-AS), acetone insoluble-THF soluble (AcI-THFS), and THF insoluble (THFI) substances were defined as oil(O), asphaltene(A), preasphaltene(PA), and residue(R), respectively. The gas yield was calculated by the difference between weights of the initial coal and recovered product.

RESULTS AND DISCUSSIONS

Liquefaction of Wyoming Coal with KB-supported NiMo Catalyst

Figure 1 illustrates the effects of reaction temperatures on the liquefaction of Wyoming coal with KB-ED-supported NiMo catalyst under initial H₂ pressure of 6.6 MPa at 380 - 460°C. The oil yield increased with reaction temperature in the range of 380 - 440°C, reaching the maximum oil yield of 40 % at 440°C, and then decreased at 460°C with a significant increase of gas yield.

Figure 2 shows the comparative activity of the KB JD-O-supported NiMo catalyst prepared by the successive impregnation method with the commercial NiMo/Al₂O₃ catalyst and synthesized pyrite for the liquefaction of Wyoming coal at 440°C for 20 min. The KB-supported NiMo catalyst gave the higher oil and asphaltene yields with less yields of preasphaltene and residue. The commercial NiMo and pyrite catalysts provided the lower oil plus asphaltene yields with higher gas and preasphaltene yields and higher asphaltene yield, respectively.

Liquefaction of Tanitohalm Coal with Recoverable Catalysts

Figures 3 and 4 compare liquefaction results of Tanitohalm coal without and with sulfided Fe₃Al(Fe₃Al-S), NiMo/KB-JD, and synthetic pyrite at 450°C for 60 min under the initial H₂ pressures of 6.0 and 9.3 MPa, respectively. The sulfided NiMo/KB-JD catalyst exhibited the highest activity for the much higher oil yield over 60 % under the higher hydrogen pressure. It is noted that the much lower yields of preasphaltene and residue were obtained in the liquefaction of Tanitohalm coal compared to those of Wyoming coal. The pyrite showed the similar activity as NiMo/KB-JD under the lower hydrogen pressure, although it failed in increasing the oil yield under the higher hydrogen pressure. Sulfided Fe₃Al particles do not essentially show any activity even after the grinding to smaller particle size under the present reaction conditions.

Figures 5 and 6 illustrate the liquefaction of Tanitohalm coal with NiMo/KB-JD catalyst at 380 - 450°C under the initial H₂ pressures of 6.0 and 9.3 MPa, respectively. The oil yield increased very much with reaction temperatures under the higher hydrogen pressure, reaching the maximum yield of 62% with least yields of preasphaltene and residue. In contrast, the oil yield appeared to be saturated around 45% in the temperature range of 420 - 450 °C, while the yields of asphaltene, preasphaltene and residue decreased and the gas yield increased sharply.

Recovery and repeated use of recoverable catalysts

The magnetically recoverable Fe₃Al particles were found to be more easily recovered from the whole liquefaction product than from the THFI residue, because the mineral matters and organic residue in THFI were strongly adhered together to include the catalyst in the grains, making it difficult to recover the catalyst separately.

Ketjen black supporting catalysts were found to be recovered from the whole product by gravimetric floatation technique using methanol, hexane and water in this order, although the weight of recovered catalyst was gained to some extent probably due to the inclusion of organic materials on the catalyst.

The KB-supported catalyst and Fe₃Al were found recoverable after the liquefaction, although some carbon adhesion took place. The KB-supported catalyst exhibited an excellent activity for the coal liquefaction. Addition of acidic properties may provide higher activity for the asphaltene conversion. Fe₃Al is found to have very small activity. Its application as the catalyst support can be examined.

The multi-stage approach consisting of coal pretreatment, solvent-mediated dissolution, and catalytic hydrocracking steps should be further developed to suppress the catalyst deactivation.

References

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Table 1 Some properties of KB carbon blacks and Fe₃Al particles

Samples	Particle size (μm)	Surface area (m^2/g)	Specific gravity (-, $\text{H}_2\text{O}=1$)
Fe ₃ Al	7.2(<500 mesh)	0.5	6.5 - 7.9
KB-EC	30×10^{-3}	800	0.145
KB-JD	30×10^{-3}	1270	0.115

Table 2 Elemental analyses of coals

	wt%, daf basis				H/C (-)	Ash (wt%)
	C	H	N	(O+S)		
Wyoming	68.9	5.4	1.0	24.7	0.94	3.7
Tanitohalm	75.9	5.6	1.5	17.1	0.87	4.8

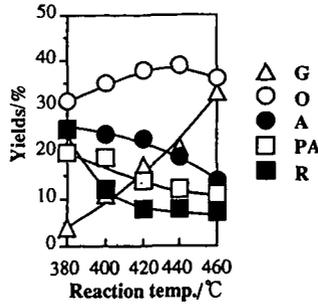


Fig.1 Effect of reaction temperature on the liquefaction of Wyoming coal.

solvent(Tetralin)/coal=1.5
 reaction time : 40min
 H₂ initial pressure : 6.6MPa
 catalyst : Ni-Mo/KB EC(Ni2wt%,Mo10wt%/simultaneous
 impregnation from Ni(NO₃)₂ and (NH₄)₆Mo₇O₂₄)
 3%addition based on coal presulfided at 360°C for 3h

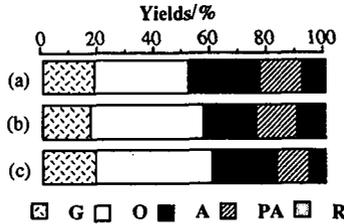


Fig.2 Effect of catalysts species on the liquefaction of Wyoming coal at 440°C

(a) Synthesized FeS₂
 (b) Commercial Ni-Mo/Al₂O₃
 (Ni:3wt%,Mo:15wt%)
 (c)Ni-Mo/KB JD-O(MoO₂-AA, Ni(OAc)₂
 successive impregnation)
 reaction temperature : 440°C
 reaction time : 20min
 (Other conditions are same as Fig.1)

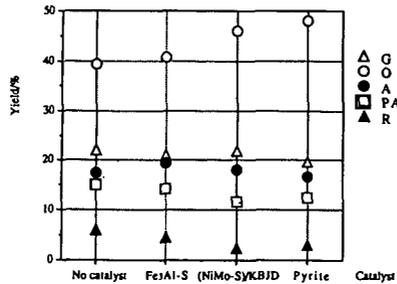


Fig. 3 Activity of catalysts for the liquefaction of Tanitohalm coal under lower H₂ pressure

solvent(Tetralin)/coal(Tanitohalm)=1.5
 Reaction time 60min, Reaction temp. 450°C
 Heating rate 20°C/min, H₂ initial press. 6.0MPa

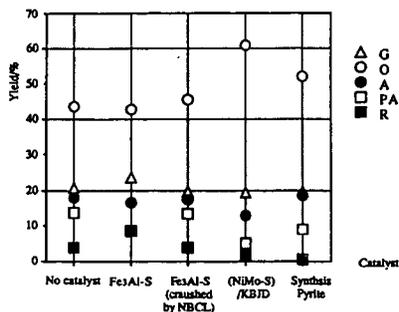


Fig. 4 Activity of catalysts for the liquefaction of Tanitohalm coal under higher H₂ pressure
 solvent(TetraIn)/coal(Tanitohalm)=1.5
 Reaction time 60min, Reaction temp. 450°C
 Heating rate 20°C/min, H₂ initial press. 9.3MPa

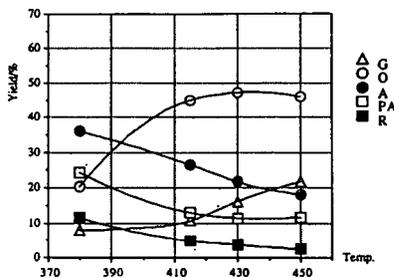


Fig. 5 Effect of reaction temperature on the liquefaction of Tanitohalm coal under lower H₂ pressure
 solvent(TetraIn)/coal(Tanitohalm)=1.5
 Reaction time 60min, Heating rate 20°C/min
 H₂ initial press. 6.0MPa
 catalyst:NiMo/KB JD(Ni:2wt%,Mo10wt%)
 3wt% addition based on coal presulfided at 360°C for 2h

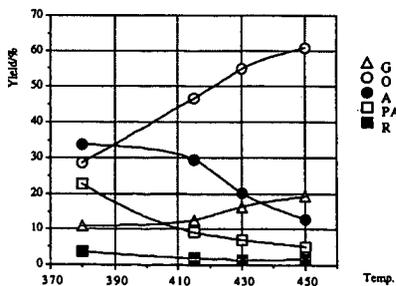


Fig. 6 Effect of reaction temperatures on the liquefaction of Tanitohalm coal under higher H₂ pressure
 solvent/coal=1.5
 Reaction time 60min, Heating rate 20°C/min
 H₂ initial press. 9.3MPa
 catalyst:NiMo/KB JD(Ni:2wt%,Mo10wt%)
 3wt% addition based on coal presulfided at 360°C for 2h