

## Design of Coal Liquefaction Catalysts with Functions for Recovery and Repeated Use

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### Abstract

Active catalysts with functions for recovery and repeated use are expected to reduce the cost and waste in the coal liquefaction. The authors are going to propose basically two types of catalysts which are recoverable for the repeated use. The first type is acid-proof iron catalysts which are recoverable from the mixture with carbonate and chloride minerals. Such catalysts are applicable to particular coals such as Australian brown coal which is completely liquefied, carrying calcium and magnesium carbonates as the major minerals after the primary liquefaction.

Second type is characterized by its sulfur-proof ferromagnetism for the recovery from the minerals and carbons by gradient magnetic field. The authors are going to describe the performances of Fe<sub>3</sub>Al powder and carbon-coated ferrite. Fine powders are essential for their high activity.

The deactivation of the catalyst by carbon and minerals in the liquefaction should be clarified, and a multi-step liquefaction scheme including coal pretreatment can be designed to minimize the deactivation.

### Introduction

Coal liquefaction has been rather extensively investigated for longer than several decades to provide clean liquid fuel from coal in order to meet the increasing demand expected in early next century. However the cost of the liquid fuel is still too high to substitute the fuel from petroleum. Several break-through ideas are strongly wanted to cut the cost currently estimated.

Cut of installation cost appears most effective. The ways are  
1) More moderate conditions

- 2) Better yields per installation, more change of coal and better conversion
- 3) Simpler scheme,
  1. hydrogen source
  2. solid-liquid separation
- 4) Stable operation for years
- 5) Cheaper catalyst and residue handling

The present authors have been studying a complete conversion of coal (no organic residue), with least amount of hydrogen donor in the reactor by multi-stage scheme which includes the coal pretreatment, coal dissolution, catalytic up-grading. The catalyst of primary liquefaction stage is a key to be developed. The authors assumed that the recovery and recycle of the catalyst from the residue is as approach to reach the objective described above.

In the present report, recovery and recycle of the catalyst for the primary liquefaction stage were studied. The basic idea is to recover the catalyst from the inorganic residues which come from the feed coal. According to the natures of inorganic residue, two approaches were examined in the present study.

1. Washing out the inorganic residues such as carbonates which are principally found in Australian brown coal

2. Recovery of the ferromagnetic catalyst from the diamagnetic residue by applying the magnetic gradient.

The catalyst deactivation and adhesion of the catalyst and minerals should be avoided by designing the scheme. The pretreatment and hydrogen transferring liquefaction as the prior to the catalytic steps are responsible. The catalyst and organic residue can be recycled to the liquefaction stage when the organic residue still carries significant amount of reactive portions.

## Experimental

### Materials

The liquefaction (hydrogen donating) solvent was a hydrogenated fluoranthene prepared by catalytic hydrogenation of commercial fluoranthene (FL) using a commercial Ni-Mo catalyst in an autoclave at 250°C, under initial hydrogen pressure of 13.5 MPa. The major component of the solvent was 1,2,3,10b-tetrahydrofluoranthene (4HFL),

which was identified by  $^1\text{H}$  and  $^{13}\text{C}$  n.m.r., quantified by g.c., and purified by recrystallization with n-hexane, removing perhydrofluoranthenes (PHFL).

#### Liquefaction procedure

Liquefaction was carried out in an autoclave (50ml volume). The ground coal (3.0g), the solvent (4.5g) and catalyst (0.9g) were transferred to the autoclave. The products remaining in the autoclave were extracted with THF, benzene and hexane. The hexane soluble (HS), hexane insoluble but benzene soluble (HI-BS), benzene insoluble but THF soluble (BI-THFS), and THF insoluble (THFI) substances were defined as oil, asphaltene, preasphaltene, and residue, respectively. A small amount (<5%) of solvent derived products, which remained in the HI-BS fraction, was corrected by g.c. analysis. The gas yield was calculated by the difference between the initial (dry ash free base) and recovered residual weights. Thus, the weight loss during the experiment was included in the gas yield.

#### Hydrogenation of 1-MN procedure

Hydrogenation of 1-MN was carried out in an autoclave (50ml volume). 1-Methylnaphthalene (1.0g), Decahydronaphthalene (9.0g) and catalyst(0.3g) were transferred to the autoclave. The reaction products were washed out with acetone. Hydrogenation conversion and products were determined with GC and GC-MS, respectively.

### Results

#### Catalytic activity of washed residue in the liquefaction of Australian brown coal.

Figure 1 summarizes the catalytic activity of the residue in the solvent washing, and ones resultfided, S-added or washed followed by resultfiding in the liquefaction of the brown coal. Basically the residues indicated similar activities, although the resultfiding enhanced activity to produce more gases. The point is that the washing removed almost completely the inorganic carbonates, concentrating the ion catalyst. Thus, the bottom recycle can be performed by avoiding the accumulation of the inorganic residues. Even if the catalyst is covered by the carbonates, such washing can remove the carbonates without diferialating the catalytic performances.

### Ferromagnetic catalysts

Two kinds of ferromagnetic catalysts are examined in the present study, Fe<sub>3</sub>Al and carbon-magnetite composite. Their catalytic activities are illustrated in Figure 2. Both of them exhibited significant activities and maintained ferromagnetic susceptibility after the liquefaction. Their susceptibility stood in H<sub>2</sub>-H<sub>2</sub>S atmosphere at 400 °C.

### Ferromagnetic support

Table 1 shows the activity of NiMo supported on Fe<sub>3</sub>Al for the hydrogenation of 1-methylnaphthalene at 380°C for 40min under H<sub>2</sub> pressure of 10MPa ; Non-trivial activities were induced by supporting NiMo on Fe<sub>3</sub>Al. The catalyst maintained the ferromagnetic susceptibility.

### Discussion

The present study indicated that the recovery and recycle of the catalyst are basically possible after the primary coal liquefaction where the inorganic residues are present to contaminate the iron catalyst. Although the catalytic activity so far revealed is not super yet, more elaborate preparation of the catalyst can improve the activity without losing functions of recovery. Smaller particle size, better dispersion and favorable catalyst-support interaction are applicable ways to enhance the activity.

The reaction scheme including coal pretreatment procedure should be also examined for further development to avoid the catalytic deactivation.

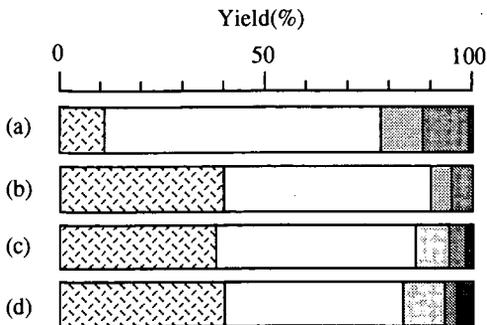


Fig.1 Effects of pretreatment for several recoverable catalyst to the liquefaction yields

catalyst: 3% addition to coal  
 solvent(75%4HFL/25% Py)/ coal= 1.5  
 single-stage used autoclave  
 380°C-40min,H<sub>2</sub>Press.10MPa

- (a) ; non-treatment Y-coal PI
- (b) ; presulfided Y-coal PI
- (c) ; presulfided and S-additon Y-coal PI
- (d) ; acetic acid washing and presulfided Y-coal PI

☑ :G   □ :O   ▨ :A   ▩ :P   ■ :R

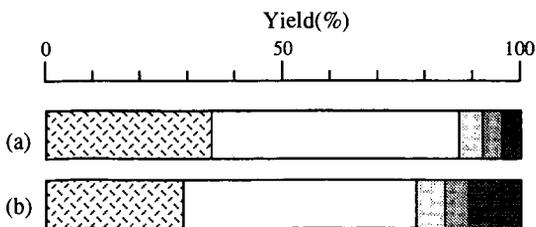


Fig.2 Effects of Fe<sub>3</sub>Al catalyst to the liquefaction yields

catalyst: 3% addition to coal  
 solvent(75%4HFL/25% Py)/ coal= 1.5  
 single-stage used autoclave  
 380°C-40min,H<sub>2</sub>Press.10MPa

- (a) ; C/Coated Magnetite, (b) ; Fe<sub>3</sub>Al

☑ :G   □ :O   ▨ :A   ▩ :P   ■ :R

Table 1 Catalysttype and 1-MN hydrogenating conversion

Catalyst (NiMo/Fe <sub>3</sub> Al)	Mo wt%	Ni wt%	Conversion %
A	10	2	9
B	10	5	13
C	5	1	5
D	10	5	20
E	10	5	23

Sulfiding conditions ( ABC:360°C 6hr D: 300 °C 3hr

E: 360 °C 3hr after 300 °C 3hr)

Reaction conditions (1-MN:1.0g DHN:9.0g

catalyst:0.3g used autoclave

380°C-40min, H<sub>2</sub>press. 10Mpa.