

Enhancement of liquefaction of low rank coal by the catalytic effects of cation exchanged to coal

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The exchange of Na^+ , K^+ , Mg^{2+} or Ca^{2+} did not affect liquefaction of coal. Because three kinds of cations (Fe^{2+} , Ni^{2+} and Co^{2+}) dispersed finely into the coal matrix through the ion exchange with carboxylic groups in coal macromolecules, these exchanged cations enhanced the upgrading reaction of coal significantly. However, the added oxide or sulfide of iron, nickel or cobalt did not. In particular, Co^{2+} exchanged coal was converted completely to acetone soluble constituent upon liquefaction with tetralin solvent and sulfur addition.

1. Introduction

It is well known that carboxylic (-COOH) group bonded to polyaromatic cluster exists dominantly in lower rank coals, uni- and di-valent metal cations can easily exchange with proton of -COOH group. It was clarified that gasification and pyrolysis reaction of coal were promoted, when the specific cation was exchanged to coal. On the liquefaction of Morwell brown coal, the upgrading reaction, such as the decrease of dichloromethane insoluble yield, was enhanced by exchanges of several kinds of cations (Sn, Fe [Hatswell, et al., 1980, Cassidy, et al., 1986], Co, Ni, Zn and Pb [Cassidy, et al., 1986]) to coal. Compared with the liquefaction of lignite, brown or subbituminous coal with any one of Fe_2O_3 (Taghiei, et al., 1993, 1994), FeCl_2 (Joseph and Forrai, 1992) or pyrite (Murakami, et al., 1998) additive, it was also reported that the upgrading reaction, such as the decrease of THF insoluble yield, was enhanced on that of Fe^{2+} exchanged lignite or coal. It is well recognized that catalyst containing nickel or cobalt exhibits excellent activity for hydrogenolysis reaction of crude oil or coal. In this study, the catalytic effects of exchanged cations on the liquefactions of Adaro subbituminous coal were discussed by using tetralin or decalin after the cation exchange treatments of the demineralized coal. For comparison, the liquefaction of demineralized coal with oxide or sulfide of iron, nickel or cobalt was also carried out.

2. Experimental

2.1 Demineralization

A subbituminous coal, Adaro (Indonesia), was pulverized to pass through a 200 mesh screen, and dried for 3 h under vacuum at 110 °C before use. After magnetically stirring raw coal (30 g) in deionized water (300 ml) at 70 °C for 1 h, the coal was stirred successively with 600 ml of 2.3N HCl and 2.3N HF aqueous solutions at 25 °C for 1 h, respectively. After each treatment, the suspension was filtered and rinsed with deionized water until the disappearance of Cl⁻ and F⁻ in filtrate. The residual demineralized coal was dried for 10 h under vacuum at 110 °C.

2.2 Cation exchange treatment

Each aqueous solution of 3.0N of sodium, magnesium, potassium or calcium acetate, 1.0N of nickel or cobalt acetate, or 5.0N of iron(II) chloride was prepared. The demineralized coal (11 g) with 880 ml of desired metal salt aqueous solution was magnetically stirred in a sealed flask at 25 °C for 24 h. The suspension was filtered and rinsed with 6000 ml of deionized water, however, in a treatment using iron(II) chloride solution, rinsed until the disappearance of Cl⁻ in filtrate. The residual cation exchanged coal was dried for 10 h under vacuum at 110 °C.

2.3 Coal liquefaction

Each coal sample (3 g) and 7 g of solvent (decalin or tetralin) were placed in a 100 cm³ autoclave under an initial hydrogen pressure of 5.9 MPa. On the liquefaction of demineralized coal, 1.5 mmol of metal powder was added. In several liquefactions of coal, 3.0 mmol of sulfur was also fed to the reactor. The reactor was heated and maintained at 420 °C for 1 h. After cooling, the gaseous products (Gas) were analyzed. The products remaining in the reactor were filtered and rinsed successively with acetone and n-hexane. The acetone insoluble (Residue), and n-hexane insoluble but acetone soluble (HIAS) materials were prepared from the respective residues by drying. After the solvents were evaporated from the filtrate, the heavy oil material was obtained. Since the range of boiling point of the heavy oil constituent was above 250 °C, the light oil material isolated from the oil constituent was evaporated with the solvents. Therefore, the yield of acetone soluble and n-hexane soluble (Oil) constituent was calculated from the difference between the weights of the fed coal and the sum of the recovered constituents (Gas, HIAS and Residue) on a d.a.f. basis. After the liquefaction with sulfur addition, the difference between the amount of fed sulfur and the amount of sulfur evolved as H₂S after the reaction is expected to be the amount of sulfur used in sulfurization of the exchanged cation or added metal during the liquefaction. Therefore, the yield of Residue was calculated by subtracting the amount of sulfur used in the sulfurization.

2.4 Analysis

The contents of -COOH group in coals were measured as reported previously (Sugano, et al., 1999). The content of exchanged cation (CEC; mmol/ g d.a.f. coal) for the exchanged coal was calculated as reported previously (Sugano, et al., 1999). The gas chromatographic analyses of gaseous components (CH₄, C₂H₆, C₃H₈, C₄H₁₀, CO and CO₂) evolved on the liquefaction were performed on a Shimadzu GC-9A instrument

equipped with a thermal conductivity detector and a dual-column molecular sieve and Porapak N (Sugano, et al., 2004).

3. Results and Discussion

3.1 Cation exchange treatments

The analytical data of raw and demineralized Adaro coals are given in Table 1. The demineralized efficiency of coal was 81 %. As listed in Table 2, the CEC values ranged between 0.4 and 0.7 (mmol/g d.a.f. coal). Therefore, 1.5 mmol of oxide or sulfide of any one of iron, nickel or cobalt was added on the liquefaction of 3.0 g (d.a.f. basis) of demineralized coal to compare the catalytic effect of these metal powders.

Table 1 Analytical data of Adaro coal

Coal	Ultimate analyses ¹					Ash ²
	C	H	N	O		
				-COOH ³	others ⁴	
Raw	68.8	5.2	0.8	4.3	20.9	1.6
Demineralized	68.7	5.2	1.2	6.4	18.5	0.3

¹ wt% d.a.f. coal basis ² wt% dry coal basis

³ content of carboxyl group ⁴ by difference

Table 2 Used metallic salts and the content of exchanged cation in Adaro coal

Cation	Metallic salt	Concentration (N)	CEC ¹
Na ⁺	acetate	3.0	0.7
K ⁺	acetate	3.0	0.6
Mg ²⁺	acetate	3.0	0.6
Ca ²⁺	acetate	3.0	0.6
Fe ²⁺	chloride	5.0	0.5
Ni ²⁺	acetate	1.0	0.4
Co ²⁺	acetate	1.0	0.5

¹ mmol / g d.a.f. coal

3.2 Catalytic effects of exchanged Na⁺, K⁺, Mg²⁺ and Ca²⁺

The product yields on the liquefactions of cation exchanged coals using decalin are shown in Figure 1. There was almost no difference between the product yields on the liquefactions of demineralized and several cation (Na⁺, K⁺, Mg²⁺ and Ca²⁺) exchanged coals. It was reported that the exchange of Na⁺, K⁺ or Ca²⁺ did not affect the liquefaction of Wyodak subbituminous coal or North Dakota lignite with tetralin (Taghiei, et al., 1993). Therefore, it was anticipated that the exchange of Na⁺, K⁺, Mg²⁺ or Ca²⁺ did not affect the liquefaction of lower rank coal, such as Adaro coal, with both decalin and tetralin.

3.3 Catalytic effects of exchanged Fe^{2+} , Co^{2+} and Ni^{2+}

As shown in Figure 1, on the liquefaction of any one of Fe^{2+} , Co^{2+} or Ni^{2+} exchanged coal using decalin, the yield of Residue decreased and that of Oil increased in comparison with the liquefaction of demineralized coal. Further, on the liquefactions of these cation exchanged coals, Residue yield decreased by adding sulfur. Among the liquefactions of these cation exchanged coals, the decrease of Residue yield and the increases of Oil yield were higher for Co^{2+} and Ni^{2+} exchanged coals than Fe^{2+}

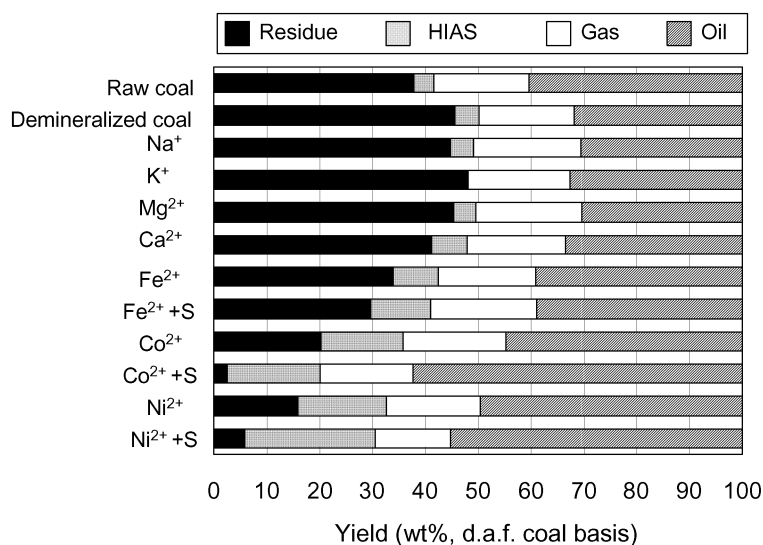


Figure 1 Product yields on the liquefactions of cation exchanged coals using decalin

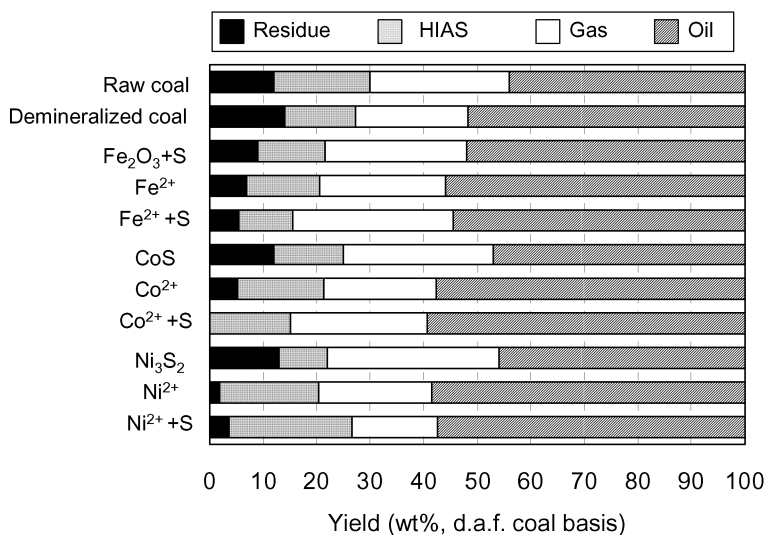


Figure 2 Product yields on the liquefactions of cation exchanged coals using tetralin

exchanged coal. In particular, 80% of coal (d.a.f. basis) was converted to nonpolar constituents (Oil + Gas) on the liquefaction of Co^{2+} exchanged coal with sulfur addition. The product yields on the liquefactions of cation exchanged coals using tetralin are shown in Figure 2. The differences of product yields between the liquefactions of demineralized and cation (Fe^{2+} , Co^{2+} and Ni^{2+}) exchanged coals with tetralin were smaller than those with decalin (Figure 1). However, on the liquefactions of these cation exchanged coals, the Residue yield decreased and the Oil yield increased in comparison with the liquefaction of demineralized coal. Further, the yield of Residue decreased by adding sulfur on the liquefaction of Fe^{2+} or Co^{2+} exchanged coal. In particular, on the liquefaction of Co^{2+} exchanged coal with sulfur addition, the coal was converted completely to acetone soluble constituents on a d.a.f. coal basis, and 85% of coal was converted to the nonpolar constituents. The yield of Residue increased slightly by adding sulfur on the liquefaction of Ni^{2+} exchanged coal. On the other hand, the decrease of Residue yield was slight on the liquefaction of demineralized coal with any one of Ni_3S_2 , CoS and Fe_2O_3 with sulfur.

Taghiei et al. (1993, 1994) reported that the yield of THF insoluble decreased on the liquefaction of Fe^{2+} exchanged Beulah or Hagel lignite. They considered that aggregation of iron suppressed during the liquefaction because iron dispersed finely in the lignite macromolecule on the Fe^{2+} exchange pretreatment (Murakami, et al., 1998). It is well known that iron is sulfurized to pyrrhotite under a conventional coal liquefaction condition, which enhances the liquefaction of coal. On the liquefactions of NiO and CoO with H_2 - H_2S gas mixture below 420 °C, it was reported that these oxides were sulfurized to Ni_7S_6 and Co_6S_5 (Okutani, et al., 1983), respectively, which were known as excellent hydrogenation catalysts (Okutani, et al., 1983, Hulston, et al., 1997). Therefore, during the liquefactions in this study, Fe^{2+} , Co^{2+} and Ni^{2+} exchanged to demineralized coal were also sulfurized to pyrrhotite, Ni_7S_6 and Co_6S_5 , respectively, by the added sulfur or sulfur in coal macromolecules. It was clarified that carboxylates between one divalent cation and two $-\text{COOH}$ groups in coal macromolecule were formed under the cation exchange condition (Sugano, et al., 1999) same as this study. Accordingly, it was considered that the hydrogen transfer from gaseous hydrogen and tetralin to coal radicals by the catalytic activity of sulfurized Fe^{2+} , Co^{2+} or Ni^{2+} appeared significantly due to the fine dispersion of these cations into coal macromolecules through the ion exchange with $-\text{COOH}$ groups. However, on the liquefaction of Ni^{2+} exchanged coal, addition of sulfur promoted the upgrading of coal in decalin solvent, but did not in tetralin solvent. It was reported that the liquefaction of coal was inhibited slightly owing to the preferential adsorption of tetralin on the surface of sulfurized nickel particle (Hulston, et al., 1997). Therefore, on the liquefaction of Ni^{2+} exchanged coal with sulfur, it was considered that cracking of tetralin occurred slightly due to the preferential adsorption of tetralin on the sulfurized Ni^{2+} surface. As a result, hydrogen transfer from tetralin to coal radical was prevented, followed by the inhibition of upgrading of the exchanged coal. On the other hand, the additive effect of any one of Ni_3S_2 , CoS and Fe_2O_3 with sulfur was not observed on the liquefaction of demineralized coal because these metal powders could not easily disperse to coal macromolecules during the liquefaction. Comparing the yields on the liquefactions of demineralized coal with these metal powders, the differences of catalytic effects between iron, nickel and cobalt were small. However, it was clarified that the catalytic effects of exchanged Co^{2+}

and Ni^{2+} for upgrading of coal were superior to that of Fe^{2+} . Accordingly, it was considered that the catalytic effect of the exchanged Co^{2+} caused not only the liquefaction of coal but also the upgrading of the liquefaction product from coal.

4. Conclusions

The exchange of Na^+ , K^+ , Mg^{2+} or Ca^{2+} did not affect the liquefaction of coal. Because three kinds of cations (Fe^{2+} , Ni^{2+} and Co^{2+}) dispersed finely into the coal matrix through the ion exchange with $-\text{COOH}$ groups in coal macromolecules, the exchanged cations enhanced significantly the upgrading reaction of coal. However, the addition of Ni_3S_2 , CoS and Fe_2O_3 with sulfur did not. In particular, Co^{2+} exchanged coal was converted completely to acetone soluble constituent on the liquefaction with tetralin solvent and sulfur addition.

References

- Cassidy, P.J., Jackson, W.R., Larkins, F.P., Sakurovs R.J. and Sutton, J.F., 1986, Hydrogenation of brown coal: 8, *Fuel* 65, 374-379.
- Hatswell, M.R., Jackson, W.R., Larkins, F.P., Marshall, M., Rash D. and Rogers, D.E., 1980, Hydrogenation of ion-exchanged Victorian brown coals, *Fuel* 59, 442-444.
- Hulston, C.K.J., Redlich, P.J., Jackson, W.R., Larkins F.P. and Marshall, M., 1997, Hydrogenation of a brown coal pretreated with water-soluble nickel/molybdenum and cobalt/molybdenum catalysts, *Fuel* 76, 1465-1469.
- Joseph J.T. and Forrai, T.R., 1992, Effect of exchangeable cations on liquefaction of low rank coals, *Fuel* 71, 75-80.
- Murakami, K., Shirato, H., Hanada, N. and Nishiyama, Y., 1998, Influences of exchanged metal ions on coal liquefaction, *Energy Fuels* 12, 843-848.
- Okutani, T., Yokoyama, S., Maekawa, Y., Furuichi, R. and Ishii, T., 1983, Coal liquefaction with hydrogen sulfide-hydrogen gas mixture and metal oxide catalysts, *Ind. Eng. Chem. Proc. Des. Dev.* 22, 306-312.
- Sugano, M., Mashimo K. and Wainai, T., 1998, Upgrading reactions of coal liquefaction residue with basic coal liquid related model compounds, *Fuel* 77, 447-451.
- Sugano, M., Mashimo K. and Wainai, T., 1999, Structural changes of lower rank coals by cation exchange, *Fuel* 78, 945-951.
- Sugano, M., Hirano K. and Mashimo, K., 2004, Effects of reaction conditions on the hydrogenolyses of cation exchanged coals, *Fuel Processing Technology* 85, 837-848.
- Taghiei, M.M., Huggins, F.E., Ganguly, B., and Huffman, G.P., 1993, Liquefaction of lignite containing cation-exchanged iron, *Energy Fuels* 7, 399-405.
- Taghiei, M.M., Huggins, F.E., Mahajan, V., and Huffman, G.P., 1994, Evaluation of cation-exchange iron for catalytic liquefaction of a subbituminous coal, *Energy Fuels* 8, 31-37.