The Effects of Catalysts on the Mean Structure of Solvent-Refined Coal in Coal Liquefaction

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The effects of MoO_3, Fe_2O_3, or SnO on the conversion and the solvent-refined coal (SRC) yield of Taiheiyo coal were small, whereas their effects on the structure of SRC were large. SRC was separated into four fractions by successive extraction in order to clarify the differences in SRC's among the catalysts. The formation of SnO_2 after the liquefaction was confirmed. It was considered that the oxygen-abstraction ability and the radical-stabilization ability of SnO prevented the retrogressive reaction of coal, SRC, and model compounds. MoO_3 and Fe_2O_3 have a higher ability to hydrogenate and accelerate the hydrocracking of coal and coal-model compounds than does SnO, but their ability to suppress the retrogressive reaction producing heavier compounds is small.

Although many attempts have been made to find more effective coal-liquefaction catalysts, most of them have been limited to the purpose of increasing the conversion to the liquid products of coal.[1,2] However, in order to evaluate a coal-liquefaction reaction and the use of its products, the difference in the structure of the liquefaction products obtained by the use of the different catalysts needs also to be investigated.

In this paper, three different metal oxides, MoO_3, Fe_2O_3, and SnO, were used as catalysts for Taiheiyo-coal liquefaction in tetralin or decalin under a hydrogen or nitrogen atmosphere. In order to clarify the differences in the structures of the products, solvent-refined coal (SRC) was separated into four fractions by successive extraction and their structural parameters were calculated using the Brown-Ladner method.[3]

SRC was treated in the presence of a catalyst in order to correlate the results with the results of coal liquefaction. Further, the reactions of coal model compounds were also examined in order to obtain information about the roles of the catalysts.

Experimental

Taiheiyo coal-1, -2, and -D (Table 1) were ground, passed through a 100-mesh (149 μm) screen and then dried at 107 °C under a nitrogen atmosphere. Taiheiyo coal-2 was deashed to prepare Taiheiyo coal-D by the method of Fan et al.[4] The ash content decreased from 14.4 to 2.2%. For coal liquefaction, a mixture of coal (5 g), a solvent (15 g), and a catalyst (0.5 g) was placed in a Pyrex glass liner, inserted into a 100-ml magnetdriven autoclave; this autoclave was then pressurized to 5.1 MPa at room temperature with hydrogen or nitrogen. It is well-known that the autoclave wall acts as a catalyst. So a Pyrex glass liner was used. The nominal reaction time was 60 min at 400 °C. The materials remaining in the autoclave after the liquefaction were extracted with benzene. A benzene-insoluble material was weighed after drying and then further extracted with THF. The liquefaction solvent was recovered from the benzene extract by vacuum distillation. The distillation residue was weighed as SRC.[5] The conversions to a benzene-soluble material (BC) and to a THF-soluble material (TC) were calculated according to the following equation:

$$\text{Conversion to BC or TC (wt\% daf coal basis)} = \frac{(\text{Coal-charged} - \text{benzene or THF-insoluble material}) \times 100}{\text{daf coal}}$$

The SRC was separated into four fractions by successive extractions; when benzene 4%-heptane 96% (Solvent 1), benzene 15%-heptane 85% (Solvent 2), benzene 50%-hexane 50% (Solvent 3), benzene 60%-methanol 40% (Solvent 4) were used successively as the extraction solvents, Fractions 1—4 were thus obtained.

The ^{1}H NMR spectra were recorded at 90MHz on a Hitachi R 22 apparatus. The solution for the measurements of the ^{1}H NMR spectra was prepared by dissolving 40 mg of a sample in 0.4 ml of chloroform-*d*, using tetramethylsilane as the internal standard.

Results

The liquefaction reactions of Taiheiyo coal-1, -2, and -D in tetralin under a hydrogen atmosphere using different catalysts at 400 °C are shown in Table 2. When no catalyst was used, the conversions to BC and the SRC yields were in the following order: Taiheiyo-D>Taiheiyo-2>Taiheiyo-1. The same order was observed when MoO_3, Fe_2O_3, or SnO was used as the catalyst. The use of catalysts was effective for coal liquefaction, and the conversions to BC with catalysts were from 12 to 18% higher than those without catalysts, even in tetralin. Although SnO was a more effec-

Table 1. Analysis of Coals (wt%)

Coal	Ultimate analysis				Proximate analysis[a]			
	C	H	N	Odiff	Ash	Mois	V.M.	F.C.
Taiheiyo-1	76.7	5.6	0.7	17.0	13.1	3.9	39.6	43.4
Taiheiyo-2	76.6	6.3	0.9	16.2	14.4	4.7	49.6	31.1
Taiheiyo-D[b]	77.0	6.5	1.2	15.3	2.2	2.2	52.4	43.2

a) Mois: Moisture, V.M.: Volatile matter, F.C.: Fixed carbon. b) Taiheiyo-D is Taiheiyo-2 deashed.

Table 2. Liquefaction of Taiheiyo Coal-1, 2 and D at 400 °C under a Hydrogen Atmosphere for 60 min in Tetralin

Coal	Catalyst	Conversion to		SRC yield	O[a] of SRC	fa[b]
		BC	TC			
Taiheiyo-1	None	55.7	83.0	31.8	6.31	0.615
	MoO_3	61.2	84.9	38.9	4.79	0.619
	Fe_2O_3	61.9	88.1	38.5	6.52	0.605
	SnO	67.7	92.2	44.4	3.43	0.600
Taiheiyo-2	None	58.6	81.7	40.7	5.10	0.564
	MoO_3	69.9	85.5	48.4	4.13	0.581
	Fe_2O_3	68.0	92.3	43.9	5.96	0.578
	SnO	76.2	91.4	51.4	3.70	0.578
Taiheiyo-D	None	74.1	84.7	46.4	4.87	0.577
	MoO_3	76.4	85.6	51.7	4.25	0.564
	Fe_2O_3	76.8	87.2	49.2	4.29	0.584
	SnO	80.5	90.0	55.6	4.33	0.560

a) Oxygen content. b) Carbon aromaticity.

Table 3. Effects of Catalysts, Solvents, and Atmospheres on the Liquefaction of Taiheiyo Coal-1

Catalyst	Solvent		Conversion		SRC yield[a]	Aromaticity (fa)[b]
			to BC[a]	to TC[a]		
None	Tetralin	H_2	55.7	83.0	31.8	0.615
		N_2	52.2	78.5	32.0	0.614
	Decalin	H_2	37.5	48.6	23.9	0.571
		N_2	28.3	34.0	14.3	0.539
MoO_3	Tetralin	H_2	61.2	84.9	38.9	0.619
		N_2	49.7	73.4	30.2	0.599
	Decalin	H_2	40.5	46.8	24.9	0.569
		N_2	24.4	26.3	11.7	0.513
Fe_2O_3	Tetralin	H_2	61.9	88.1	38.5	0.605
		N_2	37.3	61.9	25.6	0.566
	Decalin	H_2	23.5	38.8	18.1	0.559
		N_2	20.5	22.3	13.4	0.496
SnO	Tetralin	H_2	67.7	92.2	44.4	0.600
		N_2	43.0	72.5	26.5	0.589
	Decalin	H_2	44.9	62.3	23.9	0.597
		N_2	31.8	35.4	19.8	0.560

a) Wt% daf basis. b) Carbon aromaticity of SRC calculated using Brown–Ladner method.

tive catalyst than MoO_3 and Fe_2O_3, the differences between them were only from 4 to 6%. The highest conversion to BC was always obtained with Taiheiyo-D, and the tendency of conversion to BC with catalysts was not affected by the removal of coal minerals. On the other hand, the differences in the conversions to TC among the catalysts used were relatively small. This indicated that the interaction between coal minerals of Taiheiyo coal and the added catalyst was small. Taiheiyo coal-1 was exclusively used in the latter part of this study.

Taiheiyo coal-1 was liquefied at 400 °C for 60 min in tetralin or decalin under a hydrogen or nitrogen atmosphere using three different kind of catalysts, as is shown in Table 3. Irrespective of the catalyst, the conversion to BC, the TC, and the SRC yields were in the following order:

in tetralin under hydrogen > in tetralin under nitrogen >
in decalin under hydrogen > in decalin under nitrogen.

From Table 3, it may seem that two important factors in the conversion to BC, and to TC, and in the SRC yield were the solvent and the atmosphere. To quantify the effects of the liquefaction conditions, variance analysis[6] was applied to these results. The conversions on repeated runs at 440 °C in tetralin were 64.5 and 66.4% for conversion to BC, and 92.1, and 91.9% for conversion to TC. These runs indicated that the experimental data were applicable to the analysis. In the three-way model, we investigated the effects of sixteen different combinations of four catalysts (none, MoO_3, Fe_2O_3, SnO), two solvents (tetralin, decalin), and two atmospheres (hydrogen, nitrogen). The significance at the $\alpha=0.01$ level showed that the main effects of the conversion and the SRC yields were due to the solvent and the atmosphere, not to the catalyst. The SRC's were analyzed by the use of ^1H NMR, and the structural parameters of the SRC's were then calculated. The three-way variance analysis was also applied to the structural parameter, fa (aromaticity), of

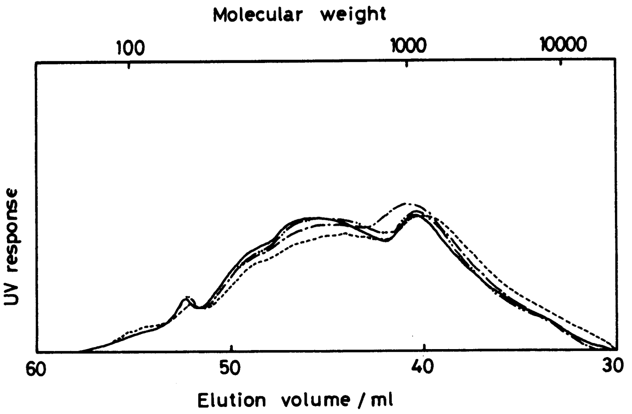

Fig. 1. Molecular weight distributions of SRC's measured by GPC.
Catalyst
None: ——, MoO_3: -··-··-, Fe_2O_3: ······, SnO: -·-·-.

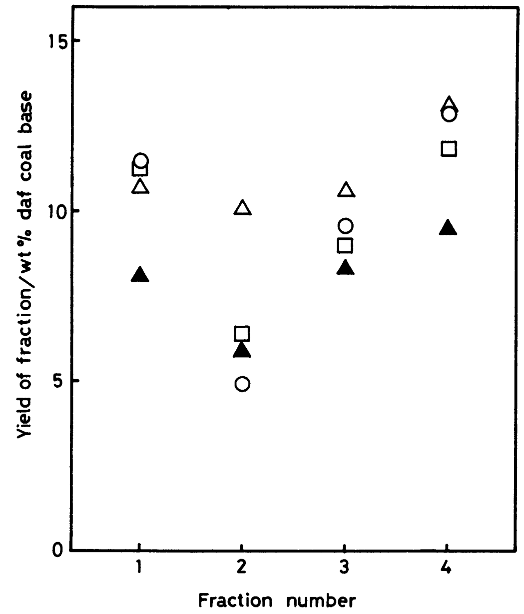

Fig. 2. Yield of fraction 1—4 obtained by successive extraction of SRC. Catalyst None: ▲, MoO_3: ○, Fe_2O_3: □, SnO: △.

SRC. In this case, even with catalysts, a significance at the $\alpha=0.01$ level was observed. It was concluded that, under these liquefaction conditions, the effects of catalysts on the conversion and the SRC yield were small, whereas the effects of the catalysts on the structure of SRC were large and important.

To obtain information about the difference in the SRC structure, the molecular-weight distributions of the SRC's were measured by means of GPC; the results are shown in Fig. 1. When a catalyst, especially Fe_2O_3, was used, the heavier compounds (with molecular weights of around 10000) were larger than those with no catalyst. Moreover, when SnO was used, the compounds whose molecular weights were around 1000 were larger than those of the SRC with other catalysts. However, we could not clarify the differences in distribution among them and the difference in the role of the catalyst in the course of coal liquefaction, for the SRC contains many compounds. Therefore, the SRC was separated into four fractions by means of successive extractions.

The SRC yields of Taiheiyo coal in tetralin under a hydrogen atmosphere were 39, 39, and 44% with MoO_3, Fe_2O_3, and SnO, respectively. They were extracted successively using Solvents 1—4, whose compositions have already been described in the Experimental section. The fraction yields based on daf coal are shown in Fig. 2.

The SRC yield without a catalyst was 32%, approximately 12% smaller than that with SnO, but the distributions of the SRC without a catalyst were almost identical with those with SnO; the yields were in the following order: Fraction 4>Fraction 3≥Fraction 1> Fraction 2.

When MoO_3 or Fe_2O_3 was used, both the lighter (Fraction 1) and the heavier (Fraction 4) components were larger than those in the SRC with no catalyst.

To compare the structure of the SRC, all fractions were analyzed by means of ^{1}H NMR. The results of the elemental analysis and their structural parameters are shown in Table 4. The hydrogen/carbon ratio (H/C) decreased, and the oxygen content, the carbon aromaticity (fa), and the number of rings (Ra, Rn, Rt) increased, with an increase in the fraction number, irrespective of the kind of catalyst. The oxygen contents of Fractions 1—4 which were obtained using SnO were smaller than those obtained using no catalyst or Fe_2O_3. When MoO_3 was used, the oxygen contents of Fractions 1 and 2 were smaller than those obtained using SnO, but those of Fractions 3 and 4 were larger. Not only the smallest number of aromatic rings (Ra), but also the smallest number of non-aromatic rings (Rn), of all fractions were obtained when SnO was used. When MoO_3 or Fe_2O_3 was used, the numbers of total rings of Fractions 3 and 4 were 4.94 and 7.01, and 4.98 and 5.39, respectively; these numbers were larger than those when no catalyst or SnO was used. The yield of Fraction 3 was from 8.5 to 10.5 wt%, and the effect of the kind of catalyst used on the yield was relatively small. The mean molecular weight of Fraction 3 was measured by means of VPO. Values of 420 with MoO_3 and 520 with Fe_2O_3 were obtained; these values were larger than those of 320 without a catalyst and 350 with SnO.

In this way, we can clarify the differences among catalysts in the structure of SRC; when SnO was used, lighter compounds than those with other catalysts were obtained, despite the larger SRC yield.

To obtain further information on the liquefaction products, SRC was treated in the presence of a catalyst. The SRC had been obtained by the liquefaction of Taiheiyo coal without a catalyst at 420 °C for 60 min under a hydrogen atmosphere. In the reaction of SRC,

Table 4. Structural Parameters of Fractionated SRC

Catalyst	Fraction No	Extract	O	H/C	fa[a)]	Ra[b)]	Rn[b)]	Rt[b)]	Mn[c)]
None	All	100	6.31	1.05	0.62	2.62	1.85	4.48	
	1	25.5	3.01	1.31	0.47	1.86	1.53	3.39	
	2	18.4	5.21	1.17	0.78	2.21	1.88	4.09	
	3	26.1	7.05	1.10	0.60	2.22	1.67	3.89	370
	4	29.9	9.66	0.91	0.71	2.95	1.84	4.80	
MoO_3	All	100	4.79	1.09	0.62	2.76	1.93	4.68	
	1	29.5	1.38	1.33	0.47	1.63	1.31	2.95	
	2	12.7	3.38	1.18	0.53	2.11	1.81	3.92	
	3	24.7	5.69	1.06	0.59	2.82	2.12	4.94	420
	4	33.2	7.94	0.93	0.66	4.13	2.87	7.01	
Fe_2O_3	All	100	6.52	1.08	0.61	2.13	1.70	3.83	
	1	29.4	2.55	1.30	0.48	1.73	1.39	3.12	
	2	16.5	4.75	1.12	0.56	2.45	2.00	4.44	
	3	23.3	5.81	1.01	0.63	2.92	2.06	4.98	520
	4	30.9	8.86	0.90	0.69	3.16	2.23	5.39	
SnO	All	100	3.43	1.06	0.60	1.47	1.58	3.05	
	1	24.0	1.89	1.40	0.45	1.04	1.12	2.17	
	2	22.8	3.70	1.16	0.54	2.10	1.88	3.97	
	3	23.9	4.95	1.09	0.56	1.97	1.60	3.57	350
	4	29.3	7.12	0.93	0.69	2.82	1.89	4.71	

a) fa: carbon aromaticity. b) Ra, Rn, Rt: number of aromatic, nonaromatic, and total rings per structural unit. c) Mn: mean molecular weight as measured by vapor-pressure osmometry (VPO).

Table 5. Effects of Treatment[a)] of SRC with Catalysts on SRC Structure

Catalyst	fa[b)]	σ[c)]	n[c)]	Ra[b)]	Rn[b)]	Rt[b)]	Mn[b)]
Feed SRC	0.57	0.52	3.08	2.61	1.88	4.48	320
None	0.58	0.50	2.58	2.72	2.01	4.73	310
MoO_3	0.55	0.54	2.63	2.92	2.37	5.29	350
Fe_2O_3	0.56	0.49	2.60	3.01	2.26	5.26	340
SnO	0.56	0.54	2.52	1.97	1.80	3.76	250

a) SRC's were treated at 400 °C under a hydrogen atmosphere for 60 min in tetralin. b) Abbreviation as in Table 4. c) σ: degree of substitution for aromatic nucleus, n: number of carbon atoms of side chain.

few gaseous compounds were produced during the treatment, and most of the SRC was recovered as benzene-soluble. The structural parameters are shown in Table 5. Without a catalyst, the H/C ratio of SRC decreased from 1.2 to 1.1, and the chain length decreased from 3.1 to 2.6; this indicates the presence of a slight retrogressive reaction. When MoO_3 or Fe_2O_3 was used, the retrogressive reaction was confirmed by the increases in the total rings per structural unit and in the mean molecular weight. On the other hand, when SnO was used, the mean molecular weight and the total number of rings decreased from 320 to 250, and from 4.48 to 3.76, respectively.

The retrogressive reaction for MoO_3 and Fe_2O_3 was also confirmed from model-compound studies. MoO_3 and Fe_2O_3 were more effective than was SnO for the hydrogenation reaction of naphthalene and benzophenone to tetralin and diphenylmethane. The results were identical with those reported previously.[7)] Furthermore, the reactions of dibenzyl ether at 360 °C and of biphenyl at 400 °C were accelerated in the presence of MoO_3 or Fe_2O_3, as is shown in Table 6. However, the yields of unknown compounds were larger with MoO_3 or Fe_2O_3 than with no catalyst or with SnO. For example, although DBE reacted completely in the presence of MoO_3, 78.2% of the products were unknown, and some of them were insoluble to a solvent like acetone. The GPC data showed that most of the unknown products were compounds whose molecular weights were larger than that of DBE, indicating the presence of a retrogressive reaction.

Discussion

It is well-known that coal minerals catalyze liquefaction and hydrogenation in coal-conversion processes.[8–10)] Guin et al. reported that certain coal minerals, particularly iron compounds, catalyze hydrogenation.[9)] Atomic-absorption analysis has shown that the content of iron in Taiheiyo coal is 0.65 wt%, based on dry coal. The hydrogenation ability of coal minerals was affected by the degree of their dispersion in the coal. Therefore, we could not estimate the degree of

Table 6. Effects of Catalysts on the Decomposition Reaction of Dibenzyl Ether (DBE) at 360 °C and Biphenyl (DP) at 400 °C

Catalyst	Model compounds	Conversion	Reaction products					
			Benzene	Toluene	Benzaldehyde	Benzylalcohol	Dibenzyl	Others
None	DBE	73.5	3.8	36.4	28.9	—	4.2	0.2
	DP	9.4	1.5					7.9
MoO_3	DBE	100	1.4	13.5	trace	trace	6.9	78.2
	DP	24.8	2.5					22.3
Fe_2O_3	DBE	68.1	3.7	32.8	28.5	3.0	trace	0.1
	DP	26.9	2.4					24.5
SnO	DBE	85.9	3.2	51.5	7.1	13.1	7.5	3.5
	DP	4.3	1.7					2.6

coal-mineral effects only from the content,[11] 0.65 wt%. Conversions to BC and TC with no catalyst in decalin were larger under a hydrogen atmosphere than under a nitrogen atmosphere, as is shown in Table 3. This suggests that the participation of hydrogen molecules in coal liquefaction promotes the coal conversion. Namely, in a non-donor solvent like decalin, organic radicals react directly with hydrogen molecules.[12] Other explanation that coal minerals, the autoclave wall or the blade catalyze the liquefaction is also possible. Wall participation has been called the "memory effect."[13,14] We could not clarify this situation. However, from the liquefaction results of Taiheiyo-D, which consisted of deashed coal of Taiheiyo-2, the interaction between coal minerals and the catalyst added might be small, for the effects of an added catalyst on conversion and on the SRC yields were not affected by the deashing. Therefore, the effects of coal minerals on the following catalyst study were excluded.

The composition of the recycle solvent is an important factor in the liquefaction of coal.[15,16] One of the functions of a liquefaction solvent is to donate hydrogen to the coal.

Under a hydrogen atmosphere, the conversions to TC in the donor solvent, tetralin, were from 30 to 40% larger than those in the non-donor solvent, decalin, irrespective of the kind of catalyst. The contribution of the donor solvent to conversion was large even in the presence of a catalyst. Under a nitrogen atmosphere, the contribution of the donor solvent increased, and the differences in the conversion to TC between solvents were from 40 to 50%. These results indicated that the catalyst suppressed somewhat the contribution of the solvent donor. The structure of Taiheiyo coal SRC was directly affected by coal conversion; we have previously reported that the aromaticity, fa, of SRC tended to increase with an increase in the conversion.[17] Therefore, we could not ascertain the relationship between the solvent used and the structure of SRC.

Variance analysis was very helpful in clarifying the relationship between them. Statistical analysis, such as variance analysis, has been applied to coal chemistry, usually, applying multiple-regression analysis to coal liquefaction.[17-19] Statistical analysis gives quantitative considerations, and intuitive conclusions could be excluded. That the effects of the catalysts on the structure of SRC were large and important was concluded from the variance analysis. In order to evaluate coal liquefaction, information about the effects of catalysts on liquid-product structures was essential. Because SRC contains many compounds,[20] the fractionation of SRC before structure analysis is effective. Figure 3 shows the molecular-weight distribution of Fractions 1—4 of SRC with no catalyst; it indicates that SRC is effectively fractionated. In our fractionation method, heavier compounds were extracted increasingly with the extract solvent numbered from 1 to 4. Although the yields of Fractions 2 and 3 without a catalyst were almost identical with those with MoO_3 or Fe_2O_3, their structures were different, as is shown in Table 4. Such a difference was caused by the difference in the catalytic action of the catalysts.

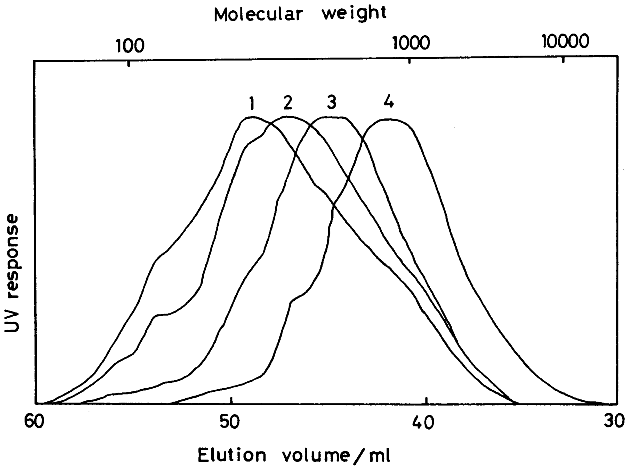

Fig. 3. Molecular weight distribution of Fractions 1—4 of SRC with no catalyst. Number in the Figure shows fraction number.

The oxygen content and ring numbers of the extract were mostly affected by the catalyst used. Lower oxygen contents were obtained with SnO. This indicates the greater ability of SnO to disrupt a linkage such as ether bonding efficiently. DBE was decomposed more with SnO than with no catalyst, as is shown in Table 6. The yield of toluene was 51.5%, and it was the main product of the reaction. It also showed an imbalance of oxygen content between reactant and products. The oxygen contents of the products were less than that of DBE. The solution of this imbalance was obtained by means of the X-ray diffraction pattern of the liquefaction residue. SnO was oxidized to SnO_2 in the course of liquefaction. The oxygen abstraction of SnO caused the lower oxygen content of the SRC extract. On the other hand, α-Fe_2O_3 (hematite) changed to γ-Fe_2O_3 (maghemite) in the course of liquefaction, but the oxygen content of the catalyst did not change. Although the X-ray diffraction pattern of the residue with MoO_3 was not very clear because of the overlapping of plural compounds, the presence of MoO_2 after the liquefaction was confirmed. Oxygen functional groups related to hydrogen bonding between coal molecules and the extractability of coal was highly affected by the hydrogen bonding.[21] The removal of the oxygen might mean the acceleration of the dissociation of the association molecules. Furthermore, it has been reported that phenolic OH condensed to form an ether linkage, eliminating water.[22] It is possible that the oxygen release of MoO_3 to MoO_2 causes the condensation reaction. The oxygen contents of the extract with MoO_3 were not very large, but the condensation reaction produced an insoluble residue.

SRC was chosen as the more appropriate coal model. It is well-known that the reactivity of liquefaction products like SRC was less than that of coal itself,[23] but it was possible to observe the structure change in the whole compounds. In coal liquefaction, the smallest number of aromatic and nonaromatic rings was obtained with SnO. The ring number of SRC decreased when SnO was used, as is shown in Table 5. The ability of SnO to hydrogenate aromatic rings was less than that of MoO_3; this was confirmed by the hydrogenation of naphthalene.

These results indicate that SnO is effective for the cleavage reaction of a linkage like an ether bond and that, further, it possesses the ability to suppress the condensation reaction. The oxygen-removal reaction relates to the latter ability. Bacand et al. has reported that Al_2O_3 could stabilize free radicals by means of adsorption.[24] SnO could possess such a radical stabilization ability to suppress condensation reactions.

MoO_3 and Fe_2O_3, especially MoO_3, have higher abilities to hydrogenate or accelerate the hydrocracking of coal structures similar to coal-model compounds, as is shown in Table 6. However, they could not prevent the retrogressive reactions of coal, which were confirmed by the structures of the SRC extracts and by model-compound studies.

The difference in SRC structure appears to result from the inherent ability of a catalyst to liquefy coal.

Conclusions

From the three-way variance analysis, it was concluded that the effects of catalysts on conversion and on the SRC yield were small, whereas the effects of catalysts on the structure of SRC were large and important. The fractionation of SRC into four fractions was very effective for comparing the structures of SRC. The oxygen content and ring numbers of the extracts were mostly affected by the catalyst used. The formation of SnO_2 after the liquefaction shows the oxygen-abstraction reaction of SnO, which cause the oxygen content of the extract to be lower. The decomposition of SRC, dibenzyl ether, and biphenyl as coal-model compounds was also accelerated by the catalysts, but retrogressive reactions were observed when MoO_3 or Fe_2O_3 was used.

More effective catalysts for coal liquefaction can be prepared by investigating the structures of liquid products obtained with other catalysts and by selecting combinations of catalysts suitable for producing the desired liquid products. Studies of this point are under way.

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