Catalytic Hydrogenation and Cracking of Anthracene over $MoCl_3$-LiCl-KCl and $NiCl_2$-LiCl-KCl Salts

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Synopsis. The $MoCl_3$- and $NiCl_2$-LiCl-KCl salts, which are effective coal liquefaction catalysts, promoted the hydrogenation of anthracene (at 400 °C for 1 h with 9.8 MPa H_2) and afforded tetrahydro- and octahydro- as well as dihydroanthracene as major products. However, these catalysts did not remarkably enhance the ring-opening cracking reactions. A comparative examination suggested that the addition of LiCl-KCl to $MoCl_3$ and $NiCl_2$ suppressed their cracking ability and improved their hydrogenation selectivity.

Because of the complexity of coal structures and catalytic coal liquefaction reaction systems, hydrogenation and cracking reactions of polycyclic aromatic compounds have been taken as model test reactions for clarifying the effects of various catalysts for coal hydroliquefaction and upgrading of coal-derived products.[1–4] Recently, $MoCl_3$-LiCl-KCl and $NiCl_2$-LiCl-KCl salts have been found to be effective catalysts for the hydroliquefaction of brown, subbituminous and bituminous coals.[5,6] The most interesting features of these new catalysts are that they significantly promote oil production but do not remarkably enhance gas formation. This work was undertaken in order to develop a better understanding of their catalytic effects in promoting the hydrogenation and cracking of polycyclic aromatics.

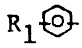
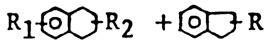
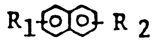
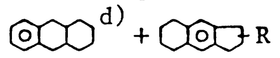
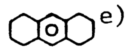
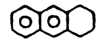
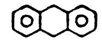
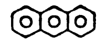
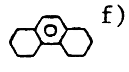
Experimental

The synthesized and purified $MoCl_3$[5] and reagent grade $NiCl_2$, LiCl, and KCl were used in preparing $MoCl_3$-LiCl-KCl (molar composition, 12 : 51 : 37) and $NiCl_2$-LiCl-KCl (14 : 50 : 36) ternary salts and LiCl-KCl (58 : 42) binary salt.[5,6] The amounts of the salt catalysts used in the reactions, MCl_n-LiCl-KCl and MCl_n (MCl_n=$MoCl_3$, $NiCl_2$), were maintained at MCl_n/anthracene (3 g, 16.85 mmol)=0.3 (molar ratio). Hydrogenation was carried out in a 60-ml SUS-316 rocking autoclave at 400 °C for 1 h with an initial H_2 pressure of 9.8 MPa. The gaseous products were analyzed by GC. The liquid and solid products were analyzed quantitatively by GLC (Shimadzu GC-4C), with the aid of GC-MS (Hitachi RMU-6MG) analyses for product identification. The experimental and analytical procedures used in this work are similar to those described elsewhere.[2]

Results and Discussion

Hydrogenation and cracking of anthracene at 400 °C for 1 h produced various hydrocarbons. These prod-

Table 1. Results of Hydrogenation and Cracking of Anthracene

Run No. Catalyst	1 None	2 LiCl-KCl	3[a)] $MoCl_3$-LiCl-KCl	4[b)] $NiCl_2$-LiCl-KCl	5 $MoCl_3$	6 $NiCl_2$
Products[c)] (wt%)						
C_1—C_4	0.1	0.2	0.9	0.2	2.6	0.2
C_5—C_9	—	—	0.1	—	2.1	0.7
	—	—	0.9	—	1.1	—
	0.1	0.1	3.0	0.8	40.2	1.6
	0.2	0.1	0.6	0.1	1.8	0.1
 d)	0.3	0.1	7.7	4.3	15.6	11.4
 e)	—	—	10.4	8.0	9.7	15.8
	14.9	15.8	44.9	41.0	6.4	37.3
	69.3	66.4	19.9	30.2	—	21.0
	14.4	13.8	6.4	12.1	2.4	7.6
 f)	—	—	2.1	1.6	8.7	4.0
Conversion	85.6	86.2	93.6	87.9	97.6	92.4

a, b) Molar contents of $MoCl_3$ (a) and $NiCl_2$ (b) are 12% and 14%, respectively. c) R, R_1 and R_2 mean alkyl groups or hydrogen. d) *unsym*-Octahydroanthracene. e) *sym*-Octahydroanthracene. f) *sym*-Octahydrophenanthrene.

ucts were grouped into 1) C_1—C_4 gases; 2) C_5—C_9 paraffins and cycloparaffins; 3) alkylbenzenes; 4) alkyltetralins and indans; 5) alkylnaphthalenes; 6) *unsym*-octahydro-, 7) *sym*-octahydro-, 8) tetrahydro-, and 9) dihydroanthracene; 10) anthracene; 11) isomerized tricyclic hydroaromatics (*sym*-octahydrophenanthrene). The results are given in Table 1. Among the 3-ring aromatics, anthracene is known to show a relatively high reactivity.[2,3] About 86% of anthracene was converted, even in a noncatalytic run. The run with LiCl-KCl (Run 2) alone, gave very similar results to those of a noncatalytic run. However, the major product in these runs was dihydroanthracene. The use of $MoCl_3$-LiCl-KCl (Run 3) and $NiCl_2$-LiCl-KCl (Run 4) considerably promoted the hydrogenation of anthracene and/or dihydroanthracene and increased the yield of tetrahydroanthracene. Moreover, the formation of *sym*- and *unsym*-octahydroanthracene was also enhanced by these catalysts; the yields of these products were somewhat higher with $MoCl_3$-LiCl-KCl (Run 3) than those with $NiCl_2$-LiCl-KCl (Run 4). The appearance of small amounts of bicyclic and monocyclic products in these runs (Runs 3, 4) indicates that ring-opening cracking reactions occurred, but only to a very limited degree, as can be seen from Table 1.

To examine the influence of the content of $MoCl_3$ and $NiCl_2$, runs with an increased content of MCl_n (25 mol%) in MCl_n-LiCl-KCl (MCl_n=$MoCl_3$, $NiCl_2$) at a constant mol ratio of MCl_n/anthracene (0.3) were also carried out. The results shown in Fig. 1 indicate that an increase in the molar content of $MoCl_3$ (from 12 to 25%, Fig. 1A) and $NiCl_2$ (from 14 to 25%, Fig. 1B) decreased the yield of tetrahydroanthracene and increased the yields of octahydroanthracene, without any remarkable increase of cracking products. These results suggest that increasing the content of $MoCl_3$ and $NiCl_2$ in $MoCl_3$- and $NiCl_2$-LiCl-KCl ternary salts could increase their hydrogenation activity without a remarkable change in the cracking ability. On the other hand, the runs with $MoCl_3$ and $NiCl_2$ alone converted more than 92% of the reactant, and produced more octahydroanthracene and hydrocracked products than their corresponding ternary salts (Table 1, Fig. 1). Especially in a run with $MoCl_3$, alone, dihydroanthracene disappeared and only a small amount of tetrahydroanthracene remained, whereas large quantities of products derived from extensive hydrogenation and cracking, such as *sym*- and *unsym*-octahydroanthracenes, bicyclic and monocyclic compounds and paraffins were formed (Table 1). It is worth while noting that in the catalytic runs of anthracene, *sym*-octahydrophenanthrene was also produced, as can be seen from Table 1. This is considered to be due to the isomerization of *sym*-octahydroanthracene, which is known to occur in the presence of Lewis acids, such as $ZnCl_2$ and $AlCl_3$.[2,3] The isomerization extent could be indicative of the relative Lewis acidity of the salt catalysts. As shown in Fig. 2, the yield of *sym*-octahydrophenanthrene increased as the molar content of MCl_n of MCl_n-LiCl-KCl increased, which appeared to be more remarkable with the $MoCl_3$-containing salts than with the $NiCl_2$-containing salts.

A comparison of the runs using $MoCl_3$- or $NiCl_2$-LiCl-KCl with runs using $MoCl_3$ or $NiCl_2$ (Table 1) indicates that the former promoted hydrogenation reactions and suppressed cracking reactions. This difference was most remarkable between $MoCl_3$-LiCl-KCl and $MoCl_3$ (Table 1, Fig. 1). Since the reactions were carried out at a constant MCl_n/anthracene ratio for both MCl_n-LiCl-KCl and MCl_n salt catalysts and LiCl-KCl showed essentially no catalytic effect, the comparative examination revealed that $MoCl_3$-LiCl-KCl and $NiCl_2$-LiCl-KCl have a lower cracking ability and a higher hydrogenation selectivity than their corresponding $MoCl_3$ and $NiCl_2$ single salts. This suggests that the addition of LiCl- KCl to $MoCl_3$ and $NiCl_2$ suppressed their cracking ability and improved

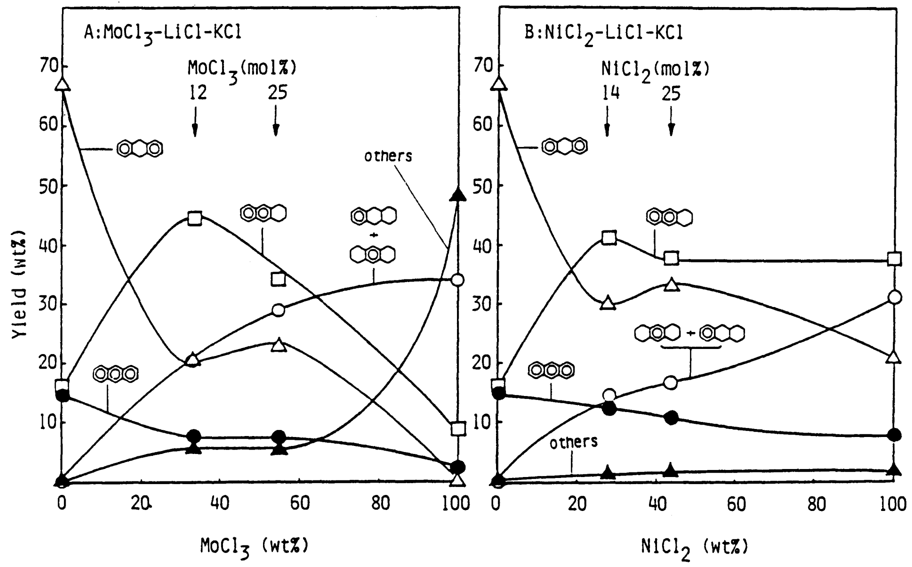


Fig. 1. The influence of MCl_n content in MCl_n-LiCl-KCl on hydrogenation of anthracene. Yields of octahydroanthracenes (○) include those of the isomerized octahydroanthracenes.

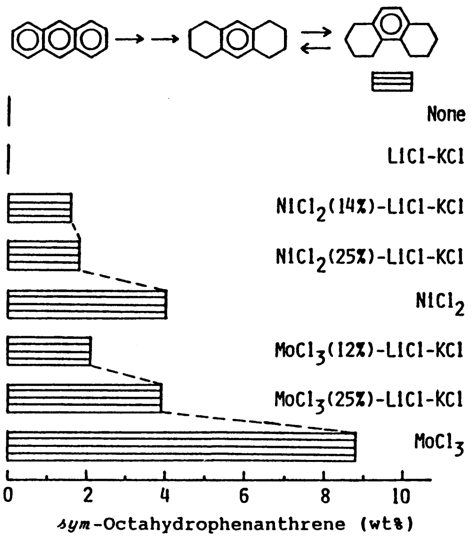


Fig. 2. Yield of *sym*-octahydrophenanthrene formed from hydrogenation of anthracene over MCl_n-LiCl-KCl. The number in the parenthesis indicates the molar content of MCl_n.

their hydrogenation selectivity.[7)] This was probably because addition of LiCl-KCl to $MoCl_3$ or $NiCl_2$ led to the formation of some complex species[8)] such as $MCl_m{}^{n-}$ (M=Mo or Ni), which decreased the Lewis acidity of the catalyst. In addition, the hydrogenation of phenanthrene was also performed. Although it showed a lower reactivity, as is well-known,[2,3)] the trend for difference between MCl_n-LiCl-KCl and MCl_n (MCl_n=$MoCl_3$, $NiCl_2$) appeared to be similar to that observed in the runs involving anthracene.

In our previous papers[5,6)] we demonstrated that $MoCl_3$- and $NiCl_2$-LiCl-KCl salt catalysts greatly enhanced coal conversion with relatively low hydrogen consumption, and significantly increased yield of oil products, without any remarkable increase of C_1—C_4 gas yields. ^{1}H NMR analysis of the oil products revealed that the use of these catalysts increased the content of α- and β-methylene hydrogens present in hydroaromatic structures.[6)] The present results show that these catalysts remarkably enhanced the production of partially hydrogenated aromatics without extensive cracking reactions, being consistent with the above-mentioned ^{1}H NMR analyses. Therefore, the results of this study provided a basis for assessing the extent of hydrogenation and cracking of polyaromatics occurring during coal hydroliquefaction using $MoCl_3$- and $NiCl_2$-based salt catalysts.

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7) Moreover, without LiCl-KCl, a part of $MoCl_3$ disproportionates (to form $MoCl_2$ and strongly Lewis acidic $MoCl_5$) and $NiCl_2$ is reduced at 400 °C, whereas the disproportionation of $MoCl_3$ and reduction of $NiCl_2$ are greatly suppressed by the addition of LiCl-KCl.[5)]

8) For the formation of complex $MCl_m{}^{n-}$, see K. E. Johnson and J. R. Dickinson, "Advances In Molten Salt Chemistry," ed by J. Braunstein, G. Mamantov and G. P. Smith, Plenum Press, New York (1973), Vol. 2, p. 83; G. P. Smith and J. Brynestad, "Molten Salts," ed by G. Mamantov, Marcel Dekker, New York (1969), p.143; H. Kuhnel, *Angew. Chem., Int. Ed. Engl.*, **6**, 64 (1967).