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ACTIVE MOLTEN SALTS CATALYST FOR HYDROCRACKING OF ANTHRACENE

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It was found that $ZnCl_2$-CuCl melts showed an excellent hydrocracking activity for anthracene compared with that of molten $ZnCl_2$ catalyst in view of increasing the yield of low boiling hydrocracked products. The difference of activities between $ZnCl_2$-CuCl melts and $ZnCl_2$ melts is discussed primarily based on the product distribution.

Recently we have shown that the higher yield of benzene derivatives was obtained by hydrocracking a heavy anthracene oil$^{1)}$ using $ZnCl_2$-CuCl melts as a catalyst compared with that over $ZnCl_2$ melts well known as an effective catalyst for hydrocracking of coal and coal extracts$^{2,3)}$.

As a part of studies on the hydrocracking of coal derivatives over molten salts catalyst, it would be desirable to carry out the hydrocracking of a pure aromatic compound such as anthracene since it simplifies analytical interpretation of the results. The molten salts employed here were $ZnCl_2$(a standard molten salt catalyst), 80 % $ZnCl_2$-20 % CuCl, 60 % $ZnCl_2$-40 % CuCl, and 80 % CuCl-20 % KCl. Experiments were carried out in a 500 ml stainless steel autoclave being shaken in horizontal direction (70 strokes/min). In the autoclave about 10 g of anthracene was charged along with equimolar amounts of molten salts$^{4)}$ and hydrogen pressured up to 100 kg/cm^2. The reaction temperature was held at 400°C for 1 hr. After the end of the reaction, gaseous products were collected in a gas holder and analyzed by glc(3.0 m × 3.0 mm column packed with 60-80 mesh silica gel, 150°C, TCD, N_2 carrier). The solid products(dissolved in acetone) and the liquid products were also analyzed by glc(4.5 m X 3.0 mm column packed with 20 % SE-30 on Uniport B 60-80 mesh, 30-270°C, TCD, H_2 carrier).

Hydrocracking of anthracene over molten zinc chloride(Run No. 2 in Table 1) gave primarily five partially hydrogenated anthracenes which were separated by a preparative gas chromatography. On the basis of their NMR spectra the structures of these compounds were assigned to unsym-octahydroanthracene, 9,10-dihydroanthracene, sym-octahydroanthracene, sym-octahydrophenanthrene and 1,2,3,4-tetrahydroanthracene, respectively, in the eluted order.

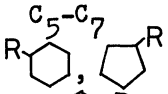
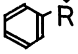
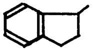
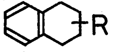
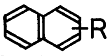
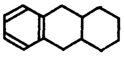
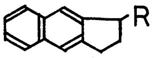
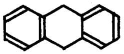
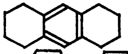
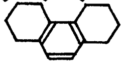
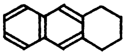
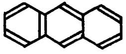
The NMR data(CCl_4) of these compounds were as follows. unsym-Octahydroanthracene (M^+ m/e 186);[δ 0.88-2.10(10 H, m), 2.38(2 H, dd, J=10, 16 Hz), 2.71(2 H, duplicate of dd, J=6, 12, 3, 16 Hz), 6.88(4 H, s) mixture of two isomers], 9,10-Dihydroanthracene (M^+ m/e 180);[δ 3.84(4 H, s), 7.06(8 H, m)], sym-Octahydroanthracene(M^+ m/e 186); [δ 1.74(8 H, m), 2.60(8 H, m), 6.73(2 H, s)], sym-Octahydrophenanthrene(M^+ m/e 186); [δ 1.75(8 H, m), 2.48(4 H, t, J=6 Hz), 2.66(4 H, t, J=6 Hz), 6.60(2 H, s)], Tetrahydroanthracene(M^+ m/e 182); [δ 1.84(4 H, m), 2.91(4 H, m), 7.00-7.60(6 H, m)].

In this treatment, significant quantities of sym-octahydrophenanthrene were isolated and the presence of small amounts of tetrahydrophenanthrene was observed in the NMR spectrum of tetrahydroanthracene-fraction prepared by glc. These hydrophenanthrenes are probably produced via such an α-ring opening of saturated portions of the corresponding hydroanthracenes as suggested by Schroeter[5)] in studies of the skeletal isomerization between octahydroanthracene and octahydrophenanthrene in the presence of $AlCl_3$. Another hydrocracked products were same as identified in the previous paper[6)].

Table 1 shows the product distributions of anthracene hydrocracking over various molten salts together with the result under the absence of molten salts. The product distribution indicates that the principal reactions in the anthracene hydrocracking are hydrogenation, skeletal isomerization and cracking as also suggested in the previous paper[6)]. It was seen from Table 1 that anthracene was very readily hydrogenated and very little remained unconverted under the experimental conditions.

In this case hydrocracking activity of molten salt may be evaluated by the yield of low boiling hydrocracked products(or the extent to which hydrogenated anthracenes were cracked). Low boiling hydrocracked products here refer to hydrocarbons(C_5-C_7), cycloalkanes and benzene derivatives. Over molten $ZnCl_2$, the combined yield of hydroanthracene is 66.0 % and the yield of low boiling hydrocracked products is 7.9 %. In this case main reaction appears to be hydrogenation of anthracene to partially hydrogenated anthracenes. On the other hand, hydrogenation in the presence of $ZnCl_2$-CuCl melts yields much larger quantities of low boiling hydrocracked products (28.8 % in Run No. 3). The yield of gaseous products(C_1-C_4) was 13.4 % in the case of 80 % $ZnCl_2$-20 % CuCl melts and only 6.8 % for 60 % $ZnCl_2$-40 % CuCl melts.

Table 1 Hydrocracking of anthracene(400°C, 100 kg/cm^2, 1 hr)

Run No.	1	2a)	3a)	4	5a)	6	7b)
Molten salt	-	$ZnCl_2$	60 % $ZnCl_2$ 40 % CuCl		80 % $ZnCl_2$ 20 % CuCl		80 % CuCl 20 % KCl
Conv %	96.0	97.9	99.1	99.8	99.0	99.0	96.1
C_1-C_4	3.0	9.6	6.8	15.8	13.4	23.5	11.5
C_5-C_7	-	0.7	4.8	8.6	4.8	6.2	-
	-	3.7	13.1	16.9	13.7	10.5	0.1
	-	3.5	10.9	12.7	9.9	13.2	0.3
	-	1.8	6.5	5.0	5.6	6.9	-
	1.7	8.1	27.2	17.3	19.3	14.5	2.4
	-	0.9	2.8	1.6	2.1	3.4	0.3
	5.4	14.6	10.6	5.9	10.8	5.7	11.5
	0.5	1.2	1.8	0.9	1.1	1.9	1.1
	22.9	9.1	-	-	-	0.3	18.8
	15.2	11.3	3.8	3.0	5.6	3.4	8.9
	1.5	7.4	2.8	1.8	4.0	2.2	4.8
	44.3	23.6	2.4	1.1	2.6	2.5	30.2
	4.0	2.1	0.9	0.2	1.0	1.0	3.9
Higher boiling constituents	1.4	2.1	3.7	2.7	2.8	4.0	3.3
Coke	0.1	0.3	1.9	6.5	3.3	0.8	2.9

a) In this case, the dried molten salts and anthracene were transferred to a stainless steel container under the dry nitrogen atmosphere.

b) Some elemental Cu was found in the stainless steel container after the experiment.

Judging from above observation, 60 % $ZnCl_2$-40 % CuCl melts is better than 80 % $ZnCl_2$-20 % CuCl melts in view of increasing the yield of low boiling hydrocracked products. These results along with the increased yield of indane and tetrahydronaphtalene point to the clear superiority of $ZnCl_2$ melts containing CuCl as a hydrocracking catalyst.

Both $ZnCl_2$ melts and $ZnCl_2$-CuCl melts have strong hygroscopic character so that they absorbed some water even under the quick work up in the atmosphere. Run 4 and Run 6 were conducted to observe the effect of this absorbed water on the hydrocracking reactions. The considerable amounts of water increase the proportion of hydrocracked products(especially gaseous products) to converted anthracene. These findings strongly suggest that the reaction proceeds via a mechanism which is similar to that proposed by Zielke et al7). When 80 % CuCl-20 % KCl melts were used as catalyst, the combined yield of hydroanthracene amounted up to 74.2 %. The distinctive feature of CuCl-KCl catalyst is the relativly high ratio of tetrahydro and dihydroanthracene to octahydroanthracene and its product distribution similar to that without molten salt(Run No. 1). These results indicate CuCl-KCl melts to be less active than $ZnCl_2$ melts for hydrocracking. Accordingly the reason why the addition of CuCl(less active than $ZnCl_2$) improved the hydrocracking activity of $ZnCl_2$ remains uncertain. However in view of the above results of hydrccracking over $ZnCl_2$ and CuCl-KCl melts giving the high yield of partially hydrogenated anthracene, it is considered that the addition of CuCl brought about a kind of synergistic effect to improve the intrinsic hydrocracking activities of $ZnCl_2$.

References and Notes

1) Presented at the Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1976; Proceedings Vol. II, p 958.

2) D. M. Bodily, H. D. Lee, and G. R. Hill, Preprints, Div. Fuel Chem., Am. Chem. Soc., 17, (1), 28 (1972).

3) C. W. Zielke, R. T. Struck, J. M. Evans, C. P. Costanza, and E. Gorin, I & EC Process Design and Development 5, 158 (1966).

4) The molten salts were dried in a Pyrex vessel before use for 3 hrs by bubbling dry N_2 and then poured into stainless steel container(which will be inserted into autoclave) while hot, the solidified melts subsequently being covered by equimolar amounts of anthracene. The above container was used to prevent molten salt to corrode the inner wall of autoclave.

5) G. Schroeter, Ber., 57, 1990 (1924).

6) S. Kikkawa, M. Nomura, and K. Murase, Sekiyu Gakkaishi(J. Japan Petro. Inst.), 19, 863 (1976).

7) C. W. Zielke, R. T. Struck, J. M. Evans, C. P. Costanza, and E. Gorin, I & EC Process Design and Development 5, 151 (1966).

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