Supported Molten Zinc Chloride Catalysts (Part 3)

Changes in Catalytic Hydrocracking Activities with Reaction Time

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Changes in catalytic hydrocracking activities with reaction time were investigated on four kinds of supported molten zinc chloride catalysts impregnated on N631-HN(28%Al₂O₃–72%SiO₂) and Neobead-C(100%Al₂O₃) as carriers for the hydrocracking reaction of anthracene, explored as a test reaction. The supported catalysts prepared by impregnating an aqueous zinc chloride solution and drying at 140°C gave a high rate of conversion into gaseous and low boiling liquid products, but they were rapidly deactivated with reaction time. The catalysts pretreated at higher temperatures increased the conversion of anthracene into smaller products and the catalytic life was longer than that of those prepared at 140°C. The reduction in the activity of supported molten zinc chloride catalysts was stemmed from the loss of molten zinc chloride on the catalysts by vaporization and dissolution into the liquid products and also to the deactivation of the carriers induced by carbon deposition on and irreversible changes in their solid surfaces.

1. Introduction

In previous papers^{1),2)}, we have reported that in the hydrocracking of anthracene or of coal extract, supported molten zinc chloride catalysts were more efficient than molten zinc chloride alone, because the activity of the former was a function of the activity of molten zinc chloride and that of the carrier and because the contact surface area was increased. In fact, it was found that N631-HN (28%Al₂O₃–72%SiO₂) was the most suitable carrier so far examined, and that catalytic activity was improved by pretreatment at higher temperatures after impregnation. Furthermore, the supported molten zinc chloride can behave like a solid instead of a liquid in handling and transporting that proved to be of great advantage in practical applications. Nevertheless, it is important to know how long the supported molten zinc chloride catalysts would be catalytically active in actual use.

In the present work, changes in the activities of supported molten zinc chloride catalysts were measured for hydrocracking of anthracene taken as an exploratory reaction. The loss of zinc chloride from the solid surface and the change in the activities of the carriers themselves were

determined, as these factors were considered to contribute to the drop in the activity. Also, tests of these catalysts on the reduction in hydrocracking activities for coal extract were carried out.

2. Experimental

Equipment, procedure, analysis of the products, chemicals and carriers are the same as those described in the previous papers^{1),2)}.

The supported molten zinc chloride catalysts used for the tests were prepared as follows: (1) impregnation of an aqueous zinc chloride solution of a given concentration on N631-HN (28%Al₂O₃–72%SiO₂) and on Neobead-C (100%Al₂O₃) and drying in air at 140 °C for 2 hrs. (2) pretreatment of the dried products at 400 °C in a stream of N₂ for 2 hrs. in a tubular furnace.

Changes in the catalytic activities with reaction time were evaluated in the following manner: 3 g of anthracene, 1 g of the prepared catalyst and 100 kg/cm² of hydrogen were introduced into an autoclave at room temperature. It was heated at the rate of 4 °C/min. up to 400 °C and kept at this temperature for one hour. After cooling the autoclave down to room temperature, only the reaction products were taken out therefrom. Then 3 g of fresh anthracene was charged into the autoclave in which the catalyst remained and the reaction was carried out in a similar manner for seven hours. After the reaction products only were taken out, the same amount of fresh anthracene was charged again and the reaction was repeated for one hour. Sometimes, the one-hour reaction

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was repeated once more.

The hydrocracking products of anthracene were classified into four groups, namely, compounds smaller than tricyclic aromatics (gaseous, saturated, monocyclic, bicyclic, isomer of bicyclic compounds), tricyclic aromatics (partially hydrogenated anthracenes and benzindanes), unreacted anthracene and carbonaceous products; the change in catalytic

activity of each catalyst with reaction time was compared with the degree of conversion into compounds smaller than tricyclic aromatics of the first and the third (or fourth) reaction products.

IR spectra of hydroxyl groups on a carrier surface were measured by the method described by Hino et al.³⁾ to investigate changes in the active sites.

Table 1 Changes in Activities of Supported Molten Zinc Chloride Catalysts with Reaction Time
Reaction conditions : Temperature 400°C, Init. press. 100 kg/cm², Sample/Catalyst = 3 g/1 g

(a) N631-HN (pretreated at 400°C for 2 hrs. under N ₂ flow)				
Experiment	No. 21	No. 22	No. 23	No. 24
Time (hr)	1	7	1	1
H ₂ Consumed (g/g-sample)	0.047	0.117	0.064	0.059
Products Smaller than Tricyclic Aromatics (wt%)	41.7	62.2	24.6	17.4
Tricyclic Aromatics (wt%)	50.2	35.1	72.5	79.6
Unreacted (wt%)	8.1	2.7	2.9	3.0
Coke (wt% for sample)				(2.2)*
Deposited Coke (wt% for catalyst)				20.9
(b) 28.5%ZnCl ₂ -71.5%N631-HN (pretreated at 400°C for 2 hrs. under N ₂ flow)				
Experiment	No. 25	No. 26	No. 27	No. 28
Time (hr)	1	7	1	1
H ₂ Consumed (g/g-sample)	0.119	0.092	0.057	0.058
Products Smaller than Tricyclic Aromatics (wt%)	72.0	95.8	39.1	21.7
Tricyclic Aromatics (wt%)	27.3	4.19	60.2	77.6
Unreacted (wt%)	0.7	0.01	0.7	0.7
Coke (wt% for sample)				(1.0)*
Deposited Coke (wt% for catalyst)				10.8
(c) Neobead-C, 28.5%ZnCl ₂ -71.5% Neobead-C (each was pretreated at 400°C for 2 hrs. under N ₂ flow)				
Catalyst	Neobead-C	ZnCl ₂ -Neobead-C		
Experiment	No. 29	No. 30	No. 31	No. 32
Time (hr)	1	1	7	1
H ₂ Consumed (g/g-sample)	0.082	0.148	0.117	0.076
Products Smaller than Tricyclic Aromatics (wt%)	5.9	68.0	92.0	27.0
Tricyclic Aromatics (wt%)	93.1	29.4	7.9	71.8
Unreacted (wt%)	1.0	2.5	0.1	1.2
Coke (wt% for sample)	0.01			(1.2)*
Deposited Coke (wt% for catalyst)				10.9
(d) 50%ZnCl ₂ -50%N631-HN (dried at 140°C for 2 hrs. after impregnation)				
Experiment	No. 33	No. 34	No. 35	
Time (hr)	1	7	1	
H ₂ Consumed (g/g sample)	0.077	0.075	0.055	
Products Smaller than Tricyclic Aromatics (wt%)	67.7	64.0	22.3	
Tricyclic Aromatics (wt%)	30.9	35.3	77.0	
Unreacted (wt%)	1.4	0.7	0.7	
Coke (wt% for sample)			(1.9)*	
Deposited Coke (wt% for catalyst)			16.3	
(e) 50%ZnCl ₂ -50%Neobead-C (dried at 140°C for 2 hrs. after impregnation)				
Experiment	No. 36	No. 37	No. 38	
Time (hr)	1	7	1	
H ₂ Consumed (g/g sample)	0.066	0.078	0.049	
Products Smaller than Tricyclic Aromatics (wt%)	49.6	31.2	21.5	
Tricyclic Aromatics (wt%)	48.3	67.3	76.9	
Unreacted (wt%)	2.1	1.5	1.6	
Coke (wt% for sample)			(0.6)*	
Deposited Coke (wt% for catalyst)			9.7	

* Based on the total amount used.

3. Results and Discussion

3.1 Changes in Catalytic Activities of Carriers

The N631-HN carrier pretreated alone at 400 °C in a N₂ stream exhibited high catalytic activity for hydrocracking of anthracene as shown in **Table 1** (a), and in the first one-hour reaction, about 40 wt% of anthracene was hydrocracked into smaller compounds such as gaseous products, saturated hydrocarbons, monocyclic aromatics and bicyclic aromatics. In the next one-hour reaction, after the seven-hour reaction, conversion into smaller compounds was reduced to 25 wt% and in another one-hour reaction, it was further reduced to 17 wt%.

The deposition of carbonaceous products on the active sites of the catalyst brought about this decrease in catalytic activity, because 0.21 g of the carbonaceous products was formed on 1 g of the catalyst, about 350 m²/g of the surface area of the catalyst dropped to 10 m²/g after an overall ten-hour reaction and the surface area and catalytic activity could be recovered nearly to the previous levels, when the carbonaceous products were burnt

off at 500 °C in air, as shown in **Table 3** (Experiment No. 42) and **Table 2**.

The Neobead-C carrier itself was found to be of poor activity for hydrocracking of anthracene (**Table 1** (c)). Accordingly, the catalytic properties may not be affected by reaction time.

3.2 Changes in Activities of Supported Molten Zinc Chloride Catalysts

As shown in **Table 1** (b) and **1** (c), the supported molten zinc chloride catalysts prepared by pretreatment at 400 °C after impregnation of 1.2 g of zinc chloride on 3 g of the carrier were highly active in the first one-hour reaction. But in the next one-hour reaction, after the seven-hour reaction, the rate of hydrocracking decreased substantially. This decrease in the activity of the Neobead-C supported catalyst was larger than that of the N631-HN. Nevertheless, the activity of the supported molten zinc chloride catalysts was maintained definitely for a longer reaction period, compared with that of N631-HN alone (**Table 1** (a)).

Table 1 (d) and **1** (e) show the results of the supported molten zinc chloride catalysts prepared

Table 2 Changes in Surface Area of a Supported Molten Zinc Chloride Catalyst and Carriers before and after Reaction

Catalyst	Treatment	Surface Area (m ² /g)
(A) 28.5%ZnCl ₂ -71.5% N631-HN	Heated at 400°C for 2 hrs. in N ₂ flow after impregnation of ZnCl ₂	97
(B) Carbon Deposited (A) Catalyst	Extracted with ethanol and benzene after the ten hours reaction	42
(C) Carbon Burnt off (B) Catalyst	Deposited carbon on (B) was burnt off at 500°C in air	116
(D) Acid Leached (C) Catalyst	After leaching twice with 12N-HCl and 14N-HNO ₃ and then treated at 400°C for 2 hrs.	140
(E) N631-HN Carrier	Treated at 320°C and 600°C	303, 387
(F) Carbon Deposited (E) Catalyst	Extracted with benzene after ten-hour reaction	10
(G) Carbon Burnt off (F) Catalyst	Deposited carbon was burnt off at 500°C in air	264

Table 3 Comparison of Activities of Regenerated Catalysts

Reaction conditions : Temperature 400°C, Init. press. 100 kg/cm², Time 1 hr., Sample/Catalyst=3 g/1g

Experiment	No. 39	No. 40	No. 41	No. 42
Catalyst	(H)	(I)	(D)	(G)
H ₂ Consumed (g/g-sample)	0.034	0.049	0.038	0.047
Products Smaller than Tricyclic Aromatics (wt%)	11.9	8.8	27.7	60.5
Tricyclic Aromatics (wt%)	86.3	89.6	71.7	35.8
Unreacted (wt%)	1.8	1.6	0.6	3.7
Coke (wt% for sample)	4.0	0.9	0.1	8.8

Methods of catalyst preparation

- (H) 10.8 wt% of carbon was deposited on 28.5%ZnCl₂-71.5%N631-HN catalyst after ten-hour reaction. This was washed with ethanol and benzene in a Soxhlet extraction apparatus to remove the ZnCl₂ and products and then 1 g of zinc chloride was impregnated on the washed and carbon deposited N631-HN.
- (I) The above deposited carbon was burnt off at 500°C in air for 2 hrs. and 1 g of zinc chloride was impregnated on 1 g of the burnt N631-HN(C).
- (D) As the above burnt N631-HN carrier (C) contained 6.33 wt% of zinc (determined by a X-ray fluorescence method), it was leached with 12N-HCl and 14N-HNO₃ twice. Zn content dropped to 0.91%.
- (G) 20.9 wt% of carbon deposited on the N631-HN catalyst after ten hours reaction. This coke was burnt off at 500°C in air for 2 hrs.

by drying at 140 °C after impregnation of 5 g of zinc chloride on 5 g of the carrier without pretreatment. In the first one-hour reaction, the conversion of anthracene into products smaller than tricyclic aromatics was 67.7 wt% with the N631-HN supported catalyst and it was 49.6 wt% with the Neobead-C supported catalyst. But in the next seven-hour reaction and in the following one-hour reaction conversions into smaller products were 64.0 wt% and 22.3 wt% with the N631-HN supported catalyst and 31.2 wt% and 21.5 wt% with the Neobead-C supported catalyst, respectively. These results indicate a rapid reduction in the activities of the supported molten zinc chloride catalysts without pretreatment and this reduction with reaction time is more remarkable than that of the catalyst pretreated at 400 °C. Causes for this difference are not clear. However, since there are differences between pretreated catalyst and dried one as regards water content, distribution of zinc chloride on the surface or in the pores, interaction between zinc chloride and the solid surface and formation of carbonaceous products by combination of these factors, some of them could be the causes.

In this manner the activity of supported molten zinc chloride catalysts changes with reaction time, and the rate of reduction depends on the method of preparation.

As the overall activity of supported molten zinc chloride catalysts is the result of the additional activities of molten zinc chloride and carriers and it also depends on increased contact surface area, reduction in the activity would be affected by changes in any of these factors.

With regard to the change in activity of N631-HN as the carrier after an overall ten hours' reaction, 10 to 20 wt% of carbonaceous products was formed on the solid surface, whose area had decreased to 42 m²/g. The covering of the active sites on the carrier and the decrease in the contact surface area by the carbonaceous substances are causes of reduction in the activity as confirmed above. But as shown in the results of experiments No. 39 to No. 42 (**Table 3**), the N631-HN carrier which was regenerated from the used N631-HN supported molten zinc chloride catalysts by extraction of zinc chloride with ethanol and then by burning off the carbonaceous products at 500 °C in air, or by acid-treatment with 12*N*-HCl and 14*N*-HNO₃ followed by removal of the carbonaceous products was considerably less active than the

original N631-HN carrier and the molten zinc chloride supported on the regenerated carrier was also less active than the original supported molten zinc chloride catalyst. Furthermore, their surface area did not recover to the original level. Under the present reaction conditions, fresh molten zinc chloride should always be supplied to the solid surface wherever and whenever carbonaceous products were formed because zinc chloride melts at about 280 °C. Accordingly, it is certain that there are other causes to prevent the recovery of activity of the carriers.

Fig. 1 shows changes in hydroxyl groups on the N631-HN carrier surface before and after the reaction or after the acid-treatment.

The surface hydroxyl groups of silica-alumina (N631-HN) are classified into single OH groups (which on silica surface give a sharp absorption band at 3,740 cm⁻¹) and hydrogen bonded or paired OH groups (which gave a broad absorption

(a) Original, (b) after extraction of ZnCl₂ on (a) with ethanol, (c) after the ten hours reaction, supported ZnCl₂ was extracted with ethanol and then the carbonaceous products were burnt off, (d) after residual ZnCl₂ on (c) was leached out with 12*N*-HCl and 14*N*-HNO₃; each was prepared by evacuation at 510 ± 20 °C for 1 hr.

Fig. 1 Changes in Hydroxyl Groups on N631-HN Carrier Surface before and after Reaction

band at about $3,640\text{ cm}^{-1}$)^{4),5)}. On the other hand, zinc chloride is known to react with metal oxides to form a surface complex with ZnCl_4^{2-} ⁶⁾. The relative intensity of the band at $3,640\text{ cm}^{-1}$ to that at $3,740\text{ cm}^{-1}$ of the hydroxyl groups on the N631-HN surface, which was subjected to contacting with molten zinc chloride at 400°C for 2 hours and then to extracting zinc chloride with ethanol, was weaker than that of the original (**Fig. 1** (a), (b)). Furthermore, the treated carrier contained 3.86 wt% of zinc and 0.34 wt% of chlorine. These results indicate the formation of some complex on the surface. **Fig. 1** (c) is a spectrum of the catalyst after ten hours' reaction from which zinc chloride was extracted with ethanol and then the carbonaceous products were burnt off at 500°C in air. The pattern of the spectrum was the same as that of the original but the surface area decreased to $116\text{ m}^2/\text{g}$. The zinc content was 6.33 wt% whereas that of chlorine was less than 0.1 wt%. These results suggest that the number of active sites of Brönsted acid on the carrier surface was remarkably reduced and that the active sites were zinc-poisoned in the following manner as deduced by Kaji et al.⁷⁾;

Fig. 1 (d) is the spectrum of the regenerated N631-HN which was leached twice with 12*N*-HCl and 14*N*-HNO₃ to remove the residual zinc. By this acid treatment, the surface hydroxyl groups were found to be affected and the zinc content of 6.33 wt% was reduced to about 1 wt%. But the surface area of $116\text{ m}^2/\text{g}$ increased to $140\text{ m}^2/\text{g}$ and the catalytic activity for hydrocracking of anthracene did not recover to the original level. From these results, some cleavage of the pore structure seemed to have occurred during the hydrocracking reaction.

As hydrocracking of anthracene is promoted mainly by the activity of the carrier, the life of a supported molten zinc chloride catalyst depends on that of the carrier when a sufficient amount of zinc chloride is present on the catalyst. Nevertheless, another possibility affecting the catalytic life could be the concentration of zinc chloride on

Fig. 2(a) An Example of Evaporation Curve of Zinc Chloride on N631-HN (42.2 wt% ZnCl_2 supported catalyst pretreated at 400°C)

Fig. 2(b) An Example of Evaporation Curve of Zinc Chloride on Neobead-C (25.5 wt% ZnCl_2 supported catalyst pretreated at 400°C)

the catalyst.

Fig. 2 (a) and (b) show examples of weight loss curves of molten zinc chloride supported on N631-HN and on Neobead-C. Molten zinc chloride has some vapor pressure at the reaction temperature and for example, at 400°C zinc chloride evaporates at the rate of about 1 wt%/hr from the supported catalyst. This evaporation rate does not depend on the species of a carrier and the amount of zinc chloride supported but on the temperature of treatment. There seems to be another factor concerned with the decrease in zinc chloride on the catalyst. It is supposed that zinc chloride dissolves into the liquid phase because it reacts with the aromatics to form EDA-complexes⁸⁾.

The combined effects of these factors can decrease the activity of the supported molten zinc chloride catalysts.

Table 4 shows the change in the activity of the 42% ZnCl_2 -58% N631-HN supported catalyst for hydrocracking of coal extract.

Table 4 Changes in Catalytic Activities for Hydrocracking of Coal Extract with Reaction Time

Reaction conditions : Temperature 400°C, Init. pressure 100 kg/cm², Sample/Catalyst=5 g/2 g

Experiment	No. 68	No. 69	No. 70
Time (hr)	1	7	1
H ₂ Consumed (g/(-sample))	0.054	0.073	0.048
Gas Produced (wt%)	8.2	14.6	13.0
Gas Composition (mol%)			
Methane	43.3	45.5	49.8
Ethane	21.9	21.9	22.6
Propane	17.1	17.8	16.0
<i>i</i> -Butane	2.5	1.6	1.1
Butane	10.6	10.0	8.2
<i>i</i> -Pentane	2.4	1.5	1.0
Pentane	2.2	1.7	1.3
Liquid Fractions (wt%)			
~200°C	38.5	50.5	46.5
200~300°C	39.5	40.0	33.0
300~400°C	9.5	5.5	7.5
400°C ~	12.5	4.0	13.0
Coke Deposited+Unreacted (wt% for 15 g of sample)			5.3

The activity of the catalyst for hydrocracking of coal extract changed a little during the period of test reaction or rather increased somewhat with reaction time.

An explanation for this observation could be that, for hydrocracking of coal extract the activity of the supported molten zinc chlorides does not depend so much on the active sites of the carrier surfaces but depends mainly on the activity of molten zinc chloride. Also, water, which is produced by the reaction of oxygen atom in the coal extract with hydrogen during the reaction, is supposed to promote the hydrocracking reaction. Accordingly, the life of the supported molten zinc chloride catalysts for hydrocracking of coal extract may depend mainly on the life of the molten zinc chloride supported.

4. Conclusion

The life of the supported molten zinc chloride catalysts depends mainly on that of the carriers and of molten zinc chloride, because the activity is a function of that of molten zinc chloride and that of the carrier. The decrease in activity

caused by these carriers was found to be the covering of the active sites and the decrease of the contact surface area with carbon deposition, and irreversible changes in the surface structures caused by the reaction of zinc chloride with the surface Brönsted acid sites. The decrease in activity caused by molten zinc chloride was found to be the decrease in the zinc chloride concentration on the solid surface induced by evaporation of the chloride and its dissolution into the products. These factors seem to contribute to deactivation of the supported molten zinc chloride catalysts. Nevertheless, the rate of deactivation of the supported molten zinc chloride catalysts depends on the species of carriers and the method of catalyst preparation. The supported molten zinc chloride on N631-HN carrier pretreated at higher temperatures after impregnation gave a longer catalytic life than that prepared at 140 °C or the catalyst supported on Neobead-C. But hydrocracking activity for anthracene rapidly decreased; on the other hand, hydrocracking activity for coal extract changed a little because it depended mainly on the activity of molten zinc chloride supported.

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要 旨

担 持 溶 融 塩 化 亜 鉛 触 媒 (第 3 報)
反 応 時 間 に よ る 水 素 化 分 解 活 性 の 変 化

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既報の如く、担持溶融塩化亜鉛触媒はアントラセンのみならず石炭分解抽出物の水素化分解にも効果的に作用することが明らかになったので、本研究では、N631-HN と Neobead-C 担体に担持した塩化亜鉛触媒の活性変化をアントラセンの水素化分解をモデル反応として、回分実験の繰返し試験によって比較検討した。

N 631-HN 担体単独の触媒活性は、反応時間とともに顕著に減少し (Table 1(a))、炭素質の沈着とともに触媒表面積の大幅な減少が確認された (Table 2)。これら沈着炭素質を燃焼除去すると、表面積や分解活性が回復することから (Table 3) 本実験においても固体表面への炭素質の沈着が活性低下の一因となることが明らかとなった。

塩化亜鉛を担持すると、アントラセンの水素化分解に対する分解活性は、担体単独の場合よりもその低下が緩慢になった

(Table 1 (b)), (c), (d), (e))。同じく炭素質の沈着があることから、これが活性低下の原因となっている。しかし、炭素質燃焼除去後も表面積は回復せず (Table 2) 分解活性も回復しない (Table 3)。さらには、酸洗いによっても亜鉛の除去が困難であることや固体表面水酸基の変化から (Fig. 1)、亜鉛イオンによる担体活性点の被毒や担持塩化亜鉛による固体細孔構造の不可逆的变化が示唆された。

以上は、担体側からの活性低下の原因であるが、担持体塩化亜鉛側からの活性低下には、生成物への溶解や揮発による固体表面の塩化亜鉛濃度の低下が要因として示される。熱天びんによると、塩化亜鉛の蒸発速度は担持量や担体の種類には影響されず、処理温度に依存することがわかった (Fig. 2)。

石炭抽出物に対する担持溶融塩化亜鉛触媒の分解活性は、主に塩化亜鉛の分解活性に依存しているために、繰返し試験した反応時間内ではほとんど活性低下は観察されなかった (Table 4)。

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