

Preparation and performance of rare earth Zr catalyst for reforming waste plastics cracking product^①

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Abstract: The rare earth Zr catalyst, whose carrier was Al_2O_3 , was prepared by co-precipitation with $\text{Zr}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, and $(\text{NH}_2)_2\text{CO}$ as the raw materials. The obtained catalyst was used to reform the waste plastic cracking product. As the Zr content in the catalyst increases, the yields of gasoline, gas, and the rate of carbon deposition increase, but the yields of diesel and heavy oil decrease. The optimum Zr content of the catalyst is 5%. At 290 °C, with this most suitable catalyst, the yield of liquid fuel oil is the highest, about 86.10%, and research octane number (RON) of the gasoline is 92.15.

Key words: rare earth Zr catalyst; co-precipitation; waste plastic cracking

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1 INTRODUCTION

As a solution for “white pollution”, production of fuel oil by cracking waste plastic has been paid much more attention. A lot of studies on waste plastic cracking process and facility have been conducted, but not so much on the related catalyst. The catalysts used in the waste plastic cracking process are those used in the process of crude oil refinery, such as HY^[1], Ni-REY^[2], and HZSM-5^[3] molecular sieve catalyst, because these two processes are a little similar. In fact, the composition of crude oil is much more complicated than that of waste plastic, so many problems while using the catalyst used in the process of crude oil to reform waste plastic cracking product would be encountered. The objective of this research is to prepare a catalyst, which is suitable for cracking waste plastic inexpensively and effectively in reforming waste plastic cracking product.

Most parts of waste plastic cracking product is heavy fraction^[4], for instance, heavy oil takes 30%, and diesel takes 35%. So the objective of catalytic reforming is to increase the quantity of light fraction and decrease the quantity of heavy fraction. This requires the reforming catalyst to have bigger pore size, wider specific surface area and sound distribution of the surface acidic site. Too strong acidic site is unnecessary because it is possible to deactivate catalyst by carbon deposition^[5]. Al_2O_3 has wide and adjustable specific surface area, stable absorptivity, and strong thermal stability. Zirconia has moderate

acidic site, so the surface acidic site distribution of the co-precipitation formed by zirconia and Al_2O_3 may be sound, and the co-precipitation could catalytically reform the waste plastic cracking product. In our research, Al_2O_3 as carrier, zirconia as main component, the reforming catalyst for cracking waste plastic is prepared by co-precipitation.

Agglomeration may take place in the course of dryness of Al_2O_3 , resulting in the inhomogeneity of the catalyst particle. Addition of a surfactant^[6] and dispersant S^[7] can avoid cluster and agglomeration of the particles, and make the catalyst particle more homogeneous and disperse. So in our study, dispersant A is added, and the co-precipitation is dewatered by isopropanol.

2 EXPERIMENTAL

2.1 Experimental materials

$(\text{NH}_2)_2\text{CO}$; $\text{Al}(\text{NO}_3)_3 \cdot 3\text{H}_2\text{O}$; $\text{Zr}(\text{NO}_3)_4 \cdot 5\text{H}_2\text{O}$; dispersant A, whose main component is poly-isoamylol; absolute ethanol; absolute isopropanol; ammonia; high-density polyethylene, polypropylene, and polystyrene particle, produced by No. 2 chemical factory of Beijing Yansan Petroleum Stock Limited Company; waste bag made of polypropylene and polyethylene; waste shockproof package material made of polystyrene were used in this experiment.

2.2 Experimental methods

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2. 2. 1 Experimental flow and methods of catalyst preparation

The method of catalyst preparation is as follows. 1) Measure the mass of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $(\text{NH}_2)_2\text{CO}$ according to the mass ratio of 1: 3, then add $\text{Zr}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ proportionally, and mix with distilled water in the three-neck flask to make solution with Al^{3+} concentration of 0.5 mol/L. At the same time, prepare dispersant A. Mix the solution, heat it in the water bath, keep the reaction temperature in the range of 90 – 100 °C, measure pH value of the solution frequently. 2) When pH reaches 4, a little gelatin comes into being. Then add ammonia with concentration of 0.1 mol/L to adjust pH to 7. At this point the reaction is nearly finished, so stop heating. Wash the mixture of gelatin by water ten times to remove NO_3^- and NH_4^+ . Then clean the gelatin by absolute ethanol or isopropanol, until the water in the gelatin has been removed completely. 3) Dry the cleaned gelatin for 4 h at 120 °C in the vacuum drier. Then calcine it at different temperatures. So catalyst from different calcine temperatures is prepared. 4) Measure the bulk density, apparent density and actual density of the catalysts^[8]; measure the specific surface area of the catalysts by BET method^[8]; measure the strength and quantity of acid of the catalysts by Hammett indicator method^[9].

2. 2. 2 Catalytic experimental flow and method

Performance of the rare earth Zr catalyst is tested by application of the catalyst directly to catalytically reform the product derived from thermal pyrolysis of the mixture of waste plastic and heavy oil. The catalytic capability is determined by the yields of gasoline, diesel, and heavy oil, and the rate of carbon deposition. The activity of the catalyst is expressed by the transformation ratio of diesel and heavy oil^[10]. Analysis of the gasoline is done with chromatogram-mass spectrometry apparatus (GC-17A and QP-5000), and the product distribution is identified.

3 RESULTS AND DISCUSSION

3. 1 Determination of end point for catalyst preparation reaction

In the preparation reaction, cool the reaction solution to room temperature rapidly and stop the reaction, when the pH of it is 5 or 6. Then separate the solution by centrifugation. Adding ammonia to the upper layer clear solution, sedimentation will come into being. If reaction is stopped when pH is 7 or 8, by the same procedure, sedimentation will not come into being. So when pH of reaction solution is 7, the reaction has completed and ions have settled completely. In a word, the end point of the preparation reaction of catalyst can be determined by mea-

suring the pH of the reaction solution.

3. 2 Effect of washing on preparation of catalyst

To study the effect of dewatering by absolute isopropanol or ethanol on catalyst, wash the gelatin 0 – 4 times respectively. Then the water removal rate is calculated and compared, as shown in Fig. 1.

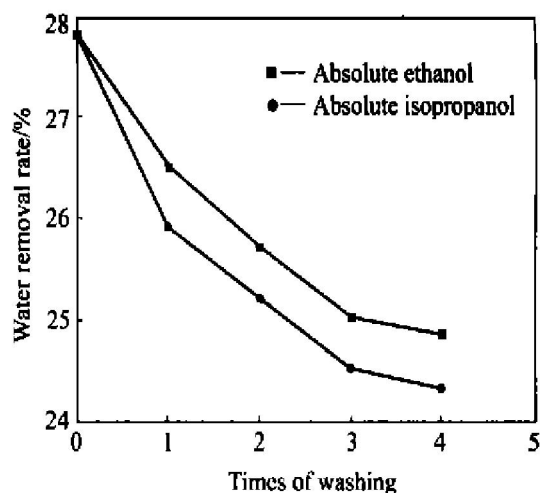


Fig. 1 Effect of washing times on water removal rate

Fig. 1 shows that with the increase of the washing times by absolute isopropanol or ethanol, the water removal rate decreases gradually; but after three or four times, the water removal rate does not change so much. With the same times of washing, the water removal rate obtained by absolute isopropanol is 0.5% less than that obtained by absolute ethanol, so the dewater efficiency of absolute isopropanol is better than that of absolute ethanol. The above description means that the water in the gelatin is nearly completely removed after three times of washing. So after four times of washing, the remain water in the gelatin is crystal water and water absorbed in hydrate (water removed when the hydrate is calcined). If the gelatin is not washed or washed one time, after calcination, the catalyst particles agglomerate; and washed three or four times, after calcination, the catalyst particle is much smaller and homogeneous. So three times of washing can decrease agglomeration of hydrate greatly, avoid agglomeration, decrease the particle size, and increase the specific surface area.

3. 3 Effect of calcine temperature on catalyst

3. 3. 1 Effect of calcine temperature on specific surface area of catalyst

Specific surface area is an important index of catalyst. It is affected not only by water in the catalyst, but also by the calcine temperature. After washing the gelatin three times with absolute isopropanol, drying it at 120 °C, and calcining it at 200, 300, 400, 500, 700, 900

and 1 100 °C, respectively, the specific surface area of each calcine was measured. As shown in Fig. 2, when the calcine temperature is 300 °C, the specific surface area is the biggest. As calcine temperature increase from 200 °C to 300 °C, the catalyst specific surface area increases from 1.8 m²/g to 153.5 m²/g rapidly. Because calcination makes Al(OH)₃ dewatered and its surface loose, the flaw and fine grain is formed, and the specific surface area is enlarged. As calcine temperature increases from 300 °C to 1 100 °C, the catalyst specific surface area decreases slowly. The variation of calcine temperature directly affects the transformation of α-Al(OH)₃ to α-Al₂O₃. Before the completion of transformation of α-Al(OH)₃ to α-Al₂O₃, a series of phases(X-, Y-, K-, θ-, α-Al₂O₃) and crystal variation take place. These variations lead to the change of physical and chemical characters of Al₂O₃. When the temperature is 300 °C, Al₂O₃ crystal consists of α-Al(OH)₃, AlOOH, and X-Al₂O₃. If the temperature is above 400 °C, Al₂O₃ crystal changes into Y-, K-, θ-, α-Al₂O₃.

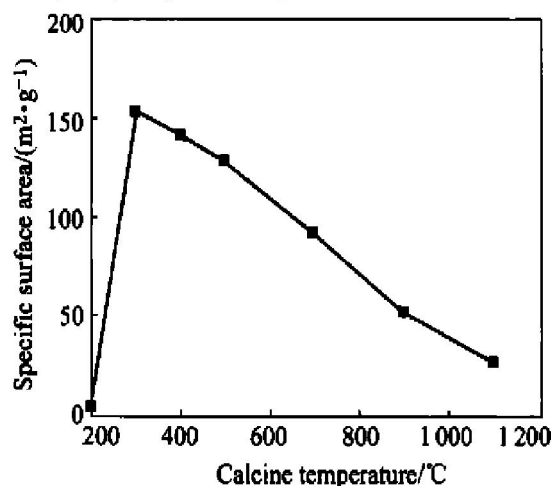


Fig. 2 Effect of calcine temperature on specific surface area of catalyst

3.3.2 Effect of calcine temperature on density of catalyst

Actual density, bulk density, and apparent density of catalyst are indexes relating to the crystal variation. As calcine temperature increases from 100 °C to 1 300 °C, actual density of catalyst increases from 2.49 g/mL to 3.98 g/mL; while from 500 °C to 1 000 °C, actual density increases a little. Apparent density and bulk density decrease firstly, then increase as formation of α-Al₂O₃. This principle, as shown in Fig. 3 and Fig. 4, is related to water removal and shape variation of particle.

3.4 Effect of Zr content on catalyst performance

In order to investigate the effect of catalyst with different Zr content on the composition of

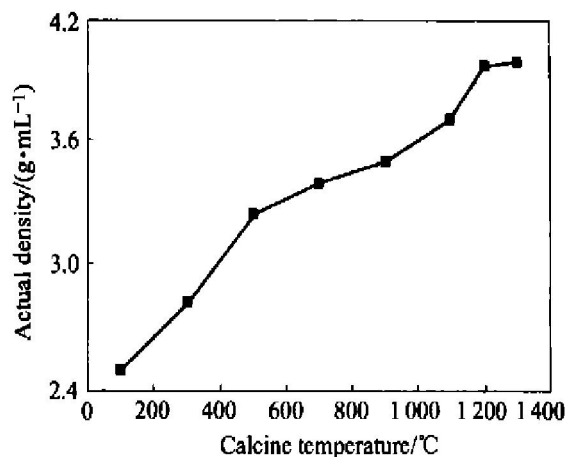


Fig. 3 Effect of calcine temperature on actual density

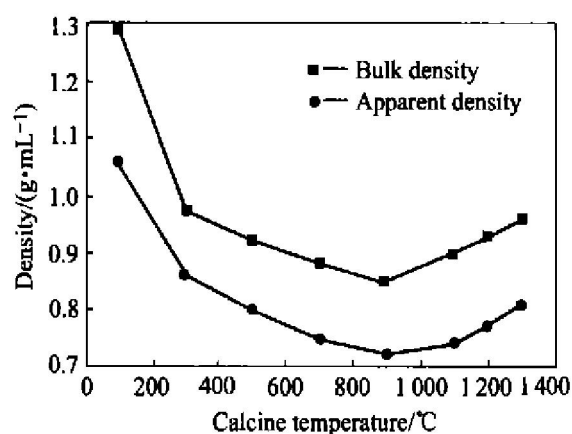


Fig. 4 Effect of calcine temperature on apparent density and bulk density

catalytically reforming product, the rare earth Zr catalyst I, II, III and IV (the Zr content increase in turn) are used to catalytically reform the product derived from thermal pyrolysis of the mixture of heavy oil and PP. That is using 100 g PP and 100 g heavy oil as material and three-neck flask as reactor to prepare a catalytic pipe of 30 cm long for charging the catalyst and then connect the instruments, and check the gas-tightness, keep temperature of reactor and catalytic pipe at 500 °C and 350 °C respectively, and measure the catalytic capability of catalyst as listed in Table 1.

Table 1 shows that: 1) as the Zr content in the catalyst increases from 2% to 15%, the acidity and activity of the catalyst increase, so the yields of liquid, diesel, and heavy oil decrease; but the yields of gasoline and gas, and the rate of carbon deposition increase; 2) the activity of catalyst I is the lowest one, resulting in the lowest yields of gasoline, gas and carbon deposition. The activities of catalyst III and IV are much higher, resulting in the much lower yield of liquid, and the much higher yield of gas and the carbon deposition rate. The activity of catalyst II is moderate, resulting in high yield of liquid and gasoline, 86.10% for liquid and 48.90% for gas-

line, and low rate of carbon deposition. There isn't so much difference between the yield of gasoline obtained by catalyst II and that obtained by catalyst III or IV. In conclusion, the catalyst II with Zr content of 5% is the best one for producing liquid oil from waste plastic.

3.5 Effect of dispersant on catalyst

To determine the effect of dispersant A on the indexes of catalyst and the catalytic performance, both catalyst II with dispersant A and catalyst II-A without dispersant A are calcined at 300 °C, then their indexes are measured. The two catalysts are used to catalytically reform the cracking product of the mixture of waste plastic and heavy oil at 290 °C, and the results obtained are shown in Table 2. Table 2 shows that dispersant A can enlarge specific surface area and lessen density of catalyst. As far as catalytic effect is concerned, catalyst II with larger specific surface area has much stronger catalytic capability. Through catalysis, the quality of liquid oil, light fraction (gasoline), and the yield of gas have been improved, and the yield of heavy oil and the rate of carbon deposition have been reduced obviously.

3.6 Temperature characteristic of rare earth Zr catalyst

In order to investigate temperature characteristic of rare earth Zr catalyst, rare earth Zr catalyst II was used to catalytically reform mixture of thermal cracking product of PP and heavy oil, with the catalytic temperature ranging from 240 °C to 365 °C. The ratio of the two materials is 1 : 1. The catalytic pipe is 30 cm long (30 g of catalyst loaded). The cracking temperature is 500 °C. The catalytic result is compared with that of catalyst FC at its most suitable temperature (315 °C), which is shown in Table 3.

At 290 °C, the rare earth Zr catalyst II can produce the highest yield of liquid fuel oil, 86.1%. The yield of gasoline increases slowly as the catalytically reforming temperature increases. When the catalytic reforming temperature is 290 °C, the yield of diesel is the highest, about 34.10%; but the yield of gas is the lowest, about 10.65%. The yield of heavy oil and the rate of carbon deposition decrease as the catalytic reforming temperature increases. The yield of gas increases as the catalytic temperature increases. So the most suitable catalytic reforming temperature of rare earth Zr catalyst

Table 1 Difference of catalysts capacity with different Zr contents

Catalyst	$w(\text{Zr})/\%$	Acid quantity ¹⁾ / (mmol·g ⁻¹)	Catalytic activity / %	$w(\text{Liquid})/\%$	$w(\text{Gasoline})/\%$	$w(\text{Diesel})/\%$	$w(\text{Heavy oil})/\%$	$w(\text{Gas})/\%$	Carbon deposition / %
No ²⁾	—	—		93.55	28.48	40.06	27.87	6.45	—
I	2	0.01	13.59	90.20	30.50	38.40	20.30	8.15	1.10
II	5	0.04	45.24	86.10	48.90	34.10	3.10	10.65	2.8
III	10	0.08	52.01	84.20	50.60	30.10	2.50	12.50	3.5
IV	15	0.12	64.38	79.40	51.20	22.10	2.10	15.60	4.2

1) —Acid strength $H_0 \leq +3.3$; 2) —Composition of thermal pyrolysis product

Table 2 Effect of dispersant A on indexes of catalyst

Catalyst	Specific surface area / (m ² ·g ⁻¹)	Effective density / (g·mL ⁻¹)	Tight density / (g·mL ⁻¹)	Loose density / (g·mL ⁻¹)	Yield of liquid / %	Yield of gasoline / %	Yield of diesel / %	Yield of heavy oil / %	Yield of gas / %	Rate of carbon deposition / %	Catalyst activity / %
II	153.5	2.80	0.97	0.85	86.10	48.90	34.10	3.10	10.65	2.80	43.64
II-A	95.60	3.10	1.15	0.96	83.25	39.50	31.40	12.35	8.75	5.70	33.85

Table 3 Catalytic effect of rare earth Zr catalyst at different temperatures

Catalyst	Catalyst activity	Catalytic reforming temperature / °C	Yield of liquid / %	Yield of gasoline / %	Yield of diesel / %	Yield of heavy oil / %	Yield of gas / %	Rate of carbon deposition / %
II	42.81	240	84.60	47.75	35.00	3.85	11.50	4.05
II	43.99	265	85.50	48.45	34.65	3.40	11.10	3.30
II	45.24	290	86.10	48.90	34.10	3.10	10.65	2.80
II	45.83	315	85.85	49.05	33.90	2.90	11.15	2.90
II	47.15	340	85.10	49.20	33.15	2.75	11.35	2.70
II	47.74	365	84.75	49.25	33.05	2.45	11.95	2.60
FC	48.84	315	87.50	52.75	32.30	2.45	11.05	2.90

II is 290 °C. Comparison of the reforming product obtained by rare earth Zr catalyst II at 290 °C with that obtained by FC at 315 °C indicates that the activity of the former is lower than that of the latter.

3.7 Effect of rare earth Zr catalyst on quality of gasoline

Gasoline, produced by catalytic reforming of the thermal cracking product derived from PP and heavy oil, using the rare earth Zr catalyst II at 290 °C, is analyzed by gas chromatogram-mass spectrometry apparatus. Table 4 shows the composition of the gasoline. It shows that the gasoline produced by catalytic reforming and thermal cracking mainly consists of hydrocarbon with carbon number ranging from 8 to 11 (indicated as C₈-C₁₁ in Table 4). However, the content of light fraction with a few of carbon numbers in the gasoline obtained by catalytic reforming is higher than that obtained by thermal cracking, and the content of heavy fraction with much more carbon numbers in the gasoline obtained by catalytic reforming is lower than that obtained by thermal cracking. Because a lot of long chain hydrocarbon is catalytically reformed to short chain hydrocarbon, the catalyst prepared by this experiment has good performance.

Table 4 Composition of gasoline reformed by rare earth Zr catalyst

Component	Content/ %	Component	Content/ %
C ₄ - C ₅	4.77	C ₉	34.25
C ₆	20.09	C ₁₀ - C ₁₁	1.24
C ₇	19.17	C ₁₂	8.46
C ₈	11.46	C ₁₃ - C ₁₅	1.17

Calculation according to formula of Lovasic^[11] works out that both the value of Y_{NP2} , which is the content of linear paraffin except C₅ and the value of Y_{IP1} , the content of isoparaffin with carbon numbers ranging from 5 to 7 are 0; the value of Y_{IP2} , the content of isoparaffin except C₅ - C₇ is 10.16; the value of Y_{CP} , the content of cycloparaffin, is 12.91 and the value of Y_{AR} , the content of total aromatics, is 4.76. Substitute those parameters in equation (1):

$$\begin{aligned} \text{RON} = & -1.0729Y_{NP2} + 0.7875Y_{IP1} + \\ & 0.0976Y_{IP2} + 0.3395Y_{CP} + \\ & 0.4049Y_{AR} + 69.006 \end{aligned} \quad (1)$$

works out that the RON of gasoline is 92.15.

4 CONCLUSIONS

1) With Zr(NO₃)₂ and Al(NO₃)₃, and (NH₂)₂CO as raw materials, ZrO₂ catalyst, whose carrier is Al₂O₃, is prepared. Dewater of gelatin by absolute isopropanol

with better dewater capability avoids the agglomeration of hydrate, makes the particle size distribution more homogeneous and active center distribution sounder.

2) When the calcine temperature is 300 °C, the specific surface area of the catalyst is the highest, about 153.5 m²/g. As calcine temperature increases from 100 °C to 1300 °C, the actual density increases from 2.49 g/mL to 3.98 g/mL accordingly; but apparent density and bulk density decrease firstly, then increase with the formation of α -Al₂O₃.

3) The most optimum Zr content of the rare earth Zr catalyst is 5%, and the most suitable catalytic temperature is 290 °C. Under this condition, the yield of liquid oil is much high, about 86.1%; the quality of gasoline is improved obviously, the yield reach 48.90%; the yield of diesel is 34.10%; the carbon deposition is low, about 2.8%.

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