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Hydroisomerization of long chain \( n \)-paraffins: the role for the acidity of zeolite

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The transformation of \( n \)-hexadecane (\( n-C_{16} \)) was tested by two series of experiments over the bifunctional catalysts with noble metal Pt and one dimensional ZSM-22 zeolite to investigate the role for the acidity of zeolite during the hydroisomerization of long chain \( n \)-paraffin. The series 1, varying the Si/Al of the zeolite but fixing the zeolite content, reveals that high acid strength of the zeolite can deteriorate the selectivity of the corresponding catalyst even at an initial conversion and the low concentration of acid sites on the zeolite is beneficial to the improvement of maximal value of isomer yield. The series 2, varying the zeolite content but fixing the Si/Al, reveals that the change of the zeolite content can not affect the selectivity of the catalyst. Both series 1 and series 2 reveal that the activity of the catalyst linearly increases with the acid strength, the concentration of acid sites and content of the employed zeolite.

Therefore, only mono-branched isomers with a smaller molecule size can be formed and multi-branched isomers that are susceptible to cracking are suppressed.

Although these theories work well for the explanation of the high isomer yield and the predication of branched distribution in the product, the role for other aspects of a catalyst should not be ignored. Over the past decades, many researchers have pointed out that the acidity characteristics of the zeolite contained in the hydroisomerization catalyst has a major influence on the activity and selectivity. Furthermore, a common idea is that the proper balance of hydrogenation function and acid function is critical to maximize the isomer yield. However, a further conclusion is under debate due to the different types of the employed zeolite structure and reaction conditions, especially for the role of acid site density and strength. For example, the hydrogen spill over mechanism emphasized that the olefinic intermediates formed on acidic sites could be hydrogenated by a far Pt cluster, so even a physical mixture of Pt/SiO\(_2\) and zeolite can show a good selectivity. However, N. Batalha et al considered that the selectivity of a catalyst is determined by the intimacy between metal and protonic sites i.e., the number of acid sites encountered by the olefinic intermediates during their diffusion between two metallic sites.

In this paper, the hydroisomerization activities and selectivities of various catalysts containing the shape selective zeolite ZSM-22, standing as one of the most successful \( n \)-paraffin isomerization zeolite, were investigated using \( n \)-hexadecane as model molecule. Due to the elimination of the influence from the pore structure of the zeolite, the relationship between hydroisomerization behaviors of a catalyst and the acidity characteristics on it was well recognized. It is revealed that the acidity characteristics like the acid strength, the concentration of acid sites and the

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1. Introduction

Usually, petroleum fractions contain significant amounts of \( n \)-paraffin with high pour/melting point, which great deteriorates their cold flow properties. Thus, hydroisomerization that can transform long chain \( n \)-paraffins into branched paraffins is an important industrial process, special for the production of high quality lube oil or diesel fuel.\(^{1,4}\) Generally, the hydroisomerization reaction takes place over the bifunctional catalysts containing metallic sites for hydrogenation/dehydrogenation and acidic sites for skeletal isomerization via carbenium ions.\(^{5,6}\) Due to the acid sites, the hydroisomerization reaction is always accompanied by a hydrocracking reaction that can lower more or less the yield of the isomerized molecules and cause the degradation of the long chain \( n \)-paraffins to less valuable and lighter products.\(^{7,10}\) Therefore, an efficient hydroisomerization catalyst should minimize the side reaction.

In this sense, more effort has been paid and some achievements have been obtained. For example, it has been reported that high yield of branched isomers can be obtained when the catalysts containing the zeolites with 1-dimensional pore and 10-membered ring channels such as ZSM-22, ZSM-23, and SAPO-11 were employed.\(^{11-13}\) To explain the high selectivity of these materials, many attempts have been done. Amongst them, the pore mouth catalysis and the key-lock catalysis have been popular.\(^{14,15}\) According to them, hydroisomerization of \( n \)-paraffins can happen on the pore opening due to the small pore size of these materials.

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amount of acid sites play different role in the hydroisomerization of \( n \)-paraffin.

2. Experimental

2.1 Zeolite synthesis

The synthesis of ZSM-22 was carried out using 1,6-diaminohexane as template following the procedure reported in reference.\(^{19}\) It works like followings: 10.64 g of Ludox AS40 (40 wt\% silica) was diluted with 18.40 g of distilled water. To this sol, a solution containing \( X \) g of \( \text{Al}_2(\text{SO}_4)_3\cdot18\text{H}_2\text{O} \), 1.16 g of KOH, 2.48 g of 1,6-diaminohexane, and 26.20 g of distilled water was added under continuous vigorous magnetic stirring, where \( X \) was determined by the targeting Si/Al ratio. The gel with molar composition was \( 27\text{NH}_3\cdot\text{CH}_2\text{NHNH}_2\cdot13\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 : 91.5\text{SiO}_2\cdot3670\text{H}_2\text{O} \). The gel was aged for 90 min at room temperature and subsequently the synthesis was carried out in the static conditions for 4 days. Finally, the template in the as-synthesized zeolites was removed by calcination in static air at 550 °C for 4 h using a heating rate of 3 °C·min\(^{-1}\). Subsequently, the as-made solid was ion exchanged with 1 M \( \text{NH}_4\text{NO}_3 \) solution at 60 °C for 24 h, filtered and dried at 120 °C for 4 h.

2.2 Catalyst Preparation

To prepare hydroisomerization catalysts, the different amount of zeolite in the ammonium form was mixed with binder (\( \gamma \)-alumina), kneaded with the addition of water containing peptization agents nitric acid. After that, the mixture was extruded in the form of cylindrical pellets (5 mm length, 1.5 mm diameter), dried at 120 °C for 6 h, and, in a further step, calcined at 600 °C for 3 h to obtain the catalyst containing the zeolite in its acidic form. Pt loading was done by wet impregnation using \( \text{Pt}(\text{NH}_3)_2\text{Cl}_2 \). For all catalysts, the targeted Pt loading is fixed at 0.5 wt\%. The oxidation and reduction of the catalysts to disperse the metal was done at 400 °C for 4 h before starting the reaction.

2.3 Materials characterization

The crystalline phase identification and phase purity of the ZSM-22 zeolites were carried out by XRD (Philips, Holland) using nickel-filtered Cu \( K_\alpha \) radiation (\( \lambda = 1.5406 \) Å). The surface areas and pore volumes were determined from \( N_2 \) adsorption isotherms using a Coulter (Omnisorp 100 CX) instrument. \(^{27}\)Al NMR spectra of the samples were recorded on a Bruker MSL 300 NMR spectrometer. Scanning electron microscopy (SEM) was employed to observe the morphologies of ZSM-22 zeolites. \( \text{NH}_3 \) temperature programmed desorption (TPD) experiments were carried out to test the total acidity of the zeolites at atmospheric pressure in a tubular flow reactor using a fixed bed. The Brunsted acid sites of the zeolites and the corresponding catalysts was determined by temperature programmed desorption of pyridine. The dispersion of platinum was estimated by CO adsorption followed by infrared spectroscopy.

2.4 Catalytic test

The catalytic experiment was examined using a single-pass microreactor. The catalysts were crushed and sieved to select particles with the size in the 40–60 mesh range in order to eliminate diffusive effects. 1.5 g of catalyst was loaded in the constant temperature zone. Prior to the catalytic tests, the catalysts were reduced again under the hydrogen pressure of 4.0 MPa (300 mL/min) for 30 min at 350 °C. After that, the feed was injected. The flow rate of feed is 0.2 mL.min\(^{-1}\). The reaction temperatures were determined by the targeted conversions and hydrogen pressure kept at 4.0 MPa. The whole reaction products were analyzed off-line using a gas chromatograph (CE 2000) equipped with a capillary column (OV-17, length 25 m, internal diameter 0.25 mm). The data reported in this paper were collected when the steady state was reached (ca. 5 h).

3. Results and discussion,

It is well known that the Si/Al ratio is a key factor to affect the acidity characteristics of a zeolite and strongly related to the catalytic activity and selectivity of the corresponding catalyst. Therefore, the first series of experiments were arranged by varying the Si/Al ratios of the ZSM-22 contained in the catalysts. Since other properties of a zeolite can be changed due to the varied Si/Al ratio, it is necessary to firstly investigate the consistency of some key parameters for the employed zeolites. Fig. 1 lists the XRD patterns of the employed ZSM-22 zeolites with various Si/Al. It is clearly revealed that all patterns are well defined and there is no apparent difference whatever diffraction patterns, crystallinities and crystal sizes. Further, the solid state \(^{27}\)Al NMR was employed to characterize the coordination information about the Al in the samples, as presented in Fig. 2. For \(^{27}\)Al NMR spectra, a strong signal at around 58 ppm was the only observed prominent peak for all zeolite samples. This peak can be corresponded to tetrahedral coordination of aluminum and confirms that all aluminum atoms are located in the framework of ZSM-22 zeolites. This indicates that the Si/Al ratios of the samples can accurately reflect the number of acid sites in the zeolites. On the other hand, SEM images (Fig.3) reveal that the similar morphologies and sizes can be observed over these zeolites. Thus, it is reasonable to eliminate the influence from them on the catalytic behaviours of the corresponding catalysts.

The difference of the acidic properties in the zeolites with various Si/Al was evaluated by NH\(_3\)-TPD and shown in Fig.4.

![Fig. 1 XRD patterns of the ZSM-22 zeolite samples. (a) Si/Al=28.6; (b) Si/Al=39.2; (c) Si/Al=55.4.](image)
The profiles can be differentiated by both the peak areas and the shift in the peak position. The former corresponds to the amount of acidic sites and the latter indicates the strength of the acidic sites. Fig. 4 shows that two \( \text{NH}_3 \) desorption peaks are observed over all profiles of zeolites. One peak is centred at about 180 °C, the other is centred at 380 °C, corresponding to weak and strong acid sites, respectively. Further, it can be observed that the peak areas whatever at low or high temperature are increased with the decreasing Si/Al in the zeolites, indicating more acid sites in the zeolite with a lower Si/Al. On the other hand, there is also obvious peak position shift toward higher temperature on these profiles with the decreasing Si/Al in the zeolites, suggesting that the strong acid sites is less in the zeolite with high Si/Al.

The TPD of pyridine was employed to assist the identification of the weak and strong Brønsted acid sites in the ZSM-22 zeolites and the results are listed in Table 1. Reasonably, the Brønsted acid sites are increased with the decreasing Si/Al in the zeolite samples. However, it should be emphasized that Table 1 also revealed a slightly increasing trend for the ratios of strong Brønsted acid sites to total Brønsted acid sites (defined as S/T) with the decreasing Si/Al in the zeolite samples, indicating more strong Brønsted acid sites in the zeolite with a lower Si/Al.

Basing on the similar textural properties and different acidity characteristics of the employed zeolites, the hydroisomerization catalysts were prepared at a fixed zeolite content (about 60 wt%) and tested for the transformation of \( n \)-hexadecane to investigate the role of Si/Al ratio of a zeolite.

Table 2 lists the main physical and chemical properties of the corresponding catalysts. As shown in Table 2, all key parameters of these catalysts are similar in spite of the different zeolites employed in them, so it is possible that only acidity characteristics is considered for the interpretation of the different hydroisomerization behaviours of these catalysts.

Fig. 5 shows the catalytic activities of these catalysts for the conversion of \( n \)-hexadecane. Combining with the Si/Al ratios listed in Table 1, it is clearly revealed that the catalytic activities of these catalysts are strongly related to their concentrations of acid sites and the acid strength on the contained zeolites and increase with the decreasing Si/Al ratios whatever the reaction temperature. According to the hydroisomerization/ hydrocracking scheme, this is reasonable considering the more formation of carbenium ions on the more acid sites and strong acid sites. However, the previous works have pointed out that this easily caused more hydrocracking of carbenium ions. Thus, it is necessary to investigate the selectivities of these catalysts. Fig. 6 shows the relationship for the isomerized \( n \)-hexadecane yield V vs. the conversion of \( n \)-hexadecane over various catalysts. As shown in Fig. 6, the curves representing the yields of isomers firstly increase as a function of the conversion and then they rapidly decrease after passing through a maximum over all catalysts. After a close examination, two interesting points are observed in Fig. 6. Firstly, it can be seen that the curve a for Cata-1 is lower than the curve b for Cata-2 and the curve c for Cata-3 even at a low conversion. About this, it should be explained basing on the strong acid strength on the zeolite contained in it as listed in Table 1. According to previous works, the isomerization proceeds through several successive steps. Amongst them, the isomerization of \( n \)-alkenes into \( i \)-alkenes on the acid site is a key step. High acid strength allows relatively longer residence time of the \( i \)-alkenes intermediate on the acid sites, thus providing sufficient time for the intermediates to be cracked. Overall, the first conclusion in our case is drawn like

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Results from pyridine adsorption-desorption(^{a,b})</th>
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<tbody>
<tr>
<td>Zeolites</td>
<td>Si/Al</td>
</tr>
<tr>
<td>Z-1</td>
<td>28.6</td>
</tr>
<tr>
<td>Z-2</td>
<td>39.2</td>
</tr>
<tr>
<td>Z-3</td>
<td>55.4</td>
</tr>
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</table>

\(^{a}\) obtained by the desorption of pyridine at 200 °C.  
\(^{b}\) obtained by the desorption of pyridine at 350 °C.  
\(^{c}\) defined as strong Brønsted to total Brønsted.

Table 2 | Physical and chemical properties of the prepared catalysts. |
<table>
<thead>
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<th></th>
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<tbody>
<tr>
<td>Catalysts</td>
<td>Zeolites</td>
</tr>
<tr>
<td>Cata-1</td>
<td>Z-1</td>
</tr>
<tr>
<td>Cata-2</td>
<td>Z-2</td>
</tr>
</tbody>
</table>
Cata-3  Z-3  0.51  68  221  0.47

Fig. 5 Activities of the catalysts containing ZSM-22 with different Si/Al ratios at various temperatures. (a) Cata-1; (b) Cata-2; (c) Cata-3.

Table 3  Physical and chemical properties of the catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Zeolite content</th>
<th>$S_{BET}$ (m$^2$/g)</th>
<th>$V_{pore}$ (mL/g)</th>
<th>Total Bronsted acid/ (µmol/g)$^a$</th>
<th>Strong Bronsted acid/ (µmol/g)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cata-40</td>
<td>40</td>
<td>224</td>
<td>0.44</td>
<td>153.6</td>
<td>88.2</td>
</tr>
<tr>
<td>Cata-60</td>
<td>60</td>
<td>217</td>
<td>0.43</td>
<td>247.6</td>
<td>149.1</td>
</tr>
<tr>
<td>Cata-70</td>
<td>70</td>
<td>208</td>
<td>0.43</td>
<td>287.5</td>
<td>166.2</td>
</tr>
</tbody>
</table>

$^a$ obtained by the desorption of pyridine at 200 ºC.
$^b$ obtained by the desorption of pyridine at 350 ºC.

maximal isomer yield of the corresponding catalysts. Additionally, this conclusion implies that we can obtain the maximal isomer yield by increasing the Si/Al of the zeolite. However, it should be reminded that this will cause higher reaction temperature and more energy consume.

Beside the acid strength and the concentration of acid sites, zeolite content is another key factor affecting the catalytic behaviors. Thus, the second series of experiments were arranged by the variation of the zeolite content contained in the catalysts but fixing Si/Al=55.4. Table 3 lists the main physical and chemical properties of the corresponding catalysts. As shown in Table 3, only slight change for the pore parameters of the catalysts like $S_{BET}$ and $V_{pore}$ and the dispersion of loaded Pt is observed. Apparently, a decrease for the amount of acid sites happens with the decreasing the zeolite content.

Fig. 7 shows the hydroisomerization activities of the employed catalysts. As shown in Fig. 7, it can be observed that the activities of the catalysts are strongly related to the zeolite content in them. At the same reaction temperature, the more the catalyst contains zeolite, the higher active it is. An interesting point is about the isomer yields over various catalysts. It can be inferred that the distance between acid sites in the catalysts was larger due to the decrease of zeolite content. On the other hand, the amount and the dispersion of loading Pt keep stable for all catalysts. Thus, the more hydrogenation of olefinic intermediates during their diffusion, giving the final $i$-paraffinic products, can be expected.

However,

**Fig. 6** Isomer yield vs. $n$-C$_{16}$ conversion for the catalysts containing ZSM-22 with different Si/Al ratios. (a) Cata-1; (b) Cata-2; (c) Cata-3.

**Fig. 7** Activities of the catalysts containing different zeolite contents at various temperatures (a) Cata-70; (b) Cata-60; (c) Cata-40.
Fig. 8 Isomer yield vs. n-C_{16} conversion for the catalysts containing different zeolite contents at various temperatures. (a) Cata-70; (b) Cata-60; (c) Cata-40.

A similar trend for isomer yields over all catalysts is observed in our case (as shown in Fig. 8), indicating the same lifetime of the olefinic intermediate for all catalysts. About this, it should be explained basing on the local environment of acid sites in the catalysts. Actually, there is no change about the number of metallic sites surrounding each acid site in spite of the varied zeolite content in the catalysts. This means that the degree of intimacy between acidic sites and Pt is invariable in our case. Overall, the third conclusion is drawn like this: the zeolite content cannot affect the selectivity of the corresponding catalyst due to the unchanged intimacy between acid sites and metal sites. Additionally, this means that to compensate the low activity caused by high Si/Al of the zeolite contained in the catalyst, we can increase zeolite content in it until the crushing strength of the support is allowed. This is meaningful to prepare an efficient hydroisomerization.

4. Conclusions

The hydroisomerization activities and selectivities of the catalysts containing various ZSM-22 zeolites with different acidity characteristics have been tested. Basing on them, the role for the acidity characteristics of a zeolite contained in the catalyst during the hydroisomerization of long n-paraffin was investigated and several points have been clearly ruled out due to the elimination of textual difference: Firstly, high acid strength of the zeolite can deteriorate the selectivity of the catalyst even at an initial conversion. Secondly, the low concentration of acid sites in a zeolite is beneficial to obtain a maximal value of isomer yield at a similar acid strength. Thirdly, the zeolite content in the catalyst can not affect the selectivity. Finally, the activity of the catalysts linearly increase with the increase of acid strength, the concentration of acid sites and the zeolite content. We think these results path a way to develop an efficient hydroisomerization catalyst.

Acknowledgements

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References

Hydroisomerization of long chain n-paraffins: the role for the acidity of zeolite

Graphic abstract

This work clarifies the role for the acidity of zeolite during the hydroisomerization of \( n \)-paraffin including in the acid strength, acid concentration and zeolite content.