Effect of Dealumination of Citric Acid-Modified Hβ Molecular Sieve on Hydroisomerization Performance of n-Hexadecane

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Abstract. Hβ molecular sieves with SiO₂/Al₂O₃ ratio of 40 were modified by citric acid dealumination (Hβ-Cn) and Hβ-Cn loading Pd (0.5 wt%) bifunctional catalysts(Pd/Hβ-Cn) were prepared by hydrothermal synthesis and incipient wetness impregnation. The structure, morphology, pore and acid properties of Hβ-Cn and Pd dispersion for Pd/Hβ-Cn were characterized using XRD, SEM, N₂ physical adsorption, NH₃-TPD and H₂ chemical absorption. The skeleton structure of all Hβ-Cn was not damaged and their relative crystallinity increased somewhat after the treatment of citric acid. With the increase of citric acid concentration, the change of morphology,structure and pore properties of Hβ-Cn was very little, but the amount of weak acid, strong acid and total acid of Hβ-Cn, and Pd dispersion for Pd/Hβ-Cn decreased significantly. It was known from hydroisomerization performance of n-C₁₆H₃₄ that the hydroisomerization reaction temperature over Pd/Hβ-Cn slightly rises under the condition of the same conversion of n-C₁₆H₃₄, but the amount of multi-branched iso-C₁₆H₃₄ over Pd/Hβ-Cn, especially Pd/Hβ-C₂ (60.51%) and Pd/Hβ-C₃ (57.84%) was much higher than that over Pd/Hβ (36.99%). This could be due to the remove of partial skeleton aluminum species with strong acid sites to effectively inhibit the further cracking of the multi-branched isomerized products.

1. Introduction

Biodiesel is a kind of renewable, efficient and safe clean energy, which has been greatly developed in recent years [1]. The hydroisomerization of n-alkanes is the key to produce all kinds of high quality fuel oil [2]. In hydroisomerization reaction process, the cracking reaction of the long carbon chain alkanes will produce light hydrocarbon component content,which reduce the selectivity of alkane isomer and liquid yield of diesel fuel [3]. The development of efficient hydroisomerization bifunctional catalysts for skeletal branching of long n-alkanes without cracking is core research topic [4]. Beta molecular sieves have been widely used in the fields of catalytic cracking, hydroisomerization, alkylation because of thier strong acidity and unique three-dimensional pore structure, good thermal stability and hydrothermal stability. But the strong acidity and more number of acidic sites of Hβ aggravate the cracking reaction in the hydroisomerization of n-hexadecane [7]. In this paper, Hβ were modified by citric acid dealumination to reduce appropriately acid strength and number of acid sites and investigted the performance of the hydroisomerization reaction of n-hexadecane.
2. Experimental Section

2.1. Synthesis of Hβ Molecular Sieve and its Dealumination by Citric Acid

Hβ molecular sieves were hydrothermally synthesized using NaAlO₂ (CP, Sinopharm chemical reagent co. LTD), ludox (26.85 wt% SiO₂, Qingdao Yumin Company, China) and tetraethylammonium hydroxide (CP, Sinopharm chemical reagent Co. LTD) according to SiO₂/Al₂O₃ ratio of 40 at 145°C for 5 days. After crystallization products were separated by centrifugation, dried at 110°C, calcined at 560°C to remove the template, treated by 0.5 mol/L NH₄NO₃ solution, then dried and roasted to obtain Hβ molecular sieves. As-prepared Hβ was mixed with citric acid solutions with concentrations of 0.5 mol/L, 1.0 mol/L and 1.5 mol/L respectively in a solid-liquid mass ratio of 1:20 at 80°C, stirred on 500 rpm for 7 h. The dealuminated Hβ molecular sieves were obtained by centrifugation and drying, labeled Hβ-Cn (n=1, 2, 3, represent three concentrations respectively).

2.2. Dealuminated Hβ Molecular Sieves Loading Palladium Bifunctional Catalysts

The bifunctional catalysts were prepared by incipient wetness impregnation with a Pd(NO₃)₂ solution according to Pd loading amount of 0.5 wt%. Then, these samples were dried at room temperature overnight and calcined at 600°C for 4 h in air, and referred to as Pd/Hβ-Cn.

2.3. Characterization of Hβ-Cn and Pd/Hβ-Cn Catalysts

XRD patterns of Hβ and Hβ-Cn shown in Figure 1 are exclusively attributed to β topological structure, indicating that the skeleton structure of all Hβ-Cn was not damaged. The relative crystallinity of Hβ-Cn samples increased somewhat after the treatment of citric acid, which was caused by the partial non-skeleton species eluted from the molecular sieve.

3. Results and Discussion

3.1. The Characterization of Hβ-Cn and Pd/Hβ-Cn Bifunctional Catalysts

3.1.1. XRD. The XRD characteristic diffraction peaks of all Hβ and Hβ-Cn shown in Figure 1 are exclusively attributed to β topological structure, indicating that the skeleton structure of all Hβ-Cn was not damaged. The relative crystallinity of Hβ-Cn samples increased somewhat after the treatment of citric acid, which was caused by the partial non-skeleton species eluted from the molecular sieve.
3.1.2. SEM. In order to investigate the effect of citric acid dealumination treatment on the morphology of Hβ molecular sieves, Hβ and Hβ-Cn samples were characterized by SEM, and the results were shown in Figure 2.

![SEM images of Hβ and Hβ-Cn samples](image)

Figure 2. SEM images of Hβ and Hβ-Cn samples

It can be seen from Figure 2 that with the change of the concentration of citric acid treatment, there was not a significant difference of the morphology and structure between Hβ and Hβ-Cn samples. All the samples present elliptical spherical aggregates with the typical morphology of β molecular sieve. The size of the aggregates is 1-1.5 μm and their diameter is about 1 μm.

3.1.3. N$_2$ physical adsorption. To investigate the effect of citric acid dealumination treatment on the specific surface area and pore volume of Hβ molecular sieves, Hβ and Hβ-Cn samples were characterized by N$_2$ physical adsorption. N$_2$ adsorption-desorption isotherms of all samples are shown in Figure 3 and the adsorption data are listed in Table 1.

As shown in Figure 3, the adsorption-desorption isotherms of all Hβ-Cn samples are corresponding to a type I isotherm, which indicating that Hβ molecular sieves modified by citric acid dealumination treatment are still microporous materials. A hysteresis loop appears at a relatively high partial pressure, which indicating the existence of mesoporous structure in Hβ-Cn samples.

The BET surface area and pore volume of Hβ-C1 sample shown in Table 1 increases slightly, which is because the dealumination treatment with low concentration of citric acid did not cause obvious damage to the skeleton structure of Hβ molecular sieve, but washed out some non-skeleton species adsorbed on the outer surface of the molecular sieve. With the increase of citric acid concentration, BET surface area, micropore surface area and micropore volume of Hβ-C3 samples
were all reduced to a certain extent, but the decrease was small. This mainly due to that the interaction between citric acid and skeleton aluminum species leads to chelate dealumination.

![Graph of Figure 3 showing the N_2 adsorption-desorption isotherm of Hβ and Hβ-Cn samples](image)

**Figure 3.** N_2 adsorption-desorption isotherm of Hβ and Hβ-Cn samples

| Sample  | Surface area (m^2/g) | Pore volume (cm^3/g) |
|---------|----------------------|----------------------|
|         | BET  | Micropore | External | Total | Micropore | Mesopore |
| Hβ      | 648  | 545       | 103      | 0.341 | 0.216     | 0.125    |
| Hβ-C1   | 661  | 548       | 113      | 0.352 | 0.218     | 0.134    |
| Hβ-C2   | 650  | 541       | 109      | 0.343 | 0.214     | 0.129    |
| Hβ-C3   | 638  | 535       | 103      | 0.338 | 0.212     | 0.126    |

**Table 1.** N_2 adsorption data of Hβ and Hβ-Cn samples

3.1.4. NH_3-TPD. In order to investigate the effect of citric acid dealumination modification with different concentration on the acid strength and acid amount of Hβ molecular sieve, Hβ-Cn samples were characterized by NH_3-TPD shown in Figure 4 and Table 2.

![Graph of Figure 4 showing the NH_3-TPD profiles of Hβ and Hβ-Cn samples](image)

**Figure 4.** NH_3-TPD profiles of Hβ and Hβ-Cn samples
Table 2. Acid data of Hβ and Hβ-Cn samples

| Sample | Acid amount (mmol/g) | T/°C |
|--------|---------------------|------|
|        | Weak    | Strong | Total | LT  | HT  |
| Hβ     | 0.29    | 0.56   | 0.85  | 218 | 365 |
| Hβ-C2  | 0.11    | 0.42   | 0.53  | 218 | 363 |
| Hβ-C3  | 0.12    | 0.43   | 0.55  | 210 | 363 |

As can be seen from Figure 4 and Table 2, the amount of weak acid, strong acid and total acid of Hβ-Cn samples treated with 1.0 mol/L and 1.5 mol/L citric acid all decreased significantly, but the strength of strong acid did not change significantly, indicating that the citric acid dealumination treatment partially removed the skeleton aluminum and non-skeleton aluminum species of Hβ.

3.1.5. $H_2$ chemical absorption. Pd/Hβ and Pd/Hβ-Cn bifunctional catalysts were characterized by $H_2$ chemical adsorption analysis to investigate the effect of citric acid dealumination on Pd dispersion shown in Table 3.

Table 3. Metal Pd dispersion and sites of Pd/Hβ and Pd/Hβ-Cn catalysts

| Catalysts | Dispersion of Pd (%) | $C_{Pd}$ (μmol/g) |
|-----------|----------------------|-------------------|
| Pd/Hβ     | 41.6                 | 19.6              |
| Pd/ Hβ-C1 | 34.8                 | 16.4              |
| Pd/ Hβ-C2 | 33.4                 | 15.8              |
| Pd/ Hβ-C3 | 31.1                 | 14.7              |

Pd dispersion on Pd/Hβ-Cn bifunctional catalysts shown in Table 3 that were lower than that on Pd/Hβ before dealumination, and inversely proportional to the concentration of citric acid, which was consistent with the change of total acid amount and surface area of bifunctional catalysts. This indicates that the acid sites are helpful to the dispersion of metal particles on surface of Hβ.

3.2. Effect of Citric Acid Dealumination on Catalytic Hydroisomerization Performance of n-Hexadecane over Pd/Hβ-Cn Bifunctional Catalysts

The isomerization (main reaction) and cracking reaction (side reaction) of n-alkanes occurs mainly at the acidic sites of bifunctional catalyst. The pore structure, acidic density and acid strength of Hβ molecular sieve all influence the selectivity of isomerization reactions and the distribution of reaction products [6]. The hydroisomerization of n-hexadecane ($n$-$C_{16}H_{34}$) over Pd/Hβ and Pd/Hβ-Cn bifunctional catalysts was carried out to investigate the effect of citric acid dealumination on catalytic performance, and the results were shown in Figure 5–6.

It can be seen from Figure 5 that the hydroisomerization reaction temperature over Pd/Hβ-Cn slightly raises under the condition of the same conversion of $n$-$C_{16}H_{34}$. This is because the acid site density and Pd dispersion decreased after dealumination. The conversion of $n$-$C_{16}H_{34}$ over all of bifunctional catalysts can reached more than 90% at the reaction temperature of 245°C. It can be seen from Figure 6 that the amount of multi-branched iso-$C_{16}H_{34}$ in hydroisomerization products over Pd/Hβ and Pd/Hβ-Cn at $n$-$C_{16}H_{34}$ conversion of 50%, especially Pd/Hβ-C2 (60.51%) and Pd/Hβ-C3 (57.84%) was much higher than that over Pd/Hβ (36.99%). The partial skeleton aluminum species with strong acid sites are removed by citric acid, which effectively inhibited the further cracking of the muti-branched isomerized products.
Figure 5. Hydroisomerization conversion of \( n-C_{16}H_{34} \) over Pd/H\( \beta \) and Pd/H\( \beta \)-C\( n \) catalysts

Figure 6. Selectivity of mono-branched iso-\( C_{16}H_{34} \) and multi-branched iso-\( C_{16}H_{34} \)

4. Conclusion
In summary, H\( \beta \) molecular sieves (Si\( \text{O}_2 \)/Al\( \text{O}_3 \) molar ratios of 40) synthesized by hydrothermal method were dealuminated by citric acid solutions with concentrations of 0.5mol/L, 1.0mol/L and 1.5mol/L respectively. The H\( \beta \) and modified H\( \beta \)-C\( n \) loading 0.5 wt% palladium bifunctional catalysts (Pd/H\( \beta \)-C\( n \)) were prepared by incipient wetness impregnation. The skeleton structure of all H\( \beta \)-C\( n \) was not damaged and their relative crystallinity increased somewhat after the treatment of citric acid. The effect of citric acid elumination on the morphology, structure and pore properties of H\( \beta \) was very little, but the amount of weak acid, strong acid and total acid of H\( \beta \)-C\( n \) samples, and Pd dispersion for Pd/H\( \beta \)-C\( n \) decreased significantly. The hydroisomerization reaction temperature over Pd/H\( \beta \)-C\( n \) slightly rises under the condition of the same conversion of \( n-C_{16}H_{34} \). The amount of multi-branched
iso-C₁₆H₃₄ over Pd/Hβ-Cn was much higher than that over Pd/Hβ. The removal of partial skeleton aluminum species with strong acid sites effectively inhibited the further cracking of the multi-branched isomerized products.

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