Effect of Metal Precursors on the Performance of Pt/SAPO-11 Catalysts for n-Dodecane Hydroisomerization

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ABSTRACT: Pt(NH₃)₄(NO₃)₂, Pt(NH₃)₄(Ac)₂, (NH₄)₂PtCl₄, and H₂PtCl₆ were used to prepare Pt/SAPO-11 catalysts to investigate the effect of Pt precursors on the hydroisomerization of n-dodecane. The catalyst derived from Pt(NH₃)₄(NO₃)₂ displays the best hydroisomerization activity and selectivity among these precursors. The hydroisomerization conversion of n-dodecane is affected by the platinum particle size, platinum dispersion, the location of platinum, and the valence state of platinum. The selectivity of n-dodecane is determined by the number of Bronsted acid sites and Pt crystal planes. These conclusions are verified by combining transmission electron microscopy, high-resolution transmission electron microscopy, hydrogen temperature programmed reduction, NH₃-temperature programmed desorption, and Py-IR studies. The catalyst prepared with Pt(NH₃)₄(NO₃)₂ as the precursor exhibits the smallest platinum particle size and the highest platinum dispersion. Most of the platinum particles are supported on the external surface of SAPO-11 with the Pt(111) crystal face. Such a catalyst also possesses a suitable number of Bronsted acid sites and then displays the best catalytic performance. Obviously, the use of various precursors for the Pt-based catalyst can significantly affect the performance of Pt/SAPO-11 for the hydroisomerization of n-dodecane.

1. INTRODUCTION

As the population of high-performance engines used in the industrial production and the strengthening of environmental protection requirements, the demand for high-grade lubricants with low viscosity, low freezing point, and high index of the viscosity is increasing. Although the long chain n-alkanes (i.e., wax) in the lubricating oil with high viscosity index, their inferior fluidity at low-temperatures is a drawback. Therefore, the wax must be partially or completely removed to give a good fluidity lubricant at low temperatures.

Isomerization dewaxing technology is derived from catalytic dewaxing technology, which could convert the long chain n-alkanes into isoparaffins with side chains by hydroisomerization. This isomerization dewaxing technology is an ideal solution for producing high-grade lubricants, and the core of the isomerization dewaxing technology is the development of the catalysts.

Metal/acid bifunctional catalysts for alkane isomerization reactions have been studied extensively, such as Pt, Ni, and other metals loaded on molecular sieves. The metals provide hydrogenation and dehydrogenation active centers, while the molecular sieves supply acidic centers. The key to make this combination become an excellent catalyst to achieve the above goal is to balance the acidic and the metallic properties of the catalysts.

For the metal/acid bifunctional catalysts, the frequently used acid supports are ZSM series and SAPO-like molecular sieves, such as ZSM-5, ZSM-12, and ZSM-22, and SAPO-11, SAPO-31, and SAPO-41. As the representative of SAPO-like molecular sieves, SAPO-11 has been widely considered as a support because of its unique pore structure, especially its excellent catalytic performance in the long-chain alkanes hydroisomerization reactions.

Summarizing the relevant literature, it can be seen that platinum is the most commonly used active component for the hydroisomerization of n-alkanes, and 0.5 wt % Pt loading can generally provide sufficient (de)hydrogenation activity sites. Moreover, the incipient wetness impregnation method makes the catalysts perform higher isomerization activity and selectivity as most of the platinum particles could be distributed on the external surface of the support. However, as there are many different Pt precursors, such as H₂PtCl₆, Pt(NH₃)₄Cl₂, Pt(NH₃)₄(OH)₂, Pt(NH₃)₄(NO₃)₂, Pt(NO₃)₃, etc., the performance of the platinum catalysts could be various when different precursors are applied according to the reported literature. Aristizábal et al. used

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Pt–Ag/AC catalysts for the catalytic reduction of nitrates, they found that the metal precursors and the metal loading could significantly affect the catalytic performance. Wang et al. revealed that the three catalysts using Pt(NO$_3$)$_2$, Pt(NH$_3$)$_4$Cl$_2$, and H$_2$PtCl$_6$ as platinum precursors, respectively, behaved very different catalytic performance for $n$-hexadecane hydroisomerization. The catalyst derived from H$_2$PtCl$_6$ exhibits better isomerization activity and selectivity. The results could be attributed to the fact that H$_2$PtCl$_6$ as the Pt precursor was more favorable for dispersing Pt and increased the density of the active metal sites. However, Regalbuto et al. reported that Pt(NH$_3$)$_4$$^{2+}$ as the Pt precursor could effectively inhibit the agglomeration of Pt particles and increase the dispersion of the metal platinum, while (PtCl$_6$)$_{2}^{-}$ formed larger platinum particles. Whatever the conclusions in the literature, different precursors of Pt could result in various Pt-molecular sieve catalysts for hydroisomerization.

Considering that different Pt precursors does have a significant effect on the performance of the catalysts in the hydroisomerization of $n$-alkanes, Pt/SAPO-11 catalysts were prepared with Pt(NH$_3$)$_4$Cl$_2$, Pt(NH$_3$)$_4$(Ac)$_2$, (NH$_4$)$_2$PtCl$_4$, and H$_2$PtCl$_6$ as the metal precursors, a self-made SAPO-11 molecular sieve as the support. The catalytic performance of Pt/SAPO-11 prepared with different Pt precursors were investigated in the $n$-dodecane hydroisomerization here. The texture properties, the surface metal/acid functions, and the impact of the precursors on the performance of the catalysts were studied and characterized using various techniques.

2. RESULTS AND DISCUSSION

2.1. Phase Structure of Catalysts. The X-ray diffraction (XRD) patterns of Pt/SAPO-11 catalysts synthesized with different platinum precursors were displayed in Figure 1. The XRD patterns of Pt/SAPO-11 with different Pt precursors are shown in Figure 1. The diffraction peaks for the samples located at $2\theta$ = 9.84, 12.78, 16.10, 21.93, 22.49, 25.78, and 29.68$^\circ$ attributed to the typical SAPO-11 phase. However, it could be seen that the intensity of these peaks decreased in the order of SAPO-11 > Pt–Cl > Pt–NCl > Pt–C > Pt–N. This reveals that the addition of Pt destroyed the crystallinity of the molecular sieves to a certain extent, that is, the process of impregnating platinum had effects on the basic structure of the support. Moreover, no platinum

diffraction peaks could be detected, which may be due to the 0.5 wt % platinum loading was lower than the detection limit of the XRD technique.

2.2. Textural Properties. The nitrogen adsorption–desorption isotherms of the samples were showed in Figure 2. When the relative pressure $P/P_0 < 0.02$, there was a typical microporous adsorption. As the $P/P_0 > 0.7$, a hysteresis loop appeared in the isotherms, which indicates that the presence of the mesopores in the samples. It can be seen that the support of SAPO-11 displayed the largest amount of adsorption capacity, while the adsorption capacity of all Pt/SAPO-11 catalysts decreased. This is the expected result as platinum particles blocked part of the pores of the catalysts, accordingly Pt/SAPO-11 with H$_2$PtCl$_6$ as the precursor showed the minimum amount of adsorption. Figure 3 displayed the pore size distributions of the catalysts. It was clear that there were a small number of micropores in the catalysts but mainly with mesopores. The calculated Brunauer–Emmett–Teller (BET) specific surface area, pore volume, $t$-plot micro-pore volume, and average pore diameter were listed in Table 1 for the catalysts.

Figure 1. XRD patterns of Pt/SAPO-11 with different Pt precursors.

Figure 2. Nitrogen adsorption–desorption isotherms of Pt/SAPO-11 with different Pt precursors.

Figure 3. Pore size distributions of Pt/SAPO-11 with different Pt precursors.
2.3. Morphology. In order to further investigate the effect of the platinum particle size and platinum crystal face on the hydroisomerization of the catalysts, Pt/SAPO-11 catalysts were analyzed by transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM). From Figure 4, it could be seen that Pt metal particles were uniformly dispersed on the support. Pt\textsuperscript{−N} and Pt\textsuperscript{−C} showed the same Pt(II) valence in the precursors and smaller platinum particle size. For the catalyst of Pt\textsuperscript{−NCl}, Pt\textsuperscript{2+} and NH\textsubscript{4}\textsuperscript{+} formed complex compounds and presented the largest platinum particle size. The order of the platinum particle size from big to small was Pt\textsuperscript{−NCl} > Pt\textsuperscript{−Cl} > Pt\textsuperscript{−N}, and Pt\textsuperscript{−N} exhibited the smallest Pt particle size, which was 1.78 nm. The HRTEM of the catalysts were also illustrated in Figure 4. It was found that the lattice fringe spacing of Pt\textsuperscript{−N} and Pt\textsuperscript{−C} were 0.223 and 0.226 nm, respectively, corresponding to the Pt(111) face, while Pt\textsuperscript{−NCl} and Pt\textsuperscript{−Cl} exposed mainly the Pt(100) face.\textsuperscript{32,35} Moreover, the size of platinum particles and the crystal planes of platinum may affect the performance of the catalysts for hydroisomerization.

2.4. Hydrogen Temperature Programmed Reduction and CO Chemisorption Characterization. Figure 5 illustrated the hydrogen temperature programmed reduction (H\textsubscript{2}-TPR) profiles of the samples. It can be seen that the peaks centered around 130 °C for all the samples can be attributed to the reduction of Pt\textsuperscript{2+}(Pt\textsuperscript{−NCl}, Pt\textsuperscript{−C}, Pt\textsuperscript{−N}) or Pt\textsuperscript{4+}(Pt\textsuperscript{−Cl}), which are loaded on the external surface of the support. The peaks among 320–365 °C could be seen as the reduction of platinum in the internal pores.\textsuperscript{36} Because of a strong metal-support interaction, the peaks appeared at 424 °C for Pt\textsuperscript{−NCl} and 447 °C for Pt\textsuperscript{−C} reveals that some platinum species in the catalysts are difficult to reduce.\textsuperscript{37} Moreover, both Pt\textsuperscript{−Cl} and Pt\textsuperscript{−N} catalysts exhibited large low temperature reduction peaks, indicating that a large number of platinum species were supported on the external surface of the molecular sieves.

CO chemisorption was employed to study the dispersion of platinum particles for Pt/SAPO-11 catalysts and the results were listed in Table 2. The Pt\textsuperscript{−N} catalyst showed the highest metal dispersion, which was up to 77%, followed by the Pt\textsuperscript{−C} catalyst. Their higher metal dispersion was consistent with the

| catalysts | S\textsubscript{BET} (m\textsuperscript{2}·g\textsuperscript{−1}) | V\textsubscript{pore} (cm\textsuperscript{3}·g\textsuperscript{−1}) | V\textsubscript{micro·pore} (cm\textsuperscript{3}·g\textsuperscript{−1}) | D\textsubscript{pore} (nm) |
|-----------|-----------------|-----------------|-------------------|-----------------|
| SAPO-11   | 168             | 0.3450          | 0.0431            | 10.97           |
| Pt−Cl     | 123             | 0.2539          | 0.0218            | 9.86            |
| Pt−NCl    | 153             | 0.3057          | 0.0353            | 12.66           |
| Pt−C      | 148             | 0.3230          | 0.0240            | 10.53           |
| Pt−N      | 144             | 0.3011          | 0.0204            | 9.16            |

Figure 4. TEM, HRTEM, and corresponding particle distribution: (a,e,i) Pt−N, (b,f,j) Pt−C, (c,g,k) Pt−Cl, and (d,h,l) Pt−NCl.
smaller platinum particles (Figure 4). For the Pt−Cl catalyst, platinum species may be more likely to agglomerate although the platinum species were easily to be reduced on the external surface of the support, resulting in a lower dispersion. Pt−NCl behaved as the lowest metal dispersion, which was related to its large metal particle size (∼2.74 nm) as well as lots of platinum particles in the pores of the support.

In the light of both Pt−N and Pt−C having amine groups in the platinum precursors, research studies revealed that the amine groups would intend to decompose to NH3 in the calcination process, and small platinum particles will be formed by the reduction of Pt(II) in the presence of NH3. However, the platinum particles are prone to agglomerate if the autocatalytic processes were too fast or at too high temperatures.32,38 In our research, the catalysts prepared from Pt(NH3)4(NO3)2 and Pt(NH3)4(Ac)2 had a higher platinum dispersion and smaller platinum particle size. We considered that autocatalytic reduction of Pt2+ by NH3 might happen during the calcination process and the platinum particles would intend to be formed. However, as there are nitrate and acetate in the platinum precursors, it is possible that they would have effects on the dispersion of platinum and the size of platinum particles.

2.5. Acidic Properties. NH3-perature programmed desorption (NH3-TPD) profiles of the samples were shown in Figure 6. It was clear that two desorption peaks could be seen in all the samples, and the peaks centered at around 160 and 270 ºC correspond to weak and medium acid sites, respectively.39

Table 3. Content of Lewis Acid (L) and Bronsted Acid (B) of Catalysts with Different Pt Precursors

| catalyst | acidity (mmolPy/g) |
|----------|------------------|
|          | L    | B    | B + L | B/(B + L) |
| SAPO-11  | 0.005 | 0.024 | 0.029 | 0.83   |
| Pt−N     | 0.003 | 0.021 | 0.024 | 0.88   |
| Pt−C     | 0.004 | 0.021 | 0.025 | 0.84   |
| Pt−NCl   | 0.003 | 0.016 | 0.019 | 0.84   |
| Pt−Cl    | 0.006 | 0.043 | 0.049 | 0.88   |

sites and Bronsted acid sites, respectively, while the band at 1490 cm−1 was related to the pyridine molecule adsorbed on both Lewis and Bronsted acid sites.40 The number of the acid sites for the catalysts were showed in Table 3. The number of Lewis and Bronsted acid sites of Pt−N, Pt−C and Pt−NCl decreased compared to SAPO-11, Pt−Cl increased on the other hand. This could be attributed to the Cl residues in the Pt−Cl catalyst. Platinum was supposed to have been modified.
over the acidity of the support by covering the acid sites. In summary, an effective catalyst for the hydroisomerization of \(n\)-alkanes requires a suitable number of Brønsted acid sites.

### 2.6. Catalytic Performance

The hydroisomerization of \(n\)-dodecane was used as a probe reaction to evaluate the catalytic performance of these Pt/SAPO-11 catalysts. The conversion of \(n\)-dodecane and the isomerization selectivity of iso-dodecane was demonstrated in Figure 8. Among the four catalysts, Pt−N exhibited the highest hydroisomerization conversion and selectivity, which up to 76 and 84\%, respectively. The conversion of the \(n\)-dodecane was mainly correlated with the platinum particle size, the location of Pt on the support and the valence state of platinum in the metal precursors. As the Pt particle size increased, the conversion of the catalysts decreased in the order of Pt−N (1.78 nm) > Pt−Cl (1.88 nm) > Pt−NCl (2.74 nm). The Pt−NCl catalyst displayed the largest particle size and therefore with the lowest catalytic activity. In addition, the increase in the Pt particle size also led to a decrease in metal dispersion, which in turn affected the conversion of \(n\)-dodecane. Combined with the characterization results of \(H_2\)-TPR, it was clear that Pt mostly existed on the external surface of the support for catalysts of Pt−N and Pt−Cl, while quite a lot of platinum particles located in the internal pores of SAPO-11 for Pt−NCl and these platinum particles are difficult to reduce at a low temperature. Consequently, Pt−N and Pt−Cl show better hydroisomerization conversion up to 76 and 63\%, respectively. Although Pt−Cl with the most platinum particles on the external surface of the support, its hydroisomerization conversion was lower than Pt−N, this may be due to the valence state of Pt in the metal precursors. Pt−N with Pt(II) while Pt−Cl with Pt(IV) in the precursors, combines with the hydroisomerization conversion, it is clear that Pt(II) in the precursors is more favorable for the isomerization reaction than Pt(IV).

The hydroisomerization selectivity of the iso-dodecane could be related to the number of Brønsted acid sites and Pt crystal planes. The number of Lewis acid sites seemed that no direct effect on the hydroisomerization selectivity. On the other hand, when the number of Brønsted acid sites is reduced, the hydroisomerization selectivity of the catalysts increased in the order of Pt−NCl < Pt−C ≈ Pt−N. The Pt−Cl catalyst owned the largest number of acid sites, but it displayed the worst hydroisomerization selectivity. Therefore, the number of Brønsted acid sites is a key factor to improve the hydroisomerization selectivity. More importantly, Pt-N and Pt−Cl catalysts with Pt(111) face showing better hydroisomerization selectivity than the catalyst of Pt−NCl and Pt−Cl with the Pt(100) face. The yield of the products over different catalysts exhibited a similar trend. As can be seen in Figure 9, hydroisomerization was the dominant reaction, and Pt−N displayed the highest percentage of i-C12 (63\%) and the lowest n-C12 (24\%), but Pt−NCl performed just the opposite, which were 32\% i-C12 and 59\% n-C12, respectively. The cracking products of \(n\)-dodecane included C1 ≈ C5, C6, C7, C8, C9, C10, and C11 fractions. Except for a small amount of the C6 component in the products, the other cracking components were nearly unable to be detected. According to the above results, Pt−N is an effective catalyst for the isomerization of \(n\)-dodecane, further indicating that the Pt precursors affect the catalytic activity of the catalysts in the hydroisomerization of \(n\)-dodecane.

### 2.7. Mechanism of \(n\)-Dodecane Hydroisomerization on Pt/SAPO-11

The mechanism of hydroisomerization of normal paraffin in literature was summarized as follows: bifunctional mechanism,\(^{31}\) shape selective catalytic mechanism,\(^{32,42}\) and chain reaction mechanism.\(^{33}\) The classic dual-functional mechanism is currently used to guide the design of the catalysis and investigate the hydroisomerization reactions.\(^{13−15}\) The process of hydroisomerization of \(n\)-dodecane on Pt/SAPO-11 with bifunctional active sites was shown in Figure 10. The \(n\)-dodecane is first adsorbed on the metal of Pt and dehydration to \(n\)-dodecene. The \(n\)-dodecane is then transferred from the metal center to the acid center, and forms the corresponding alkylcarbenium ions. These ions undergo...
skeletal rearrangement, alkyl shify and hydride shify then form the branched olefin. At the same time, the fracture of the alkylcarbenium ions is also carried out on the acidic center of the Bronsted acid. The isomerizing and cracking products are iso-dodecene and hydrocarbons with less than 12 carbon atoms, respectively. The iso-dodecene is then transferred to the metal center for hydrogenation to form iso-dodecane and desorption, then the process of the hydroisomerization is complete.

3. CONCLUSIONS

Pt(NH3)4(NO3)2, Pt(NH3)4(Ac)2, (NH4)2PtCl4, and H2PtCl6 were used as Pt precursors to investigate their effects on the performance of Pt/SAPO-11 catalysts for n-dodecane hydroisomerization. The results indicated that the platinum precursors significantly affected the performance of the catalysts for hydroisomerization of n-dodecane. The catalyst derived from Pt (NH3)4(NO3)2 displayed the best hydroisomerization activity and selectivity of 76.1 and 84.2%, respectively.

The hydroisomerization conversion of n-dodecane is mainly affected by the platinum particle size, platinum dispersion, the location of platinum whether the internal or external surface of SAPO-11, and the valence state of platinum. In general, as the Pt particle size increases, the conversion of n-dodecane decreases in the order of Pt>N > Pt–Cl ≥ Pt–C > Pt–NCl. The results of H2-TPR reveal that Pt exists on the outer surface of the support and is beneficial for the catalyst performance, and Pt(II) in the precursors is more favorable for the isomerization reaction than Pt(IV). The hydroisomerization selectivity of n-dodecane is determined by the number of Bronsted acid sites and platinum crystal planes. The experiments showed that a suitable number of Bronsted acid sites and Pt(111) face of the catalysts are in favor of improving the hydroisomerization selectivity of the n-dodecane.

Overall, the platinum particle size, platinum dispersion, the location, and valence states of Pt, the number of Bronsted acid sites and Pt crystal planes are influenced by Pt precursors, which in turn affect the performance of the catalysts for the hydroisomerization of n-dodecane.

4. EXPERIMENTAL SECTION

4.1. Materials. Pseudoboethmite (78.4 wt % Al2O3, Chalco Shandong Co., Ltd), silica colloidal gel (30 wt % SiO2, Jiangyin Saiwei Electronics Co., Ltd), and phosphoric acid (85 wt % H3PO4, Sinopharm Chemical Reagent Co., Ltd) were used as sources of Al, Si, and P. Di-n-propylamine (DPA, chemically pure) was used as structure-directing agents. Pt(NH3)4(NO3)2 (AR) and Pt(NH3)4(Ac)2 (AR) were supplied by Kunming Institute of Precious Metals. (NH4)2PtCl4 (AR) was purchased from Sinopharm Chemical Reagent Co., Ltd and H2PtCl6·6H2O (AR) was purchased from Aladdin.

4.2. Catalyst Preparation. SAPO-11 molecular sieve was prepared by the hydrothermal synthesis method and the procedures of the method can be found in the literature. The synthesis procedure was described as follows: first, phosphoric acid was mixed with a certain amount of water to get a phosphoric acid solution, then aluminum was slowly added to the phosphoric acid solution and the mixture solution was kept stirring for 2 h to obtain phosphorus–aluminum colloid; second, the template DPA were added drop-wise into the colloid and the mixture was still kept stirring until it became homogeneous. After that, the silicon source was slowly added and the pH of the colloid was adjusted to 5 with 1 mol·L−1 H2SO4 or 1 mol·L−1 NH3·H2O. Keep stirring until the colloid was uniformly mixed, and retain all the materials in the mixture in a molar composition of 1.0Al2O3/0.3SiO2/1.0P2O5/2.0DPA/50H2O; third, the mixture was transferred into a PTFE-containing stainless-steel autoclave and maintained the stability for crystallization at 180 °C for 96 h. After that, the samples were centrifuged and washed, dried at 120 °C overnight. Finally, the as-synthesized SAPO-11 was calcined at 600 °C for 6 h to remove the organic template and the SAPO-11 molecular sieve was obtained.

This self-made SAPO-11 molecular sieve was used as the support, Pt(NH3)4(NO3)2, Pt(NH3)4(Ac)2, (NH4)2PtCl4, and H2PtCl6 were selected as the platinum precursors, denoted as Pt–N, Pt–C, Pt–NCl, and Pt–Cl, respectively. All the Pt/SAPO-11 catalysts were prepared by an impregnation method and the Pt loading was 0.5 wt %. After being dried at 120 °C overnight, the samples were calcined at 500 °C for 4 h.

4.3. Characterization. X-ray powder diffraction patterns were obtained on a Rigaku X-ray diffractometer with Cu Kα radiation (40 kV, 30 mA). The samples were scanned with a rate of 5°·min−1 from 5° to 60°.

The nitrogen adsorption–desorption test was operated on a Micromeritics ASAP 3020 apparatus. The samples were degassed at 300 °C for 3 h in vacuum before the measurement. The specific surface area was calculated by the BET equation. The total pore volume (Vpore) was estimated at a relative pressure of 0.99. The micropore volume (Vmicropore) was calculated using the t-plot method. The mean pore diameter (Dpore) was calculated using Dpore = 4Vpore/SBET.

TEM was operated on the Tecnai F30 with an acceleration voltage of 300 kV. The samples were first reduced with H2 at 400 °C for 4 h, then suspended in ethanol, and sonicating for 20 min. The dispersed samples were dried on the carbon-coated copper grid and dried at room temperature.

H2-TPR was operated on a Micromeritics AutoChem II 2920 instrument and a TCD detector was used for the signal detection. 100 mg of the samples were loaded into a quartz U-tube reactor and pretreated with helium at 150 °C for 60 min with a flow rate of 40 mL·min−1. After the temperature was cooled down to 50 °C, the gas was switched to 5% H2/Ar at the same flow rate until the TCD signal was level. The temperature was then raised from 50 to 800 °C at a ramp of 10 °C·min−1.

CO chemisorption was performed on a Micromeritics ASAP 2020C instrument. 100 mg of samples were loaded into the reactor and reduced with H2 at 400 °C for 4 h, followed by flushing with a helium flow at the same temperature for 1 h. Afterward, the temperature was cooled to room temperature and maintained at that temperature for some time until the...
and the specific information was shown in the literature.  

4.4. Catalytic Performance Assessment. Prior to the reaction, the catalysts were first reduced in H2 at 400 °C for 4 h. The hydrosisomerization of n-dodecane was operated in a fixed bed reactor at atmospheric. The reaction conditions were H2/n-C12 (mol/mol) = 15.0, liquid hourly space velocity (LHSV) = 4.0 h⁻¹ and gas hourly space velocity (GHSV) = 6000 h⁻¹. The reaction temperature was 320 °C. In the assessment of catalyst performance, 0.5 g of (20–40 mesh) catalysts were loaded into a tubular reactor, and both ends of the bed were filled with a certain amount of 20–40 mesh quartz sand. n-dodecane was pumped continuously into the reactor, together with a co-feed H2. The reactant and the products were analyzed on-line by a GC-950 equipped with a flame ionization detector and a PONA-50 m column.

The conversion ($X_{n-C12}$) of n-dodecane, the selectivity to isododecane ($S_{iso}$), the cracking products ($S_{cr}$), the yield of isododecane ($Y_{iso}$), and the cracking products ($Y_{cr}$) were calculated as follows

\[ X_{n-C12} = \frac{F_{n-C12,0} - F_{n-C12}}{F_{n-C12,0}} \]

\[ S_{iso} = \frac{F_{iso}}{F_{n-C12,0} - F_{n-C12}} \]

\[ S_{cr} = \frac{F_{cr}}{F_{n-C12,0} - F_{n-C12}} \]

\[ Y_{iso} = X_{n-C12} \times S_{iso} \times 100\% \]

\[ Y_{cr} = X_{n-C12} \times S_{cr} \times 100\% \]

where $F_{n-C12,0}$ and $F_{n-C12}$ denote the flow rate of n-C12 in the feed and the product (g/h), respectively; $F_{iso}$ and $F_{cr}$ denote the flow rate of i-C12 and the cracking components in the product (g/h), respectively; $Y_{iso}$ and $Y_{cr}$ denote the yield of i-C12 and the cracking components in the product.

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**Notes**

The authors declare no competing financial interest.

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