Sn-Modified Pt/SAPO-11 Catalysts for Selective Hydroisomerization of n-Paraffins

Yunqi Liu,*,† Chunying Liu,† Chenguang Liu,† Zhijian Tian,‡ and Liwu Lin‡

College of Chemistry & Chemical Engineering, University of Petroleum, Shandong 257061, China, and Institute of Chemical Physics, The Chinese Academy of Science, Dalian 116023, China

Received January 28, 2004. Revised Manuscript Received May 6, 2004

The hydroconversion of n-paraffins is a key reaction in hydrodewaxing of lubricating base oil. In this paper, we investigate the performance of Pt/SAPO-11 catalysts for isomerization of n-paraffins by the model compound of n-dodecane. Under this experimental condition, yields of feed isomers as well as cracking products are a function of the total n-dodecane conversion. Primary products are methylundecane while multi-brancheds and cracking products are formed in successive reactions. The result shows that the addition of Sn increases the selectivity for isomerization reaction. The most ideal experimental data for hydroconversion of n-dodecane is that the selectivity of isomerized products gets 90% when conversion of n-dodecane is 90% for the Sn-promoted Pt/SAPO-11 catalyst.

1. Introduction

Lubricating oils are being used under increasingly severe conditions. Meanwhile, the growing use of synthetic and unconventional base stocks make it more difficult to produce lube oils by simply modifying addition technology.1 Hydroisomerization of n-paraffins over solid acid catalysts is used to produce high octane gasoline blending components, to increase the low temperature performance of diesel and to obtain high viscosity index lube oils.2-4 These isomerization reactions are generally carried out over bifunctional catalysts containing metallic sites for hydrogenation/dehydrogenation and acid sites for skeletal isomerization via carbenium ions. Catalytic dewaxing is probably the first industrial application of selectivity properties of zeolite catalysts, which selectively crack long-chain n-paraffins contained in lube base oil.5 The presence of acidic and the shape selective features of zeolites has spurred a widespread interest in new catalytic materials such as silicoaluminophosphate molecular sieves as solid catalysts for the hydroisomerization of paraffinic feedstocks. An attractive dewaxing procedure6,7 results through isomerization of the n-paraffins to branched isoparaffins, eliminating the yield loss associated with n-paraffin removal by cracking or solvent extraction. Shape-selective molecular sieves suppress formation of multibranched isomers which are more susceptible to hydrocracking, thereby leading to high isomerization selectivity. In the so-called isode waxing process, the pour point is lowered by the introduction of a limited number of methyl branches in the long n-alkanes, while preserving the high quality associated with the paraffinic nature of the molecules.

The framework of SAPO-11 is isotopic to that of ALPO-11, with AEL-type structure. The void volume consists of nonintersecting elliptic 10-membered ring pores of 0.39 × 0.63 nm pore opening. Recently, evidence of selectivity in some hydrocarbon reactions using silicoaluminophosphate molecular sieves as solid catalysts has been reported,8-12 indicating that conversions involving C8 range hydrocarbons on SAPO-11 are potentially shape-selective. But little attention has been paid to metallic component. In this work, we have studied and compared the catalytic properties of the bifunctional

‡ The Chinese Academy of Science.
† University of Petroleum.
* Corresponding author. E-mail: liuyq@mail.hdpu.edu.cn.

10.1021/ef049968x CCC: $27.50 © 2004 American Chemical Society
Published on Web 07/07/2004
catalyst Sn-modified Pt/SAPO-11 with Pt/SAPO-11 in n-dodecane hydroconversion. The result shows that the addition of Sn promotes the isomerization selectivity under n-dodecane deep conversion.

2. Experimental Section

2.1. Catalyst Preparation. SAPO-11 is hydrothermally synthesized according to ref 13 and the typical gel composition is Al₂O₃/P₂O₅/SiO₂ is 1:1:0.3. The XRD of the crystal phase is shown in Figure 1. The main surface properties are surface area, 217 m²/g; pore volume, 0.24 cm³/g; median pore diameter, 0.59 nm. The catalysts employed in this work are SAPO-11 containing 0.5 wt % of platinum or Tin-platinum as hydrogenating metal. In Pt–Sn/SAPO-11 catalyst, the atomic ratio of Sn to Pt is 1:1. The Pt and Sn were loaded on the SAPO-11 by wet impregnation with an aqueous solution of H₂PtCl₆ and SnCl₂. The resulting materials were dried at 393 K for 4 h and calcined at 823 K for 4 h in air.

Metal dispersions were measured using hydrogen chemisorption. Prior to the chemisorption experiment, the catalyst was pretreated at 400 °C under flowing helium. Chemisorptions were carried out at room temperature. In the calculation of the metal dispersion, it was assumed that every surface atom of platinum chemisorbs one hydrogen atom. The dispersions, d(%), were calculated as the number of platinum atoms at the surface divided by the total number of platinum atoms in the sample.

2.2. Catalytic Activity Measurements and Products Analysis. The measurements of reaction activities of catalysts for conversion of n-dodecane were accomplished in a stainless steel microreactor at medium pressure (4.0 MPa). The reaction feed was introduced into the reactor by a pulseless pump. The liquid hourly space velocity (LHSV) was 1–2.5 h⁻¹ and the volume ratio of hydrogen to liquid was 1000. The reaction temperature was 593–673 K. The products were collected and analyzed off-line by a Varian-3400 gas chromatograph equipped with a 0.32 mm × 100 m HP CP-1 capillary column and a flame ionization detector, and the product identification was carried out by gas chromatography–mass spectrometry (GC-MS).

3. Results and Discussion

3.1. Identification of the Products from Hydroconversion of n-Dodecane. The high resolution GC-MS analysis shows that the mixture of isododecane was formed mainly of mono-branched isomers in different positions of the paraffinic chain at lower conversion levels, which consist of 2-methylundecane, 3-methylundecane, 4-methylundecane, and 5- or 6-methylundecane (unresolved). At higher conversion degrees, a decrease in the relative concentration of mono-branched isomers and an increase in the di-branched isomers were observed. There are scarcely any tri-branched isomers in the products. The typical chromatograms of the products from hydroconversion of n-dodecane on Pt(Sn)/SAPO-11 catalysts were shown in Figure 2b. In the di-branched isomers, the composition of the fraction of dimethyl isomers slightly varies with the global conversion (specially 2,3-dimethyl-, 2,4-dimethyl-, 2,5-dimethyl-, and 2,6-dimethyldecane), and it substantially deviates from that observed in selective SAPO-11 zeolites.

3.2. The Relationship of Conversion with Selectivity of Isomerized Products. In the hydroconversion reaction of n-dodecane, the products include mono-branched isomers, multi-branched isomers, and cracked products. In the multi-branched products, the di-branched isomers are the main products and the tri-branched isomers hardly exist in the isomer products. In cracked products, which indicated the molecules with carbon number less than dodecane, there is scarcely any methane. These are benefit to iso-waxing processing. So, the isomer selectivity is defined as the percentage of isomers (including mono-branched and multi-branched isomers) in the total products. Table 1 and Table 2 show the percentage of different kinds of products vs n-dodecane conversion.

The results indicate that the isomerization conversion of n-dodecane over Pt/SAPO-11 or Pt-Sn/SAPO-11 is a unique function of the total conversion. Initially, the conversion into isododecane is more than 94%, reaching the highest isomer selectivity, but on continuing to increase the n-dodecane conversion the selectivity decreases. Over the Pt–Sn/SAPO-11 catalyst, we obtained more than 90% isomerization selectivity at 90% n-dodecane conversion. Meanwhile, only 85% isomerization selectivity at 87% n-dodecane conversion over Pt/SAPO-11 has been obtained. When the conversion of n-dodecane is more than the 87%, the isomerization selectivity obviously decreases. The better catalytic
performance may be attributed to the addition of a second metal to the metallic catalyst composition.

3.3. The Effects from Different Composition of Molecular Sieve. In Table 3, we present the products distribution on different compositions of molecular sieves. The results show that the activity and selectivity is strongly affected by the silica content in gel composition of synthesized zeolites.

As we know, the acidity of SAPO molecular sieves is attributed to the substitution Si for Al or P in the skeleton of the microporous wall. With the addition of silica in gel composition, the silicon content in the skeleton of the microporous wall and acidity will increase, so the higher acidity of as-synthesized zeolite contributes to the increase in n-dodecane hydroconversion on Pt/SAPO-11 catalysts. However the selectivity of isomerized products decreases when the content of silica reaches a certain value, so it is necessary to control the acidity or acidity distribution in the skeleton of the zeolite microporous wall.

**Figure 2.** (a) Chromatogram of typical products of hydroconversion of n-dodecane on Pt(Sn)/SAPO-11. 1–11: C₄–C₉ alkane and their isomers; 12–15: 2,3-dimethyl-, 2,4-dimethyl-, 2,5-dimethyl-, and 2,6-dimethyldecane; 16: 5(6)-methyldecane; 17: 4-methyldecane; 18: 2-methyldecane; 19: 3-methyldecane; 20: dodecane. (b) The reaction network of hydroconversion of n-dodecane on Pt/SAPO-11 catalysts.

**Table 1. Isomer Selectivity vs Conversion of n-Dodecane on Pt–Sn/SAPO-11 Catalyst**

<table>
<thead>
<tr>
<th>Conversion</th>
<th>41.2%</th>
<th>49.9%</th>
<th>60.1%</th>
<th>72.0%</th>
<th>83.0%</th>
<th>91.1%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-branched products %</td>
<td>35.2</td>
<td>42.0</td>
<td>48.8</td>
<td>55.2</td>
<td>58.3</td>
<td>54.1</td>
</tr>
<tr>
<td>Multi-branched products %</td>
<td>4.5</td>
<td>6.0</td>
<td>8.7</td>
<td>12.7</td>
<td>20.0</td>
<td>29.2</td>
</tr>
<tr>
<td>Cracked products %</td>
<td>1.5</td>
<td>1.9</td>
<td>2.6</td>
<td>4.1</td>
<td>4.7</td>
<td>7.8</td>
</tr>
<tr>
<td>Selectivity %</td>
<td>96.3</td>
<td>96.2</td>
<td>95.7</td>
<td>94.3</td>
<td>94.3</td>
<td>91.4</td>
</tr>
</tbody>
</table>

**Table 2. Isomer Selectivity vs Conversion of n-Dodecane on Pt/SAPO-11 Catalyst**

<table>
<thead>
<tr>
<th>Conversion</th>
<th>41.0%</th>
<th>59.6%</th>
<th>71.6%</th>
<th>79.1%</th>
<th>87.4%</th>
<th>90.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mono-branched products %</td>
<td>35.5</td>
<td>52.3</td>
<td>59.4</td>
<td>52.1</td>
<td>47.1</td>
<td>43.2</td>
</tr>
<tr>
<td>Multi-branched products %</td>
<td>3.8</td>
<td>5.4</td>
<td>10.1</td>
<td>22.6</td>
<td>27.6</td>
<td>32.6</td>
</tr>
<tr>
<td>Cracked products %</td>
<td>1.7</td>
<td>1.9</td>
<td>2.1</td>
<td>4.4</td>
<td>12.7</td>
<td>14.7</td>
</tr>
<tr>
<td>Isomerized selectivity %</td>
<td>95.5</td>
<td>96.8</td>
<td>97.1</td>
<td>94.4</td>
<td>85.5</td>
<td>83.8</td>
</tr>
</tbody>
</table>
Table 3. The Effects on Product Distribution from Different Gel Composition of Molecular Sievea

<table>
<thead>
<tr>
<th>catalysts</th>
<th>gel composition SiO2/Al2O3/P2O5</th>
<th>cracked products %</th>
<th>isomerized products %</th>
<th>conversion %</th>
<th>isomer selectivity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SAPO-11(1)</td>
<td>0.1:1:1:1</td>
<td>7.1</td>
<td>71.7</td>
<td>78.8</td>
<td>91.0</td>
</tr>
<tr>
<td>Pt/SAPO-11(2)</td>
<td>0.2:1:1:1</td>
<td>7.7</td>
<td>74.6</td>
<td>82.3</td>
<td>90.6</td>
</tr>
<tr>
<td>Pt/SAPO-11(3)</td>
<td>0.3:1:1:1</td>
<td>7.4</td>
<td>78.0</td>
<td>85.4</td>
<td>91.3</td>
</tr>
<tr>
<td>Pt/SAPO-11(4)</td>
<td>0.4:1:1:1</td>
<td>13.2</td>
<td>76.5</td>
<td>89.7</td>
<td>85.2</td>
</tr>
</tbody>
</table>

a The reaction conditions: T = 360 °C, P = 4.0 MPa, LHVS = 1 h⁻¹.

Table 4. The Effects on Products Distribution with Varied Ratios of Sn/Pt

<table>
<thead>
<tr>
<th>catalysts</th>
<th>metal dispersion D %</th>
<th>micropore (nm)</th>
<th>cracked products %</th>
<th>isomerized products %</th>
<th>conversion %</th>
<th>isomer selectivity %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5Pt–0.05n</td>
<td>57</td>
<td>0.59</td>
<td>14.7</td>
<td>75.8</td>
<td>90.5</td>
<td>83.8</td>
</tr>
<tr>
<td>0.5Pt–0.5n</td>
<td>79</td>
<td>0.59</td>
<td>7.8</td>
<td>83.8</td>
<td>91.0</td>
<td>91.4</td>
</tr>
<tr>
<td>0.5Pt–1.0n</td>
<td>83</td>
<td>0.58</td>
<td>5.9</td>
<td>81.2</td>
<td>87.1</td>
<td>93.2</td>
</tr>
<tr>
<td>0.5Pt–2.0n</td>
<td>82</td>
<td>0.58</td>
<td>4.7</td>
<td>78.3</td>
<td>83.0</td>
<td>94.3</td>
</tr>
</tbody>
</table>

a The reaction conditions: T = 360 °C, P = 4.0 MPa, LHVS = 1 h⁻¹; micropore indicates the pore diameter of Pt(Sn)/SAPO-11 catalysts corresponding to loading volume.

3.4. The Effect of Sn Promoter on Pt(Sn)/SAPO-11 with Varied Ratios of Sn/Pt. To obtain information about the beneficial effect of Sn as a promoter if there is a truly synergistic phenomenon, we investigated the effect of varying the ratio of Sn/Pt and the result is listed in Table 4.

The selectivity of isomerized products increases with the addition of Sn promoter in the range of lower than 1 of Sn/Pt ratio. When the ratio of Sn/Pt goes beyond the limits of 1:1, the conversion decreases with the increase of the ratio of Sn/Pt, but the selectivity of isomerized products has hardly any decrease in trend but has an increase in trend. The decrease in conversion may be attributed to the cover of acidity on the porous surface of zeolite, while the increased selectivity of isomerized products may be attributed to high metal dispersion and the modification to the pore mouth of the molecular sieve from the Sn promoter.

3.5. The Mechanism of Hydroconversion of n-Dodecane on Bifunctional Catalyst. If an n-alkane is converted to a bifunctional catalyst in the presence of hydrogen, two principal reactions take place: isomerization into isoparaffins, and hydrocracked into products with a lower carbon atom number than the feed. A simplified reaction network of long-chain n-alkane hydroconversion over bifunctional catalysts is that in which hydroisomerization and hydrocracking occur in series. In the first step, the n-alkane is isomerized to a set of its isomers with single branches. In a consecutive step, these isomers are again isomerized, whereby di-branched isoparaffins are produced. If further isomerization occurs, however, the tri-branched species is produced under a very rapid hydrocracking referred to as type A β-scission. In addition to this main pathway of hydrocracking via tri-branched species, there is some contribution to hydrocracking reactions starting from di-branched species referred to as type B β-scission. Figure 2 shows the reaction network from hydroconversion of n-dodecane on Pt/SAPO-11 catalysts. Due to the selective effect of the SAPO-11 molecular sieve, the tri-branched species hardly form in this catalytic reaction. Figure 3, parts a and b, give the composition of the isododecane and cracked products from n-dodecane hydroconversion over Pt/SAPO-11 and Pt–Sn/SAPO-11 catalysts. The results indicate that the isododecanes obtained through isomerization of n-dodecane can be either mono-branched or di-branched; the tri-branched isomers do not appear with the two catalysts in the experimental range studied. These results also indicate the isomer distribution is a function of the total conversion and di-branched isomers are formed in successive reaction from methylundecane and only appear at high values of n-dodecane conversion and in small quantities. The multi-branched isomers obviously increase at conversion levels more than 60%. On Pt/SAPO-11 and Pt–Sn/SAPO-11 catalysts, even at 90% n-dodecane conversion, the cracking yields are limited and amount to lower than 10% on Sn-modified Pt/SAPO-11 catalyst. Much higher reaction severities are necessary to crack the isododecane molecules on the two catalysts. This is attributed to the feature of 10-membered ring zeolite. The key feature of the SAPO-11 is the limited penetration of branched molecules into this zeolite. According to pore mouth catalysis and key-lock catalysis concepts, the product distribution from the n-dodecane hydroconversion can be explained as follows. The catalytic conversion of alkane on SAPO-11 base catalysts does not involve diffusion transportation through the micropores. Skeletal isomerization occurs on molecules absorbed in pore mouths and on the external surfaces of the zeolite crystals. The mono-branched reaction of n-alkane, only part of the molecule penetrates into a micropore opening. The skeletal rearrangement takes place in the pore mouth where there is less steric hindrance (pore mouth catalysis). Further branching in the carbon skeleton is introduced when the mono-branched molecule is stretched across the external crystal surface. With the first branching pinned into one pore mouth, additional branchings are generated at positions where the carbon chains face neighboring pore mouths (key-lock concept). In di-branched isomers, the content of 2-methylundecane is relatively less than other methylundecane product, but the content of 2-methyl (including 2,3-dimethyl-, 2,4-dimethyl-, 2,5-...
dimethyl-, and 2,6-dimethyldecane) in di-branched isomers obviously increased, which substantiates the key-lock reaction mechanism. According to the reaction pathway, although the selectivity of isomers depends mainly on the properties of zeolite, but the balance of acidic vs metallic function in the catalyst is also an important factor. Owing to the as-synthesized zeolite having an appropriate porous mouth, we obtained better isomer selectivity in two catalysts. Considering that we have used the same molecular sieve in two different catalysts, the improved selectivity should be ascribed to the Sn promoter. The promoter may modify the acidity or porous pathway in the synthesized molecular sieve, which helps to avoid the deep isomerization and cracking reaction in the surface of the molecular sieve.

3.6. Product Composition and Cracking Reaction Mechanism. In Tables 1 and 2, we list the content of cracking products on Pt/SAPO-11 and Pt(Sn)/SAPO-11, respectively. The results show that cracking products exclusively consisted of alkane and both n-alkane and isoalkane with one methyl branching were obtained, which substantially deviates from that observed in selective SAPO-11 zeolites with a key-lock mechanism. In cracked products, which indicated the molecules with carbon number less than dodecane, there is scarcely any methane. The carbon-number distribution of cracked products is shown in Figure 4. On the SAPO-11 base catalysts, linear fragments predominated in the cracked products of lower carbon number. This suggests that cracking occurs according to B1-, B2-, and C-type mechanisms. The content of branched isomer in the cracked products increases with increasing carbon number of the fraction. Souverijns et al.\textsuperscript{17} have investigated the hydroconversion of heptadecane on Pt/ZSM-

22 catalyst and also found a similar phenomenon. Hydrocracking involves the β-scission of alkylcarbenium ion. In a β-scission, two electrons of a β carbon–carbon bond are transferred toward the positively charged R carbon atom to form an olefin and a smaller alkylcarbenium ion, charged at the γ carbon atom of the parent ion. The rival β-scission modes that exist depend on the nature of the parent ion. β-scission is extremely rapid for a specific tri-branched ion for which both the starting and product ions are tertiary ion (type A). Other β-scission modes can operate also di-branched (B1 and B2) and mono-branched ions (C), which involve secondary ions and are much slower. The rate of β-scission decreases in the order A ≫ B1 = B2 > C. Type A β-scission generates branched fragments with four and more than four carbon number atom, whereas the type B and C mechanisms yield propane and larger linear and branched fragments. According to the pore mouth catalysis model, mechanism C appears to be the most likely mechanism for β-scission on SAPO-11 base catalysts. This is due to the fact that the parent and product alkylcarbenium ions can interact favorably with the micropore wall.

4. Conclusion

On SAPO-11 base catalysts, n-dodecane can be intensively isomerized with very limited cracking. Hydroisomerization and hydrocracking of n-dodecane in SAPO-11 base catalysts occur in the pore mouth, being governed by shape selectivity imposed by the SAPO-11 structure strongly affecting the product distribution. Preferential formation of mono- or di-branched isododecane is observed. The isomerization selectivity depends on the properties of synthesized zeolite and the balance of acidic vs metallic functions in the catalysts. The addition of Sn improves the isomerization reaction selectivity. On Pt–Sn/SAPO-11 catalysts, the yield of isododecane reaches 81 at 90% n-dodecane conversion, compared to 76 at 90% conversion on Pt/SAPO-11 catalyst. Further investigation on the function of Sn promoter in Sn-modified Pt/SAPO-11 catalysts is made in our laboratory.

Acknowledgment. The authors are particularly grateful to the Chinese National Petroleum and Gas Group Corporation for financial support of this work.

EF049968X