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Hydroisomerization of *n*-tetradecane over Pt/SAPO-11 catalyst

Cheng-Hui Geng, Fei Zhang, Zhi-Xian Gao*, Liang-Fu Zhao, Jing-Lai Zhou

Institute of Coal Chemistry, Chinese Academy of Sciences, South Taoyuan Road 27, Taiyuan 030001, Shanxi Province, PR China

Abstract

The hydroisomerization of *n*-tetradecane over SAPO-11 supported Pt catalyst have been investigated in a fixed bed reactor by changing reaction parameters such as temperature, pressure and WHSV, as well as the H_2/HC ratio. High yields of branched feed isomers, which had high mono-branched to multi-branched ratio, were achieved with Pt/SAPO-11 catalyst of 0.4% Pt loading. The catalyst showed high stability and good regeneration property. The unique characteristic of the catalyst is its high selectivity to the branched isomers under relatively low reaction pressures. It has been proposed that the high selectivity to feed isomers and good catalyst stability result from the combination of steric constraints of the micropores of SAPO-11 and high Pt dispersion as well as the mild acidity. A pore channel catalysis mechanism has also been proposed to account for the formation of feed isomers.

Keywords: Pt/SAPO-11; *n*-Tetradecane; Hydroisomerization; Selectivity

1. Introduction

Isomerization of normal paraffin plays an important role in the petroleum industry [1]. The isomerization of C_4–C_7 hydrocarbons has found wide applications in the production of gasoline with high octane numbers, while that of long-chain alkanes has been used in the dewaxing processes for production of high quality diesel fuel and lube base oil [2]. The isomerization process usually takes place in the presence of hydrogen, and in this case it is referred as hydroisomerization. As is well known, hydroisomerization employs a metal/acid zeolite catalyst that has been described as bifunctional [3]. Molecular sieves, such as ZSM-12, Mordenite, USY, L-zeolite and β-zeolite, loaded with noble metal are preferred catalysts because of their good shape-selectivity and high stability, as well as the resistant to poisons such as sulfur and water. Recently, using microporous molecular sieve, such as silicoaluminophosphates (SAPO) [4] and ZSM-22, supported noble metal Pd or Pt catalysts, great improvements have been achieved. SAPO materials generally have a lower acidity than zeolites [5], and have been proved to more suitable for constituting catalysts that manifest better performance for long-chain hydrocarbon isomerization.

In the open literature, C_7–C_{10} hydrocarbons, both pure and binary mixtures, have been used as feed to demonstrate the mechanism of isomerization reactions in the presence of bifunctional catalysts [6]. It is well established that selectivity of paraffin isomerization depends primarily on the balance between metal and acid functions. According to the classical isomerization mechanism [7,8], paraffins are dehydrogenated on the metal sites, and the formed olefins are protonated on the acid sites to form the corresponding alkylcarbenium ions. These carbenium ions undergo skeletal rearrangement and β-scission followed by deprotonation and hydrogenation over metal sites to produce the isomerization and cracking products. Essentially, the above mechanism involves diffusion steps of the olefin intermediates from the acid sites to the metallic sites, and vice versa. However, the transportation of olefin intermediates is questionable, and is hardly proved by any direct evidences. In fact, olefin intermediates have never been detected in the gas phase during alkane hydroconversion. So it seems necessary that the classical mechanism should be reconsidered and revised.

One can easily formulates that if the two functional sites, acid site and metal site, have a close contact, there will be no need for the diffusion processes. Based on this idea, we have prepared a Pt/SAPO-11 catalyst that was presumed to have close proximity of the two functional sites, and this catalyst shown pretty good isomerization selectivity even at high conversions of *n*-heptane [9]. In this work we have

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* Corresponding author. Fax: +86 351 4067440.
E-mail address: gaozx@sxicc.ac.cn (Z.-X. Gao).

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further investigated the hydroisomerization of *n*-tetradecane on this Pt/SAPO-11 catalyst of 0.4% Pt loading. The aims were to investigate the effect of chain length and reaction variables on reactivity, stability and hydroisomerization selectivity, and to determine the possible reasons that account for the catalytic behavior of the new catalyst system.

2. Experimental

2.1. Catalyst

SAPO-11 microporous molecular sieve was synthesized hydrothermally according to the established procedure. Pseudo-boehmite and silica sol were used as the aluminum and silicon source, respectively. The as-synthesized sample was dried at 100 °C and then calcined in air at 500 °C for 4 h to burn the occluded template. XRD characterization of the obtained powder confirmed that it was a SAPO-11.

The powder was mixed with a certain amount of alumina, and extruded into cylindrical shape at moderate pressures. After drying at 120 °C, the sample was crushed and sieved to obtain particles with a diameter of about 0.5 mm.

The particle was then impregnated with an H_2PtCl_6 solution by incipient wetness method. The solution was added dropwise to the particle and kept at room temperature overnight, and subsequently dried for 4 h at 100 °C. The obtained catalyst sample contains 0.4% of platinum.

The acidity of the catalyst was characterized by NH_3-TPD method, and quantitative measurement of the total acidity was obtained by chemical titration of the desorbed ammonia in aqueous solution. Dispersion of Pt was estimated by H_2 chemisorption measurement at room temperature with a self-equipped apparatus system. Low temperature N_2 adsorption–desorption method was used to measure the BET surface area and porosity. The morphology and the particle size of the SAPO-11 and the catalyst were obtained from transmission electron microscopy (TEM) measurement.

2.2. Catalytic activity measurements

Hydroconversions of *n*-tetradecane were carried out in a 10 ml fixed bed reactor system. The reactor, which was surrounded by a well-insulated heater jacket, was vertically mounted, and packed with alternating layers of porcelain, with 9 ml catalyst particle placed between these layers.

n-Tetradecane (99.5%) was a custom product from Fushun Petrochemical Co. Ltd. Hydrogen, dried by molecular sieves, was employed as both carrier and reactant gas. Previous to activity measurements, the catalyst was pretreated in situ first with air, then with H_2 up to 400 °C for 2 h.

Experimental data were collected over a wide range of experimental conditions: temperature, 300–400 °C; pressure, 0.5–4.5 MPa; H_2 to hydrocarbon (HC) molar ratio of 1.4–20, WHSV $= 0.5–5\,h^{-1}$.

Reaction products, collected as gas and liquid phase, were analyzed in a GC with a flame-ionization detector. Product identification was achieved by GC–MS and by comparing the retention time of some pure compounds with separate GC injections. The carbon numbers of all the peaks were settled, but only some could be identified.

Conversion was calculated as the disappearance of n-C_{14}. Isomerization selectivity was defined as the yield of C_{14} iso-components (in wt.%) divided by n-C_{14} conversion.

3. Results and discussion

For the synthesized SAPO-11, an inhomogeneous particle containing amorphous phase was observed, and the size distribution ranged from 0.04 to 0.12 μm. Compared with literature data [10], the crystals were much small. This was what we had expected for preparing the Pt/SAPO-11 catalyst that had a close contact between acid site and metal site. The SAPO-11 was shaped using alumina as binder and loaded with platinum by impregnation method. The thus obtained catalyst had 0.4 wt.% of metal, and shown a particle size of about 0.2 μm. The main physicochemical properties were: BET surface area 173.2 m^2/g, pore volume 0.1971 ml/g; platinum dispersion 0.92, total acidity 0.1413 mmol NH_3/g. The high Pt dispersion, which might result from the small size of the SAPO-11, and the low total acidity of the catalyst, which was far more less than the reported literature data, were key features to govern the catalytic behavior of high isomerization selectivity.

Hydroconversions of *n*-tetradecane and *n*-heptane were performed over the Pt/SAPO-11 catalyst at a wide range of experimental conditions. The hydroconversion products consisted both isomerization and cracking products, but with high selectivity to feed isomers. The distribution of isomerization products was influenced by reaction variables, however it could be well correlated with conversion level. So in the following subsections, the effects of reaction parameters on the catalytic performance of *n*-tetradecane have been demonstrated by catalytic activity and isomerization selectivity. Then the distribution of isomerization products has been discussed in the last part of this section.

3.1. Effect of reaction temperature

Dependence of *n*-tetradecane conversion with temperature over the 0.4 Pt/SAPO-11 catalyst is shown in Fig. 1. As was expected, the conversion n of *n*-tetradecane increased as a function of reaction temperature, while the selectivity to feed isomers decreased gradually. Within the temperature range, the selectivity to cracking products were less than 10% even at a high temperature of 380 °C. It should be mentioned that formation of cracking product was inevitable even at low reaction temperature, indicating cracking products could be formed as primary reaction ones. In

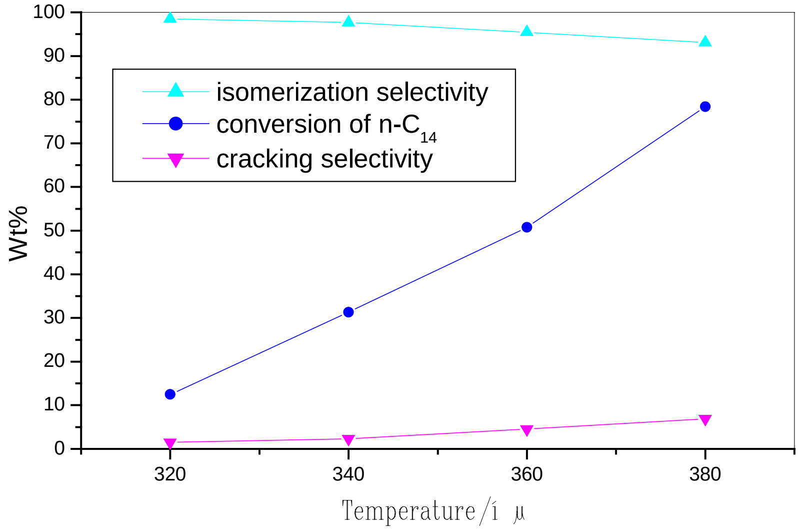

Fig. 1. Hydroisomerization of n-C_{14} as a function of temperature over Pt/SAPO-11. Conditions: pressure = 3.0 MPa; WHSV = 1.0 h^{-1}; H_2/C_{14} = 26.1 mol mol^{-1}.

other words, high isomerization selectivity toward 100% was never obtained at low conversions, which was somewhat different from literature data. Campelo et al. [11] had observed nearly isomerization products at low conversions of dodecane over Pt/SAPO-11 catalyst, but the isomerization selectivity decreased to 87% when conversion level reached up to 70%.

Over the 0.4 Pt/SAPO-11 catalyst, conversion of n-heptane presented a similar trend, but the value was lower than that of n-C_{14} hydroisomerization at the same experimental conditions [9]. In conclusion, the catalytic activity was pretty higher with long-chain hydrocarbon, which has been well proved in the open literature [12,13].

As for the isomerization products, the maximum yield of feed isomers was 55% for n-heptane hydroconversion. A maximum yield of more than 80% was obtained for n-tetradecane hydroconversion.

3.2. *Effect of reaction pressure*

There have been many papers on the isomerization of hydrocarbon, but few had dealt with the pressure effect on catalytic behavior [14]. The catalytic activity with time-on-stream showed some difference with varying reaction pressures. At pressures higher than 1.0 MPa, the isomerization process was stabilized within 30 min. However,

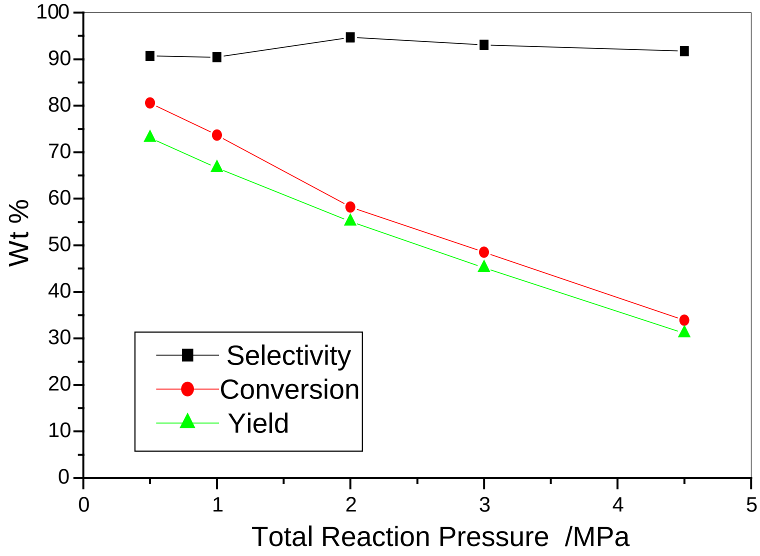

Fig. 2. Effect of reaction pressure on hydroisomerization of n-C_{14} over Pt/SAPO-11. Conditions: temperature = 360 °C; WHSV = 2.0 h^{-1}; H_2/C_{14} = 8.7 mol mol^{-1}.

noticeable catalyst deactivation was observed at a lower reaction pressure, especially at atmospheric pressure.

By keeping a constant reaction temperature of 360 °C, a H_2/HC ratio of 8.7 and a WHSV of 2.0 h^{-1}, the effect of total reaction pressure on n-C_{14} hydroconversion was investigated, and the results are depicted in Fig. 2. As shown in the figure, both the conversion of n-C_{14} and the yield of feed isomers decreased with increasing pressure. However, the isomerization selectivity was above 90% value and remained unchanged at high-pressure range.

The above results clearly indicated the participation of H_2 in the isomerization process. As has been reported in the open literature [15], a negative reaction order with respect to hydrogen was observed for hydroconversion reactions. With increasing reaction pressure, both the partial pressure of H_2 and that of *n*-tetradecane increased. So the negative pressure effect on activity, which was also observed by Chao et al. [14], suggested that absolute value of reaction order of *n*-tetradecane was smaller than that of hydrogen.

Contrary to the present result, Chao et al. had shown that the isomerization selectivity of heptane conversion on Pt/MOR was significantly improved by increasing reaction pressure, while the effect of pressure was less pronounced with Pt/Beta catalyst [14]. The disparity might result from the acidity difference between the samples. The small change in isomerization selectivity with variation of reaction pressure in this work was unique feature of the new catalyst that had low acidity. This also might be due to the high isomerization selectivity of the 0.4 Pt/SAPO-11 catalyst. The isomerization selectivity was above 90% at *n*-tetradecane conversion up to 80%. As mentioned above, similar selectivity was observed at a conversion level of 70% for dodecane conversion over Pt/SAPO-11 catalyst [11].

The carbon-number distribution of the cracked products was nearly independent of the total reaction pressure. The cracking products consist of spectra of C_1–C_{13} hydrocarbons with pretty high percentage of C_3–C_7. The presence of very small amount of methane and ethane suggested that the hydrogenolysis reaction, which is catalyzed by metal, might be negligible over the 0.4 Pt/SAPO-11 catalyst. The result shown in Fig. 2 suggested nearly the same reaction pathway within a wide pressure range. However, our recent data show that when Pt loading increased from 0.4% to 0.8%, the hydrogenolysis on metal site was noticeable, especially at high H_2 pressures. The dependence of metal loading on hydrogenolysis had also been observed over Pt/Hβ catalysts with 0.4–1.2 wt.% metal loadings. High yield of methane and ethane as hydrogenolysis product was formed over Pt/Hβ with a metal loading of 1.2%.

3.3. *Effect of space velocity*

At a reaction temperature of 360 °C, a reaction pressure of 1.0 MPa and constant H_2/HC ratio, the effect of WHSV on n-C_{14} hydroconversion was investigated by proportionally changing the flow rate of H_2 and n-C_{14}. As shown in Table 1, the conversion of n-C_{14} and the yield of feed isomers decreased with increasing WHSV, while no significant isomerization selectivity changes were observed. With the increase of WHSV, the contact time of feed on the catalyst decreased, and thus the decrease of conversion was expectable.

3.4. *Effect of H_2/HC ratio*

The influence of H_2/HC ratio on n-C_{14} hydroconversion was investigated, at a constant reaction temperature of 380 °C, a reaction pressure of 3.0 MPa and a WHSV of 1.0 h^{-1}, by changing the flow rate of H_2. As shown in Fig. 3, the conversion of n-C_{14} decreased with increasing the partial pressure of hydrogen (the H_2/n-C_{14} mole ratio from 8.5 to 45), while the isomerization selectivity was slightly increased. The changes were relatively small with higher H_2/HC ratios. The results were similar to those obtained by changing reaction pressure.

At pretty low H_2/HC ratio, catalyst deactivation became predominant, so the conversion data, which was collected with a time-on-stream of 3 h, was low as shown in Table 2. This result indicated that the isomerization was no more the principle reaction at pretty low H_2/HC ratios.

All these reflected the importance of H_2 in the isomerization process. The function of H_2 could be interpreted as facilitating isomerization by suppressing cracking reactions and keeping the catalytic activity by impeding coke formation. To maximize isomerization yield, a suitable H_2/HC ratio should be selected. The required value was found to be dependent upon reaction temperature, and higher temperature needed larger H_2/HC ratio.

3.5. *Catalytic stability*

During the catalytic transformation of *n*-tetradecane, the activity decreased gradually with time-on-stream due to catalyst deactivation. The catalytic behavior of 0.4 Pt/SAPO-11

Table 1
Effect of WHSV on n-C_{14} hydroconversion on Pt/SAPO-11 catalyst[a]

Temperature (°C)	Pressure (MPa)	H_2/HC (mol mol^{-1})	WHSV (h^{-1})	Conv[b] (%)	Y_{iso} (%)	S_{iso} (%)
360	1.0	8.7	1.0	84.1	78.4	93.2
360	1.0	8.7	2.0	73.7	66.6	90.5
360	1.0	8.7	4.0	51.2	46.2	90.4

[a] Data collected with a time-on-stream of 3 h.

[b] Conv: conversion of n-C_{14}; Y_{iso}: yield of isomers; S_{iso}: selectivity to isomers.

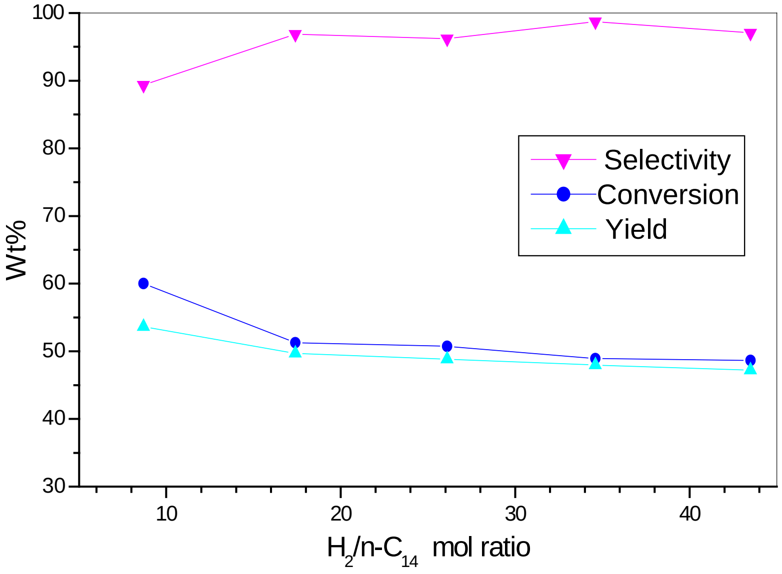

Fig. 3. Effect of H_2/HC molar ratio on hydroisomerization of n-C_{14} over Pt/SAPO-11. Conditions: temperature = 360 °C; WHSV = 1.0 h^{-1}; pressure = 3.0 MPa.

Table 2
Effect of H_2/HC ratio on the hydroisomerization of n-C_{14} on Pt/SAPO-11 catalyst[a]

Temperature (°C)	Pressure (MPa)	H_2/HC (mol mol^{-1})	WHSV (h^{-1})	Conv[b] (%)	Y_{iso} (%)	S_{iso} (%)
380	2.0	17.40	2.0	88.3	82.2	93.1
380	2.0	8.70	2.0	90.3	80.7	89.4
380	2.0	2.17	2.0	83.6	70.4	84.3

[a] Data collected with a time-on-stream of 3 h.
[b] Conv: conversion of n-C_{14}; Y_{iso}: yield of isomers; S_{iso}: selectivity to isomers.

catalyst was largely influenced by reaction parameters. A larger H_2 partial pressure inhibited the n-tetradecane conversion, while a slower deactivation had been observed. At reaction temperature of 380 °C, pressure of 3.0 MPa and H_2/C_{14} = 8.7 mol mol^{-1}, the catalyst shown good stability as shown in Fig. 4. The data were collected for a 3 h-sampling period with changing parameters in between (data not shown), and usually the liquid yield was always above 95%.

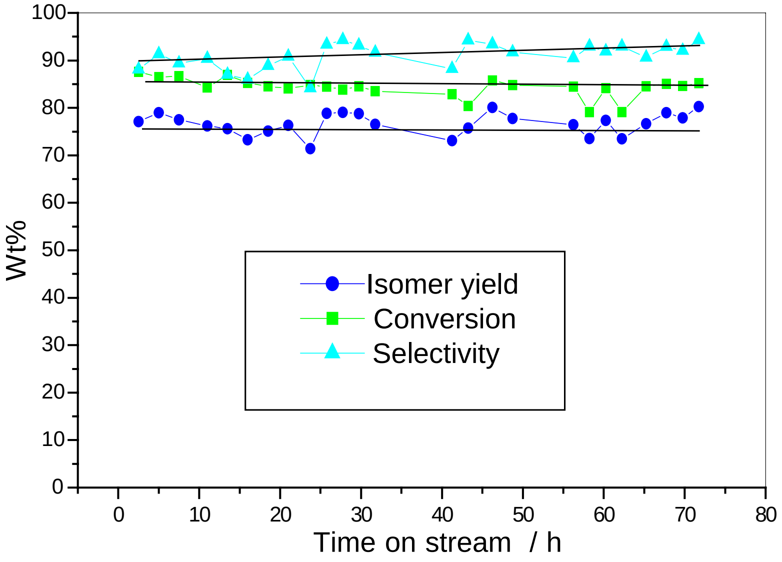

Fig. 4. Hydroisomerization of n-C_{14} as a function of time-on-stream over Pt/SAPO-11. Conditions: temperature = 380 °C; pressure = 3.0 MPa; WHSV = 2.0 h^{-1}; H_2/C_{14} = 8.7 mol mol^{-1} (notes: sampling period 3 h; data for changing reaction parameters in between not shown).

At very low H_2 partial pressure, relatively fast catalyst deactivation was observed. When the fresh sample was partially deactivated by coking, it could be regenerated by treating first with air followed by reduction with H_2 at higher temperatures.

It was found that partially deactivated coke could not be burnt up with air up to 400 °C. The activity was about 95% of original value with fresh catalyst, but the isomerization selectivity increased about 5%. Upon regeneration at 500 °C with air, the catalyst recovered more than 99% of its original activity and selectivity. Thus the change of catalytic behavior after low temperature regeneration could be attributed to fact that cracking activity was suppressed partially by coking the isolated strong acid sites.

Once the partially deactivated catalyst was treated with air, subsequent reaction-regeneration for several times by air did not affect the catalytic activity and selectivity.

3.6. Hydroconversion products and distribution of feed isomers

In the presence of H_2, normal paraffin undergoes several reactions such as isomerization, cracking and even aromatization. So a mixture of hydrocarbons is generally obtained for the hydroconversion of specific paraffin. The degree of each individual reaction is largely dependent upon the nature of catalyst. For hydrocracking catalyst, the main reaction should be cracking, which give high selectivity of lower carbon number products. For the known reforming catalyst system, both cracking and aromatization products are obtained in high selectivities, but with less selectivity to feed isomers. For an ideal isomerization catalyst, the most favored reaction is isomerization that produces feed isomers in high selectivity.

The hydroconversion of *n*-tetradecane over Pt/SAPO-11 catalyst gave both isomerization and cracking products, but with a higher selectivity to feed isomers. The cracking products consisted of spectra of C_1–C_{13} hydrocarbons with pretty high percentage of C_3–C_7. Minor amount of C_1 and C_2 were obtained, which suggested that the hydrogenolysis on the catalyst was negligible.

The isomerization products, as had been identified by MS, could be categorized into two groups as mono-branched and di-branched isomers. A high mono-branched to di-branched ratio was always observed, which was in good agreement with reported data by other researchers [4,16]. The result clearly indicates that the small pore mono-dimensional channels of SAPO-11 are highly selective for the hydroisomerization of long-chain alkanes. Over bifunctional metal/acid catalysts, activity and selectivity depend on the characteristics of the acid and of the metallic sites. The product distribution depends essentially on acidity and pore structure of the catalyst. For the transformation of longer paraffins like *n*-tetradecane, low acidity is required to minimize the cracking reaction. In our opinion, the high isomerization selectivity could also be attributed to the high dispersion of Pt in the catalyst as well as the mild acidity of SAPO-11.

The mono-branched to di-branched ratio was dependent upon the conversion level within the reaction conditions tested. At low conversion levels, the hydroisomerization product consisted of 90% mono-branched isomers. With increasing conversion level, di-branched isomers increased up to 30% of the feed isomers. As a conclusion, the degree of mono-branching and di-branching could be controlled by adjusting the reaction parameters. However, the distribution of mono-branched isomers was independent of conversion level. In the conversion range up to 90%, the distribution of mono-branched isomers remained unchanged. Among the mono-branched isomers, 2-methyl tridecane was less than 20%, while the 3-methyl tridecane was about 20%. Thus the content of 2-methyl and 3-methyl isomers was less than 40%.

Martens and coworkers [17–21] studied the hydroconversion of long *n*-alkane in the range *n*-C_{10}–*n*-C_{24} on Pt/ZSM-22 catalyst. They also found a high selectivity to mono-branched isomers, and the distribution of mono-branched isomers remained constant in the conversion range up to 60%. The authors suggested the idea of pore mouth catalysis to interpret the experimental data with respect to monomethyl-branching, and proposed that key lock catalysis also contributed to mono-branching of *n*-alkanes, whereas it was previously believed to be relevant for multibranching only. However, for the hydroconversion of *n*-tetradecane on Pt/ZSM-22, the content of 2-methyl and 3-methyl isomers was more than 50%, which was different from the present study. This might be due to the difference of the catalyst support geometry, or to different mode of catalysis. To account for the disparity, a pore channel catalysis mechanism was proposed, and this was further supported by the following experimental data.

Hydroconversion of *n*-tetradecane and other hydrocarbons did produce isomerization products characterized by high ratio of mono-branched to the multi-branched isomers and the absence of bulky structure feed isomers. The SAPO-11 channel system (0.39 nm × 0.63 nm pore opening), which favored the formation of mono-branched isomers (molecular diameter 0.5–0.6 nm), inhibited the formation of multi-branched isomers (molecular diameter >0.6 nm) especially those more bulky isomers. With large-pore zeolite β contained in SAPO-11 supported Pt catalyst, the hydroconversion of *n*-heptane produced dimethyl isomers that was about 8 times higher than that with SAPO-11 supported Pt at the same conversion level.

Furthermore, if the catalytic reactions occurred at the pore mouth, the crystal size of SAPO-11 would not influence the isomerization selectivity. However, the observed data for hydroisomerization of *n*-tetradecane and *n*-heptane shown variation of isomerization selectivity over catalysts that had prepared with SAPO-11 of different crystal sizes. Consequently, we suggested that the pore channel catalysis mechanism might be operative.

4. Conclusions

Platinum supported on SAPO-11 molecular sieve is efficient catalyst for the hydroconversion of long-chain hydrocarbons. In the hydroisomerization of *n*-tetradecane, high yields of branched feed isomers, with high mono-branched to multi-branched ratio, are achieved with Pt/SAPO-11 catalyst of 0.4% Pt loading. Among the mono-branched isomers, most methyl tridecanes are at the center positions, which is highly desired for diesel and lube base oil components. The distribution of feed isomers is tunable by varying reaction parameters. The unique characteristic of this catalyst is the high isomerization selectivity in the relatively low reaction pressure range. The catalyst also shows pretty good stability and regeneration property, which is of great industrial potentials. The high selectivity to feed isomers and good catalyst stability result from the combination of steric constraints of the micropores of SAPO-11 and high Pt dispersion as well as the mild acidity. A pore channel catalysis mechanism has also been proposed to account for the formation of feed isomers.

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