Feature Article

Skeletal isomerization of n-pentane: A comparative study on catalytic properties of Pt/WO$_x$–ZrO$_2$ and Pt/ZSM-22

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A B S T R A C T

Pt/WO$_x$–ZrO$_2$ and Pt/ZSM-22 were prepared and used as catalysts for the n-pentane hydroisomerization reactions. The physico-chemical properties of the supports were characterized by XRD, N$_2$ adsorption, NH$_3$-TPD and 1-pentene isomerization reaction. The reducibility and adsorbability of the catalysts were evaluated via H$_2$-TPR, H$_2$-TPD and CO adsorption. Under the reaction condition of WHSV = 1 h$^{-1}$, $P_n$-$pentane,0$ $=$ 0.24 bar and ambient pressure, the yields of isopentane over Pt/WO$_x$–ZrO$_2$ and Pt/ZSM-22 can reach 52% (at 300 °C) and 61% (at 340 °C) respectively. The selectivities to isopentane over these two catalysts are well above 95%. The hydroisomerization mechanisms over these catalysts are discussed.

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1. Introduction

Skeletal isomerization of light naphtha is an ideal process for the manufacture of gasoline because the obtained isomerization product has high octane number but contains few air pollutants such as olefins, aromatics and sulphur contents [1–3]. As strong Lewis acids, Friedel-Crafts catalysts can initiate the isomerization of light n-alkanes at relatively low temperatures. However, these catalysts are corrosive and unstable and therefore have been obsolete for decades [4]. Nowadays, industrial isomerization processes typically use platinum-loaded solid acids as catalysts.

Modified metal oxides are one of the most widely used acidic supports of the above catalysts. Both chlorinated alumina and sulphated zirconia are highly effective supports of low temperature isomerization catalysts. Unfortunately, the unavoidable leak of the active chlorine/sulphur species makes the lifetime of these catalysts fairly low. Tungstation is another modification method for the preparation of acidic metal oxides and it has been well known that platinum-promoted tungstated zirconia (Pt/WO$_x$–ZrO$_2$) exhibits high stability and efficiency in the catalysis of light n-alkane isomerization [5]. Nevertheless, until now no consensus has been reached on the mechanism of Pt/WO$_x$–ZrO$_2$ catalysed isomerization reactions. For example, Knözinger et al. [6,7] suggested that in the hydroisomerization reaction catalysed by Pt/WO$_x$–ZrO$_2$, alkenes as reactive intermediates are first formed and subsequently isomerized via a fast and highly selective monomolecular reaction and saturated on the tungstate surface. Meanwhile, platinum promotes the reduction of surface tungstate by hydrogen spillover and participates in the removal of coke. But because the equilibrium concentration of the alkenes is very low during the reaction, such alkene-mediated mechanisms are often questioned [8,9]. Instead, Iglesia et al. [10,11] suggested a mechanism for light n-alkane hydroisomerization on Pt/WO$_x$–ZrO$_2$, in which platinum sites are essential for the dissociation and storage of hydrogen atoms required for hydrogen transfer and alkaliium ion desorption steps. However, this mechanism does not indicate how the reactions are initiated.

Because of their adjustable acidity, zeolites, such as β, mordenite and ZSM-5, are also the appropriate catalyst supports for the hydroisomerization of light n-alkanes [9,12–14]. Comparative studies on the zeolite-based catalysts have shown that activity...
and selectivity of them are determined by their pore structures, which can affect the diffusion properties of the reacting species [12,14]. However, information is still insufficient on the relationship between the microporous properties and the catalysis mechanisms [15].

Herein is presented a comparative study on two types of catalysts, namely, Pt/WO₄–ZrO₂ and Pt/ZSM-22, for n-pentane hydroisomerization. Their physico-chemical properties were characterized by using X-ray diffraction (XRD), N₂ adsorption-desorption, NH₃ temperature-programmed desorption (NH₃-TPD), H₂ temperature-programmed reduction (H₂-TPR), H₂ temperature-programmed desorption (H₂-TPD) and CO pulse adsorption. The n-pentane hydroisomerization reaction was carried out in a continuous fixed-bed reactor under ambient pressure. For further studying the difference of reaction mechanisms over the two catalysts, the pure supports (WO₄–ZrO₂ and ZSM-22) were also characterized, and evaluated in both n-pentane hydroisomerization and 1-pentene isomerization reactions.

2. Experimental

2.1. Catalyst preparation

WO₄–ZrO₂ was prepared by a co-precipitation method modified from that of Santiesteban et al. [16]. Briefly, the aqueous solution of zirconyl chloride was drop-wise added into the vigorously stirred aqueous solution containing ammonia, ammonium chloride and ammonium metatungstate (W/Zr molar ratio = 0.072). The pH of the reaction medium was maintained at about 9.0 by the controlled addition of an aqueous solution of ammonia. The obtained slurry was aged at 80 °C for 24 h and then the solid was recovered by filtration, washed with deionized water until free from chloride ions, and dried at 120 °C overnight. The resulting solid was calcined at 800 °C for 3 h to form WO₄–ZrO₂.

ZSM-22 (Si/Al molar ratio = 35.9) was synthesized according to a published procedure [17]. The product was calcined at 550 °C for 6 h before further processing.

The platinum loaded catalysts (0.5 wt.% of Pt) were prepared by incipient wetness impregnation of the supports with an aqueous solution of chloroplatinic acid, followed by drying at 120 °C overnight and calcination 500 °C for 3 h.

2.2. Catalyst characterization

XRD patterns were recorded on a PANalytical X’pert Pro X-ray diffractometer with nickel-filtered Cu Kα radiation (λ = 1.5419 Å). The N₂ adsorption-desorption isotherms were measured at −196 °C on an ASAP 2420 physical adsorption instrument. Chemisorption studies were performed by using a Micromeritics 2920 analyser. The samples for NH₃-TPD experiments were pretreated in He flow at 500 °C for 1 h and then saturated with NH₃ at 100 °C in NH₃–He flow. The NH₃-TPD curves were measured from 100 to 500 °C in He flow with a heating rate of 10 °C/min. The samples for H₂-TPR experiments were pretreated in O₂–He flow at 500 °C for 1 h and then reduced in H₂–Ar flow from 40 to 800 °C with a heating rate of 10 °C/min. The reduction curves were obtained by measuring the H₂ concentration in the exit stream. The samples for both H₂-TPD and CO pulse adsorption experiments were pretreated in O₂–He flow at 450 °C for 1 h and then reduced in H₂–Ar flow at 250 °C for 1 h. The H₂-TPD profiles were measured from 40 to 700 °C in Ar flow with a heating rate of 10 °C/min. The saturation of CO was achieved by adding CO–He into He flow in pulse mode. The average size of platinum particles was calculated with the assumption that platinum particles are semi-spherical and the molar ratio of CO/Plurface is 1.

2.3. Catalytic evaluation

Catalytic evaluation was carried out in a continuous fixed-bed reactor under ambient pressure. The mass of catalyst was 0.50 g in each reaction. Before reaction, all the catalysts were in situ dried in N₂ or air flow at 400 °C for 30 min and the catalysts for n-pentane transformation were further reduced in H₂ at 300 °C for 1 h. After pretreatment, the feed was introduced into the reactor by a gas flow saturation method, in which the carrier gas was passed through a glass saturator filled with n-pentane (containing 3 wt.% of isopentane as impurity) or 1-pentene at 0 °C before entering into the reactor. The product was analysed after 10 min on-stream by an online Varian CP-3800 chromatograph with a CP-Sil PONA CB column.

Reaction data were calculated on the carbon basis. The accuracy of the mass balance in all experiments amounts to ±2%.

The carbon fraction of species i (Yᵢ) was calculated as

\[ Yᵢ = \frac{nᵢ \times εᵢ}{n_{\text{feed}} \times ε_{\text{feed}}} \]

where n and ε are the molar flow and the carbon number of a certain species. The subscript 0 indicates the value at the reactor inlet.

The total conversion (X) was calculated as

\[ X = 1 - Y_{\text{feed}} \]

The selectivity of species i (Sᵢ) was calculated as

\[ Sᵢ = \frac{Yᵢ}{X} \]

In 1-pentene skeletal isomerization reactions, the double bond isomerization reaction is much faster than the skeletal isomerization reaction. Therefore, the double bond isomers (cis-2-pentene and trans-2-pentene) were merged with 1-pentene as the reactant [18].

![Fig. 1. X-ray diffraction patterns of WO₄–ZrO₂ (a) and ZSM-22 (b). Cu Kα radiation.](image-url)
**3. Results and discussion**

3.1. Structure, texture and acidity of the supports

XRD patterns of WO$_x$–ZrO$_2$ and ZSM-22 are shown in Fig. 1. WO$_x$–ZrO$_2$ exhibits monoclinic (PDF#00-044-1390) and monoclinic (PDF#00-007-0343) ZrO$_2$ crystallites. No characteristic diffraction peaks of WO$_x$ can be found in the XRD pattern. The XRD pattern of ZSM-22 matches well with the reference one (PDF#00-044-1390) and reveals that the synthesized zeolite exhibits high crystallinity and phase purity.

Pure tetragonal ZrO$_2$ would transform at 650–700 °C into the monoclinic one which is thermodynamically more stable [19]. However, during the calcination of WO$_x$–ZrO$_2$, such transformation is not significant as the XRD peaks of monoclinic ZrO$_2$ are quite broad and weak. The inhibition of the transformation should be attributed to the existence of the well dispersed WO$_x$ species [11]. Compared with monoclinic ZrO$_2$, tetragonal ZrO$_2$ contributes much more efficiently to the activity of the WO$_x$–ZrO$_2$-based isomerization catalysts [20].

N$_2$ adsorption–desorption isotherms of WO$_x$–ZrO$_2$ and ZSM-22 are shown in Fig. 2 and the surface area data are listed in Table 1. WO$_x$–ZrO$_2$ exhibits type IV isotherms which indicate the mesoporous character. ZSM-22 exhibits type I isotherms with H3 hysteresis caused by slit-shaped pores. ZSM-22 contains one-dimensional 10-membered ring channels and as a result has high surface area (163 m$^2$/g). However, because aperture of the channels is as small as 5.5 Å × 4.5 Å [21], reactants with large molecular size can hardly diffuse through them. Furthermore, despite their difference in texture, WO$_x$–ZrO$_2$ and ZSM-22 have similar external surface areas (49 and 39 m$^2$/g respectively).

The acidity of WO$_x$–ZrO$_2$ and ZSM-22 was studied via NH$_3$-TPD experiments and the results are shown in Fig. 3. Two bands can be found in each NH$_3$-TPD curve. Both the low-temperature desorption bands of WO$_x$–ZrO$_2$ and ZSM-22 are at around 200 °C. These bands should be assigned to the physically or weakly chemically adsorbed NH$_3$ [22]. The high-temperature desorption bands of WO$_x$–ZrO$_2$ and ZSM-22 are at about 270 and 370 °C respectively.

![Fig. 2. N$_2$ adsorption–desorption isotherms of WO$_x$–ZrO$_2$ and ZSM-22.](image)

**Table 1**

<table>
<thead>
<tr>
<th>Support</th>
<th>BET surface area (m$^2$/g)</th>
<th>t-Plot external surface area (m$^2$/g)</th>
<th>Micropore area (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>WO$_x$–ZrO$_2$</td>
<td>48</td>
<td>49</td>
<td>–</td>
</tr>
<tr>
<td>ZSM-22</td>
<td>163</td>
<td>39</td>
<td>124</td>
</tr>
</tbody>
</table>

3.2. Reducibility and adsorbability of the catalysts

H$_2$–TPR profiles of the catalysts and WO$_x$–ZrO$_2$ are shown in Fig. 4. In the profile of Pt/ZSM-22, only a weak reduction peak centred at 52 °C can be observed. This peak should be assigned to the reduction of the oxidized platinum species [23]. The absence of reduction peaks above 300 °C indicates that the platinum species on Pt/ZSM-22 is fully reduced after the catalyst pretreatment.

The H$_2$–TPR profiles of WO$_x$–ZrO$_2$ and Pt/WO$_x$–ZrO$_2$ are more complex than that of Pt/ZSM-22. The peaks in the profile of WO$_x$–ZrO$_2$ show the stepwise reduction of WO$_x$ species in the procedure:

WO$_3$ → WO$_2.9$ → WO$_2$ → W

The 342 °C centred weak peak should be assigned to the WO$_3$ → WO$_2.9$ process, and the wide band in the high-temperature range (>600 °C) to the successive WO$_2.9$ → WO$_2$ → W reductions. For the catalyst Pt/WO$_x$–ZrO$_2$, two peaks centred at 72 and 547 °C as well as a high-temperature band can be observed. Similar H$_2$–TPR profiles of Pt/WO$_x$–ZrO$_2$ have been reported by Iglesia et al. [10,11]. They assigned the two peaks to the reduction processes of WO$_3$ → WO$_2.9$ and WO$_2.9$ → WO$_2$ respectively, and attributed the negative shift of the reduction peaks to the hydrogen spillover on Pt/WO$_x$–ZrO$_2$. A later report by Arribas et al. [24] also confirmed the facilitation effect of platinum on the reduction of WO$_x$ species. However, the authors ascribed the H$_2$–TPR peak at the temperature lower than 100 °C to the reduction of platinum cations. Despite the controversy on the attribution of the low-temperature peak in literature, the difference between the H$_2$–TPR profiles of WO$_x$–ZrO$_2$ and
Pt(WO₄–ZrO₂) doubtless demonstrates the occurrence of hydrogen spillover on Pt(WO₄–ZrO₂) [25,26].

H₂-TPD studies were applied to determine the H₂-adsorption abilities of the catalysts. The results are shown in Fig. 5. The H₂-TPD profile of Pt(WO₄–ZrO₂) can be deconvoluted into three peaks [27], which should be assigned to the hydrogen species adsorbed on platinum (centred at 81 °C), adsorbed at the platinum-support interface (centred at 108 °C) and split-over to the WO₄ clusters (centred at 228 °C) respectively. When adsorbed onto platinum, the H₂ molecule is first dissociated into two hydrogen atoms. One of the hydrogen atoms denotes an electron to the unsaturated coordinated Zr⁴⁺, and is subsequently stabilized at the adjacent WO₄ clusters as H⁺. Then the second hydrogen atom could react with the resultant Zr=H to form H₂ [28]. Furthermore, according to the colour change of WO₄–ZrO₂ exposed in hydrogen, Barton et al. [29] suggested that hydrogen atoms can release electrons directly to WO₄ clusters via redox process and form temporary Brønsted acid sites therein. The resultant acid sites are believed to be the active centres for n-alkane hydroisomerization reactions [11].

In the temperature range of our measurement (40–700 °C), no desorption peaks can be observed in the H₂-TPD profile of Pt(ZSM-22). As measured by CO pulse adsorption experiments (Table 2), the platinum dispersion of Pt(ZSM-22) is quite low and its platinum surface area is not more than 1/3 of that of Pt(WO₄–ZrO₂). Therefore, it can be concluded that Pt(ZSM-22) is much less effective in adsorbing H₂ than Pt(WO₄–ZrO₂). On the other hand, even if H₂ can be dissociatively adsorbed on Pt(ZSM-22), the resultant hydrogen species seem to be easily released below 40 °C. Moreover, as an ideal non-reducible support, ZSM-22 is not favourable for the occurrence of hydrogen spillover [30].

### 3.3. Hydroisomerization of n-pentane

Fig. 6 shows the catalytic performance of WO₄–ZrO₂, ZSM-22, Pt(WO₄–ZrO₂) and Pt(ZSM-22) for n-pentane hydroisomerization reactions as a function of reaction temperature. Taking account of the impurity concentration of the feed (3 wt.% of isopentane), the net conversions of n-pentane over WO₄–ZrO₂ and ZSM-22 are quite low. Compared with ZSM-22, WO₄–ZrO₂ shows lower selectivity to isopentane but higher selectivity to the products with less than five carbon atoms.

Platinum significantly promotes the performance of both the catalysts. Over Pt(WO₄–ZrO₂), the conversion of n-pentane increases along with the increase of reaction temperature to a maximum of 53% at 300 °C, and then slightly decreases with the further increase of the reaction temperature. By contrast, the conversion of n-pentane over Pt(ZSM-22) keeps increasing and reaches 61% at 340 °C. The selectivities to isopentane over these two catalysts are well above 95%. In the temperature range we studied, side reactions are strongly limited. As an example, the by-product yield at 280 °C is listed in Table 3. These barely detectable by-products may be formed via hydrogenolysis and dimerization–cracking reactions [7,31].

<table>
<thead>
<tr>
<th>By-product</th>
<th>Yield (%)</th>
<th>Pt/ZSM-22</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethane</td>
<td>0.025</td>
<td>0.039</td>
</tr>
<tr>
<td>Propane</td>
<td>0.069</td>
<td>0.058</td>
</tr>
<tr>
<td>n-Butane</td>
<td>0.080</td>
<td>0.047</td>
</tr>
<tr>
<td>Isobutane</td>
<td>0.377</td>
<td>(Not detected)</td>
</tr>
<tr>
<td>Hydrocarbon with more than five carbon atoms</td>
<td>0.557</td>
<td>0.154</td>
</tr>
</tbody>
</table>

#### 3.4. Skeletal isomerization of 1-pentene

As mentioned above, the alkene-mediated mechanisms of n-alkane hydroisomerization are far from clear. The illustration of the role of alkenes is prevented by their low concentration in the reactions. To overcome this drawback and deepen the understanding of n-alkane hydroisomerization, we performed further studies on the skeletal isomerization of 1-pentene.

Fig. 7 shows the product distribution of 1-pentene skeletal isomerization reactions over WO₄–ZrO₂ and ZSM-22 at 280 °C. It can be found that the conversion of 1-pentene over WO₄–ZrO₂ is lower than that over ZSM-22 and drops quickly. Meanwhile, the conversion over ZSM-22 keeps almost a constant high value. Compared with ZSM-22, WO₄–ZrO₂ shows lower selectivity to skeletal isomers (3-methyl-1-butene, 2-methyl-2-butene and 2-methyl-1-butene) but higher selectivity to the hydrogen-transfer products (n-pentane, isopentane and pentadiene).

After the skeletal isomerization reactions, colours of the catalysts WO₄–ZrO₂ and ZSM-22 changed into black and light brown respectively. This indicates the occurrence of coking during the reactions. NH₃-TPD results show that coking strongly influences the acid density of WO₄–ZrO₂. As shown in Fig. 3, the high-temperature desorption band of WO₄–ZrO₂ decreases significantly after the skeletal isomerization reaction of 1-pentene. The moderate acid sites, which correlate with this band of WO₄–ZrO₂, can improve the lifetime of alkenium ions by strong interactions. It is favourable for oligomerization and hydrogen transfer reactions and the consequent coke deposition [32]. However, the low-temperature desorption band of WO₄–ZrO₂ and the whole profile of ZSM-22 are only slightly affected by coking. The small variations of the low-temperature desorption bands of both WO₄–ZrO₂ and ZSM-22 suggest that these bands are mainly attributed to the physisorbed NH₃, the adsorption amount of which is related to the surface area of the sample and scarcely influenced by coking. On the other hand, acid sites in the micropores of ZSM-22 should be little influenced by coke because its formation involves large intermediates and demands large space [33]. Considering the small variation of the high-temperature desorption band of ZSM-22, it
can be deduced that the acid sites of ZSM-22 are mainly located in the micropores rather than on the external surface.

Considering the relationship between the coking degree and the activity loss of the catalysts, we ascribe the 1-pentene isomerization activity of \( \text{WO}_x - \text{ZrO}_2 \) and ZSM-22 to their acid sites. Furthermore, pentenes are probably poisons for the moderate acid sites on \( \text{WO}_x - \text{ZrO}_2 \).

3.5. n-Pentane activation

Pentenium ions are crucial to the isomerization of n-pentane and can be formed via various routes \([13,34]\). For example, they can be obtained by the protonation of pentene molecules, which are resulted from pentane dehydrogenation. The existence of pentene molecules should significantly improve the dimerization–cracking process and as a result, lead to the increase of the selectivity to the products with less and more than five carbon atoms. However, as shown in Fig. 6, compared with \( \text{WO}_x - \text{ZrO}_2 \), \( \text{Pt/WO}_x - \text{ZrO}_2 \) shows a much lower selectivity to the dimerization–cracking products. This phenomenon suggests that platinum species on \( \text{Pt/WO}_x - \text{ZrO}_2 \) do not result in the pentene-dominated reaction routes because dimerization–cracking reactions would be more sensitive to the concentration of alkenes.

The extremely low conversions of n-pentane over \( \text{WO}_x - \text{ZrO}_2 \) and ZSM-22 (Fig. 6) suggest that acid sites cannot activate the C–H bonds of n-pentane. Hattori et al.’s study \([35,36]\) has shown that the hydrogen/deuterium exchange process of H\(_2\)/D\(_2\) on \( \text{Pt/WO}_x - \text{ZrO}_2 \) is much faster than that on \( \text{WO}_x - \text{ZrO}_2 \). Considering the similarity of the hydrogen/deuterium exchange processes of H\(_2\)/D\(_2\) and D\(_2\)/alkane \([37]\), it can be deduced that n-pentane is activated by platinum or the cooperation of H\(_2\), platinum and \( \text{WO}_x - \text{ZrO}_2 \). Furthermore, by improving the hydrogenation of pentenes, platinum makes the local concentration of pentene intermediates low \([9]\).

Roessner and Roland \([38]\) suggested a stepwise radical–alkenium mechanism for the n-alkane isomerization reactions. According to this mechanism, hydrogen species spilt-over from the platinum sites activate alkane molecules to form radicals. The resultant radicals subsequently transform into alkenium cations on the acid sites. However, the results of our experiments show that the hydrosisomerization reaction over \( \text{Pt/WO}_x - \text{ZrO}_2 \) is initiated by the synergy of platinum and \( \text{WO}_x - \text{ZrO}_2 \) at the boundary. The catalytic performance of a mixture containing equally weighted Pt/ZSM-22 and \( \text{WO}_x - \text{ZrO}_2 \) was tested for the n-pentane hydrosisomerization reaction. As Fig. 8 shows, the yield of isopentane over the mixed catalyst resembles that over Pt/ZSM-22 rather than Pt/\( \text{WO}_x - \text{ZrO}_2 \). This result indicates that (i) the platinum amount of the mixed catalyst is sufficient for the reaction and (ii) the separation of platinum from \( \text{WO}_x - \text{ZrO}_2 \) results in an alteration in the reaction mechanism. The supported platinum particles would be electron-deficient when they interact with the acidic hydroxyls on the support surface \([39,40]\). Arribas et al.’s study \([24]\) has shown that a fraction of platinum on
Meanwhile, homolytic cleavage of H₂ occurs on the reduced platinum sites (Pt⁰). The resultant hydrogen atoms can spill over and interact with the surface WO₆ species to form temporary Brønsted acid sites, which further activate pentane molecules into pentenium ions

$$\text{Pt}^0/\text{WO}_x-\text{ZrO}_2 + \delta \text{H}_2 \rightarrow [\text{H}_3-\text{Pt}^0]/[\text{H}^+]_3 - \text{WO}_x-\text{ZrO}_2]$$

and the obtained active species can react with pentane molecules to form pentenium ions

$$[\text{H}_3-\text{Pt}^0]/[\text{H}^+]_3 - \text{WO}_x-\text{ZrO}_2] + \delta \text{RH} \rightarrow [\text{H}_8$$

$$-\text{Pt}^0]/[\text{R}^+]_3 - \text{WO}_x-\text{ZrO}_2] + \delta \text{H}_2$$

In the present work, chloroplatinic acid was used as the platinum source to prepare the catalysts. Because of their large size, solvated chloroplatinic ions can hardly enter the medium-sized pores of ZSM-22 [41]. Furthermore, the charge mismatch between these anions and the anionic zeolite framework inhibits the migration of the chloroplatinic ions into the micropores of zeolite. As a result, platinum particles can only be situated on the external surface of ZSM-22 and easily aggregate into larger ones. As discussed above, few acid sites exist on the external surface of ZSM-22. Therefore, the hydroisomerization reaction over Pt/ZSM-22 is difficult to be initiated in a route similar to that of the electron-deficient platinum on Pt/WOₓ–ZrO₂ (Reaction 1). Additionally, on the non-reducible ZSM-22, analogous process to Reaction 3 will not occur. Overall, Pt/ZSM-22 can not promote the n-pentane isomerization through a way similar to those of Pt/WZ. As shown in Fig. 7, ZSM-22 is effective for the skeletal isomerization of 1-pentene. Therefore, n-pentane can be activated over Pt/ZSM-22 via dehydrogenation on the platinum sites. The resultant pentene molecules then migrate onto the acid sites and are protonated into pentenium ions, which would further transform into isopentane molecules. However, at low temperatures, the equilibrium concentration of pentenes in the presence of H₂ is too low to be detected and the conversion of n-pentane is consequently depressed (Fig. 6). Along with the increase of the reaction temperature, the formation of pentenes is improved and thus the activity of Pt/ZSM-22 is promoted.

### 3.6. Pentenium ion transformation

It has been widely accepted that pentenium ions can skeletally rearrange via either the monomolecular or bimolecular approach, and then the obtained isomerized cations are de-protonated into branched-pentene molecules, which are further hydrogenated over platinum to form isopentanes [32,34]. In the bimolecular approach, ß-cleavage of the dimeric cations frequently occurs and results in the high yield of by-products besides isopentanes. Considering the extremely low yields of the products with less and more than five carbon atoms (Fig. 6 and Table 3), it can be deduced that the skeletal rearrangement processes over both Pt/ZSM-22 and Pt/WOₓ–ZrO₂ mainly follow the monomolecular mechanism [31].

The dominance of the monomolecular approach over Pt/ZSM-22 should be attributed to the spatial confinement effect of the zeolite [42]. The progress of the rearrangement–deprotonation–hydrogenation reactions is determined by the concentration of the intermediate pentenes, which is improved by elevating the reaction temperature. As a typical example of such effect, the conversion of n-pentane over Pt/ZSM-22 increases along with the reaction temperature. However, the temperature range we explored does not reach the point for the maximum conver-
sion, which is optimum for both the thermodynamic equilibrium and the catalyst activity.

Unlike Pt/ZSM-22, Pt/WO₃-ZrO₂ can promote the transformation of pentenium ions via the hydrogen transfer between pentenium ions and n-pentane/H₂ molecules [13]. At 200 °C, the skeletal rearrangement rate of pentenium ions is limited by the acidity of Pt/WO₃-ZrO₂ and thus is very low. Temperature elevation can significantly improve the skeletal rearrangement rate. However, even at 300 °C, the yield for n-pentane hydroisomerization is only 52% (Fig. 8), which is quite lower than the thermodynamically equilibrated yield at this temperature (65%) [43]. This phenomenon suggests that hydrogen transfer is always much faster than skeletal rearrangement, and the skeletal rearrangement of pentenium ions on the surface of Pt/WO₃-ZrO₂ is the rate-determining step [11]. Further increase of the reaction temperature (>300 °C) may cause a loss of the active sites and consequently the decrease of n-pentane conversion [26].

4. Conclusion

n-Pentane hydroisomerization reactions over Pt/WO₃-ZrO₂ and Pt/ZSM-22 were studied. It has been found that Pt/WO₃-ZrO₂ shows low-temperature activity, while Pt/ZSM-22 is highly efficient at high temperatures. The hydroisomerization mechanisms over these catalysts are different from each other at least in the steps of the n-pentane activation and the pentenium ion transformation. Over Pt/WO₃-ZrO₂, pentenium ions are formed via hydrogen spillover and finally transformed into isopentane molecules via hydrogen transfer. In contrast, after formed on platinum sites of Pt/ZSM-22 by n-pentane dehydrogenation, the pentene molecules transform into isopentane molecules via a monomolecular process. The spatial confinement effect of the micropores limits the occurrence of hydrogen transfer on Pt/ZSM-22. Over both catalysts, the formation of dimeric cations, which would be cleaved into the by-products besides isopentanes, is not noticeable.

References