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Factors affecting isomer yield for *n*-heptane hydroisomerization over as-synthesized and dealuminated zeolite catalysts loaded with platinum

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Abstract

Pt loaded Y, USY, beta, mordenite, ZSM-12, and ZSM-5 zeolites with different Si/Al ratios and a USY and ZSM-12 sample having enhanced activity were studied for the hydroisomerization of *n*-heptane. All the possible heptane isomers were obtained over Pt/H-ZSM-12 and the product distribution was closer to that over Y and beta catalysts, but very different from that over Pt/H-ZSM-5. Shape-selective effects in ZSM-12 resulted in a significantly higher isomer yield than the beta and Y-zeolite catalysts. For Y, beta, and ZSM-12 samples having very little extraframework aluminum, changing the Si/Al ratio did not affect the isomer yield. However, USY and ZSM-12 samples that showed enhanced activity were very sensitive to the Pt precursor and Pt loading, which caused huge differences in their activity and isomer selectivity. The Pt dispersion in the enhanced activity catalysts was also much lower. A careful optimization of the precursor, amount of Pt loaded, and pretreatment conditions is essential to achieve good balance between the metal and the acid functions in these catalysts. The optimized enhanced activity catalyst is able to provide isomer yields approaching that obtained over the regular catalysts, which suggests that zeolite acidity is not directly affecting the isomer selectivity. These results indicate that the maximum isomer yield for a Pt/H-zeolite catalyst is obtained when the metal and acidic functions of the catalysts are well balanced. Therefore, it may not be possible to increase the isomer yield beyond this maximum by modifying the acidity characteristics of the catalyst. Mordenite and ZSM-5 catalysts showed low isomer yields, but acid dealumination of the parent mordenite improved the isomer yield, possibly due to creation of mesopores.

Keywords: Alkane hydroisomerization; ZSM-12; Shape selectivity; Steam dealumination; Enhanced activity; Metal-acidity balance; Hydroconversion; Bifunctional catalyst

1. Introduction

Hydroisomerization of straight-chain paraffins into highly branched paraffins to boost the octane number of gasoline is an environmentally more acceptable alternative compared to other technologies such as blending with oxygenates and aromatics [1]. Paraffin hydroisomerization is typically carried over bifunctional metal/acid catalysts and it is well established that isomerization proceeds through consecutive branching reactions. The traditional isomerization catalyst, Pt loaded chlorided alumina, is very active and can operate at lower temperatures, but these catalysts cause corrosion and pollution problems and are very sensitive to poisons such as water, aromatics, and sulfur [2,3]. Pt/H-mordenite can overcome these disadvantages and can successfully isomerize smaller alkanes such as *n*-pentane and *n*-hexane with a high yield of isomers, however it is much less selective for *n*-heptane isomerization as cracking occurs to a large extent [3,4]. No industrial hydroisomerization process exists for C_7 or C_8 paraffins due to their high tendency to crack [5]. Several studies have focused on various zeolite catalysts for hydroisomerization and the effects of acid site density on the isomer selectivity have been described [6–8]. Meriaudeau and co-workers [9–11] utilized medium-pore one-dimensional zeolites to obtain a high yield of the monobranched isomers. A higher isomer selectivity on a nanocrystalline beta zeolite sample compared to a beta zeolite having much larger crystallites has been reported [3,4].

Although several studies have attempted to investigate the effect of zeolite acidity characteristics on the isomerization selectivity, no clear result has emerged. Moreover, there are not many detailed reports on hydroisomerization over ze-

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olite catalysts having enhanced activity. The phenomenon of enhanced activity is observed when a zeolite is steam-dealuminated under certain conditions [12–14]; however, the exact chemical nature of the enhanced activity sites is still unresolved and under debate. Recent explanations for enhanced activity include the presence of several types of Al coordinations in the framework [14], many of these Al atoms having reversible coordination [15]; and a synergistic effect between extraframework aluminum and framework Brönsted sites, resulting in the dramatically enhanced activity has also been proposed [12]. Kung et al. [13] proposed an increase in the rates of pore diffusion limited bimolecular and oligomeric cracking reactions due to formation of mesopores as part of the reason for enhanced activity. van Bokhoven et al. [16] have proposed that the increased reaction rate is due to an increase in the initial enthalpy of adsorption on the extraframework Lewis acid sites which increases the concentration of reactants in the steamed zeolites under reaction conditions.

Denayer et al. [17] studied the hydroconversion of C_6 to C_9 n-alkanes over Y and USY zeolites and found no influence of the zeolite Si/Al ratio on the selectivity; however, the catalysts they studied primarily consisted of Brönsted acid sites, and did not show dramatically enhanced activity. Our goal therefore was to carefully examine the variation of isomer selectivity with conversion in different zeolites at various Si/Al ratios and also in USY and ZSM-12 catalysts with enhanced activity. The other objective of this study is to evaluate the performance of Pt/H-ZSM-12 as a potential hydroisomerization catalyst and compare it with P-loaded zeolite Y, beta, and mordenite and ZSM-5 catalysts.

2. Experimental

2.1. Catalyst preparation

The details of the samples used in this study are listed in Table 1 and 2. The ZSM-12 samples were synthesized hydrothermally using tetraethylammonium hydroxide (TEAOH) as the template. The procedure used for the synthesis of ZSM-12 has been described in detail elsewhere [18]. The beta zeolite samples were also synthesized in our laboratory with TEAOH as the template. The template was removed from the synthesized zeolites by calcination in air at 550 °C for 4 h. Y and USY zeolites (CBV series) as well as ZSM-5 (CBV-8020) were obtained from Zeolyst International. Mordenite was kindly donated to us by UOP. Dealumination of the as-received mordenite (Mor-10) was carried out using 1 N HCl at 90 °C for 4 h to yield the Mor-35 sample. For samples not in ammonium or proton form, a cation exchange was performed with 2 N NH_4Cl solution at 90 °C for 4 h. For the Y-zeolite sample (CBV-100), the ammonium exchange was performed three times. Finally, the zeolites were converted to their protonated forms by calcination in air at 500 °C for 1 h. Platinum loading was done by wet impregnation using H_2PtCl_6 (Aldrich) or $Pt(NH_3)_4Cl_2$ (Johnson Matthey). The impregnated catalysts were dried overnight in an oven at 120 °C. Oxidation and reduction of the catalysts to disperse the metal was done in situ before starting the reaction.

Table 1
Characteristics of the Pt/H-zeolite catalysts

Zeolite	Si/Al ratio	Percentage crystallinity	No. of acid sites[b] (mmol/g)	Percentage Pt dispersion
Y-2.5 (CBV-100)	2.5[a]	100	2.21	62
Y-15 (CBV-720)	15[a]	70	0.79	46
Y-30 (CBV-760)	30[a]	72	0.40	95
Beta-15	15	100	0.69	87
Beta-30	30	100	0.49	70
Mor-10	10	100	1.31	84
Mor-35	35	109	0.51	102
ZSM-12–31	31	100	0.49	79
ZSM-12–45	45	100	0.34	76
ZSM-12–58	58	100	0.25	86
ZSM-5–40 (CBV-8020)	40	–	–	–

All zeolites were loaded with 0.5 wt% Pt using H_2PtCl_6.

[a] Nominal Si/Al ratio reported by the company.

[b] The number of acid sites was measured by NH_3-STPD using the protonated form of the zeolite, before platinum was loaded.

Table 2
Details of the catalysts prepared using the enhanced activity USY and ZSM-12 samples

Sample	Pt precursor	Pt loading (wt%)	Oxidation and reduction temperature, °C	Percentage Pt dispersion
EY-1	H_2PtCl_6	0.5	450	–
EY-2	H_2PtCl_6	1.0	450	13
EY-3	$Pt(NH_3)_4Cl_2$	1.0	450	15
EY-4	$Pt(NH_3)_4Cl_2$	1.5	450	–
EY-5	$Pt(NH_3)_4Cl_2$	1.0	400	–
EZ12–1	H_2PtCl_6	0.5	450	18
EZ12–2	$Pt(NH_3)_4Cl_2$	0.5	450	20
EZ12–3	$Pt(NH_3)_4Cl_2$	0.75	450	–
EZ12–4	$Pt(NH_3)_4Cl_2$	0.5	400	–
EZ12–M	Physical mixture with Pt/SiO_2		450	–

EZ12–M is a mechanical mixture of 0.5 wt% Pt/SiO_2 and the enhanced activity ZSM-12 in a 2:1 ratio. For the experiment a mixture of 100 mg Pt/SiO_2 and 50 mg zeolite was used.

The enhanced activity USY sample studied was the CBV-500 sample (Si/Al = 2.6) from Zeolyst International. Remy et al. [14] have shown that CBV-500 possesses dramatically enhanced activity compared to the parent nondealuminated sample. A ZSM-12 sample with enhanced activity was prepared by calcining the synthesized zeolite (Si/Al = 35) containing template at 850 °C in a flow of air, under carefully controlled conditions. The activity of this sample was compared with other ZSM-12 samples by carrying out an n-hexane cracking reaction at 420 °C. The sample calcined at 850 °C showed a hexane cracking activity about 5 times higher than the regular ZSM-12 sample calcined at 550 °C. Several different catalyst samples were prepared using these enhanced activity USY and ZSM-12 zeolites by varying the platinum precursor and the amount of Pt loading. The oxidation and reduction temperature was also varied in certain cases. The details of these catalysts are provided in Table 2. The enhanced activity USY and ZSM-12 catalysts have been named EY-1 through 5 and EZ12-1 through 4, respectively. The ZSM-12 catalyst named EZ12-M is a mechanical mixture of 0.5 wt% Pt/SiO_2 and the enhanced activity ZSM-12 in a 2:1 ratio.

2.2. *Catalyst characterizations*

X-ray diffraction (XRD) was employed for identification of the synthesized zeolite phases and quantification of the crystallinities of dealuminated zeolites. The XRD patterns were collected with a Siemens D-500 powder X-ray diffractometer using Cu-K_α radiation. The bulk Si/Al ratios of the zeolites were determined by inductively coupled plasma (ICP) spectroscopy. NH_3-stepwise temperature programmed desorption (STPD) was used for the measurement of acid site density [19]. To check for the presence of extraframework aluminum, FTIR measurements were performed on selected samples using a Bio-Rad FTS-40 spectrometer equipped with a high temperature flow cell having CaF_2 windows. After purging with helium at 500 °C, the sample was cooled down to 150 °C and pyridine was adsorbed until saturation was achieved. The sample was then purged with helium for 1 h to remove the physisorbed pyridine and a spectrum was collected. A spectrum was also collected after desorption of pyridine at 200 °C. Nitrogen adsorption isotherms were measured for selected samples at 77 K using a Micromeritics ASAP 2000 instrument; samples were degassed at 250 °C for 2 h. Dispersion of platinum on the catalysts was determined by hydrogen chemisorption. The analysis was carried out using a Micromeritics Autochem 2910 automated catalyst characterization system. Before analysis the catalyst was first oxidized in situ at 450 °C for 1 h and then reduced at 450 °C for 4 h. The oxidation and reduction conditions were the same as that used to activate the catalyst before the reaction. After reduction, helium was allowed to flow over the catalyst at 450 °C for 1.5 h. The catalyst was cooled down to 50 °C and a 1 ml pulse of 10% hydrogen in argon was repeatedly injected until no hydrogen was chemisorbed. The volume of hydrogen chemisorbed was determined by summing the fraction of hydrogen consumed in each pulse. The platinum dispersion was calculated assuming a H:Pt stoichiometry of 1:1.

2.3. *Catalytic experiments*

The n-heptane hydroconversion experiments were carried out in a fixed-bed flow reactor system loaded with 50 mg of the catalyst at a pressure of 100 psig (6.9 bar). The catalysts were activated in situ by oxidation with high-purity oxygen for 1 h at 450 (or 400) °C, followed by purging with high-purity helium for 15 min. The reduction of the catalyst was carried out at 450 (or 400) °C in high-purity H_2 for 1 h at atmospheric pressure. The WHSV for the n-heptane hydroconversion experiments was 7 h^{-1}, unless otherwise specified, and $H_2/n\text{-}C_7$ was 16; conversion was varied by varying the temperature in the range from 210 to 360 °C. The same catalyst sample was used to obtain the data at different temperatures. The first analysis was performed after 1 h on stream and subsequent analyses (with reaction occurring at different temperatures) were performed after at least 45 min had elapsed at the set temperature. No deactivation of the catalysts was observed after 1 h on stream. Repeat experiments confirmed that the data obtained were closely reproducible. Product identification was accomplished using a gas chromatograph (Hewlett-Packard, 5890 Series II) equipped with a mass spectrometer (Hewlett-Packard, 5972 Series II). Separation was achieved using a capillary column (SUPELCO Petrocol DH50.2). The concentrations of products were obtained by using a calibration factor for each product.

3. Results

3.1. *n-C_7 conversion versus temperature*

The variation of n-heptane conversion with temperature for different Pt/H-zeolites having similar Si/Al ratios has been compared in Fig. 1. It can be seen that ZSM-5 and beta zeolite which have a three-dimensional pore structure require a much lower temperature to achieve a certain conversion level than one-dimensional mordenite and ZSM-12. It has been suggested that in one-dimensional zeolites like mordenite and ZSM-12, the reaction essentially occurs in

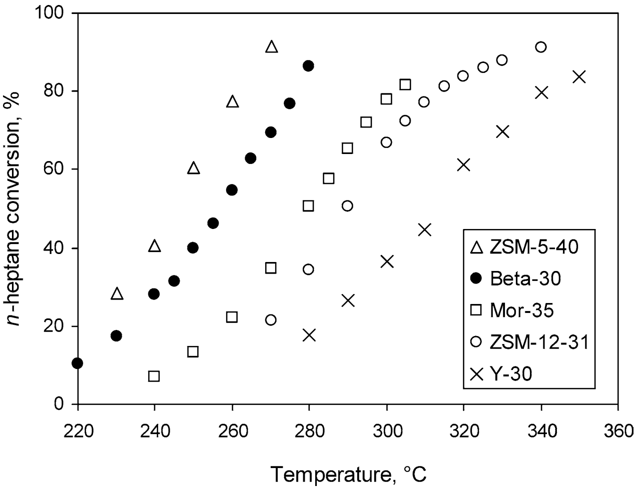


Fig. 1. Variation of the n-heptane conversion with temperature for various Pt/H-zeolite catalysts with comparable Si/Al ratios. WHSV = 7 h^{-1}, $H_2/n\text{-}C_7$ (molar) = 16, total pressure = 100 psig, and 0.5 wt% Pt loading (using H_2PtCl_6) on all catalysts.

a region close to the pore mouth, resulting in a lower activity [2,9,20]. Differences in activities of the various zeolite catalysts could also be attributed to intrinsic differences in zeolite acidity. However, recent explanations for the differences in activity of various zeolites in hydroisomerization have focused on the adsorption enthalpies of the alkanes in the zeolite [21]. In general, zeolites having smaller pores have been found to possess a higher adsorption enthalpy. This results in an increased concentration of the reactants within the pores, which leads to higher isomerization rates [16,21]. Therefore, the smaller pores present in ZSM-5 and zeolite beta would result in a higher adsorption enthalpy and higher n-heptane loadings, which would explain their higher activity compared to mordenite. Moreover, it is also possible that the beta and ZSM-5 samples studied had enhanced activity. Even for enhanced activity catalysts, the high activity has been explained using the high initial heat of alkane adsorption, which increases the concentration of the reactant in the zeolite [16]. A reasoning based on the adsorption enthalpy could again be used to explain the lower activity of the Y-30 catalyst. Our goal in this paper was to focus on the effect of differences in zeolite properties on the isomer selectivity. These results are discussed in the following sections.

3.2. Variation of isomer yield with conversion

Based on their performance in the n-C_7 hydroconversion, the catalysts studied in this work could be separated into three distinct types. Further details of the performance of these catalysts are presented below.

3.2.1. Y (and USY), beta, and ZSM-12 catalysts

The zeolite catalysts discussed in this section show high isomer yields and for each zeolite changing the Si/Al ratio does not appear to have an effect on the variation of the isomer yield with conversion. The Y and USY zeolites, CBV-100, CBV-720, and CBV-760, are well-known commercial samples and have been well characterized. ^{27}Al MAS NMR data of Remy et al. [14] showed that the above Y-zeolite samples have only a small amount of octahedral aluminum; most of the aluminum is present in the framework, resulting in Brönsted sites. The beta and ZSM-12 samples were directly synthesized, and after calcination at 550 °C to remove the template, they are likely to contain only a small amount of extraframework aluminum and consequently a very small number of Lewis sites. For the ZSM-12 samples, ^{27}Al MAS NMR confirmed that almost all the aluminum was present in tetrahedral coordination in the calcined samples [22].

The hydroisomerization of n-heptane was studied over these zeolite catalysts, each at different Si/Al ratios, and the total yield of branched C_7 isomers (in mol%) obtained as a function of heptane conversion is shown in Fig. 2. For a particular zeolite, the yield of heptane isomers follows almost the same trend regardless of the Si/Al ratio of the zeolite. From Fig. 2a, the maximum obtainable isomer yield in the case of Y zeolites, obtained with the Y-15 sample appears to be around 61 mol%; when a plot is made with wt% (not shown) the maximum is around 68 wt%, an observation also made by other researchers [23,24]. For beta zeolite (Fig. 2b) the trend for variation of isomer yield with conversion and the maximum isomer yield is very similar to that obtained over the Y zeolites. Patrigeon et al. [25] have also reported that the same maximum isomer yield is obtained over Y and beta zeolites. In the case of ZSM-12 catalysts (Fig. 2c), the maximum isomer yield achieved is around 66 mol% (73 wt%). This is significantly higher than the maximum obtained over the "open" pore systems like Y and beta zeolites. Interestingly, the yield of dibranched isomers is also high over the ZSM-12 catalysts and comparable to that obtained over beta and Y zeolites, especially at the higher conversions.

3.2.2. Mordenite and ZSM-5 catalysts

The results of the mordenite and ZSM-5 catalysts are presented here in a separate section since they both show much lower isomer yields than the other zeolites studied. The Pt/H-mordenite catalysts with different Si/Al ratios show different trends in the variation of i-C_7 yield with heptane conversion, with the dealuminated mordenite sample showing a higher yield (Fig. 3). Over the parent Mor-10 sample the isomer yield was particularly low and it remained low even when the Pt loading was varied (data not shown). To investigate the reasons for this difference, nitrogen adsorption studies were done to obtain information about the porosity of the mordenite samples. The Mor-10 sample had a micropore area of 346 m^2/g and external surface area of 68 m^2/g, determined by the t-plot method. To check if this sample was a steamed sample having extraframework aluminum, an FTIR experiment was performed on this sample. The FTIR absorbance spectra of pyridine adsorbed on the Mor-10 sample did not show a peak at 1455 cm^{-1}, which is characteristic of Lewis acidic extraframework aluminum. However, there was a prominent peak at 1545 cm^{-1}, indicating that the Mor-10 sample had mostly Brönsted acidic sites.

The Mor-35 sample had an even larger external surface area of 113 m^2/g and micropore area of 288 m^2/g, suggesting that acid leaching might have caused the formation of mesopores. Dealumination of a zeolite by leaching with HCl is known to remove all extraframework aluminum [26], therefore, it is likely that the Mor-35 sample obtained by leaching of Mor-10 with 1 N HCl will also primarily contain Brönsted sites. Therefore, it appears that the higher isomer yield over Mor-35 is obtained due to the creation of mesopores by acid leaching. For ZSM-5, Fig. 3 shows that the maximum yield of heptane isomers is much lower than that obtained over ZSM-12, Y, and beta catalysts. ZSM-5 has a straight channel and a sinusoidal channel, and a bigger space, larger than its pore opening, is available at the intersection of these channels. The occurrence of equimolar amounts of propane and isobutane in the products over the ZSM-5 catalyst confirms that almost all the cracked products

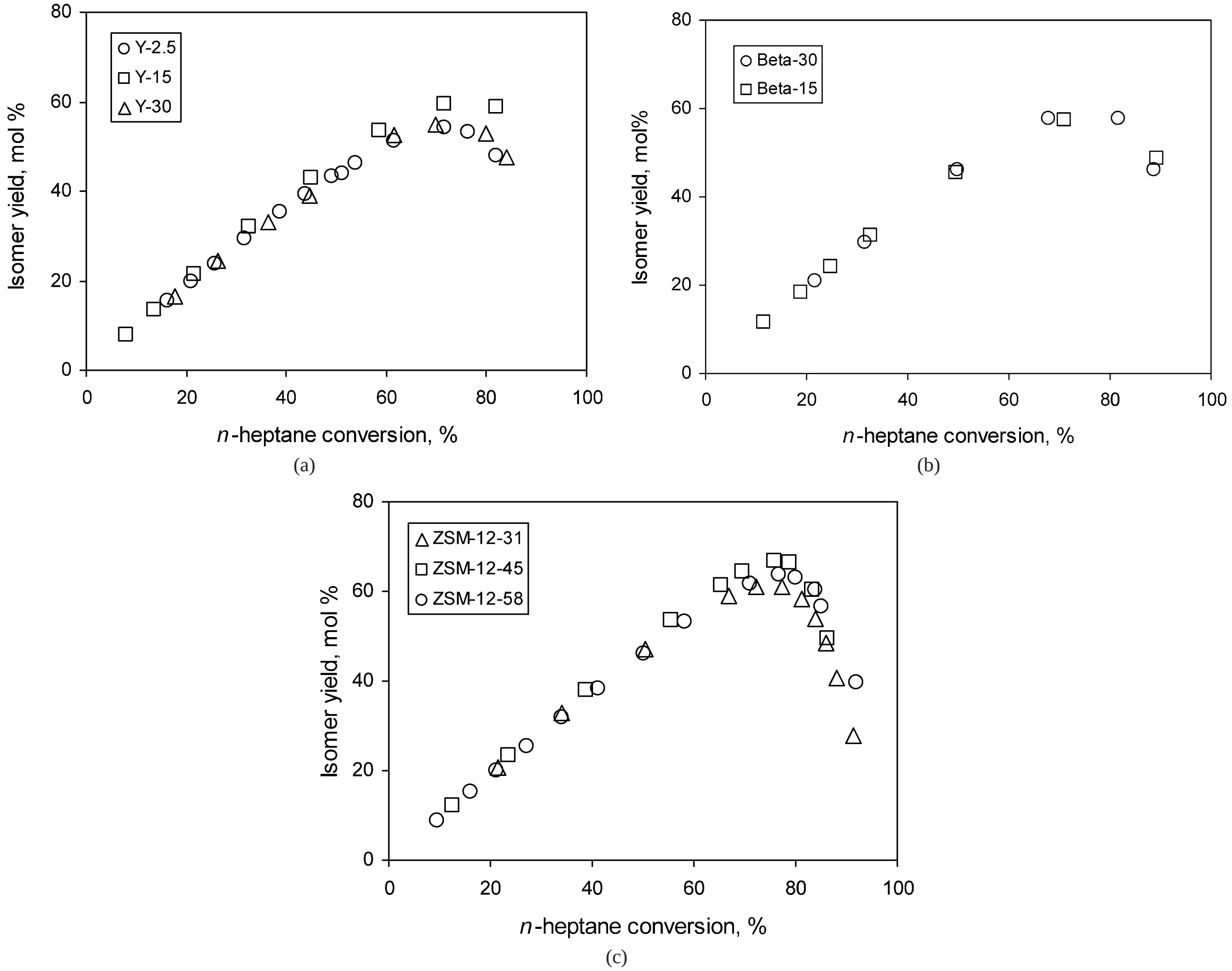


Fig. 2. Total yield of C_7 isomers (mono + di + tribranched isomers) as a function of n-heptane conversion over (a) Pt/H-Y zeolite, (b) Pt/H-Beta zeolite, (c) Pt/H-ZSM-12 catalysts. WHSV $= 7\ h^{-1}$, $H_2/n\text{-}C_7$ (molar) $= 16$, total pressure $= 100$ psig and 0.5 wt% Pt loading (using H_2PtCl_6) on all catalysts.

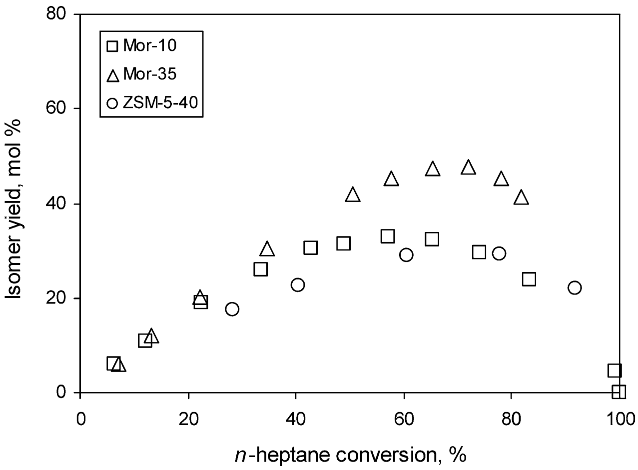


Fig. 3. Total yield of C_7 isomers (mono + di + tribranched isomers) as a function of n-heptane conversion over two Pt/H-Mordenite catalysts and a Pt/H-ZSM-5 catalyst. WHSV $= 7\ h^{-1}$, H_2/C_7 (molar) $= 16$, total pressure $= 100$ psig and 0.5 wt% Pt loading (using H_2PtCl_6) on all catalysts.

are obtained from β-scission of dibranched isomers. Therefore, it appears that the low isomer selectivity of ZSM-5 is due to the inability of the dibranched heptane isomers, which form at the channel intersections, to come out of the pore. The performance of ZSM-5 and mordenite is discussed in more detail in the later sections.

3.2.3. Enhanced activity USY and ZSM-12

It is well known in the literature that subjecting a zeolite to steam treatment can greatly enhance the catalytic activity of the zeolite, which is generally attributed to generation of extraframework aluminum [12]. This behavior has been observed even for a high silica zeolite like ZSM-5 after mild steam treatment [27]. As noted earlier, one of our objectives in this study was to determine how the isomer yield is affected in these enhanced activity catalysts; the samples we studied were an enhanced activity USY (CBV-500) and a ZSM-12 sample prepared in our laboratory. First, the results obtained with the enhanced activity Y-zeolite (EY)

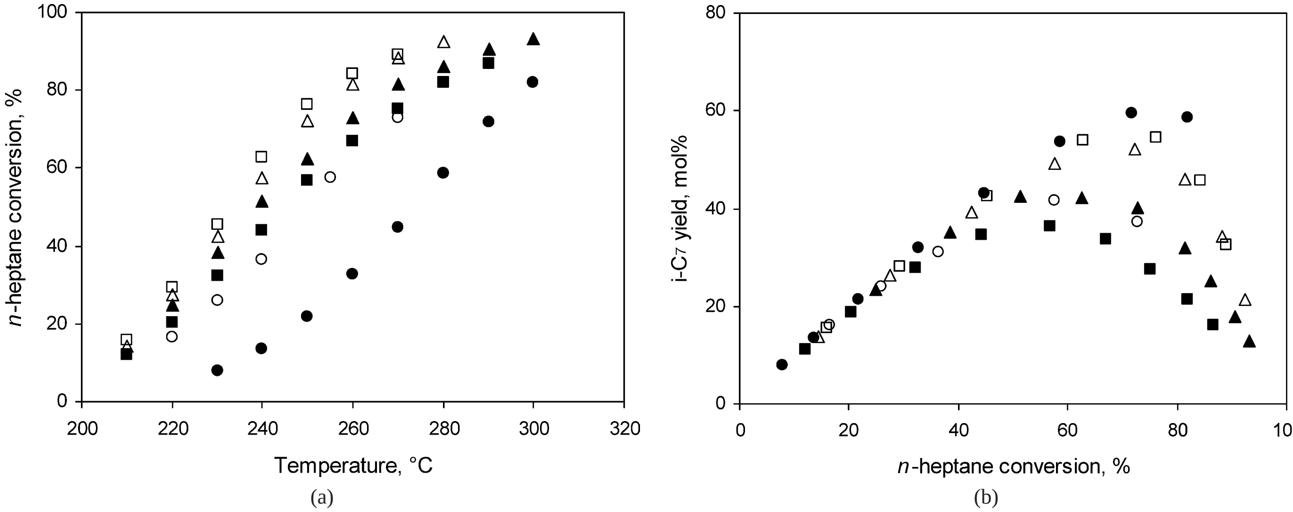
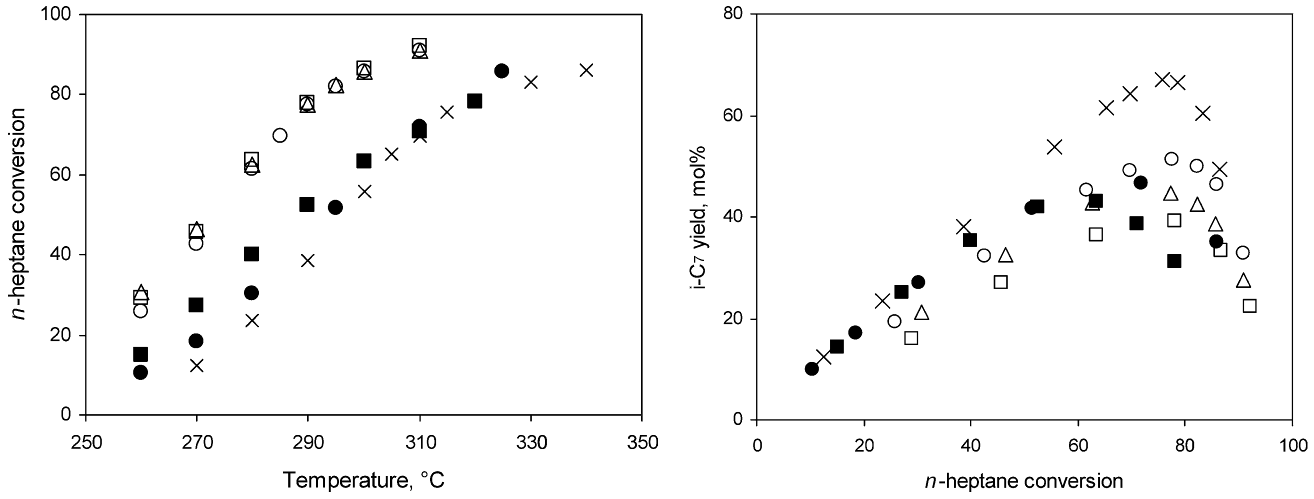


Fig. 4. (a) Variation of n-heptane conversion with temperature and (b) total yield of C_7 isomers as a function of n-heptane conversion, for the enhanced activity USY catalysts (▲) EY-1, (■) EY-2, (△) EY-3, (□) EY-4, and (○) EY-5 catalysts. The Y-15 catalyst (●) is shown for comparison. WHSV = 7 h^{-1}, $H_2/n\text{-}C_7$ (molar) = 16, total pressure = 100 psig.

samples are discussed. The acidity characteristics and catalytic activity in heptane and decane hydroisomerization of the CBV-500 sample have been reported by Remy et al. [14]. They observed a large amount of octahedral aluminum and aluminum with unknown coordination, in addition to framework tetrahedral aluminum, and the sample showed a dramatically higher turnover frequency (TOF) in heptane hydroisomerization compared to the parent nondealuminated sample [14]. In our experiments, we observed that some of the catalysts prepared using the CBV-500 sample (EY-3 and 4) are so active that they require about 80 °C lower than the Y-2.5 catalyst and about 30 °C lower than Y-15 to achieve the same level of heptane conversion (Fig. 4a). van Bokhoven et al. [16] have suggested that the increased reaction rate in these catalysts is due to an increase in the initial heat of alkane adsorption on the Lewis acid sites, which increases the concentration of reactants within the pores. Unlike the Y-zeolite and USY catalysts discussed in the earlier section (which were all loaded with 0.5 wt% Pt using H_2PtCl_6), we found that the performance of the EY catalysts was highly dependent on the Pt loading and the precursor used. Therefore, the performance of the EY sample was studied with different amounts of Pt, loaded using the two different precursors—H_2PtCl_6 and $Pt(NH_3)_4Cl_2$.

The variation of the heptane conversion with temperature and the variation of the branched C_7 yield with conversion for the EY catalyst samples are shown in Figs. 4a and 4b, respectively. Both figures clearly show the differences when different Pt precursors and loadings are used. From Fig. 4a, $Pt(NH_3)_4Cl_2$ appears to be a better precursor than H_2PtCl_6 for loading Pt, since it results in a more active catalyst. Increase in the Pt loading from 1.0 to 1.5 wt% using $Pt(NH_3)_4Cl_2$ further improves the activity of the catalyst, which suggests that a higher loading of platinum is necessary to balance the high activity of acid sites. Dispersion measurements carried out on selected EY samples (Table 2) show that the Pt dispersion on these samples is quite low compared to the samples listed in Table 1, suggesting that migration of Pt to the external surface and sintering might be occurring in these catalysts. This is true for the catalyst samples prepared by loading Pt using H_2PtCl_6 as well as $Pt(NH_3)_4Cl_2$. However, it is unusual to note that increasing the Pt loading from 0.5 to 1.0 wt% with H_2PtCl_6 actually results in lower conversions at the same temperatures. The pH of the H_2PtCl_6 solution used for impregnating platinum was around 3.2. Since extraframework aluminum can be removed by acid treatment [26], it is possible that using H_2PtCl_6 somehow disrupts the extraframework aluminum, thereby affecting enhanced activity sites and lowering the activity of the catalyst. This is supported by the fact that increasing the Pt loading using H_2PtCl_6 decreases the activity even further. The temperature at which the oxidation and reduction treatment to disperse the platinum is carried out also affects the catalyst performance. The EY-5 sample, which had 1.0 wt% Pt loaded using $Pt(NH_3)_4Cl_2$ but oxidized and reduced at 400 °C, showed a much lower activity compared to the EY-3 catalyst.

The isomer yield also showed different trends with respect to heptane conversion over the EY catalysts (Fig. 4b); the sample that showed a higher conversion at a particular temperature (in Fig. 4a), also shows a higher isomer yield. In the EY catalysts that show a lower yield, this behavior is an indication of the lack of balance between the metal and acid functions [28]. Therefore, using H_2PtCl_6 to load Pt on the enhanced activity USY sample does not result in an efficient hydrogenation/dehydrogenation function. Loading platinum using $Pt(NH_3)Cl_2$ does not appear to affect the enhanced activity zeolite and increasing the Pt loading to 1.5 wt% gives the highest activity as well as isomer yield. The maximum isomer yield obtained with the EY-4 catalyst is around 56 mol% (64 wt%), which is very close to that obtained with the other Y-zeolite catalysts discussed earlier.



(a) (b)

Fig. 5. (a) Variation of n-heptane conversion with temperature and (b) total yield of C_7 isomers as a function of n-heptane conversion, for the enhanced activity ZSM-12 catalysts. (■) EZ12–1, (△) EZ12–2, (○) EZ12–3, (□) EZ12–4, and (●) EZ12–M. The ZSM-12–45 catalyst (×) is shown for comparison. WHSV = 7 h^{-1}, H_2/nC_7 (molar) = 16, total pressure = 100 psig.

The difference between EY and other Y-zeolite catalysts is that in addition to requiring a higher metal loading, the EY (CBV-500) catalysts also appear to be quite sensitive to the Pt precursor used and the pretreatment conditions.

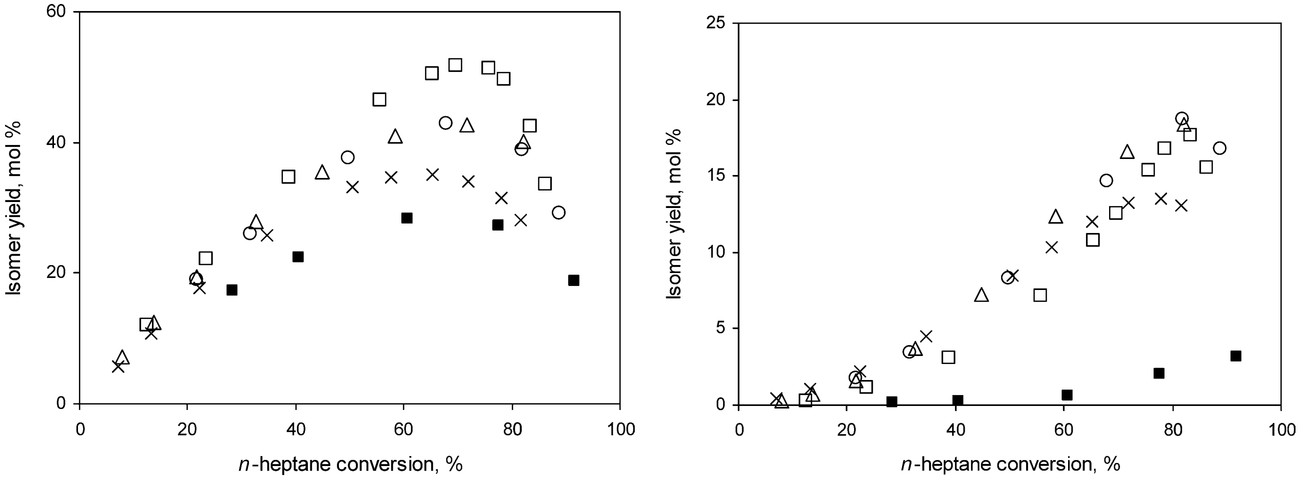
The performance of the enhanced activity ZSM-12 sample was also studied with Pt loaded using different precursors. FTIR of pyridine adsorbed on the enhanced activity ZSM-12 sample confirmed the presence of Lewis acid sites, by the appearance of a peak at 1455 cm^{-1}. The variation of the heptane conversion with temperature and i-C_7 yield with conversion for the enhanced activity ZSM-12 catalysts, EZ12–1 to EZ12–4 and EZ12–M, are shown in Figs. 5a and 5b, respectively. It can be clearly seen in Fig. 5a that the EZ12 catalysts prepared by loading Pt using $Pt(NH_3)_4Cl_2$ show a significantly higher activity than the ZSM-12–45 catalyst, which is shown for comparison. However, the EZ12–1 catalyst prepared by H_2PtCl_6 loading and a mechanical mixture of the enhanced activity ZSM-12 with Pt/SiO_2 (EZ12–M) are not more active. Examination of the isomer yields over these EZ12 catalysts (Fig. 5b) shows that the yields are much lower than that over the ZSM-12–45 catalyst, the closest being the EZ12–3 catalyst which gave a maximum yield of about 52 mol%. The overall trends in variation of the activity and isomer yield of the EZ12 catalysts with respect to Pt loading and precursor are very similar to those observed for the EY catalysts, which again proves that H_2PtCl_6 is not a good precursor for loading Pt on zeolites with enhanced activity. The platinum dispersions on the EZ12 samples are again much lower than the dispersions on the ZSM-12 samples listed in Table 1. Also, similar to the EY-5 sample, the EZ12–4 sample, which was oxidized and reduced at 400 °C shows a poor performance. The above data serve to illustrate the highly sensitive nature of the enhanced activity catalysts. Even though the EZ12–3 catalyst showed a reasonably high isomer yield, there is still a substantial improvement that needs to be made to achieve a maximum yield close to that of ZSM-12–45. Further optimization of the Pt loading (using $Pt(NH_3)_4Cl_2$) and pretreatment conditions for the enhanced activity ZSM-12 catalyst is necessary to obtain a better balance between the metal and the acid functions and this optimized catalyst can be expected to show a higher activity and isomer yield than the EZ12–3 catalyst.

4. Discussion

For the Y and ZSM-12 zeolites that did not show enhanced activity, as well as beta zeolites, a loading of 0.5 wt% Pt using H_2PtCl_6 was enough to achieve good metal/acidity balance and the performance of these catalysts showed that they were close to the “ideal hydrocracking” behavior. Regardless of the Si/Al ratio and the reaction temperature, each zeolite gives a specific maximum isomer yield. For the zeolites with enhanced activity, it was observed that the catalyst is very sensitive to the Pt precursor used and the pretreatment conditions. The product distributions obtained over some of the EY and EZ12 samples are compared with the Y-15 and ZSM-12–45 catalysts at a n-heptane conversion of about 75% in Table 3. It can be seen that higher amounts of methane and ethane are formed over the EY-5 catalyst which shows a low isomer yield, which could be an indication of the lack of metal/acidity balance or lack of proximity between the metal and acid sites. In the EY-4 catalyst, there is no methane or ethane formed and product distribution is closer to the Y-15 catalyst. In the case of ZSM-12, the product distributions for ZSM-12–45 and the EZ12 catalysts are drastically different. Substantial amounts of methane, ethane, pentane, and even hexane are observed over EZ12–2 and EZ12–3 catalysts, which suggests hydrogenolysis; however, the EZ12–3 catalyst which has a higher Pt loading than

Table 3
Product selectivities (in mol%) at about 75% n-heptane conversion over selected Y-zeolite and ZSM-12 catalysts

	Y-15	EY-4	EY-5	Z12–45	EZ12–1	EZ12–2	EZ12–3
Conversion (%)	71.7	76.2	72.7	78.7	78.1	77.4	77.6
Methane	0.2	0.0	0.5	0.6	1.7	3.6	2.5
Ethane	0.2	0.0	0.2	0.2	0.7	4.1	3.3
Propane	8.1	14.1	24.4	7.2	28.9	14.1	11.2
Isobutane	7.3	13.4	22.1	5.9	24.9	7.4	6.1
Butane	0.8	0.4	1.3	1.1	2.6	6.1	5.0
2-Methylbutane	0.1	0.1	0.2	0.1	0.3	0.8	0.6
Pentane	0.1	0.2	0.1	0.1	0.5	3.3	2.8
2-Methylpentane	0.1	0.1	0.1	0.1	0.2	0.6	0.5
3-Methylpentane	0.0	0.0	0.0	0.0	0.1	0.4	0.3
Hexane	0.1	0.1	0.0	0.1	0.2	1.7	1.6
2,2-Dimethylpentane	5.9	5.6	3.7	4.5	1.8	2.6	2.9
2,4-Dimethylpentane	5.8	5.6	3.5	5.8	2.8	3.7	4.2
2,2,3-Trimethylbutane	0.6	0.8	0.6	0.2	0.2	0.1	0.1
3,3-Dimethylpentane	3.8	3.2	2.2	2.7	1.1	1.3	1.4
2-Methylhexane	27.3	23.6	17.3	29.2	14.5	21.2	24.5
2,3-Dimethylpentane	7.1	6.8	4.5	8.1	3.6	4.8	5.3
3-Methylhexane	29.2	23.9	17.9	31.2	14.9	22.2	25.5
3-Ethylpentane	2.9	1.9	1.3	2.7	1.0	1.7	2.0
Methylcyclohexane	0.3	0.2	0.1	0.2	0.1	0.1	0.1



(a)

(b)

Fig. 6. (a) Best yields of monobranched C_7 isomers and (b) multibranched C_7 isomers that could be obtained over the various Pt/H-zeolite catalysts in this study. (□) ZSM-12–45, (△) Y-15, (○) Beta-30, (×) Mor-35, and (■) ZSM-5–40.

the EZ12–2 catalyst gives lower amounts of these products. This observation again suggests that lack of intimate contact between the metal and acid functions might be responsible for this behavior. According to Lago et al. [27], the enhanced activity acid sites can be 45 to 75 times more active than the normal acid sites. If this is the case, then a very strong hydrogenation function in close proximity to the acid site would be necessary to achieve an ideal hydrocracking catalyst, which explains why the enhanced activity catalysts are so sensitive to Pt precursor, loading and pretreatment conditions. When a good metal/acidity balance is achieved in the enhanced activity USY, such as in the EY-4 catalyst, the maximum isomer yield achieved was comparable to that obtained over the catalysts having mainly framework aluminum. Based on these observations it is reasonable to conclude, at least in the case of the enhanced activity USY, that the presence of enhanced activity is not affecting the selectivity properties of the catalyst in hydroisomerization if good metal/acidity balance is achieved.

The best yields of monobranched and dibranched C_7 isomers that could be obtained with respect to conversion over various zeolite catalysts in this study are shown in Figs. 6a and 6b, respectively. In these figures, the better isomer selectivity of ZSM-12 can again be seen. The yield of monobranched isomers is higher over ZSM-12 and the yield of multibranched isomers approaches that of Y zeolite at high conversions. The open structures Y and beta zeolites show very similar trends. Only in the case of mordenite, as noted earlier, there was a substantial increase in the isomer yield after acid dealumination. It has been suggested that the lower selectivities for bulkier isomers in certain mordenite samples could be due to channel blockage by extraframework species in the pores [29]. This could very well be the case with the Mor-10 sample. Therefore, it appears that the higher isomer yield over Mor-35 compared to Mor-10 is not due to a better metal/acid balance or the lower acid site concentration, but might be due to the creation of mesopores which would increase the contribution of the external surface to the reaction, and also improve accessibility of the acid sites and facilitate faster diffusion of the products. Tromp et al. [30] also observed an increase in selectivity, in n-C_6 hydroisomerization after acid leaching of mordenite, and utilized a similar reasoning to explain their results. The maximum isomer yield in Mor-35 is still much lower than that of the Y and beta zeolite catalysts. The very low yield of dibranched isomers over ZSM-5 (Fig. 6b) illustrates its shape-selective behavior. However, the cracked products obtained over ZSM-5 contained only a very small amount of n-butane (not shown); most of the C_4 produced was isobutane, which indicated that cracking was occurring by the more favorable B_1 and B_2-type β-scissions of the dibranched C_7 isomers. Therefore, dibranched C_7 isomers are able to form inside the pores of ZSM-5; this must be occurring at the channel intersections as there would be large enough space available for the dibranched isomers to form. However, these molecules are not able to come out of the pore due to the narrower channel openings. A product shape selectivity is therefore in effect in the case of ZSM-5. If extraframework (silica or Al) debris is present in the Mor-10 sample, then an effect similar to that occurring in ZSM-5 would occur, which would explain the lower isomer yield and the increased selectivity to cracked products. In ZSM-12, transition-state shape selectivity, which slightly hinders the formation of dibranched isomers and possibly also their further cracking is the reason for the higher isomer yield. In another study on the conversion of individual octane isomers over a ZSM-12 catalyst [31], we observed that the less bulky isomers were the more favored products, and the bulkier 3,3-, 3,4-, and 2,3-dimethyloctane isomers were hindered. The backward debranching reactions of monobranched isomers to n-C_8 and dibranched isomers to monobranched occurred to a substantially greater extent over ZSM-12 compared to USY. These observations led us to suggest the above reason for the higher isomer yield over ZSM-12.

The maximum isomer yields over the open structures, zeolites Y and beta, are identical. Even the Y-30 catalyst, a USY sample containing mesopores and reduced crystallinity, shows the same trend for variation in isomer yield with n-C_7 conversion as the other Y and USY catalysts, regardless of the reaction temperature. This prompted us to look at how non-zeolitic solid acids perform in the hydroisomerization of heptane. Pope et al. [24] studied a Pt-loaded chlorided alumina catalyst for n-heptane hydroisomerization and the maximum isomer yield obtained over this catalyst (68 wt%) was identical to that over Y zeolite; this was despite the operating temperature being much lower for this catalyst. Patrigeon et al. [25] studied Pt loaded silica–alumina and observed that the maximum yield over this catalyst was lower than that of Y zeolite only because of the very high operating temperature which caused formation of aromatics instead of isomers. These observations seem to indicate that the maximum isomer yield for heptane conversion over bifunctional catalysts consisting of open pore systems which do not show any shape selectivity is limited by the reaction kinetics itself, since the onset of hydrocracking reactions does not allow the isomers to reach thermodynamic equilibrium. It should be noted again that for this to be true, the catalyst must be well balanced and behave as an “ideal hydroconversion catalyst”; i.e., the metal function should be strong enough to ensure equilibrium between a paraffin and its corresponding olefin.

In zeolites that show shape selectivity, the pore structure of the zeolite determines the kind of shape selectivity that prevails, as was the case for ZSM-5 and ZSM-12. Therefore, for a shape-selective zeolite, any increase in contribution of the external surface area to the reaction, and decrease in the diffusion path length, such as creation of mesopores and nanocrystallinity, would cause the maximum isomer yield to change. In a zeolite such as ZSM-5, which shows an inherent maximum isomer yield much lower than that of Y zeolite, an increase in the external surface area and decrease in the diffusion path length would result in an increase in the isomer yield. In fact, this is what was recently observed for decane hydroconversion over nanocrystalline ZSM-5 [32]. However, for open pore systems such as zeolites Y and beta, it appears that the creation of mesopores or preparation of a nanocrystalline zeolite would not help in improving the isomer yield well beyond the maximum obtained in Y zeolite. In ZSM-12, increase in contribution of the external surface would cause its maximum isomer yield to decrease and approach that of Y zeolite. Therefore, to obtain isomer yields higher than that of the open pore structures, the shape-selective properties of zeolites must be utilized.

5. Conclusions

The performance of large-pore zeolites having different Si/Al ratios and activity characteristics, and a ZSM-5 catalyst, was studied in n-heptane hydroisomerization. In zeolites that showed enhanced activity, the catalyst was very sensitive to the Pt precursor used and pretreatment conditions and $Pt(NH_3)_4Cl_2$ was found to be a better precursor than H_2PtCl_6 for loading Pt on these zeolites. If a sufficient amount of metal is loaded on these zeolites using $Pt(NH_3)_4Cl_2$, and the catalyst is optimized to provide close proximity between metal and acid sites to ensure a strong hydrogenation function and good metal/acidity balance, the variation of isomer yield with heptane conversion over these catalysts is similar to that over the other zeolite catalysts that do not show such enhanced activity. Therefore, for any zeolite, the maximum isomer yield is obtained when the catalyst meets the criteria for the ideal hydrocracking catalyst, which means that it is not possible to obtain isomer yields higher than this maximum by modifying zeolite acidity characteristics. Interestingly, the maximum isomer yield obtained in heptane hydroisomerization over open zeolite structures like Pt-loaded Y and beta zeolite catalysts is identical to the maximum yield obtained over Pt/$AlCl_3$ and Pt/SiO_2–Al_2O_3 regardless of the activity of the catalyst. The presence of mesopores in Pt/USY catalysts also does not affect the maximum isomer yield. However, the creation of mesopores or preparation of nanocrystalline zeolite is likely to affect the maximum isomer yield in zeolites that show shape selectivity. Therefore, the best way to obtain isomer yields higher than that obtained over open solids is to employ the shape selectivity of zeolites to suppress the formation of multibranched isomers that can easily undergo cracking.

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