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Catalysis Today 65 (2001) 117–122

CATALYSIS TODAY

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Simultaneous isomerization of *n*-heptane and saturation of benzene over Pt/Beta catalysts
The influence of zeolite crystal size on product selectivity and sulfur resistance

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Abstract

In this work we show that decreasing the zeolite crystal size has a clear benefit on product selectivity and sulfur resistance of Pt/Beta catalysts during the simultaneous hydroisomerization of *n*-heptane and hydrogenation of benzene. The higher isomerization selectivity of the catalyst prepared from a nanocrystalline Beta zeolite can be ascribed to a faster diffusion of the *iso*-C_7 products through the small crystallites preventing cracking reactions to occur, while the improved sulfur resistance can be related to a better dispersion of Pt owing to its higher surface area and mesoporosity. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydroisomerization; *n*-Heptane; Hydrogenation; Benzene; Zeolite; Crystal size; Beta; Pt; Sulfur

1. Introduction

As a consequence of environmental concerns, the benzene level in reformulated gasoline has to be drastically reduced while keeping or even increasing the octane ratings. Reduction of benzene can be achieved by extracting it from the reformate product and/or by eliminating the benzene precursors (C_6–C_7 paraffins and naphthenes) from the reformer naphtha feed. In order to compensate for the octane loss produced by benzene removal, it would be highly desirable to increase the contribution of high-octane branched paraffins to the gasoline pool, and even to extend the isomerization reaction to *n*-paraffins higher than C_6, such as *n*-C_7 and *n*-C_8. In such a case, the isomerization reaction has to be carried out with high selectivity to multibranched components, carrying the highest octane numbers, while minimizing undesired hydrocracking reactions.

An interesting alternative to produce benzene-free high-octane gasoline components would be to process the benzene and benzene precursor streams from the reforming units together with the light straight run (LSR) naphtha (mainly formed by C_5–C_6 *n*-paraffins) in an isomerization unit in the presence of H_2 and a bifunctional catalyst [1]. In this case, the *n*-paraffins could be isomerized while benzene could be hydrogenated to cyclohexane (CH) and this is converted into its higher octane methylcyclopentane (MCP) isomer. Unfortunately, such an ideal situation cannot be achieved with the current LSR isomerization catalysts, mostly based on Pt/Mordenite, for which the addition of even low amounts of benzene causes an inhibition of the isomerization activity [2], while the presence

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PII: S0920-5861(00)00576-9

of n-C_7 and higher n-paraffins produces a significant increase of the gas yield by extensive cracking of the multibranched isomers [3]. Consequently, it would be interesting to design new isomerization catalysts suitable to perform, in a single catalytic step, the saturation of benzene and the selective isomerization of the C_{7+} n-paraffins.

In this line of work, we have recently shown that bifunctional Pt/Beta and Pt/WO_x–ZrO_2 catalysts are effective for carrying out the simultaneous conversion of a benzene/n-C_7 mixture (25 wt.% benzene) with high selectivity to *iso*-C_7 under typical hydroisomerization conditions [4]. However, when the reaction was carried out in the presence of 200 ppm of sulfur, the zeolite-based catalyst displayed a higher sulfur resistance while maintaining high isomerization and hydrogenation activities [4].

As a continuation of that work, here we have investigated the influence of the zeolite crystal size on the catalytic performance of Pt/Beta catalysts for the simultaneous hydroconversion of n-C_7 and benzene either in the absence or in the presence of sulfur. It will be shown that decreasing the zeolite crystal size has clear advantages on both product quality and catalyst sulfur resistance.

2. Experimental

A nanocrystalline Beta zeolite (sample NB) was synthesized in the absence of alkali cations and without seeding according to the procedure described in [5]. A sample of Beta zeolite with larger crystallites was synthesized using fluoride as mineralizing agent (sample FB) following the procedure reported in [6]. The gels having the following molar composition:

NB : Al_2O_3:16 SiO_2:10.3 TEAOH :240 H_2O
FB : Al_2O_3:16 SiO_2:9.7 TEAOH :126 H_2O : 9.7 HF

were crystallized at 140°C under rotation (60 rpm) for about 30 and 6.5 days, respectively. The solids were then separated, washed, dried at 100°C, and finally calcined at 580°C to remove the organic. The zeolites were then impregnated with a solution of chloroplatinic acid in 0.2N HCl to obtain a concentration of Pt of 1 wt.%, and calcined again at 500°C for 3 h.

The catalysts were characterized by XRD, IR spectroscopy combined with adsorption–desorption of pyridine for acidity measurements, adsorption of N_2 for determination of textural properties, electron microscopy, and H_2 chemisorption.

The catalytic experiments were carried out in a down-flow fixed-bed stainless steel reactor at 30 bar total pressure, H_2/hydrocarbon molar ratio of 10, and temperature in the 230–290°C range. Before being loaded into the reactor, the catalyst (3.0 g) was crushed and sieved to a particle size of 0.25–0.42 mm, and diluted with SiC having 0.59–0.84 mm particle size until a constant bed volume of 10 cm^3. Pure n-heptane or an n-heptane/benzene mixture (25 wt.% benzene) were fed at a constant flow rate of 13.6 cm^3/h, which corresponded to a space velocity (WHSV) of 3.1 and 3.3 h^{-1}, respectively, with respect to the total hydrocarbon feed. Before starting the reaction the catalyst was reduced in situ at 450°C for 2 h in a H_2 flow of 300 cm^3/min. Reaction products were analyzed on-line at regular intervals in a GC (Varian 3800) equipped with a capillary column (Petrocol DH50.2) and an FID. For the sulfur resistance experiments, an n-heptane/benzene feed mixture containing 200 ppm sulfur added as 2-methylthiophene was used.

3. Results and discussion

3.1. Catalyst characterization

The main physicochemical properties of the calcined Beta zeolites are given in Table 1. As observed, the nanocrystalline sample (NB) has a higher surface area and much higher mesoporosity than the Beta zeolite synthesized in the presence of fluoride (FB). Such a mesoporosity is mainly due to the interparticle voids created in the NB zeolite by aggregation of the small crystallites, and was seen to present a narrow distribution of pore diameter [5]. On the other hand, the nanocrystalline zeolite shows a lower Brönsted acidity than the fluoride-made sample, despite the higher Al content (lower Si/Al ratio) of the former. This is explained by a higher dealumination of zeolite NB during the thermal activation steps, owing to the lower thermal stability of the Al in small crystallites. In fact, the Beta zeolites synthesized in the presence of

Table 1
Physicochemical characteristics of the calcined Beta zeolites

Sample	Bulk Si/Al ratio	Crystal size (nm)[a]	BET (m^2/g)	Pore volume (cm^3/g)		Acidity (μmol/g)[b]			
				Total	Mesopore	$B_{250°C}$	$B_{400°C}$	$L_{250°C}$	$L_{400°C}$
NB	8	10–20	700	0.91	0.76	44	9	62	47
FB	13	500–1000	541	0.32	0.10	50	17	30	23

[a] Estimated from SEM pictures.

[b] Calculated using the extinction coefficients given by Emeis [7].

F^- are almost free of connectivity defects, which further contribute to increase their thermal and hydrothermal stability [6]. Consequently, the Lewis acidity (associated to extraframework Al species) of sample NB is also higher than that of sample FB (Table 1).

The textural and acidic properties of the zeolites were hardly altered after Pt impregnation. Moreover, the dispersion of Pt on the zeolite surface, estimated from H_2 chemisorption, was seen to be 25 and 13% for the nanocrystalline and the fluoride-made Beta zeolites, respectively. The better dispersion of Pt on the nanocrystalline zeolite can be ascribed to its higher surface area and mesoporosity.

3.2. Hydroconversion of *n*-C_7/benzene in the absence of sulfur

In the present study we have first carried out the hydroisomerization of *n*-heptane in the absence and in the presence of 25 wt.% benzene in the feed over the two Pt/Beta catalysts having different crystal sizes. At a given reaction temperature, the *n*-C_7 conversion (both in the absence and presence of benzene) was slightly higher for the catalyst containing the large crystal size FB zeolite (not shown), which can be ascribed to its higher Brönsted acidity as compared to zeolite NB (see Table 1). As observed in Fig. 1, the catalyst based on the nanocrystalline Beta zeolite (Pt/NB) was more selective to *iso*-heptanes in the whole range of conversions studied, either in the absence or in the presence of benzene. Moreover, in the presence of 25 wt.% benzene, the *iso*-C_7 selectivity significantly decreased for the large crystal Pt/FB catalyst, while it was almost preserved in the case of the catalyst prepared from the nanocrystalline Beta zeolite. In fact, a selectivity to *iso*-heptanes of ca. 93% at ca. 75% *n*-C_7 conversion was obtained for Pt/NB with the 25 wt.% benzene-containing feed, while the selectivity was about 75% for Pt/FB at similar conversion level.

The higher isomerization selectivity of Pt/NB catalyst can be explained by a faster diffusion of the branched C_7 isomers through the small crystallites of zeolite NB, which prevents secondary cracking reactions leading to lighter products to occur. The inhibiting effect of aromatic co-feed on the isomerization efficiency of Pt/Mordenite catalysts has been explained by (a) a competition in adsorption on the acid sites between the aromatic and the olefinic intermediates of *n*-paraffin hydroisomerization, and (b) to diffusional limitations caused by adsorbed aromatic species [2,8,9]. Taking this into account, it can be suggested that the smaller inhibiting effect of benzene on the isomerization activity observed here for the Pt/NB catalyst is primarily due to the lower diffusional restrictions encountered in the small zeolite crystallites.

On the other hand, significant differences between the two Pt/Beta catalysts were also found concerning

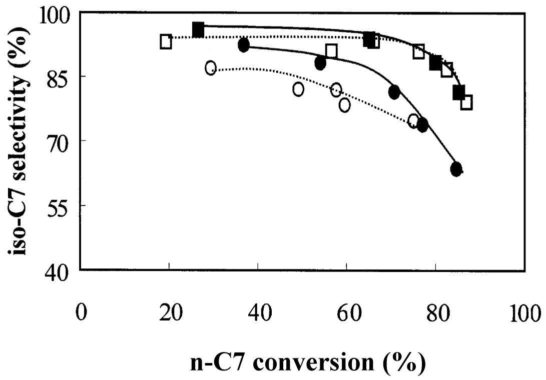

Fig. 1. Selectivity to *iso*-C_7 in the absence (filled symbols) and presence (open symbols) of 25 wt.% benzene against the *n*-C_7 conversion for the (■) Pt/NB and (●) Pt/FB catalysts.

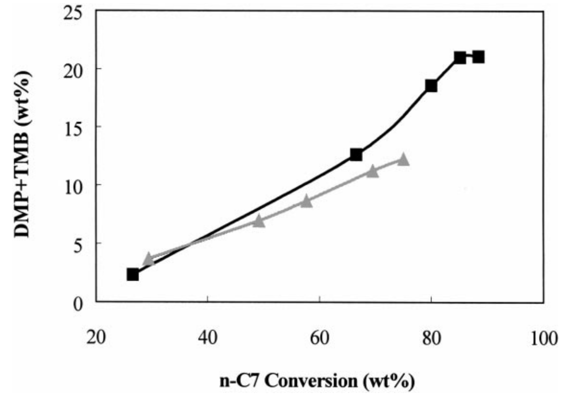

Fig. 2. Yield to multibranched *iso*-C_7 as a function of *n*-C_7 conversion for the Pt/Beta catalysts: (■) Pt/NB, (▲) Pt/FB.

Table 2
Yield to the different reaction products obtained for Pt/Beta catalysts during the hydroconversion of a sulfur-free *n*-C_7/benzene feed mixture (25 wt.% benzene)

Catalyst	Pt/NB	Pt/FB
Temperature (°C)	260	250
n-C_7 conversion (%)	66.6	69.6
Benzene conversion (%)	100	100
Yield (wt.%)		
Total C_1–C_6 (excluding CH and MCP)	3.07	10.53
$C_3 + C_4$	2.46	9.75
C_3/C_4 molar ratio	0.94	0.98
MCP + CH	24.83	25.69
MCP/CH ratio	2.16	2.25
(2,2 + 2,4 + 3,3 + 2,3)-DMP	8.89	8.19
2,3,3-TMB	0.13	0.14
2-MH + 3-MH + 3-EP	36.57	32.37
C_7 cycloalkanes[a]	0.26	0.24
Total *iso*-C_7	45.85	40.94
C_{7+}	0.03	0.04

[a] DMCPs + MCH + ECP.

the distribution of *iso*-C_7 products in the *n*-C_7/benzene experiments. Thus, a higher concentration of the multibranched isomers (DMP + TMB) was obtained with the nanocrystalline Pt/NB catalyst at a given *n*-C_7 conversion as compared to Pt/FB (Fig. 2), which could be associated with a higher octane of the reaction product for the former catalyst.

For both catalysts the conversion of benzene was found to be 100% in the whole range of temperatures and reaction times (up to ca. 8 h) studied, with a high selectivity (above 90% in the range of temperatures studied) to cyclohexane (CH) and its higher octane isomer methylcyclopentane (MCP). At a constant reaction temperature the MCP/CH ratio was slightly higher for the large crystal Pt/FB sample due to the higher acidity of the FB zeolite with respect to the nanocrystalline sample. However, when compared at constant *n*-heptane conversion, the MCP/CH ratio was almost the same for the two Pt/Beta catalysts. This is ascribed to the lower activity of the Pt/NB catalyst, which requires higher reaction temperatures to achieve a given *n*-C_7 conversion, and to the fact that the isomerization of CH into MCP becomes thermodynamically favored at higher temperatures.

The product distribution obtained for the two Pt/Beta catalysts at similar *n*-C_7 conversion during the *n*-C_7/benzene experiments is given in Table 2. It is seen that for the two Pt/Beta samples the monobranched 2-MH and 3-MH are the predominant isomers, which are formed in almost equimolar amounts. On the other hand, hydrocracking of *n*-heptane produces mainly C_3 and C_4 hydrocarbons in a C_3/C_4 molar ratio close to 1, indicating that hydrocracking occurs according to the ideal bifunctional mechanism on the two zeolite catalysts [10]. The relatively high yield to *iso*-hexanes (as compared to C_1–C_3 and C_5) suggests that these hydrocarbons are mainly formed by ring opening of the MCP and CH naphthenes produced in the hydrogenation of benzene.

3.3. Influence of sulfur on activity and selectivity of Pt/Beta catalysts

In order to study the sulfur resistance of Pt/Beta catalysts under hydroisomerization conditions, 200 ppm of sulfur was added as 2-methylthiophene to the *n*-heptane/benzene mixture. Due to the differences in catalyst activity, the reactions were carried out at 250 and 260°C for Pt/FB and Pt/NB, respectively, in order to obtain a similar *n*-C_7 conversion before the addition of sulfur. The relative *n*-C_7 and benzene conversions, X_t/X_0 (considering $X_t/X_0 = 1$, the values obtained in the absence of sulfur), obtained after starting the addition of sulfur are presented in Fig. 3 as a function of time on stream (TOS). As observed, the *n*-C_7 conversion initially decreases and then a pseudo-steady state behavior is attained. Moreover, the conversion of benzene in the presence of sulfur

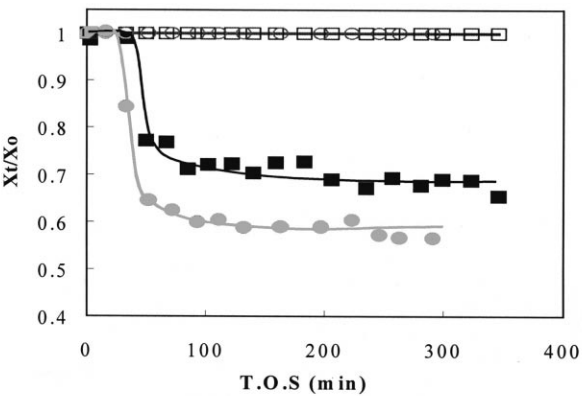

Fig. 3. Relative *n*-heptane (filled symbols) and benzene (open symbols) conversions obtained for (■) Pt/NB and (●) Pt/FB catalysts during the course of the sulfur-containing experiments.

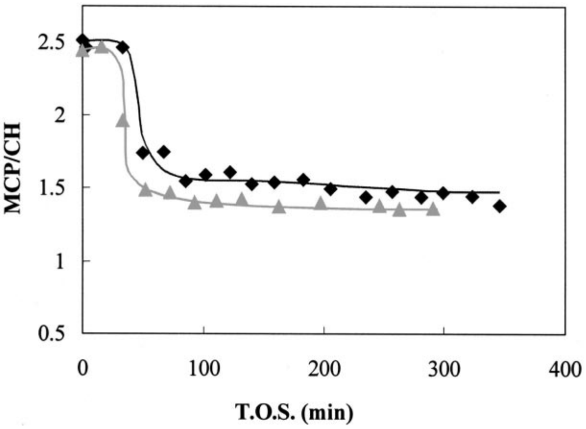

Fig. 5. Change of MCP/CH ratio with time on stream for (◆) Pt/NB and (■) Pt/FB catalysts during the hydroconversion of *n*-C_7/benzene in the presence of 200 ppm sulfur.

was maintained at 100% for the two Pt/Beta catalysts within the reaction times studied. It is seen in Fig. 3 that the nanocrystalline zeolite catalyst (Pt/NB) retains a higher relative *n*-C_7 conversion in the presence of S than the catalyst containing the large crystal size zeolite. Thus, the pseudo-steady state *n*-C_7 conversions in the presence of sulfur are about 70 and 55% of the conversions obtained with the S-free feed for Pt/NB and Pt/FB samples, respectively.

The change of selectivity to *iso*-C_7 with TOS is presented in Fig. 4. As observed, the *iso*-C_7 selectivity significantly decreases from ca. 80% to ca. 55% in the presence of sulfur for the Pt/FB catalyst, especially during the first 60 min on stream, while it still remains high (ca. 80%) for the nanocrystalline Pt/NB sample. Nevertheless, both catalysts present a lower isomerization selectivity in the presence of sulfur as compared to the S-free feed at similar conversions. The decrease of isomerization selectivity indicates that the ideal bifunctional isomerization mechanism is no longer operative in the presence of sulfur. This is probably due to a missbalance between the hydrogenating and acidic functions of the catalyst caused by poisoning of Pt surface sites by sulfur atoms. Similarly, the isomerization of CH into MCP in the hydrogenation products decreases during the initial stages of the reaction (Fig. 5), even if the benzene conversion remained 100% during the sulfur experiments. As it occurs for *n*-heptane isomerization, the nanocrystalline Pt/NB catalyst maintains a higher activity for cyclohexane isomerization than Pt/FB in the presence of sulfur. We have previously observed [4] that in the case of Pt/Beta catalyst, the original isomerization activity is almost restored when the sulfur-containing feed is stopped and the sulfur-free *n*-heptane/benzene mixture is passed again through the reactor, indicating that deactivation by sulfur is a reversible process.

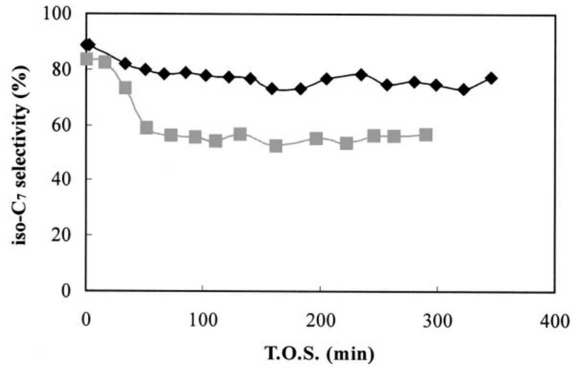

Fig. 4. Change of *iso*-C_7 selectivity with time on stream for (◆) Pt/NB and (■) Pt/FB catalysts during the hydroconversion of *n*-C_7/benzene in the presence of 200 ppm sulfur.

The higher sulfur resistance of the Pt/NB as compared to Pt/FB can be related with a better dispersion of the Pt atoms on the nanocrystalline Beta zeolite (NB), as indicated by the H_2 chemisorption results. As already discussed, this fact can be ascribed to the higher surface area and mesoporosity of the NB sample.

4. Conclusions

Bifunctional Pt/Beta catalysts (1 wt.% Pt) prepared from two Beta zeolites having similar Si/Al ratio and different crystal sizes show fairly good catalytic properties for the simultaneous isomerization of *n*-heptane and hydrogenation of benzene (25 wt.% benzene feed mixture) under typical hydroisomerization conditions ($P = 30\,\text{bar}$, $T = 230\text{–}290^{\circ}\text{C}$, $\text{H}_2/\text{feed} = 10\,\text{mol/mol}$, $\text{WHSV} = 3.3\,\text{h}^{-1}$). Under these conditions *n*-C_7 is isomerized with high selectivity, while benzene is totally hydrogenated into CH and MCP. However, the catalyst prepared from a nanocrystalline zeolite synthesized in the absence of alkali cations and without seeding (sample NB) displays, at constant *n*-C_7 conversion, a higher selectivity to *iso*-C_7 and a higher multibranched/monobranched ratio in the *iso*-heptanes than the catalyst containing a Beta zeolite synthesized in the presence of fluoride and having much larger crystallites (sample FB). For instance, at ca. 80% *n*-C_7 conversion the selectivity to *iso*-C_7 reaches ca. 90 and 70% for Pt/NB and Pt/FB, respectively. When 200 ppm sulfur is added to the *n*-C_7/benzene feed, both the *n*-C_7 conversion and the isomerization selectivity decrease for the two Pt/Beta catalysts, but the benzene conversion still remains at 100%. However, the relative decrease of activity and selectivity for *n*-C_7 conversion is significantly lower for the nanocrystalline Pt/NB catalyst.

The better *iso*-C_7 selectivity observed for the Pt/NB catalyst can be related with a faster diffusion of the branched C_7 isomers through the small zeolite crystallites, thus minimizing secondary cracking reactions. On the other hand, the higher sulfur resistance displayed by this catalyst can be ascribed to a better dispersion of Pt on the nanocrystalline zeolite owing to its much higher surface area and mesoporosity as compared to the large crystal size Beta sample.

Acknowledgements

Financial support by the Comisión Interministerial de Ciencia y Tecnología (CICYT) of Spain is gratefully acknowledged (Project MAT97-1010). M.A. Arribas thanks the Generalitat Valenciana for a postgraduate scholarship.

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