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n-Hexane isomerization over Pt–Na(H)Y catalysts obtained by different preparation methods

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Abstract

Catalysts containing 0.5 wt.% of Pt on Na(H)Y zeolite with potentially high acidity were prepared alternatively by ion exchange and wetness impregnation. Their acidity was altered by altitude of calcination temperature and by the order of calcination and Pt–acid decomposition. The catalysts were tested in *n*-hexane isomerization reaction. It was shown that optimum selectivity with the maximal isomer yield was obtained for the catalyst where calcination and Pt–acid decomposition were hold simultaneously at high temperature. This was attributed to very well-balanced acidic and metallic sites due to optimal metal–support interaction. When the sequence of generation of acid sites was followed by Pt–acid decomposition in a separated temperature sequence, the catalyst with poor activity and selectivity was obtained. This is explained by the lower acidity and poorer metal dispersion as the result of different pretreatment procedure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Isomerization; HY; Acid strength; Metal–support interaction; Preparation procedures effects

1. Introduction

High environmental standards have eliminated the usage of the lead-based additives for busting the octane number (ON) in gasoline in the most of developed countries. In addition to environmental concern this process was speed up by the fact that three-way catalysts were poisoned by lead additives. The elimination of these additives brought about the problem of gasoline blending in order to reach the high ON. The new restrictions towards aromatics content in gasoline (reformulated gasoline) [1,2], have further tight the ON issue. Boosting gasoline with oxygenates, MTB, e.g., turned out to be limited due to shortage of MTB [2]. Besides, it was found that gasoline containing extra oxygen suffers from a loss in fuel economy [3]. The answer might be in hydroisomerization of straight C_5–C_6 paraffins to corresponding isomers, particularly when combined with adsorption of left-over *n*-paraffins in product [1]. Isomerization reactions of alkanes require a bifunctional catalyst and can be achieved on Cl–Al_2O_3-type catalyst containing a noble metal [4]. However, due to sensitivity to trace impurities in feed such as water, these catalysts are being replaced by zeolite-based catalysts. Zeolites like MFI [5], L [6–8], mordenite [5,9,10], Y [5,6,11,12], with or without incorporated noble metals, have been investigated. The results indicate the importance of metal loading, acidity of the support, as well as properly balanced metallic and acidic functions.

2. Experimental

Catalysts containing 0.5 wt.% of Pt were prepared either by ion exchange (catalyst IE), or wetness

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impregnation (catalyst WI), both from commercial Y zeolite with potentially high acidity due to exchanged Na^+ with NH_4^+. For the IE catalyst the metal loading was done following the instructions in [13], and using 0.01 mol/l $Pt(NH_3)_4{\cdot}(NO_3)_2$ solution. The calcination was carried out by slow temperature ramp of 1°/min from 20 to 350°C, with additional 2 h at the final temperature [14]. In order to prevent autoreduction of Pt due to NH_3 decomposition the calcination was conducted in a high O_2 flow of 1000 ml/min g_{CAT} [15]. The catalyst IE was activated ex situ in 50 ml/min g_{CAT} H_2 stream at 250°C over 5 h. The wetness impregnation (catalyst WI) were performed from 10% solution of $H_2PtCl_6{\cdot}6H_2O$. Three WI catalysts (WI-400, WI-550 and WI-550 + 350) were prepared, differing in final temperature level and sequence of calcination. Catalysts WI-400 and WI-550 upon impregnation were calcined at temperatures as designated in order to simultaneously generate both acidic and metal sites. The catalyst WI-550 + 350 was prepared in a way that first parent zeolite was exposed to the higher temperature (550°C) in order to generate Bronsted acid sites [13]. After the wetness impregnation was done in the same manner like in two other cases, the catalyst was additionally calcined (350°C) in order to decompose Pt–acid. In all cases a temperature ramp of 2°/min in high flow of air, with additional 3 h at final calcination temperature was performed. All catalysts were palletized, crashed and sieved to particle of 1.2–1.5 mm in diameter. Prior to activity measurement WI catalysts were activated in situ in flowing H_2 at 300°C for 3 h.

Catalytic runs were carried out at temperatures from 200 to 350°C at atmospheric pressure, in a fixed-bed reactor (10 mm i.d.) containing 1 cm^3 of catalyst. The reactant mixture H_2/*n*-hexane was made by saturation of H_2 by bubbling through *n*-hexane in a bubbler which was thermostated at desired temperature. After passing through a preheating section, the reaction mixture entered the top of the reactor. The reactor was heated by means of block furnace controlled by thermocouple measuring the temperature of the outer reactor wall. The additional thermocouple measured the temperature of the outcome gases leaving the catalyst bed, and this was taken as the reaction temperature. The down part of the reactor was heated additionally in order to prevent condensation of products. Sampling was performed by means of syringe the content of which was quickly transferred to a gas chromatograph (GC — HP 5890 Series II). In order to minimize condensation in the syringe between two sampling it was kept in a thermostat. The products of the reaction from CH_4 to benzene were separated by 50 m long PONA column, and detected using both TC and FI detectors connected in line. Occasionally GC was calibrated using appropriate qualitative test samples.

The quantities and strength of acid sites in both calcined and reduced samples were measured by NH_3 desorption followed by differential scanning calorimetry (DSC — DuPont 1090 Thermal Analysis System). Initially samples were evacuated in a vacuum system providing vacuum up to 0.133 Pa, and subsequently exposed to NH_3 at room temperature for 6 h, in order for NH_3 to chemisorb onto the catalyst acid sites [16]. Before transferred to the DSC cell for the analysis, samples were evacuated to remove the physisorbed base. All DSC analyses were done at temperatures from 50 to 550°C by temperature ramp of 10°/min, in static atmosphere of air. From the temperature of ammonia desorption, and its enthalpy it was possible to conclude about the acid strength and number of acid sites [17–19]. The acidity of samples was additionally tested by means of Hammett indicators [20].

3. Results and discussion

The product distribution upon *n*-hexane isomerization in the temperature range 200–350°C is shown in Table 1. The fraction of C_1 and C_3 products in C_1–C_5 hydrocarbons, catalysts selectivity, as well as the total isomer yield are presented in Table 2. All results are given as average values calculated on the bases of several GC analyses for the particular catalyst on each reaction temperature. The catalyst IE has the lowest activity in the whole series (Table 1). Its selectivity at the optimal temperature of 250°C is considerable but due to low activity the isomer yield is the lowest. According to C_1 and C_3 fractions in sum of C_1–C_5 hydrocarbons, hydrogenolysis reaction on the primary C atom on metallic site is not favored to any extent. Instead, reaction of catalytic cracking by monomolecular mechanism [9,11], especially at higher reaction temperature is the dominant one. For this acidic centers of higher acid strength are necessary, so *n*-hexane is cracking in the middle of the molecule [21] resulting mostly in C_3 hydrocarbons

Table 1
Product distribution in *n*-hexane isomerization as a function of reaction temperature

Product (wt.%)	Catalyst				T (°C)
	IE	WI-400	WI-550	WI-550 + 350	
$\sum(C_1–C_5)$	0.20	0.26	0.20	0.17	200
i-C_5	–	0.15	–	0.02	
2,2-DMB	–	0.52	–	0.11	
2,3-DMB	0.30	0.97	0.15	0.33	
2-MP	2.05	8.45	1.39	5.35	
3-MP	2.25	6.07	1.08	3.77	
n-C_6	95.01	82.41	97.15	86.61	
Benzene	–	1.12	–	2.45	
$\sum(C_1–C_5)$	1.65	3.85	1.01	1.30	250
i-C_5	0.30	0.68	–	0.07	
2,2-DMB	0.20	8.70	1.97	1.16	
2,3-DMB	1.11	5.52	1.43	1.57	
2-MP	5.80	28.68	15.78	10.88	
3-MP	4.15	19.38	10.27	7.60	
n-C_6	87.04	32.46	69.56	76.35	
Benzene	–	0.89	–	1.14	
$\sum(C_1–C_5)$	9.54	43.25	4.35	9.55	300
i-C_5	1.05	1.59	0.47	0.93	
2,2-DMB	0.04	7.64	9.78	1.53	
2,3-DMB	1.07	3.79	6.80	2.77	
2-MP	4.44	17.22	29.84	14.60	
3-MP	3.36	11.70	20.37	9.59	
n-C_6	80.47	12.05	26.12	60.30	
Benzene	–	3.00	2.20	0.75	
$\sum(C_1–C_5)$		56.92	35.31	43.10	350
i-C_5		1.89	2.19	1.72	
2,2-DMB		4.92	6.50	1.16	
2,3-DMB		2.99	5.00	2.41	
2-MP		10.81	19.51	12.56	
3-MP		7.62	13.56	8.26	
n-C_6		8.99	13.48	30.18	
Benzene		5.83	4.85	0.64	

(Table 2). It is known that isomerization of a paraffin without required dehydrogenation on metallic sites is possible either through the carbonium-ion mechanism (strong Bronsted acid sites), or through the mechanism of hydride-ion extraction (strong Lewis acid sites) [21]. However, the sites in IE catalyst are not of such an acidity that could isomerize paraffin directly and in that way to contribute to the selectivity. The additional experiment in which hexane was premixed with N_2 (not shown) giving products with no olefins content in the mixture, pointed out the metallic function as the cause for the poor activity and selectivity of the catalyst IE. The reason for the improperly balanced metallic function could be either in low metal loading or in low dispersity of Pt. Since the applied procedures of calcination and reduction should give a highly dispersed catalyst with Pt sitting in a supercage [14,15], it is more likely that too low Pt loading, as the result of poorly done ion exchange, is the cause for low selectivity of this catalyst.

Among catalysts obtained by wetness impregnation WI-400 demonstrates the highest activity and very high selectivity. At temperatures above 250°C its selectivity, however, suffers from production of large amount of light hydrocarbons (C_1–C_5), indicating pronounced cracking activity. According to the distri-

Table 2
Catalyst selectivity in *n*-hexane isomerization as a function of reaction temperature[a]

Selectivity (% yield, mol/100 mol)	Catalyst				T (°C)
	IE	WI-400	WI-550	WI-550 + 350	
$C_1/\sum(C_1–C_5)$	–	–	–	–	
$C_3/\sum(C_1–C_5)$	–	–	30.64	30.11	
Selectivity	92.18	91.87	91.93	71.54	200
$\sum$ Isomer yield	4.60	16.16	2.62	9.58	
$C_1/\sum(C_1–C_5)$	–	8.46	10.11	20.71	
$C_3/\sum(C_1–C_5)$	53.7	40.65	36.15	37.96	
Selectivity	89.20	93.22	97.03	89.98	250
$\sum$ Isomer yield	11.56	62.81	29.54	21.28	
$C_1/\sum(C_1–C_5)$	0.58	11.82	5.01	10.46	
$C_3/\sum(C_1–C_5)$	55.12	34.04	63.26	51.44	
Selectivity	50.00	47.91	91.04	74.11	300
$\sum$ Isomer yield	9.76	42.14	67.26	29.42	
$C_1/\sum(C_1–C_5)$		18.25	2.22	21.00	
$C_3/\sum(C_1–C_5)$		56.38	71.23	56.23	
Selectivity		32.01	54.04	37.40	350
$\sum$ Isomer yield		29.13	46.75	25.83	

[a] $\sum$ Isomers $= i$-C_5+2,2-DMB + 2,3-DMB + 2-MP + 3-MP (from Table 1). Selectivity $= \sum$ isomers/$\sum$ products. $\sum$ Isomer yield = moles of $\sum$ isomers produced per 100 moles of *n*-hexane entered the reactor.

bution of light hydrocarbons it seems that hydrocracking on acidic centers is the dominant reaction. The smaller fraction of C_3 in WI-400 comparing to WI-550 catalyst indicates that calcination at lower temperature generates acid sites of lower acidity. This is in accord with the slightly higher benzene production on WI-400 reflecting its higher basic character [6]. However, the number of these acid sites in WI-400 exceeds by large the number of the sites of the same quality in WI-550; that is obvious from the total amount of C_1–C_5 hydrocarbons which for WI-400 is ten times higher than in the case of WI-550 (Table 1). This could mean that higher calcination temperature generates fewer number of acid sites, but of higher strength. The metallic sites are also function of the calcination temperature. From product distribution reflecting skeletal isomerization on Pt-sites, it is evident that two catalysts which differ in calcination temperature altitude (Wi-400 and WI-550) have the metallic sites of similar quality, reaching however their optimum at different reaction temperature. What makes WI-550 different from the similar catalyst calcined at lower temperature is its very well-balanced catalytic functions, giving more or less stable selectivity in the whole applied temperature range. Coupled with the high activity this results in the highest isomers yield among all catalysts (Table 2, 300°C). However, it is worth to notice that its optimal activity and selectivity, represented through low cracking activity and high isomers yield, were reached at higher reaction temperature. It is likely that simultaneous generation of acid sites and Pt–acid decomposition at high temperature gives very well-balanced acidic/metal functions, perhaps as the results of their interaction [12]. It has been observed previously that Pt loading with subsequent treatment at appropriate temperatures (calcination/reduction) generates acid sites in the vicinity of metal particle [22], what makes possible the assumption of the existence of metal–proton hybrid centers requiring no mobile reaction intermediates moving between centers [23].

The catalyst WI-550 + 350, in which generation of acid and metal sites were done separately, shows moderate activity but prominent cracking selectivity at temperatures above 300°C (Table 1). The cracking is mostly monomolecular on acidic sites producing C_3 [11], but as the reaction temperature increases demetilation reaction takes over (Table 2). According to the C_3 fraction which is close to that in WI-400, it seems that the acid sites in WI-550+350 are of lower strength and probably alike those in the previous catalyst. On the other hand, the difference in activity and selectivity between catalysts WI-550 + 350 and WI-550 shows that the order of Pt loading and calcination sequences influence the type of interaction. Indeed, when Pt–acid decomposition was performed on the catalyst precursor with previously generated acidic centers, catalyst with not optimally balanced catalytic functions was obtained. This difference in acid strength of WI-550 + 350 and WI-550 could be understood as the result of some "decoration" of acidic centers by Pt. This could happen either by simultaneous calcination/decomposition resulting in enhanced strength, or by consecutive processes giving lower acid strength. The lower skeletal isomerization of WI-550 + 350 catalyst (lower quantities of 2-MP and 3-MP in Table 2) indicates low metal dispersion. This could be the consequence of low second calcination temperature (350°C) following $H_2PtCl_6{\cdot}6H_2O$ impregnation on previously activated parent zeolite at high temperature (500°C). This is in accord with previous observation that samples with acid form of zeolite requires a higher calcination temperature for optimum dispersion of metal [24].

Fig. 1 shows DSC traces of catalyst samples following NH_3 adsorption for 6 h. The differences in calcination temperature and the calcination/decomposition sequences are reflected on NH_3 desorption temperature and heat of desorption. In all cases two main peaks occur: low temperature peak between 170 and 250°C, and high temperature peak between 400 and 450°C. The differences in desorption temperature point out the existence of acid sites of different strength, since stronger sites would require higher temperature to desorb the base than weaker sites [18]. As expected, DSC thermogram of catalyst IE shows a very small amounts of both weak and strong acidic sites. Besides, they are shifted to lower temperature comparing to other catalysts. The NH_3 desorption profiles of WI-400 and WI-550+350 resemble the sites of the similar strength, being exclusively in the domain of weaker sites. However, this acid sites are of the strength high enough to brake C–C bond producing light hydrocarbons. Finally, DSC profiles of catalyst WI-550 indicate very well-formatted acidic centers of higher strength. In all cases thermograms also indicate the positive influence of reduction in terms of acidic sites formation, except in the case of IE catalyst where, perhaps due to the low Pt loading, contribution of metal–support interaction is a minor one.

The colors observed while exposing the samples to Hammett indicators and corresponding acidity related to their pK_a values [20] are presented in Table 3. The order of acidity strength as: IE $\approx$ WI-550 $>$ WI-550 + 350 is in line with DSC profiles, but do not follow activity and selectivity patterns. This can be understand in terms of inappropriate method performed here, which indicates just the quality of the present acidic sites. Only some acid–base titration method would give a real picture about the catalyst acidity [20].

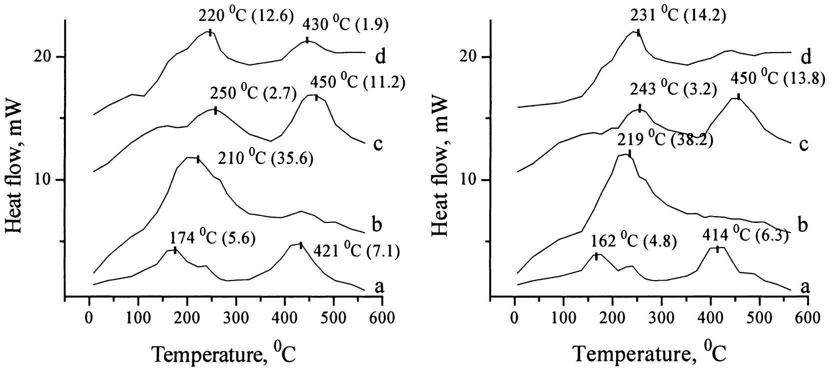

Fig. 1. DSC thermograms of catalysts IE (a), WI-400 (b), WI-550 (c) and WI-550+350 (d) following exposure to NH_3 for 6 h; corresponding ΔH (J/g) values in parentheses; on left side calcined samples, on right side calcined + reduced samples.

Table 3
Catalyst acidity measured by Hammett function

Indicators/color observed	Catalyst		
	IE	WI-550	WI-550 + 350
Crystal violet	Blue	Blue	Blue
Methyl orange	Orange	Orange	Orange
Methyl red	Red	Red	Orange
Acidity	$4.8 > H_0 > 3.3$	$4.8 > H_0 > 3.3$	$6.8 > H_0 > 3.3$

4. Conclusions

From the results it is obvious that sequence of temperature pretreatments and the height of applied temperature play an important role in activity and selectivity of Pt/HY catalyst in *n*-hexane isomerization. Catalyst pretreated at lower temperature comes to its optimal selectivity at lower reaction temperature. The simultaneous calcination and metal–precursor decomposition at high temperature is favorable for isomerization reaction resulting in high selectivity and high isomers yield. This can be explained by the presence of acidic sites of required strength and well-dispersed metal sites which both were generated simultaneously through an optimal metal–support interaction. The previous can be understand in terms of a specific synergetic effect leading to a good bifunctional catalyst.

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