Transformation of 1-hexene on Pt supported ZSM-5 zeolite modified with tin, copper or chromium

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Abstract ZSM-5 zeolite samples containing Pt and a second metal (Sn, Cu or Cr) were prepared by different impregnation procedures. All these catalysts were highly active in the transformation of 1-hexene. A great variety of hydrocarbons were obtained, whose proportion depended on the particular catalyst and the reaction conditions. In general, low temperatures (250 °C) favored the double bond shift reaction, whereas medium temperatures (350 °C) predominantly led to cracking and skeletal isomerization. However, cracking was the major reaction at temperatures above 450 °C. The addition of the second metal decreased the hydrogenating activity of Pt and so olefins constituted a considerable fraction in the product. The use of nitrogen as a carrier gas instead of hydrogen favored the formation of both internal and branched olefins while reducing cracking. The reaction products are interesting for their use in gasoline blending.

Keywords Olefins · 1-Hexene · ZSM-5 zeolite · Isomerization · Cracking · Fuel upgrading

Introduction

Olefins are produced in a variety of important industrial processes. Thus, they account for a 40–60 vol% of FCC naphthas. Among them, around 70 % contain from 5 to 7 carbon atoms and above 30 % are *n*-olefins [1]. In addition, linear

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α-olefins are major components in the Fischer–Tropsch synthesis [2]. Also, several processes have been described on the trimerization of ethylene, in some cases with a high selectivity to 1-hexene [3]. Even though 1-hexene is used as co-monomer for the synthesis of linear low density polyethylenes (LLDPE), which find important applications in packing [4] and as intermediate for the synthesis of detergents and lubricants, among other useful compounds, its content should be reduced in gasoline to improve emissions and increase the octane number. In general, internal and branched olefins are much more interesting for their use as components in fuels because they have higher RON than the corresponding terminal and linear isomers. Although the olefin content in gasoline is limited to 18 %, they can also be hydrogenated to the corresponding isoparaffins.

1-Hexene can undergo different transformations over a catalyst such as cracking, hydrogenation, double bond shift and skeletal isomerization. Other reactions such as oligomerization, hydrogen transfer, cyclization and aromatization are also feasible. These processes have been carried out in a great variety of heterogeneous catalysts.

Sulfonated ion exchange resins have been typically used as catalysts, particularly Amberlyst 15, for the double bond shift of α-olefins [5]. In addition, sulfated mixed oxides consisting of NiO, ZrO_2 and Al_2O_3 have been evaluated for the double bond shift of 1-hexene to 2-hexenes at temperatures ranging from 100 to 200 °C [6]. Furthermore, sulfated mesoporous Ti, Nb, and Ta oxides were compared to Amberlyst 15, Y and ZSM5 zeolites in 1-hexene isomerization [7, 8]. A mesoporous Ta oxide gave a 95.89 % conversion of 1-hexene to *trans/cis* 2-isomers with a ratio of *trans/cis* isomers of 3.7, close to the theoretical thermodynamic equilibrium (3.37). Furthermore, the selectivity in the isomerization of 1-hexene to 2-hexene has been related to confinement and curvature effects on MCM-41 catalysts with different pore sizes [9].

Even though extensively studied for butenes, the investigations on the skeletal isomerization of C_{5+} olefins are relatively scarce. Catalysts such as molecular sieves [10], particularly zeolites [1, 11, 12], Pt-M (M = Re, Sn, Ge) supported chlorinated aluminas [13], and zirconia-based catalysts [14] have been used. The upgrading of 1-hexene has also been carried out by its simultaneous isomerization and aromatization on different zeolites [15]. The selectivity toward aromatics was higher in zeolite ZSM-11 than in zeolite ZSM-5, whereas it was the opposite toward isoparaffins [16]. The addition of Zn and Mg species to zeolite ZSM-5 was found to promote the aromatization reaction [17]. Moreover, a Ni/HZSM-5 bifunctional catalyst converted 1-hexene into aromatics and isoparaffins [18]. A combination of cobalt-modified MCM-41 with Co–Mo/γ-Al_2O_3 converted a significant amount of 1-hexene into branched hexanes during the hydrodesulfurization (HDS) of thiophene [19].

Herein, we report the transformation of 1-hexene on different catalysts consisting of ZSM-5 zeolite supported with Pt and a second metal (Sn, Cu and Cr) synthesized by different impregnation procedures. The influence of various experimental conditions has been discussed.

Materials and methods

Catalysts

HZSM-5 zeolite with a SiO_2/Al_2O_3 ratio of 80 was purchased from Zeolyst Int. (reference CBV8014). Different metals were incorporated into the zeolite by an incipient wetness method using $Pt(NH_3)_4(NO_3)_2$, $SnCl_2$, $Cu(NO_3)_2 \cdot 3H_2O$ and/or $Cr(NO_3)_3 \cdot 9H_2O$. All these metallic salts were purchased from Aldrich. In general, the platinum content of the catalysts was 0.5 wt%, whereas those of tin, copper and chromium were 2.0 wt%.

Bimetallic catalysts were prepared following three different procedures, i.e., one co-impregnation and two consecutive impregnations, thus resulting in three catalysts with the same composition. The syntheses of catalysts consisting of platinum and chromium are given as examples.

The catalyst Pt–Cr/ZSM-5 was synthesized according to the following procedure. 25 ml of an aqueous 2.6×10^{-3} M Pt^{2+} solution and 25 ml of an aqueous 1×10^{-2} M Cr^{3+} solution were mixed and added to 5 g of ZSM-5 zeolite in a round-bottomed flask. The suspension was stirred for 2 h at room temperature. Subsequently, the flask was immersed in a water bath at 50 °C for 2 h and later the solvent was removed under reduced pressure. The resulting solid was dried in an oven at 120 °C.

Catalyst Pt/Cr/ZSM-5 was prepared by adding 5 g of ZSM-5 zeolite into 25 ml of an aqueous 1×10^{-2} M Cr^{3+} solution. After stirring the suspension for 2 h at room temperature and 2 h at 50 °C, the solvent was removed to dryness in vacuum. The solid was calcined at 580 °C for 3 h. The resulting material was added to 25 ml of an aqueous 2.6×10^{-3} M Pt^{2+} solution. After stirring at room temperature and 50 °C for 2 h each, water was removed in a rotary evaporator.

Catalyst Cr/Pt/ZSM-5 was prepared in a similar way to Pt/Cr/ZSM-5 but impregnating first Pt^{2+} and later Cr^{3+}.
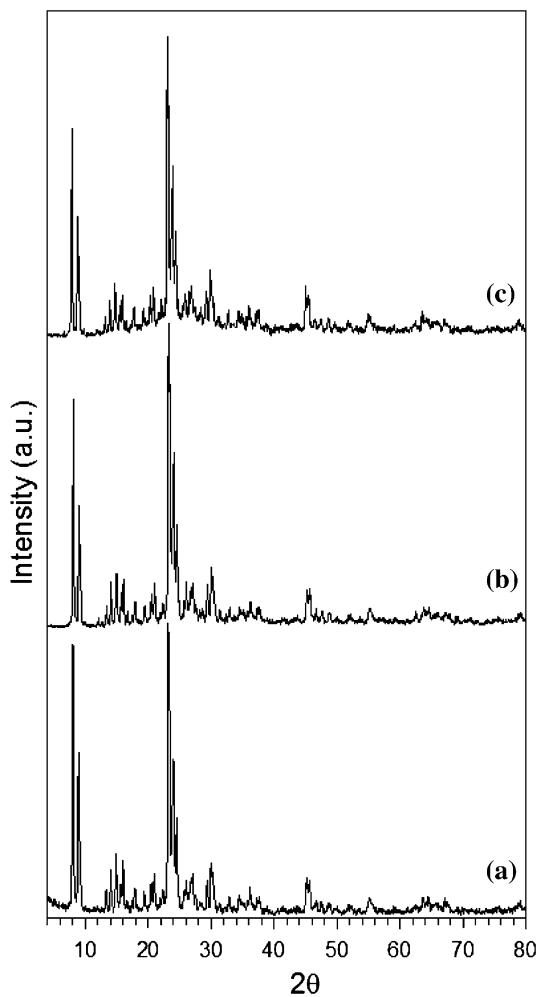
Characterization

All catalysts were characterized by different techniques. X-ray diffraction patterns were recorded on a Siemens D5000 diffractometer using Cu K_α radiation. Nitrogen adsorption isotherms were recorded on a Micromeritics ASAP 2000 analyzer. The specific surface area of each solid was determined using the BET method and the pore size distribution by the Barret–Joyner–Halenda (BJH) method. The acid properties of the catalysts were determined by temperature programmed desorption of ammonia from 100 to 500 °C (at a heating rate of 10 °C min^{-1}) in an AutoChem-2910 equipment with a thermal conductivity detector. Previously, all samples were degassed under flowing helium at 450 °C for 1 h.

Catalytic activity

The catalytic tests were performed in a fixed-bed continuous flow reactor (10 mm i.d.) connected by a thermostated pipe to a gas chromatograph (Fisons 8000;

capillary column: methyl silicone 100 m × 0.25 mm i.d. fused silica; oven program: 60–115 °C at 2 °C min^{-1}). Under the analysis conditions used, *n*-hexane and *trans*-3-hexene could not be discriminated. The reactor, charged with 200 mg of catalyst, was fed at the top with 1-hexene by means of a controlled evaporator mixer from Bronkhorst. The solids were calcined and reduced in the reactor. Calcination was done using an oxygen stream at a flow rate of 30 ml min^{-1} at 500 °C for 1 h, and reduction with a hydrogen stream at 20 ml min^{-1} at the same temperature for 1 h. The reaction temperatures ranged from 200 to 500 °C. All reactions were conducted at atmospheric pressure.

Fig. 1 XRD patterns of HZSM-5 (*a*), Pt–Cr/ZSM-5 (*b*) and Pt/Cr/ZSM-5 (*c*)

Results and discussion

Characterization of the catalysts

Fig. 1 depicts the diffractograms of some ZSM-5 zeolites containing Pt and Cr. XRD patterns, which were similar for the rest of catalysts, revealed that all catalysts preserved the structure of the ZSM-5 zeolite. No additional peaks were observed, thus suggesting that the supported metals were present as crystallites of very small size.

The textural properties of the catalysts (Table 1) remained very similar to those of the parent ZSM-5 zeolite. A slight decrease in surface area was only observed for catalysts containing Pt and Cu. Thus, the possible blockage of pores by the deposition of metals could be considered to be negligible.

The deposition of metals on the surface of zeolites usually modifies their acid properties. These metals can neutralize some Brønsted acid sites by ion exchange while generating new Lewis acid sites. Fig. 2 shows the ammonia TPD curve of HZSM-5 zeolite. Basically, it exhibited two peaks centered at around 130 and 355 °C that can be ascribed to desorption of ammonia from weak and strong acid sites, respectively. Upon deposition of Pt and Sn or Cu, the distribution of acid sites drastically changed. In such cases, the number of both weak and strong acid sites decreased while new medium-strength acid sites arose. These changes were more severe for Cu than for Sn. The role of exchanged metal cations as Lewis acid sites is well known [20]. These new sites desorbed ammonia at ca. 200 °C and close to 300 °C for the samples with Cu and Sn, respectively.

Those catalysts consisting of Pt and Cr displayed more similar profiles to that of the parent zeolite (Fig. 3). Nevertheless, the peak corresponding to weak acid sites was slightly shifted to higher temperatures. Also, the population of acid sites seemed to decrease in catalysts Pt/Cr/ZSM-5 and Cr/Pt/ZSM-5 in comparison with the sample prepared by co-impregnation, i.e., Pt–Cr/ZSM-5.

Table 1 Textural properties of catalysts

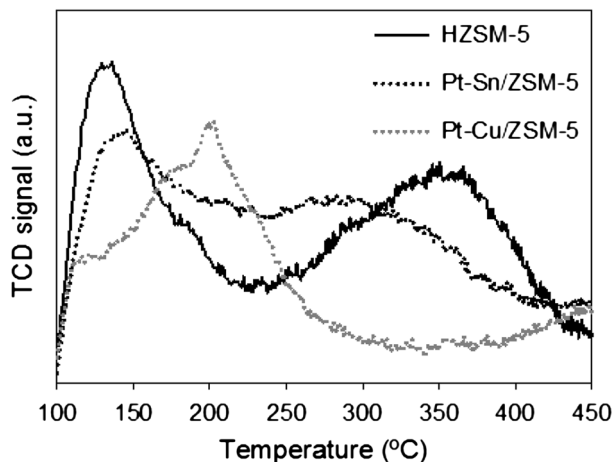| Catalyst	Surface area (m^2 g^{-1})	Pore volume (cm^3 g^{-1})	Pore diameter (Å)
ZSM-5	384	0.24	25
Pt/ZSM-5	407	0.25	25
Pt–Sn/ZSM-5	382	0.24	25
Pt/Sn/ZSM-5	389	0.24	25
Sn/Pt/ZSM-5	388	0.24	25
Pt–Cu/ZSM-5	320	0.21	27
Pt/Cu/ZSM-5	344	0.23	27
Cu/Pt/ZSM-5	350	0.23	26
Pt–Cr/ZSM-5	378	0.23	24
Pt/Cr/ZSM-5	376	0.22	24
Cr/Pt/ZSM-5	380	0.23	25

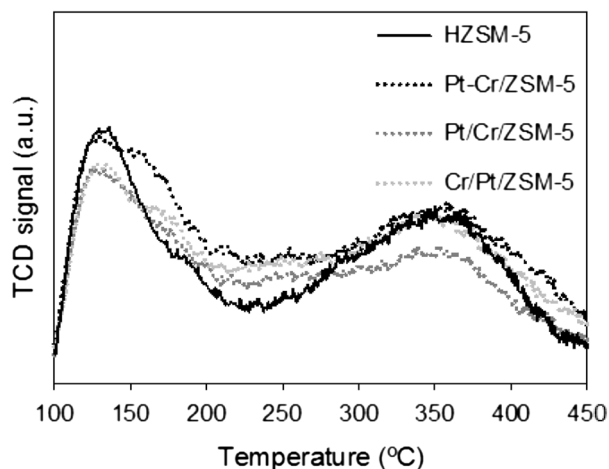**Fig. 2** NH$_3$ TPD curves for various catalysts

Fig. 3 NH$_3$ TPD curves for various catalysts ZSM-5 zeolites containing Pt and Cr

Transformation of 1-hexene

Pt-supported ZSM-5 zeolite is a highly active catalyst for the transformation of 1-hexene [12]. The conversion was quantitative at 350 °C and, as shown in Fig. 4, cracking (ca. 56 %) predominated. Also, this catalyst exhibited a high hydrogenating activity since all the products were saturated hydrocarbons. Unbranched paraffins contributed with ca. 31 %. Furthermore, it gave around 11 % isoparaffins (C5 + C6).

Fig. 5 depicts the catalytic activity in the transformation of 1-hexene of different ZSM-5 catalysts supported with platinum and tin. At 350 °C, the conversion was
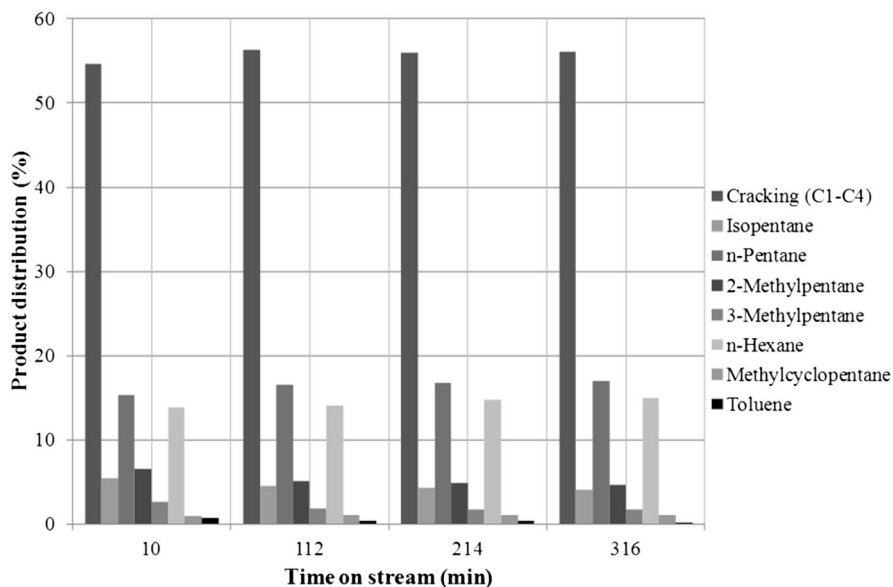
Fig. 4 Catalytic results in the transformation of 1-hexene on Pt (0.3 wt%)/ZSM-5. *Reaction conditions* temperature, 350 °C; 1-hexene mass flow, 2.0 g h^{-1}; W/F, 0.1 h; H$_2$ flow, 60 ml min^{-1}; H$_2$/1-hexene ratio, 6.2
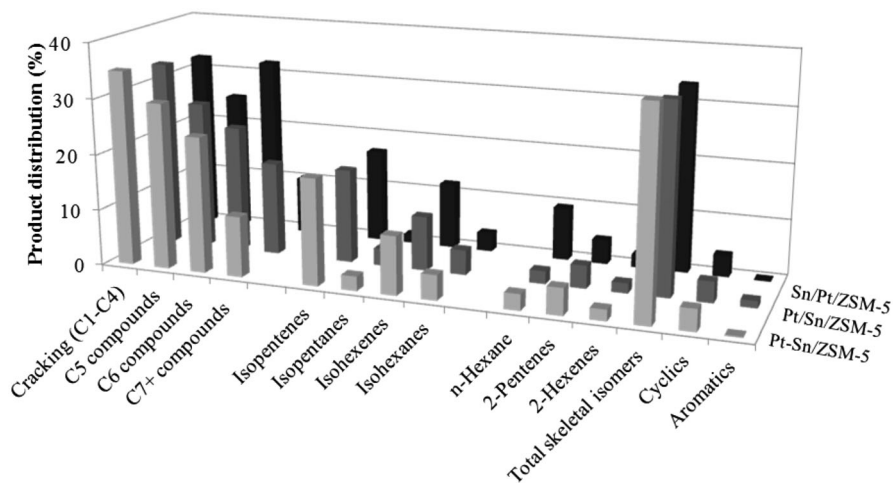

Fig. 5 Catalytic results in the transformation of 1-hexene on ZSM-5 catalysts supported with platinum and tin. *Reaction conditions* temperature, 350 °C; 1-hexene mass flow, 7.32 g h^{-1}; W/F, 0.03 h; H$_2$ flow, 60 ml min^{-1}; H$_2$/1-hexene ratio, 1.7; reaction time, 1 h

almost quantitative and the product distribution was very broad. Clearly, several reactions occurred, such as cracking, double bond shift, skeletal isomerization, hydrogenation, cyclization and aromatization. The three different impregnation

procedures led to similar catalytic results. Cracking was significant with ca. 32–35 % of C1–C4 compounds. The fraction of C5 (25–30 %) and C7+ (ca. 10 %) compounds suggested an important contribution of a dimerization-cracking mechanism [12]. Especially noteworthy was the conversion to skeletal isomers, which amounted to 34–37 %. Isopentenes predominated among the branched hydrocarbons, followed by isohexenes and, in a lower amount, by isopentanes and isohexanes. In this sense, the catalyst of this group with the highest isomerization activity was Pt–Sn/ZSM-5. The yield to C6 branched olefins followed the order: 2-methyl-2-pentene $\approx$ 3-methyl-*trans*-2-pentene > 3-methyl-*cis*-2-pentene > 3-methyl-1-pentene, whereas that of C5 branched olefins was: 2-methyl-2-butene > 2-methyl-1-butene > 3-methyl-1-butene. The formation of 2,3-dimethyl-1-butene was not observed since its formation is restricted on ZSM-5 due to its size [11].

The amounts of hexene isomers and aromatics were low. However, the former were the main reaction products at lower reaction temperatures (Table 2). Thus, at 250 °C, catalyst Pt–Sn/ZSM-5 provided 64.2 % of 2-hexenes and 17.8 % of n-hexane/3-hexenes, while cracking was only 2.2 %. The *cis*-2-hexene to *trans*-2-hexene ratio was 0.42, close to the thermodynamic value, i.e., 0.39, in agreement with the results previously found by other authors [11]. This has been explained by the equilibration that is favored by diffusional limitations in the pores of ZSM-5 (5–6 Å). The double bond shift was lower in Pt/Sn/ZSM-5 with a 51.6 % yield and a *cis* to *trans* ratio of 0.44. Also, the hydrogenating activity of this catalyst seemed to be higher.

Table 2 Catalytic results in the transformation of 1-hexene over Pt/M/ZSM-5 zeolites (M = Sn, Cu, Cr) under hydrogen at 250 °C

	Pt/Sn/ZSM-5	Pt/Cu/ZSM-5	Pt/Cr/ZSM-5
Overall conversion	93.5	94.3	98.5
Product distribution			
Cracking (1 to 4 C atoms)	–	0.5	20.4
n-pentane	–	–	2.5
1-Pentene	–	0.1	0.1
2-Pentenes	–	0.3	0.6
iC5	–	–	2.8
iC5$^=$	–	0.1	3.1
3-Hexenes + *n*-hexane	28.2	28.5	39.4
trans-2-Hexene	35.8	40.2	2.1
cis-2-Hexene	15.8	16.6	0.9
iC6	1.1	0.9	13.8
iC6$^=$	4.5	6.9	7.9
Cyclics (5–6 C atoms)	1.2	0.3	5.7
Aromatics (6–9 C atoms)	0.9	–	1.5
Other C7+ compounds	5.7	–	10.0

Reaction conditions H$_2$ flow, 60 ml min^{-1}, W/F = 0.03 h, H$_2$/1-hexene ratio = 1.7. Data are given after 1 h reaction

When increasing the temperature above 450 °C (Fig. 6), cracking was the major pathway at the expenses of all other reactions.

All catalysts consisting of platinum and copper were also active toward the conversion of 1-hexene at 350 °C (Fig. 7). Sample Pt/Cu/ZSM-5 gave a product distribution that was similar to that of catalysts containing Pt and Sn. Nevertheless, the other two catalysts of this group, Pt-Cu/ZSM-5 and Cu/Pt/ZSM-5 gave C1–C4 compounds in a higher extension (ca. 60 %). Minor amounts of isomerization and hydrogenation products were also detected. Thus, *n*-pentane was present at ca. 8 % yield on catalysts Pt-Cu/ZSM-5 and Cu/Pt/ZSM-5. Unlike the zeolites containing Pt and Sn, the impregnation procedure had a great influence on the performance of these catalysts with Pt and Cu.

Cracking greatly increased at reaction temperatures above 450 °C. For instance, it accounted for ca. 80 % in catalyst Cu/Pt/ZSM-5 at 500 °C. At this temperature, 6.5 % of aromatics were formed, particularly toluene and xylenes. At 250 °C, catalyst Pt/Cu/ZSM-5 gave a similar product distribution (Table 2) to that of catalysts containing Pt and Sn. Indeed, the yield to 2-hexenes was 56.8 % and the *cis* to *trans* ratio of 0.41. However, it resulted in a slightly higher fraction of isohexenes, which accounted for 6.9 %.

As shown in Fig. 8, catalysts Pt–Cr/ZSM-5 and Pt/Cr/ZSM-5 also yielded a significant fraction of cracking (ca. 60 %). In these catalysts, the fraction of skeletal isomers was moderate with ca. 18 %. Sample Cr/Pt/ZSM-5 led to a lower amount of cracking products and a higher proportion of skeletal isomers (ca. 25 %). The presence of Cr in these catalysts favored the formation of paraffins, which were more abundant than olefins among the skeletal isomers.

A comparison of the results obtained in the Pt/ZSM-5 catalyst with those obtained in the catalysts containing Sn, Cu or Cr revealed a higher selectivity to olefins in the latter materials. In fact, no olefins were observed as products over Pt/
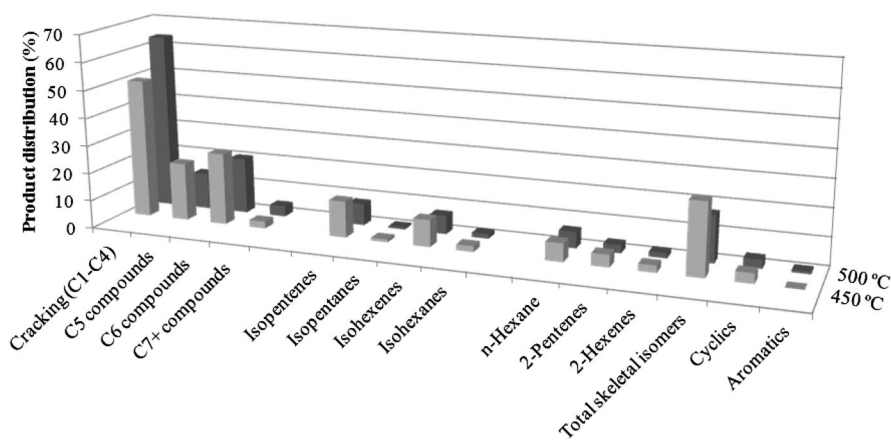

Fig. 6 Catalytic results at 450 and 500 °C in the transformation of 1-hexene on catalyst Sn/Pt/ZSM-5. *Reaction conditions* 1-hexene mass flow, 7.32 g h^{-1}; W/F, 0.03 h; H$_2$ flow, 60 ml min^{-1}; H$_2$/1-hexene ratio, 1.7; reaction time, 1 h
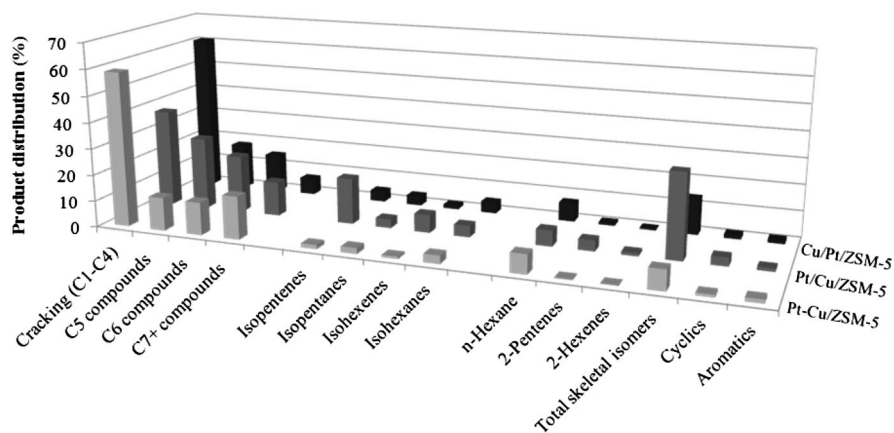
Fig. 7 Catalytic results in the transformation of 1-hexene on ZSM-5 catalysts supported with platinum and copper. *Reaction conditions* temperature, 350 °C; 1-hexene mass flow, 7.32 g h^{-1}; W/F, 0.03 h; H_2 flow, 60 ml min^{-1}; H_2/1-hexene ratio, 1.7; reaction time, 1 h
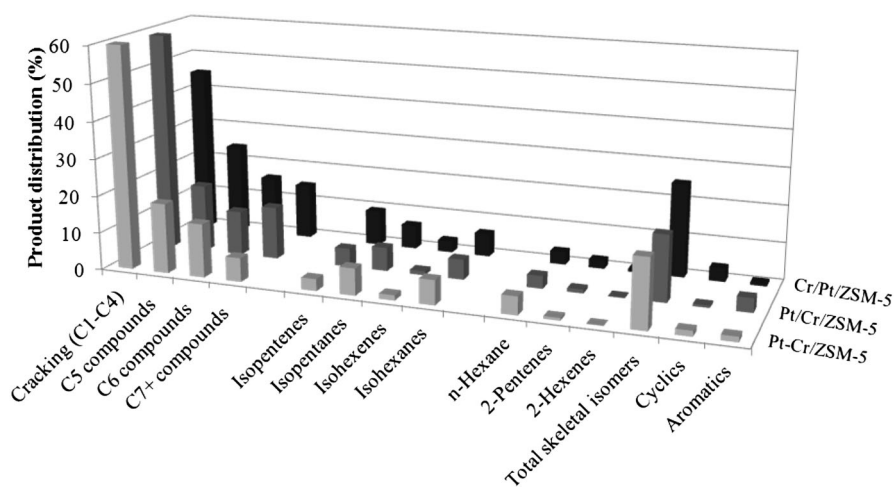

Fig. 8 Catalytic results in the transformation of 1-hexene on ZSM-5 catalysts supported with platinum and chromium. *Reaction conditions* temperature, 350 °C; 1-hexene mass flow, 7.32 g h^{-1}; W/F, 0.03 h; H_2 flow, 60 ml min^{-1}; H_2/1-hexene ratio, 1.7; reaction time, 1 h

ZSM-5 zeolite. Therefore, the addition of these metals decreased the hydrogenating activity of Pt. Consequently, intermediates can undergo isomerization reactions in the pore channels, thus yielding a considerable amount of skeletal isomers at medium temperatures.

Apparently, it is not possible to establish a clear relationship between acidity and catalytic performance. Even the catalysts containing copper, which exhibited the lowest concentration of strong acid sites, gave rise to a significant amount of

Table 3 Catalytic results in the transformation of 1-hexene over Cr/ZSM-5 zeolites under hydrogen (flow, 60 ml min^{-1})

Reaction conditions	Cr(1 wt%)/ZSM-5		Cr(2 wt%)/ZSM-5	ZSM-5
	W/F = 0.1 h, H$_2$/1-hexene ratio = 6.2		W/F = 0.03 h, H$_2$/1-hexene ratio = 1.7	W/F = 0.1 h, H$_2$/1-hexene ratio = 6.2
	T = 250 °C	T = 350 °C	T = 350 °C	T = 350 °C
Overall conversion	87.8	99.1	99.0	97.2
Product distribution				
Cracking (1–4 C atoms)	–	49.0	35.2	38.5
n-Pentane	–	1.0	1.6	0.7
1-Pentene	0.9	0.5	0.4	0.5
2-Pentenes	3.0	3.8	3.4	3.8
*i*C5	–	3.9	3.9	2.3
*i*C5$^=$	–	16.2	15.1	15.3
n-Hexane + 3-hexenes	16.1	1.1	8.5	1.9
trans-2-Hexene	45.3	0.5	0.7	1.9
cis-2-Hexene	19.1	0.4	0.3	0.8
*i*C6	0.3	3.4	4.4	4.0
*i*C6$^=$	2.9	4.2	5.5	15.3
Cyclics (5–6 C atoms)	0.2	3.0	3.0	5.6
Aromatics (6–9 C atoms)	–	1.1	1.5	0.2
Other C7+ compounds	–	10.6	13.9	5.9

Data are given after 2 h reaction

cracking products. Probably, very strong acid sites are not needed to catalyze the variety of reactions involved in the transformation of 1-hexene. In fact, the participation of medium-strength acid sites in the hydroisomerization of *n*-paraffins has previously been recognized [21].

Due to the high activity to cracking of the catalysts containing Cr, two materials consisting of Cr/ZSM-5 with different Cr content were tested under different reaction conditions (Table 3). The catalytic activity at low temperature (250 °C) was dominated by the double bond shift reaction, thus giving 2-hexenes (64.4 %) as major products with a *cis* to *trans* ratio of 0.42. These results were similar to those obtained by some of the Pt supported catalysts previously discussed. Cr species have been shown to play an active role in the oligomerization of olefins [22] and the transformation of methanol to hydrocarbons [20]. In this case, Cr caused an increase in the cracking activity of ZSM-5 zeolite at the expenses of isohexenes.

The catalytic performance in the isomerization of 1-hexene over beta zeolite has been reported using different carrier gases [23]. In this case, the catalyst worked better in nitrogen than in hydrogen, even though the deactivation was faster in the former gas. Accordingly, the catalytic activity of the Pt-M/ZSM-5 catalysts, with M = Sn, Cu and Cr, was also tested under nitrogen as carrier. When the reaction was carried out at 250 °C, conversions were much lower than those carried out

Table 4 Catalytic results in the transformation of 1-hexene over Pt-M/ZSM-5 zeolites (M = Sn, Cu, Cr) under nitrogen at 350 °C

	Pt–Sn/ZSM-5	Pt-Cu/ZSM-5	Pt–Cr/ZSM-5
Overall conversion	94.0	74.3	95.1
Product distribution			
Cracking (1–4 C atoms)	17.8	18.5	24.5
n-Pentane	0.4	0.2	0.7
1-Pentene	0.4	0.4	0.5
2-Pentenes	2.8	2.5	3.3
iC5	1.3	0.9	2.0
iC5$^=$	8.4	7.1	12.2
n-Hexane + 3-hexenes	4.7	2.6	3.7
trans-2-Hexene	10.8	10.6	7.2
cis-2-Hexene	4.8	4.6	3.1
iC6	4.1	2.4	4.0
iC6$^=$	22.3	15.5	16.4
Cyclics (5–6 C atoms)	4.4	2.9	4.1
Aromatics (6–9 C atoms)	1.1	–	1.0
Other C7+ compounds	10.5	1.6	10.5

Reaction conditions N$_2$ flow, 60 ml min^{-1}, W/F = 0.03 h, N$_2$/1-hexene ratio = 1.7. Data are given after 2 h reaction

under hydrogen. For example, Pt-Cu/ZSM-5 gave 17.6 % total conversion, whereas Pt–Cr/ZSM-5 led to 37.4 %, under identical conditions. In both cases, the major products were 2-hexenes. The conversion drastically increased at 350 °C (Table 4). Cracking did not exceed 25 % and the content of aromatics was low. Remarkably, catalyst Pt–Sn/ZSM-5 produced ca. 36 % skeletal isomers and ca. 16 % 2-hexenes. In comparison with the reaction under hydrogen, the yield to cracking compounds was lower and that to 2-hexenes was higher under nitrogen. Indeed, C6 compounds predominated under nitrogen.

Conclusions

1-Hexene can be converted into different hydrocarbons through a great variety of reactions including cracking, hydrogenation, double bond shift, skeletal isomerization, cyclization, aromatization and oligomerization. These reactions were studied on catalysts consisting in ZSM-5 supported with Pt and a second metal, i.e., Sn, Cu or Cr, which were synthesized by three different impregnation procedures. The reaction temperature was decisive and determined the outcome of the whole process. Thus, double bond shift predominated at 250 °C, whereas much more reactions occurred at 350 °C, above all cracking and skeletal isomerization. The major reaction above 450 °C was cracking. Broadly, catalysts with Pt and Sn led to

a higher amount of skeletal isomers than those catalysts composed of Pt and Cu, as well as Pt and Cr. The latter materials usually resulted in an enhanced cracking. In addition, the selectivity to internal and branched olefins can be increased by using nitrogen rather than hydrogen as carrier gas.

References

1. Li D, Li M, Chu Y, Nie H, Shi Y (2003) Catal Today 81:65–73
2. Dry ME (1996) Appl Catal A Gen 138:319–344
3. Dixon JT, Green MJ, Hess FM, Morgan DH (2004) J Organomet Chem 689:3641–3668
4. Van Grieken R, Carrero A, Suarez I, Paredes B (2007) Macromol Symp 259:243–252
5. Słomkiewicz PM (2006) Appl Catal A Gen 301:232–240
6. Pérez-Luna M, Cosultchi A, Toledo-Antonio JA, Díaz-García L (2009) Catal Lett 128:290–296
7. Rao Y, Kang J, Antonelli D (2008) J Am Chem Soc 130:394–395
8. Rao Y, Kang J, Trudeau M, Antonelli DM (2009) J Catal 266:1–8
9. Tanchoux N, Pariente S, Trens P, Fajula F (2009) J Mol Catal A Chem 305:8–15
10. Li M, Chu Y, Nie H, Shi Y, Li D (2002) Stud Surf Sci Catal 145:403–406
11. Abbot J, Corma A, Wojciechowski BW (1985) J Catal 92:398–408
12. Roldán R, Romero FJ, Jiménez-Sanchidrián C, Marinas JM, Gómez JP (2005) Appl Catal A Gen 288:104–115
13. Coleto I, Roldán R, Jiménez-Sanchidrián C, Gómez JP, Romero-Salguero FJ (2007) Fuel 86:1000–1007
14. Coleto I, Roldán R, Jiménez-Sanchidrián C, Gómez JP, Romero-Salguero FJ (2010) Catal Today 149:275–280
15. Li YN, Liu SL, Zhang ZK, Xie SJ, Zhu XX, Xu LY (2008) Appl Catal A Gen 338:100–113
16. Zhang L, Liu H, Li X, Xie S, Wang Y, Xin W, Li S, Xu L (2010) Fuel Process Technol 91:449–455
17. Li X, Liu S, Zhu X, Wang Y, Xie S, Xin W, Zhang L, Xu L (2011) Catal Lett 141:1498–1505
18. Yin C, Zhao R, Liu C (2005) Fuel 84:701–706
19. Shi G, Shen J (2009) Energy Fuels 23:320–326
20. Esquivel D, Cruz-Cabeza AJ, Jiménez-Sanchidrián C, Romero-Salguero FJ (2013) Micropor Mesopor Mater 179:30–39
21. Jiménez C, Romero FJ, Roldán R, Marinas JM, Gómez JP (2003) Appl Catal A Gen 249:175–185
22. Van Grieken R, Escola JM, Moreno J, Rodríguez R (2009) Chem Eng J 155:442–450
23. Modhera B, Chakraborty M, Parikh PA, Bajaj HC (2009) Catal Lett 132:168–173