Journal of Catalysis **184,** 19–28 (1999)
Article ID jcat.1999.2421, available online at http://www.idealibrary.com on IDEAL®

Influence of Acidity–Basicity in ^{13}C-Labeled Hexane Isomerization Reactions on Exchanged Pt-β Zeolite: Mechanistic Studies

Stéphane Siffert,* Jean-Louis Schmitt,* Jean Sommer,† and François Garin*,[1]

*Laboratoire d'Etudes de la Réactivité Catalytique, des Surfaces et Interfaces, UMR 7515 du CNRS, EPCM, Université Louis Pasteur,
25, rue Becquerel, F-67087 Strasbourg Cedex 2, France; and †Laboratoire de Physico-Chimie des Hydrocarbures,
Université Louis Pasteur, Institut Le Bel, 4 Rue Blaise Pascal, F-67070, Strasbourg cedex, France

Received March 30, 1998; revised June 15, 1998; accepted January 12, 1999

The acidity–basicity effect on the catalytic behavior of exchanged Pt-β zeolites in hexane reforming reactions has shown: (i) from X-ray photoelectron spectroscopy, that the platinum binding energy decreases when the basicity increases (therefore there is an electronic shift from zeolite to Pt particles which increases with basicity); (ii) at low hydrogen pressure ($P_{H_2} = 226$ or 38 Torr), the apparent activation energy for the 2MP reaction increases when the basicity of the zeolite increases; (iii) the ring enlargement reaction of methylcyclopentane to cyclohexane and benzene is increased when Brønsted acidity is increased; (iv) with acyclic molecules as 2-methylpentane and 4-methyl 1-pentene and *n*-hexane, the isomerization selectivity is high when the acidity is high but decreases when the basicity increases; (v) from the use of ^{13}C-labeled molecules, no cyclic mechanism was detected but only bond shifts, for which the ethyl bond shift predominates on the acidic catalyst and the methyl bond shifts on the basic catalyst. The combination of these experimental points with kinetic data suggests that the hydrocarbon rearranges at the metal–support interface and that electron donor or electron acceptor effects due to the acidity–basicity of the zeolite lead to changes of the reaction mechanism pathway. © 1999 Academic Press

Key Words: **acidity; basicity; Na$^+$ and Cs$^+$ exchanged Pt-β zeolites; ^{13}C-labeled hexanes; reforming reactions.**

INTRODUCTION

Zeolite beta, a large pore 12 MR zeolite with a three-dimensional system of channels (1), has been shown to be a very active catalyst for an important number of hydrocarbon reactions involving carbocation intermediates. Many patents (2, 3) and publications about the cracking of alkanes (4–6), the isomerization of *m*-xylene (7, 8) and dihalobenzene (9), and the alkylation of aromatics (10) describe the use of zeolite β. Moreover, zeolite β is often combined with supported platinum particles to obtain a bifunctional behavior for hydrocarbon isomerization (11–13). In this latter case, Pt particles are only assumed to have a dehydrogenation and hydrogenation function and the isomerization will occur on the acidic sites of the zeolite via carbenium ions. Therefore, according to Weisz (14), an alkane would be first dehydrogenated on a metallic site to give an alkene, and, after diffusion of this unsaturated species to an acidic site on the support, the generated carbenium will undergo rearrangement or cracking by β-scission (15).

Moreover, there is always a close connection between acidic and basic sites. The exchanged cations and the oxygens of the zeolite framework are actually acid–base pairs (16) and the more electropositive the cations are, the higher the basicity of the zeolite is. It was shown that the activity of platinum in the hydrogenation of benzene is strongly influenced by the basic character of the zeolite support (17). De Mallmann and Barthomeuf also demonstrated the existence of Pt–CO complexes similar to "Pt Chini" complexes, known to exist in basic media, with PtNaY and PtCsNaY (18) and, by the use of benzene and ethylbenzene adsorption, the high basicity of oxygen of Na and Csβ zeolites (18′).

Therefore, we have studied the dual effect of acidity and basicity of the support in the isomerization of hexanes on Pt–zeolite β, in which the protons H$^+$ are exchanged against Na$^+$ and Cs$^+$ ions, using ^{13}C-labeled hexanes and kinetic data. Moreover, in this paper, in the light of results obtained by using various linear and branched hexane and hexene and cyclic molecules, we have suggested a relationship between the acido-basic properties of the zeolite and some reaction mechanisms.

METHODS

Treatment

The system Pt–Naβ (Csβ) was obtained by exchanging the commercial $H_{1.2}Na_{3.7}(AlO_2)_{4.9}(SiO_2)_{59.2}$ zeolite purchased from P.Q. Corporation first with a solution of NaCl (CsCl) and then with a solution of $Pt(NH_3)_4Cl_2$ (10^{-2} M),

---

[1] To whom correspondence should be addressed. Fax: (33) 03 88 13 6968. E-mail: garin@chimie.u-strasbg.fr.

0021-9517/99 $30.00

TABLE 1

Chemical Elementary Analysis

Catalyst	% Pt	% Na	% Cs	Approximate Si/Al
Pt–Hβ	2.9	<200 ppm	0	10.5
Pt–Naβ	4.7	0.2	0	10.5
Pt–Csβ	3.9	<200 ppm	3.8	15.5

as described for Pt-faujasites (17). The most acidic system used, Pt-Hβ, was simply exchanged with the solution of $Pt(NH_3)_4Cl_2$. The solid was heated at 90°C for 3 h and then kept at room temperature overnight. The exchanged zeolite was washed until no Cl^- was detectable (with $AgNO_3$) and then dried at 80°C overnight.

The basicity should increase from Pt–Hβ to Pt–Naβ and to Pt–Csβ because of the increasing electropositivity of the cations.

The chemical elementary analysis (Table 1) shows that the prepared catalysts are composed of 2.9 up to 4.7 wt% of platinum for respectively the acidic system to the sodium exchanged catalyst. There is less than 200 ppm of Na^+ in the protonated catalyst and the Si/Al ratio varies from 10.5 to 15.5, indicating some extraframework alumina.

From these analyses given in Table 1, the M/Al ratios are equal to 0.08 when $M = \text{Na}$ and 0.32 when $M = \text{Cs}$. Therefore, the basic character increases only from 0 to 8% and to 32%, respectively, on Pt–Hβ, Pt–Naβ, and Pt–Csβ.

Catalytic Reaction Procedure

Following the procedure of de Mallmann and Barthomeuf (17), an aliquot of 50 mg of each catalyst is first calcined *in situ* in O_2 with a flow rate of 88 ml/min for 5 h at 320°C (heating rate, 5°C/min) and, after purging with Ar (88 ml/min, 320°C) for 0.5 h, reduced under H_2 (40 ml/min) for 15 h at 320°C.

The catalytic experiments are performed in a plug flow reactor and consecutive pulses of 5 to 15 μl of hydrocarbon are injected in the carrier gas (hydrogen in our case). The partial pressure of the hydrocarbon is kept constant during the experiments. Catharometers are used to follow the hydrocarbon flow through the catalyst. Rectangular pulses are observed and recorded; their lengths corresponding to the hydrocarbon flow. The duration of the catalytic experiments are between 5 and 20 min each. Several experiments are performed on the same catalyst during about 1 week. During the hydrocarbon flow through the catalyst, the steady state conditions are obtained on the "plateau" of the rectangular pulse. Moreover, there is actually almost no deactivation observed: the last pulse was done under the same conditions as the first one and the activity and selectivity of the catalyst never vary significantly. We have also checked very carefully that the reactions are not controlled by diffusion (19). On the other hand, we have not observed any scrambling of the ^{13}C in the labeled products which means that diffusion should not be rate limiting in the process.

IR experiments show that the Pt complex is decomposed and that metallic Pt is obtained under these conditions of treatment at the end of this process. In order to perform kinetic measurements, the catalytic experiments were performed under different partial pressures: (i) of various hydrocarbons: 2-methylpentane (2MP), 4-methyl 1-pentene (4M1P), methylcyclopentane (MCP), and *n*-hexane (nC6); (ii) of hydrogen (using H_2 mixed with He) and, (iii) at different temperatures (160–230°C). The products (cracking, isomers, and cyclic) are measured quantitatively by a VARIAN 3300–3700 gas chromatograph equipped with a FID detector and a megabore Chrompack CP-SIL-5CB column, or for studies performed with ^{13}C-labeled molecules, by the use of a FISONS GC 8000 gas chromatograph with the same kind of column as above coupled with a quadripolar FISONS MD 800 mass spectrometer.

RESULTS AND DISCUSSION

In the first part of this section, we will briefly discuss the results obtained with diverse catalyst characterization techniques. As will be seen in the second part, the characteristics of the catalysts are of major importance in the catalytic behavior.

A. Catalyst Characterization

Infrared analysis of the catalyst was performed on a BRUKER IFS 66 V to follow the calcination and reduction steps of each catalyst. We checked that the chloro–amino complex of platinum was completely decomposed at 320°C for each catalyst as shown in Fig. 1 for Pt–Naβ.

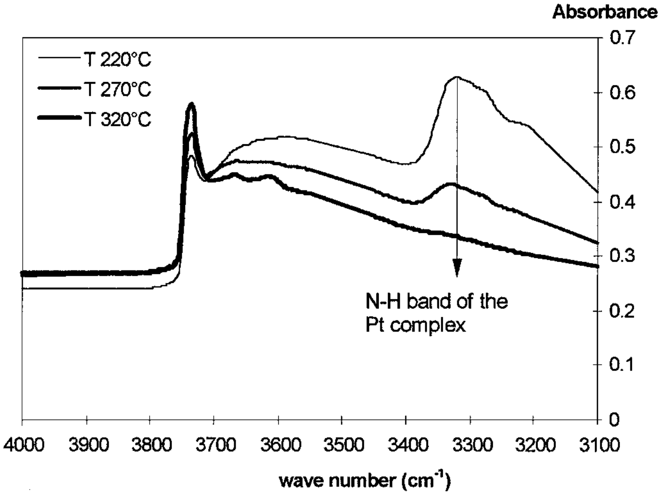


FIG. 1. Infrared analysis of the calcination (Pt–Naβ).

The Pt particle size measurement was performed by TEM using a TOPCON EM002B apparatus with a resolution of about 2 Å. The mean metallic surface particle size was determined to be about 13.7 to 32.5 Å for the acidic system to the cesium exchanged zeolite (Table 2). These measures are deduced from the histograms reported in Fig. 2 which show the appearance of large particles on the more basic catalyst.

TABLE 2

TEM and Hydrogen Chemisorption Results

Catalyst	% Pt	Dispersion D (%)	Diameter d_s (Å)^a by H chemisorption	Diameter d_s (Å)^a by TEM
Pt–Hβ	2.9	92.4	11.7	13.7
Pt–Naβ	4.7	88.6	12.4	18.0
Pt–Csβ	3.9	38.8	27.6	32.5

^{a}10 Å = 1 nm.

The chemisorption of H_2, determined on a X-SORB apparatus, confirmed the presence of well dispersed platinum particles with a dispersion of about 90% for the more acidic catalysts and of only about 40% for the more basic one. Surface particle size is deduced from the hypothesis that one platinum atom chemisorbs one hydrogen atom in our standard conditions and that platinum particles are spherical with a surface composed of an equipartition of (111), (100), and (110) planes. The mean diameter d_s is equal to 11.7 Å for the more acidic catalyst up to 27.6 Å for the Cs exchanged system (Table 2). The difference between the

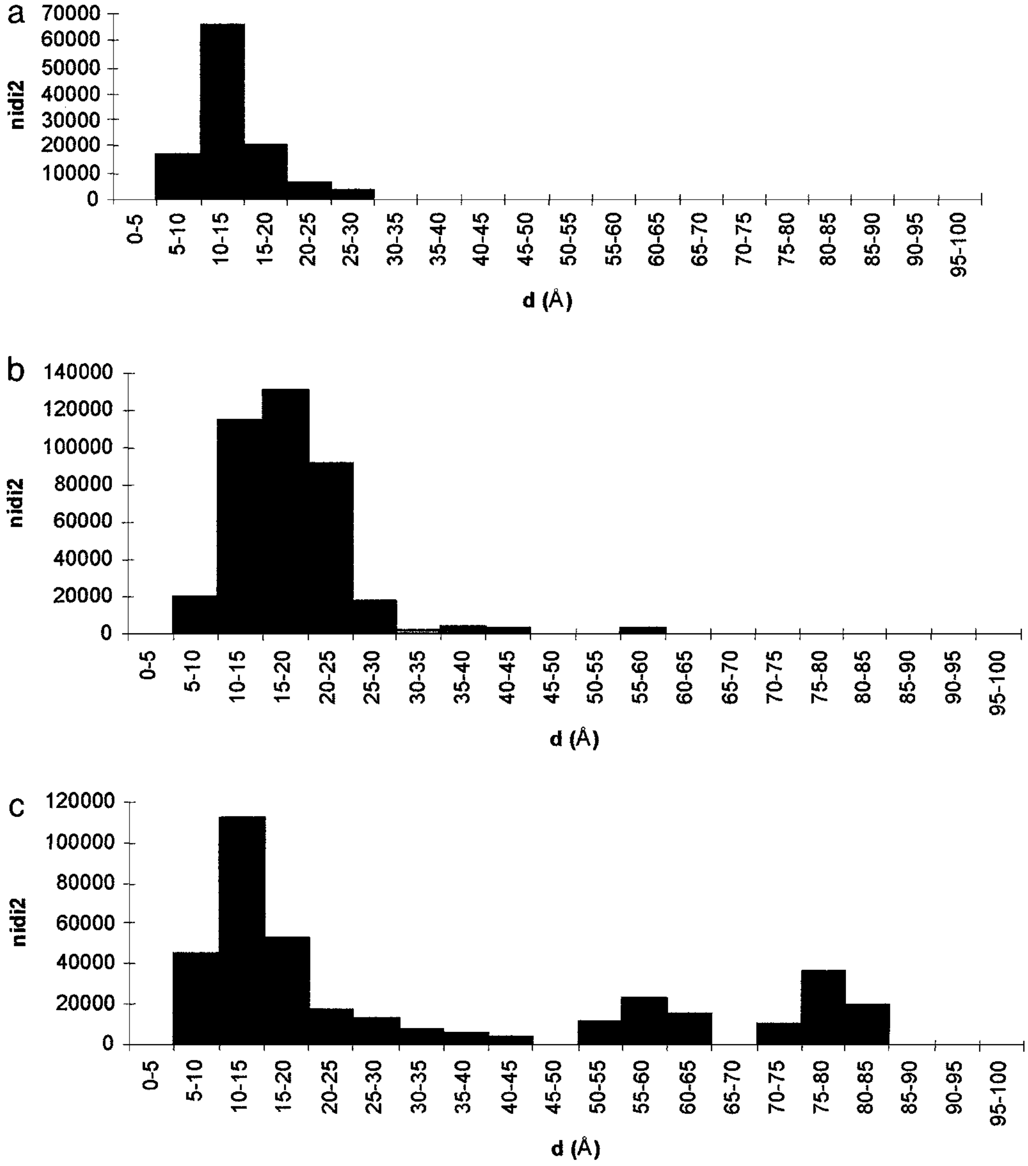


FIG. 2. Particle size distribution of Pt, $n_i d_i^2 = f(d_Å)$: (a) for Pt–Hβ, (b) for Pt–Naβ, (c) for Pt–Csβ.

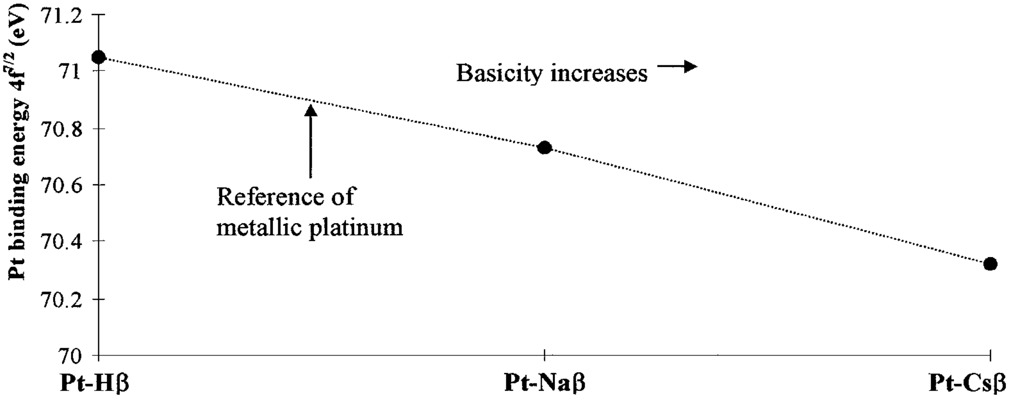


FIG. 3. Pt binding energy ($4f_{7/2}$ electrons) versus the catalytic system.

measurements of the particle diameters obtained from TEM and hydrogen chemisorption may be due to some smaller Pt particles inside the zeolite framework which are accessible for hydrogen chemisorption but are not seen by TEM.

Each activated catalytic system was analyzed by XPS, on a VG ESCA 3 instrument, to measure the electronic shift of the Pt $4f_{7/2}$ peaks due to the acidity–basicity of the support. From the XPS results, we conclude that there is an electronic shift from the zeolite framework to the Pt particles which increases when increasing basicity (Fig. 3).

B. Catalytic Results

Numerous studies have shown that the catalytic characteristics of a zeolite-supported transition metal often differ significantly from those of the same metal on an amorphous support. These differences are attributed either to the metal particle morphology or to some chemical interaction between metal and support.

To obtain information about the influence of the support in alkane reforming reactions, our experiments were performed in a temperature range where platinum metallic particles are not able to break carbon–carbon bonds (21). We tried to separate the influences of the metal and the support on the reactants; which situation may give information about the nature of the initial step in alkane activation, still under discussion. The following questions will be addressed:

1. Is the catalytic activity dependent on the structure of the hydrocarbon? With the aid of the results of the catalyst characterization, we can calculate the rates as turn over frequencies (20). We expressed the catalytic activity in μmol/g · h and also in “TOF” to see if the C–H bond rupture occurring on platinum aggregates is the slow reaction step. If the same tendencies are obtained for both activities expressed in μmol/g · h and in TOF, then the support only plays a role in the rate determining step. In Fig. 4, the same evolutions, versus the catalysts used, are observed for methylcyclopentane and 4-methyl-1 pentene as reactants; both of which belong to the C_nH_{2n} family. For alkanes, *n*-hexane and 2-methyl pentane, however, this is not true, and both metal and support may participate in the slow step of the reaction. With C_nH_{2n+2} as reactants the existing mechanisms greatly depend upon the size of the metal particles and the metal–support interface.

It turns out, as presented in Fig. 4, that:

—even at 160°C, we observe a catalytic activity which cannot be ascribed to platinum alone, because Pt is unable to induce a carbon–carbon bond rupture at this temperature (21, 21′);

—the more acid the system, the larger the difference in activity between cyclic, linear, branched alkane and alkene reactants;

—on the basic catalyst, whatever the structure of the reactant used, its activity is similar for all;

—on the acidic catalyst, methylcyclopentane is the least reactive molecule (This result is opposite to that of Pt supported on neutral alumina) (21);

—surprisingly, on the more acidic catalyst, 2MP and 4M1P react at about the same rate, but on Pt–Naβ, 4M1P reacts three times faster than 2MP;

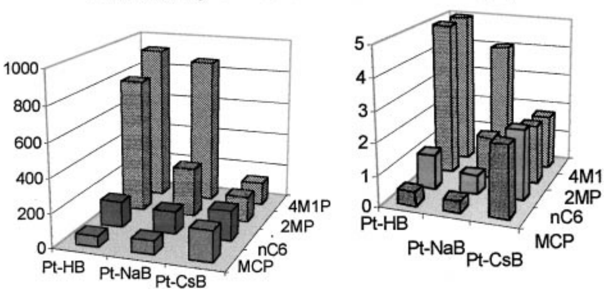


FIG. 4. Total activity of the catalysts for the hydrocarbon reactant molecules (160°C, $P_{HC} = 6 \pm 2$ Torr* and $P_{H_2} = 754 \pm 2$ Torr* (*1 Torr = 133 Pa).

TABLE 3

Hydrocracking Selectivity at 160°C for 2MP

	Demethylation	Deethylation	Depropylation
Pt on neutral alumina	3	1	1
Pt–Hβ	0 (1.5[a])	2.5 (1.9[a])	2.5 (1.5[a])
Pt–Naβ	0.9	2.5	1.6
Pt–Csβ	0.8	2.4	1.7

[a] Results at 200°C.

—on the basic catalyst, linear and cyclic molecules have a higher activity than the branched alkane and alkene;

—the reactivity of the cyclic molecule increases from acidic to basic catalyst;

—from acidic to basic catalyst, two types of variation of the TOF activity can be observed.

- for nC6 and 2MP an hyperbolic variation occurs,
- for MCP and 4M1P, respectively, a gradual increase or decrease takes place.

Moreover, whatever the catalyst used, the reaction rate increases when: (i) the temperature increases, or (ii) the partial pressure of hydrocarbon increases, or (iii) the partial pressure of hydrogen decreases (Tables 4–6). Therefore, there is an inhibiting effect of hydrogen which is tentatively explained in Ref. (19).

These results show that activity is dependent on the structure of the reactant. This point clearly confirms that the intrinsic platinum property is modified by the support. When amorphous supports are used we do not observe such differences in the activity of alkane and alkene (21). Only a higher activity is noticed with methylcyclopentane, which is a reaction intermediate (21).

2. What about the selectivity of these catalysts? With acyclic molecules, we always obtain a statistical bond rupture for the carbon–carbon bond on platinum catalysts supported on neutral alumina (21). On the other hand, the hydrocracking selectivity for these catalysts is different as shown in Table 3.

On the zeolite-supported catalysts the cracking process is different from the one obtained with a platinum catalyst supported on neutral alumina. Deethylation and depropylation reactions are favored over the demethylation reaction. This result is typical for an acid-catalyzed reaction in which the C–C bond rupture can be rationalized by the formation of secondary and tertiary carbenium intermediates (22, 23). These electrophilic entities, which are adsorbed as alkoxy species on the surface according to Kazansky *et al.* (24) explain the deethylation reaction. In Scheme 1, the positive charge appearing on oxygen is a representation which can be found in many papers on mechanistic aspects of acidic zeolite-catalysed reactions since Haag 's paper on protolytic activation of alkanes (25–27). In this scheme, the activation step relies on the concept of σ-basicity as proposed by Olah (22). In fact, this is only a schematic description borrowed from organic chemists (a trivalent oxygen having a positive charge) but does of course not describe correctly the real charge delocalization. For this reason most often a mesomeric form is used in which the positive charge does not appear on oxygen.

TABLE 4

Apparent Activation Energies for the 2MP Isomerization Reaction

		Ea (kcal/mol)		
P_{2MP} (Torr)	P_{H_2} (Torr)	Pt–Hβ	Pt–Naβ	Pt–Csβ
0.8	748 ± 11	17 ± 2	17 ± 2	16 ± 2
6.3	748 ± 11	25 ± 2	27 ± 2	25 ± 2
6.3	226 ± 11	17 ± 2	26 ± 2	29 ± 2
6.3	38 ± 11	14 ± 2	26 ± 2	31 ± 2
22.4	748 ± 11	24 ± 2	25 ± 2	21 ± 2

According to the results obtained above, the metallic part of the catalyst has to be involved as well (Scheme 1). This reaction pathway reinforces the proposed presence of the adduct $[Pt–H]^+$ on the surface of the catalyst (28, 29). The adduct could be formed either from dissociative hydrogen chemisorption or from the [OH] of the support.

With cyclic molecules, the approach is different. As was shown earlier, for alumina-supported platinum catalysts (21), methylcyclopentane is the reaction intermediate in the cyclic mechanism of alkane isomerization. It means that methylcyclopentane, at low conversion may react faster than the acyclic molecules which are formed from its ring opening. It is obvious that methylcyclopentane is no longer a reaction intermediate on these three catalysts because this cyclic molecule is not formed and is less reactive than the acyclic molecules. Moreover, on these catalysts, we have a competition between the ring opening reaction and the ring enlargement reaction (Scheme 2), which latter reaction never occurs on a neutral alumina- supported platinum catalyst. Such results were already observed by Sachtler and coworkers (30, 31), who compared nonacidic and bifunctional Pd/Y zeolites [32].

The results obtained point to a very high selectivity for ring enlargement on the more acidic catalyst (Pt–Hβ) and to a zero selectivity for the more basic system (Pt–Csβ) (Fig. 5). Therefore, the ring enlargement of MCP could be a reaction test for measuring the acidity of a catalyst via consecutive hydride shift and ring enlargement via protonated cyclopropane (23, 28, 30, 31).

According to Chow *et al.* (32), the hydrogenolysis would be due only to the platinum, although it is possible to produce the above products in low quantities by β-scission (33), whereas the ring enlargement actually depends on the Brønsted acidity of the catalyst (29, 34, 35). The products, cyclohexane and benzene, would stop the access of

TABLE 5

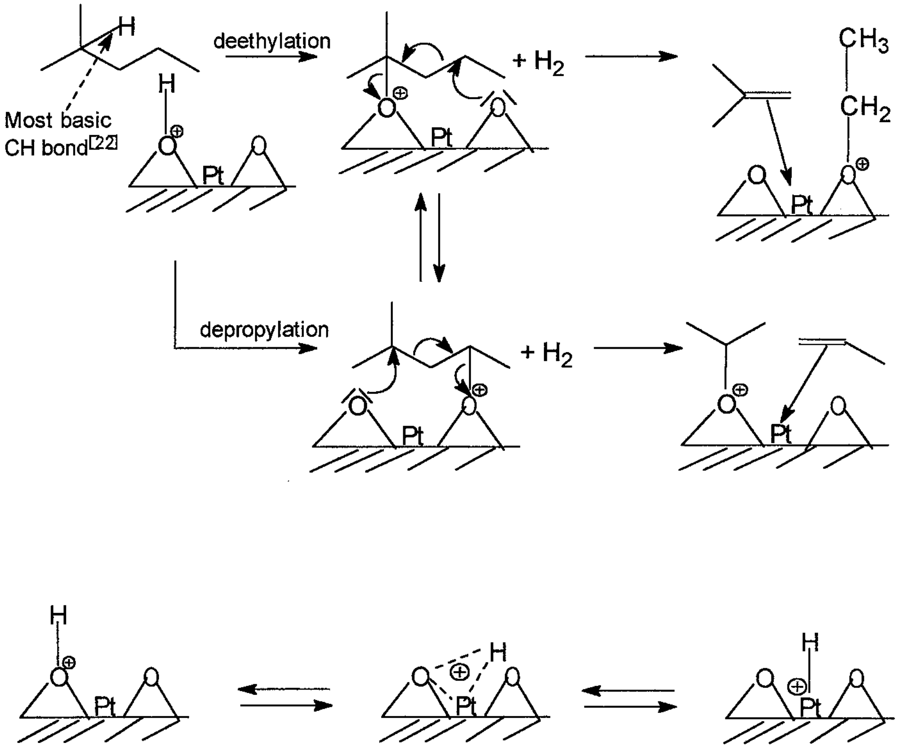
Reaction Orders for 2MP and Hydrogen (2MP Reaction)

	Order/2MP			Order/H_2		
T (°C)	Pt–Hβ	Pt–Naβ	Pt–Csβ	Pt–Hβ	Pt–Naβ	Pt–Csβ
160	0.6 ± 0.1	0.7 ± 0.1	0.2 ± 0.1	−0.3 ± 0.1	−0.2 ± 0.1	−0.2 ± 0.1
180	0.6 ± 0.1	0.7 ± 0.1	0.3 ± 0.1	−0.2 ± 0.1	−0.4 ± 0.1	−0.4 ± 0.1
200	0.7 ± 0.1	0.5 ± 0.1	0.3 ± 0.1	0 ± 0.1	0 ± 0.1	−0.4 ± 0.1

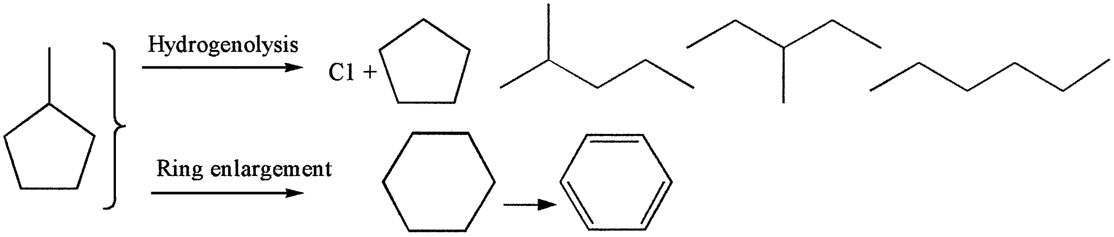
TABLE 6

Reaction Orders for MCP and Hydrogen (MCP Reaction)

	Order/MCP			Order/H_2		
T (°C)	Pt–Hβ	Pt–Naβ	Pt–Csβ	Pt–Hβ	Pt–Naβ	Pt–Csβ
160	0.3 ± 0.1	0.4 ± 0.1	0.2 ± 0.1	−0.5 ± 0.1	−0.2 ± 0.1	0.3 ± 0.1
180	0.3 ± 0.1	0.1 ± 0.1	0.3 ± 0.1	−0.4 ± 0.1	−0.2 ± 0.1	0.4 ± 0.1
200	0.2 ± 0.1	0.2 ± 0.1	0.2 ± 0.1	−0.4 ± 0.1	−0.1 ± 0.1	0.4 ± 0.1



SCHEME 1. Mechanism of deethylation and depropylation.



SCHEME 2. Reaction products from methylcyclopentane.

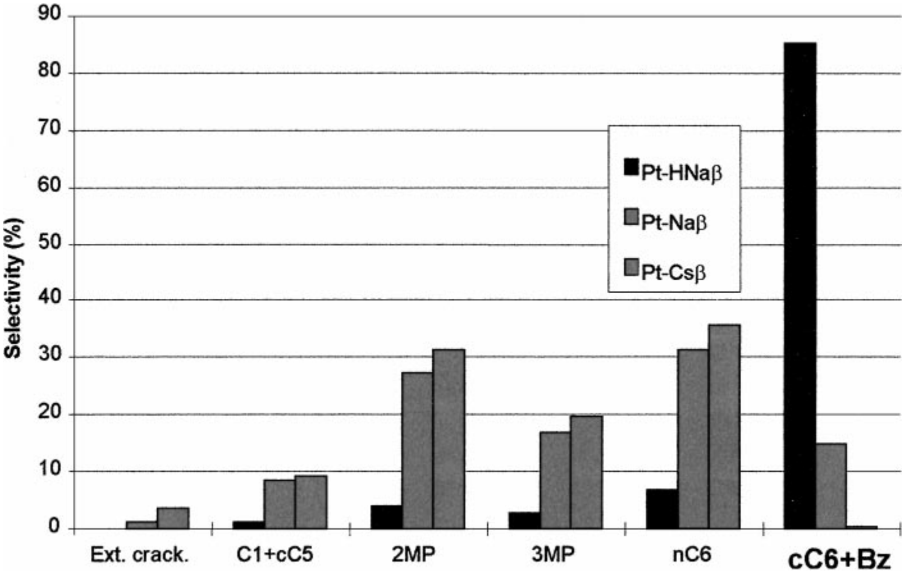


FIG. 5. Selectivities from MCP reaction (180°C, $P_{MCP} = 3.7$ Torr, $P_{H_2} = 756$ Torr) on Pt–Hβ, Pt–Naβ, and Pt–Csβ.

MCP to the metallic sites responsible for the hydrogenolysis (29).

The most intriguing point about the reactions with 2-methylpentane, 4-methyl-1-pentene, and *n*-hexane is the selectivity for isomerization. The isomerization selectivity is high when the acidity is important and decreases when the basicity increases (Fig. 6).

3. Kinetic parameters (orders and Ea). Apparent activation energies Ea and reaction orders for the reactions of 2-methylpentane (2MP) and methylcyclopentane (MCP) were obtained versus temperature and hydrocarbon and hydrogen pressures (Tables 4, 5, and 6). Only the apparent activation energy values (Ea) obtained for the isomerization reaction were considered, because only in that case, by the use of labeled compounds, can we say that they are related to the Bond Shift reactions (39).

The apparent activation energy values for the isomerization of 2MP are given in Table 4. The values are similar for all three catalysts except at low hydrogen pressure ($P_{H_2} = 226$ or 38 Torr), where the apparent activation energy values increase with increasing basicity. These results are in good agreement with those of Corma *et al.* (36) and Li Quin *et al.* (37). They observed that an increase in acidity resulted in an increase of activity and a decrease in apparent activation energy. Therefore, the exothermicity of the adsorption of the hydrocarbon species should decrease when the basicity increases.

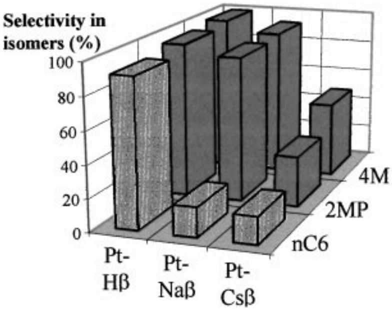


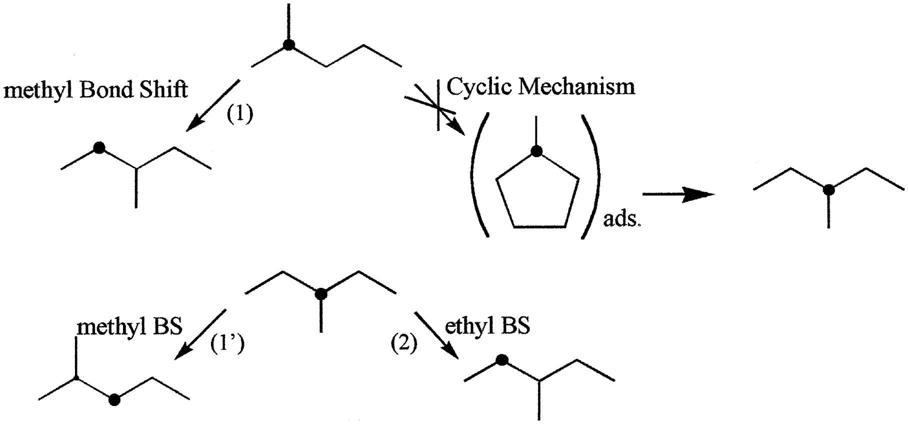
FIG. 6. Selectivity for isomerization of nC6, 2MP, and 4M1P (180°C, $P_{HC} = 6$ Torr, $P_{H_2} = 754$ Torr).

As far as the apparent activation energy values for the MCP hydrogenolysis and the MCP ring enlargement are concerned, it is difficult to draw conclusions due to the erratic results. If we analyze the average values of the apparent activation energies for hydrogenolysis and for ring enlargement, these mean values seem to be substantially higher for the ring enlargement (∼27 kcal/mol) than for hydrogenolysis (∼17 kcal/mol).

The reaction orders of the $2MP + H_2$ reaction are given in Table 5.

The orders versus hydrocarbon pressure (2MP) are always positive. They are higher (0.6 ± 0.2) for the more acidic catalysts (Pt–Hβ and Pt–Naβ) and lower for the Cs exchanged system (0.3 ± 0.1). The orders versus hydrogen pressure are negative or zero for all three catalysts, the average value being: -0.2 ± 0.2.

For the reaction orders of the $MCP + H_2$ reaction (Table 6), one can say that the orders versus MCP are always positive for all three catalysts (0.2 ± 0.2). However, the reaction orders versus hydrogen increase from a negative value (-0.4 ± 0.1) for the protonated catalyst and for the sodium exchanged system (-0.2 ± 0.1) to a positive value ($+0.4 \pm 0.1$) for the more basic system. The negative order versus hydrogen for the MCP reaction on acidic catalyst and positive on basic catalyst can be rationalized



SCHEME 3. Reactions of 2-methyl-[2-^{13}C]pentane and 3-methyl-[3-^{13}C]pentane.

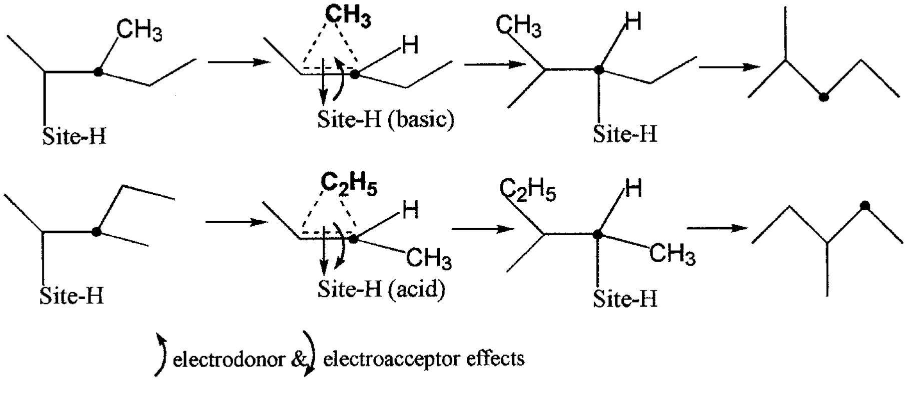
by the presence of ring enlargement on the former catalyst, while on the basic one, only ring opening occurs.

The use of the relative contributions of the labeled products obtained from studies performed with ^{13}C-labeled molecules allows us to find out which reaction mechanisms may dominate on these catalysts.

Starting with 2-methyl-[2-^{13}C]pentane, if the two isomerization reactions (bond shift (BS) and cyclic mechanism (CM)) take place, then we may expect, the formation of 3-methyl-[2-^{13}C]pentane, and 3-methyl-[3-^{13}C]pentane, respectively (38). Only the former product is found. Apparently the cyclic mechanism does not take place. With 3-methyl-[3-^{13}C]pentane as reactant only BS occurs and we obtained 2-methyl-[3-^{13}C]pentane and 3-methyl-[2-^{13}C]pentane (Scheme 3). The very small amount of *n*-hexane formed does not allow us to study the whole labeled distribution of the isotopes (39).

These carbon-13 experiments, which were performed under the same conditions as the reactions with nonlabeled molecules, indicate that there are only intramolecular isomerization reactions, because no doubly labeled products are formed. Therefore, there are only monomolecular reactions under our experimental conditions. Furthermore, there is no scrambling of the ^{13}C in the products or in the reactants on the Pt–Hβ and Pt–Naβ catalysts, and there is no cyclic mechanism but only alkyl bond shifts and there is rather: (i) ethyl bond shift on the acidic catalyst (path 2) and (ii) methyl bond shift when the basicity increases (paths 1 and 1′) as noticed in Table 7.

Such a result can be explained with cyclopropanic intermediates and by the use of the results obtained by XPS. The adsorbed intermediate would involve a comparable cyclopropane (40) (Scheme 4), and the localization of the rearrangement of the hydrocarbon would be at the metal–zeolitic support interface (39). As the acidic catalyst would imply an electron acceptor effect, the shifted ethyl group stabilizes the three center intermediate species more by an inductive effect than the leaving methyl group. It was indeed shown earlier (41) that the ethyl shift is seven times faster than the methyl shift on a superacidic catalyst. Therefore, the ethyl bond shift would be favored on the more acidic catalyst. On the other hand, the more basic catalyst would have an electron donor effect and then the substituent effect should be in the opposite direction. Therefore, the methyl



SCHEME 4. Interpretation of the alkyl bond shift mechanisms: electron donor and electron acceptor effects.

TABLE 7

Ratio of the Relative Contribution of the Ethyl Bond Shift on the Methyl Bond Shift

Catalyst	Pt–Hβ	Pt–Naβ	Pt–Csβ
Ethyl BS/methyl BS	**2.1**	**0.7**	Same tendency as for Pt–Naβ but too much erratic (some scrambling)

bond shift is favored on the more basic catalysts. Actually, even on the basic catalyst, there would be some protons coming from the reduction of the metallic phase of the catalyst and these protons would imply primary formation of protonated cyclopropane. In fact, the reduction of Pt^{2+} with hydrogen leads to the formation of metallic platinum plus some protons: $Pt^{2+} + H_2 \rightarrow Pt^0 + 2H^+$.

CONCLUSION

The acidity–basicity effect on the catalytic behavior of exchanged Pt–β zeolites is important and can be summarized by the following conclusions:

—From X-ray photoelectron spectroscopy, we noticed that the platinum binding energy decreases when the basicity increases. Therefore there is an electronic shift from zeolite to Pt particles which increases with basicity.

—At low hydrogen pressure ($P_{H_2} = 226$ or 38 Torr), the apparent activation energy for the 2MP reaction increases when the basicity of the zeolite increases. Therefore, the enthalpy of adsorption for the hydrocarbon species would decrease when the basicity increases.

—The ring enlargement reaction of methylcyclopentane to cyclohexane and benzene is increased when Brønsted acidity is increased.

—With acyclic molecules as 2-methylpentane and 4-methyl 1-pentene and *n*-hexane, the isomerization selectivity is high when the acidity is high but decreases when the basicity increases.

—The relative contributions of the cyclic and alkyl bond shift mechanisms were obtained from the study of the reaction of 2-methyl-[2-^{13}C]pentane and of 3-methyl-[3-^{13}C]pentane. No cyclic mechanism occurs but only bond shifts, for which the ethyl bond shift predominates on the acidic catalyst and the methyl bond shift on the basic catalyst.

Finally, we noticed that the order versus hydrogen for MCP reaction is negative on the acidic catalyst and positive on the basic catalyst. This result can be due either to a change of hydrogen coverage or to a change of the rate determining step from acidic to basic catalyst. These results indicate that platinum, even at 4 wt%, has lost its intrinsic behavior.

The combination of these experimental points with kinetic data suggest that the hydrocarbon rearranges at the metal–support interface and that electron donor or electron acceptor effects due to the acidity–basicity of the zeolite lead to changes of the reaction mechanism pathway.

However, although the acidity–basicity of the zeolite is important for catalysis, the metal is also active. It stops the deactivation, rehydrogenates the adsorbed hydrocarbon, and leads to simple cracking (C1=C5 and C2=C4) (38) and to the hydrogenolysis of methylcyclopentane.

ACKNOWLEDGMENTS

We thank Marguerite Briend and Pascale Massiani (Laboratoire de Réactivité de Surface, Paris VI) for IR analyses.

REFERENCES

1. Treacy, M. M. J., and Newsam, J. M., *Nature* **332**, 249 (1988).
2. Tobias, M. A., U.S. patent 3 728 408 (1973).
3. Young, L. B., European patent application 30 084 (1981).
4. Corma, A., Gonzàlez-Alfaro, V., and Orchillés, A.V., *Appl. Catal.* **129**, 203 (1995).
5. Bonetto, L., Camblor, M. A., Corma, A., and Pérez-Pariente, J., *Appl. Catal.* **82**, 37 (1992).
6. Philippou, A., and Anderson, M. W., *J. Catal.* **158**, 385 (1996).
7. Martens, J. A., Pérez-Pariente, J., Sastre, E., Corma, A., and Jacobs, P. A., *Appl. Catal.* **45**, 85 (1988).
8. Ratnasamy, P., Bhat, R. N., Pokhriyal, S. K., Hegde, S. G., and Kumar, R., *J. Catal.* **119**, 65 (1989).
9. Pardillos, J., Brunel, D., Coq, B., Massiani, P., De Ménorval, L. C., and Figueras, F., *J. Am. Chem. Soc.* **112**, 1313 (1990).
10. Jia, C., Thesis, Université de Paris VI, France, 1994.
11. Smirniotis, P. G., and Ruckenstein, E., *J. Catal.* **140**, 526 (1993).
12. Zheng, J., Dong, J.-L., Xu, Q.-H., Liu, Y., and Yan, A.-Z., *Appl. Catal.* **126**, 141 (1995).
13. Smirniotis, P. G., and Ruckenstein, E., *Appl. Catal.* **123**, 59 (1995).
14. Weisz, P. B., *Adv. Catal.* **13**, 137 (1962).
15. Ivanova, I. I., Pasau-Claerbout, A., Seirvert, M., Blom, N., and Derouane, E. G., *J. Catal.* **158**, 521 (1996).
16. Barthomeuf, D., *J. Phys. Chem.* **88**, 42 (1984).
17. de Mallmann, A., and Barthomeuf, D., *J. Chim. Phys.* **87**, 535 (1990).
18. de Mallmann, A., and Barthomeuf, D., *Catal. Lett.* **5**, 293 (1990).

18′. Dzwigaj, S., de Mallmann, A., and Barthomeuf, D., *J. Chem. Soc., Faraday Trans.* **86**, 431 (1990).

19. Siffert, S., and Garin, F., *J. Chim. Phys.* **95**, 536–560 (1998).
20. Boudard, M., and Djega-Mariadassou, G., *in* "Kinetics of Heterogeneous Catalytic Reactions." Princeton Univ. Press, Princeton, NJ, 1984.
21. Gault, F. G., *Adv. Catal.* **30**, 1 (1981).

21′. Gault, F. G., and Garin, F., *J. Am. Chem. Soc.* **97**, 4466 (1975).

22. Olah, G. A., *Angew. Chem.* **12**(3), 173 (1973).
23. Sommer, J., Sassi, A., Hachoumy, M., Jost, R., Karlsson, A., and Ahlberg, P., *J. Catal.* **171**, 391 (1997).
24. Kazansky, V. B., Frash, M. V., and van Santen, R. A., *Catal. Lett.* **28**, 211 (1994).
25. Haag, W. O., *Stud. Surf. Sci. Catal.* **84**, 1375 (1994).
26. Corma, A., *Chem. Rev.* **95**, 559 (1995).
27. Mota, C. J. A., Martins, R. L., Nogueira, L., and Kover, W. B., *J. Chem. Soc. Faraday Trans.* **90**, 2297 (1994).
28. Bai, X., and Sachtler, W. M. H., *J. Catal.* **129**, 121 (1991).

29. Moretti, G., and Sachtler, W. M. H., *J. Catal.* **116**, 350 (1989).
30. Lerner, B. A., Carvill, B. T., and Sachtler, W. M. H., *Catal. Lett.* **18**, 227 (1993).
31. Dossi, C., Psaro, R., Ugo, R., Zhang, Z. C., and Sachtler, W. M. H., *J. Catal.* **149**, 92 (1994).
32. Chow, M., Park, S. H., and Sachtler, W. M. H., *Appl. Catal.* **19**, 349 (1985).
33. de la Puente, G., and Sedran, U., *Appl. Catal.* **144**, 147 (1996).
34. Smirniotis, P. G., and Ruckenstein, E., *Appl. Catal.* **117**, 75 (1994).
35. Smirniotis, P. G., and Ruckenstein, E., *Catal. Lett.* **25**, 351 (1994).
36. Corma, A., Llopis, F., Monton, J. B., and Weller, S., *J. Catal.* **142**, 97 (1993).
37. Li Quin, S., Su, H., and Xuan-Wen, L., *Stud. Surf. Sci. Catal.* **20**, 135 (1984).
38. Barron, Y., Maire, G., Cornet, D., and Gault, F. G., *J. Catal.* **2**, 152 (1963).
39. Siffert, S., Thesis, Université Louis Pasteur de Strasbourg I, France, 1997.
40. Brouwer, D. M., and Oelderick, J. M., *Rec. Trav. Chim.* **87**, 721 (1968).
41. Le Normand, F., Fajula, F., Gault, F. G., and Sommer, J., *Nouv. J. Chim.* **6**, 417 (1982).