Catalysis on Bifunctional Pt Acid Zeolites. A Route to Cleaner Processes[*]

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The large benefit brought by the association of hydrogenating sites (Pt or Pd) with the protonic acid sites of a zeolite is shown here on three examples of reactions related to Refining, Petrochemicals and Specialty Chemicals processes: n-alkane hydroisomerization and hydrocracking, ethylbenzene (EB) isomerization, synthesis of methylisobutyl-ketone (MIBK) from acetone. Whatever the reaction, the bifunctional catalysts are more stable than the purely acidic catalysts. They are able to catalyze certain reactions, which cannot occur through acid catalysis (*e.g.* EB isomerization). They allow the synthesis in one apparent step of products, which requires several successive steps catalyzed by metallic and acidic sites (*e.g.* synthesis of MIBK). Their selectivity can be directed to the desired products (*e.g.* monobranched alkanes in isodewaxing, xylenes in EB isomerization). Moreover, the semi-quantitative relations, which were established between their physicochemical properties, especially the balance between hydrogenating and acid functions and the zeolite pore structure, and their catalytic properties constitute guidelines for a scientific design of optimal catalysts and for the development of economic and environmentally friendly processes.

Key words: bifunctional catalysis, Pt/acid zeolites, n-alkane hydroisomerization, ethylbenzene isomerization, methylisobutylketone synthesis

Introduction

Solid acid catalysts play a very important role in refining, petrochemicals and fine chemicals industries. With these catalysts, the main problem is their fast deactivation by coking, a typical example being FCC catalysts, which must be regenerated (coke removal) after a few seconds in the reactor [1]. One possible solution is to use regenerative systems, *e.g.* FCC [1], MTO [2] *etc*. Another one is to associate a redox function to the acid catalyst which, when operating under hydrogen, limits significantly coking and deactivation phenomena [3]. However, the benefit of this association of redox and acid functions is generally not limited to stability improvements. Bifunctional catalysts may catalyze reactions, which cannot occur through acid catalysis (*e.g.* ethylbenzene isomerization) [4,5]; the selectivity of bifunctional catalysts

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[*]Dedicated to the memory of Professor Stanisław Malinowski in appreciation of his outstanding contributions to acid-base catalysis.

for the desired products is often much higher than the selectivity of acid catalysts (*e.g.* long chain n-alkane isomerization [6]); certain products, the formation of which requires several successive steps catalyzed by acid or by redox sites can be synthesized in one step, with as a consequence a considerable decrease in environmental problems [7,8]. These various aspects are shown here on reactions of commercial significance catalyzed by Pt (or Pd) acid zeolite samples.

1. Bifunctional catalysis – Generalities

1.1. Bifunctional reaction scheme. n-Alkane hydroisomerization (and hydrocracking) over bifunctional Pt/acid solid catalysts was investigated by many authors [6,9–17]. As an example, the reaction scheme of n-hexane isomerization into methylpentanes is shown in Fig. 1. Although n-hexane is transformed into methylpentanes in one apparent step (only traces of olefinic intermediates can be detected by using the most sensitive analysis techniques), this bifunctional transformation requires:

– two reactions catalyzed by the metallic sites: dehydrogenation of n-hexane into n-hexenes (step 1 in Fig. 1), hydrogenation of methylpentenes into methylpentanes (step 5);
– one reaction catalyzed by the acid sites: rearrangement of n-hexenes into methylpentenes (step 2);
– and physical steps, *i.e.* diffusion of n-hexenes from the metallic sites on which they are formed to the acid ones (step 2) and of methylpentenes from the acid sites to the metallic ones (step 4).

The existence of this **bifunctional** scheme with **desorbed olefinic intermediates** was demonstrated by various experiments showing:

– the participation of both acid and hydrogenating functions *e.g.* the activity of mixtures of platinum deposited on an inert carrier with an acid catalyst was definitely greater than the sum of the activities of the components (which are generally very low) [4,18].
– the presence in the reaction mixture of traces of olefinic intermediates [19,20]: only traces can be formed, these intermediates being highly unfavored at thermodynamic equilibrium under the operating conditions (hydrogen pressure…).
– the high reactivity of alkenes over the acid component [4,19,21] of the bifunctional catalysts.
– the negative effect on the catalytic activity of an increase in the distance between acid and metal sites, *i.e.* in the diffusion path of olefinic intermediates [4].

It should however be emphasized that, over certain bifunctional catalysts, n-hexane isomerization does not occur mainly through the reaction scheme presented in Fig. 1. Indeed, alkane isomerization can be catalysed by the acid as well as by the metal components of the bifunctional catalysts [22]. Therefore, under certain operating conditions with particular characteristics of the acid and metal sites, n-hexane isomerization can occur through a purely acid or through a purely metal mechanism. Thus, over Pt chlorinated alumina catalysts, n-hexane isomerization occurs only through a purely acid mechanism [23]; indeed, the acidic component having very strong acid
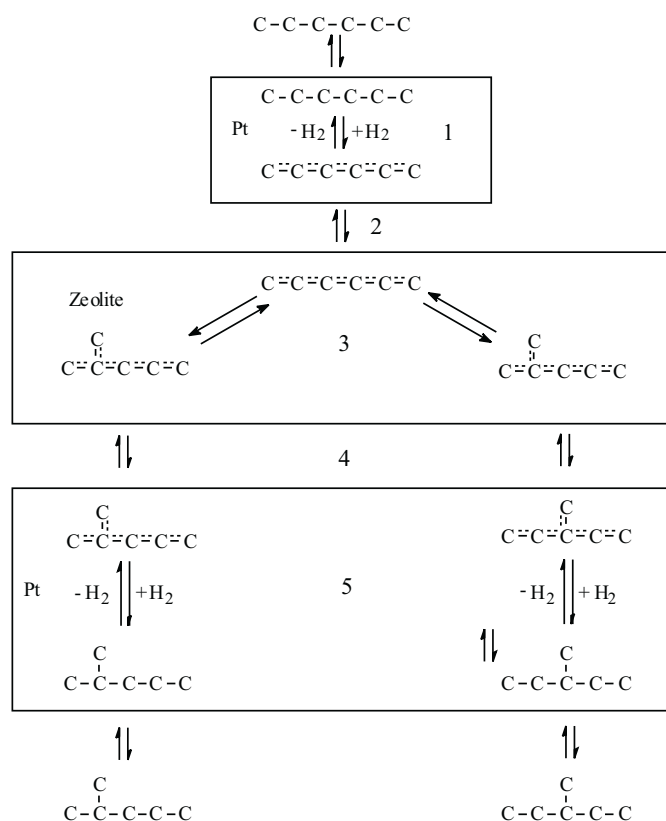
C - C - C - C - C - C

C - C - C - C - C - C

Pt   - H$_2$ ⇅ +H$_2$ 1

C=C=C=C=C=C

2

Zeolite

C=C=C=C=C=C

3

C=C=C=C=C (with C branch)   C=C=C=C=C (with C branch)

4

C=C=C=C=C (C branch)   C=C=C=C=C (C branch)

Pt   - H$_2$ ⇅ +H$_2$ 5   - H$_2$ ⇅ + H$_2$

C - C - C - C - C (C branch)   C - C - C - C - C (C branch)

C - C - C - C - C (C branch)   C - C - C - C - C (C branch)

Figure 1. Bifunctional scheme of n-hexane isomerization.

sites is active in isomerization at low temperature (100–150°C). The introduction of platinum has only a limited effect on the activity, no effect on the selectivity but improves very significantly the catalyst stability by decreasing the rate of coking [23]. Furthermore, with a weakly acid component such as silica, n-hexane isomerization occurs only at high temperatures and through a metallic mechanism: cyclic or bond shift mechanism according to the size of the Pt crystallites [24–26].

1.2. Correlations between physicochemical characteristics and catalytic properties – Generalities. When considering the bifunctional reaction scheme for n-alkane isomerization (Fig. 1), it appears clearly that the catalytic behaviour of bifunctional catalysts should depend on:

1) **the characteristics of the metallic and acid functions** which determine the relative rates of alkane dehydrogenation (step 1, Fig. 1), of alkene hydrogenation (step 5) and of alkene rearrangement (step 3). The balance between these functions can generally be considered as the determining parameter of the activity, stability and selectivity of non shape selective catalysts such as Pt large pore zeolites [6,12–14,27]. The quantification of this balance is the main problem to be solved.

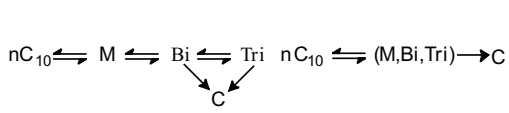Two main parameters were used for a quantitative estimation of this balance:

- the ratio between the concentrations of accessible metal and acid sites estimated by physicochemical methods. Thus, the ratio between nPt, the concentration of accessible platinum sites and nA the concentration of the acid sites for which the NH_3 adsorption heat (measured for a platinum free zeolite) was greater than 100 kJ mol^{-1} was proposed by our group to quantify this balance [13]. The choice of 100 kJ mol^{-1} was justified by the observation that, below this value, the acid sites were practically inactive for the skeletal isomerization of alkenes (step 3). Recently [28], as only protonic sites were active in step 3, n_{H+} the concentration of protonic sites able to retain pyridine adsorbed as pyridinium ions at 150°C was substituted for nA. An important remark is that nPt, nA or n_{H+} are determined over fresh catalysts, hence can be related with catalytic results obtained over fresh catalysts only and not on the stabilized catalysts.
- the ratio between the hydrogenating and acid activities for model reactions. Benzene and toluene hydrogenation at low temperatures (50–110°C) were often used for characterizing the hydrogenating function, a large variety of model reactions: alkane cracking, xylene isomerization *etc.* for the acid function. Of course, an *in situ* measurement (*i.e.* under the conditions of n-alkane hydroisomerization) would be desirable, the hydrogenating and acid activities being largely dependent on the operating conditions. An example of these in situ measurements deals with NiMoS/zeolite catalysts for which the balance of hydrogenating and acid functions was taken as the ratio between the activities for xylene hydrogenation and isomerization under hydroisomerization (hydrocracking) conditions [29]. Unfortunately, xylene hydrogenation is too fast over Pt bifunctional catalysts to be used with the hydroisomerization catalysts.

2) **the characteristics of the zeolite pores** which determine the relative rates of rearrangement (step 3) and diffusion (steps 2, 4) of olefinic intermediates from the metal to the acid sites and *vice versa* [14,30,31]. Again, these characteristics should be representative of the operating catalyst, hence should be determined after the initial period of deactivation which is generally observed. This can be made difficult by an easy elimination of "coke" during the pretreatment of the stabilized catalyst which is applied before adsorption measurements.

2. Hydroisomerization of n-alkanes

2.1. Influence of the hydrogenating/acid balance. n-Heptane and n-decane transformations [13,15] were carried out over a series of Pt/HFAU samples with framework Si/Al ratio of 5, 10 and 40 and platinum contents between 0.07 and 1.5 wt %, the platinum dispersion being between 70 and 90 %. nPt/nA was chosen for characterizing the balance between the hydrogenating and the acid functions. No shape selectivity effects were expected, the sizes of the olefinic intermediates or of the transition states being much lower than the size of the pore apertures or supercages. For the transformation of both alkanes, the activity, stability and selectivity of the catalysts

are definitely governed by the hydrogenating/acid balance. The effect of nPt/nA on the activity per acid site, on the stability and on the apparent reaction scheme is reported in Table 1 for n-decane transformation.

Table 1. Hydroisomerization and hydrocracking of n-decane over PtHFAU catalysts. Influence of the metal/acid balance (nPt/nA) on the catalytic properties.

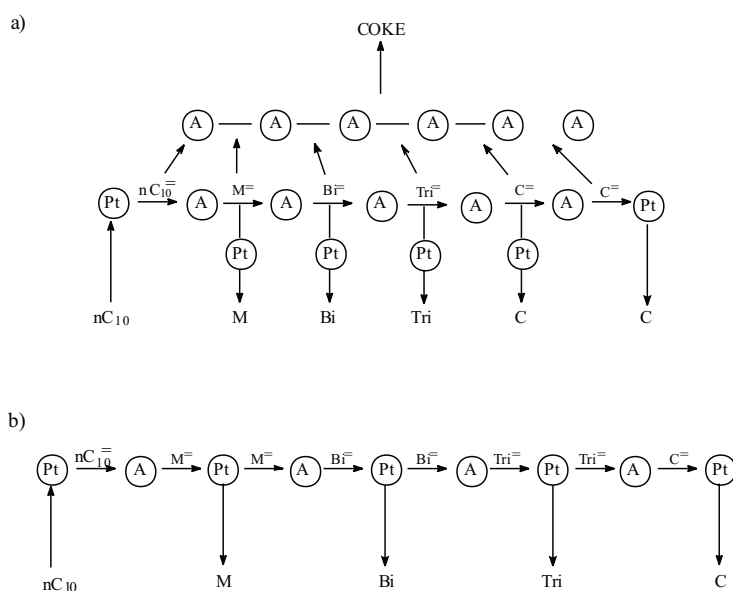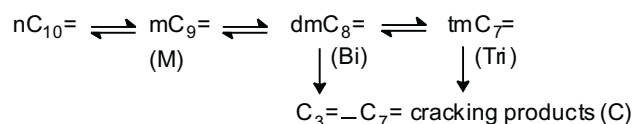| nPt/nA	≥ 0.17	> 0.03 < 0.17	< 0.03
Activity/acid site	Maximal	Maximal	Low
Stability	Perfect	Average	Low
Reaction scheme			

Figure 2. Scheme of n-decane transformation over bifunctional Pt/acid zeolite catalysts: a) with a low value of the hydrogenating/acid balance (nPt/nA < 0.03); b) with a high value of this balance (nPt/nA > 0.17); $nC_{10}^=$: n-decenes; $M^=$, $Bi^=$, $Tri^=$: mono-, bi- and tribranched decenes; $C^=$: cracking products.

- At low values of nPt/nA (< 0.03), the Pt sites are not sufficiently numerous for all the acid sites to be fed with intermediate alkenes and the activity per acid site increases with nPt/nA. This means that n-decane dehydrogenation (step 1, Fig. 1) is the limiting step of the bifunctional scheme. As the average distance between two Pt sites is large, the number of acid sites which can be encountered by decene intermediates is high, with consequently a high probability of several successive alkene transformations on the acid sites before hydrogenation (Fig. 2a). This explains why bibranched and tribranched isomers as well as cracking products ap-

pear as primary products (parallel scheme, Table 1), although on the acid sites, n-decene transformation occurs through the following successive scheme:

Scheme 1

$$nC_{10}= \;\rightleftharpoons\; mC_9= \;\rightleftharpoons\; dmC_8= \;\rightleftharpoons\; tmC_7=$$

$$(M) \qquad\qquad (Bi) \qquad\qquad (Tri)$$

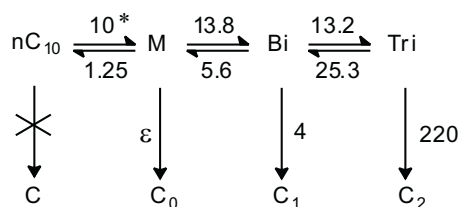$$C_3= - C_7= \text{ cracking products (C)}$$

Condensation reactions can also occur, with finally the formation of coke molecules. This explains the fast deactivation of these catalysts.

- For intermediate values of nPt/nA (between 0.03 and 0.17), the activity per acid site increases no more, which means that the Pt sites are sufficiently numerous for all the acid sites to be fed with intermediate alkenes: the alkene transformation over the acid sites (step 3) is then the limiting step of n-decane transformation. However, the number of acid sites encountered by the alkenes during their diffusion from one Pt site to another Pt site is great enough to lead to their successive transformation into monobranched, bibranched and tribranched isomers. Coke molecules can also be formed with consequently a relatively fast deactivation.

- For high values of nPt/nA ($\geq$ 0.17) the activity per acid site is maximal, the stability is perfect under the operating conditions and the apparent reaction scheme matches the scheme of transformation of alkene intermediates (Scheme 1). This means that the number of acid sites encountered by the decene intermediates during their diffusion between two Pt sites is such that only one decene transformation (skeletal rearrangement or β scission) can occur before hydrogenation (Fig. 2b). These bifunctional catalysts can be considered as **ideal hydroisomerization or hydrocracking catalysts** [14]: their activity and stability are optimal; moreover, as the reaction scheme is essentially successive, the selectivity to isomers is at the maximum which can be obtained through the classical bifunctional scheme (Fig. 1).

However, this maximum selectivity: 67% for a n-decane conversion of 75% (and the maximum yield: 50%) are too low in order that these catalysts be used in isodewaxing processes (there is too much cracking). This is due to the fact that while the rate constants for the successive branching steps are not very different, the higher the degree of substitution of decane, the faster the cracking rate (Scheme 2) [15].

Scheme 2

$$nC_{10} \;\underset{1.25}{\overset{10^*}{\rightleftharpoons}}\; M \;\underset{5.6}{\overset{13.8}{\rightleftharpoons}}\; Bi \;\underset{25.3}{\overset{13.2}{\rightleftharpoons}}\; Tri$$

$$\times\!\!\downarrow \qquad \varepsilon\!\!\downarrow \qquad 4\!\!\downarrow \qquad 220\!\!\downarrow$$

$$C \qquad\quad C_0 \qquad\quad C_1 \qquad\quad C_2$$

nC_{10} n-decane, M, Bi, Tri: mono-, bi- and tribranched isomers, C: cracking products *Reference.

On the other hand, ideal bifunctional catalysis is a good way for directing hydrocracking of heavy feeds to the production of middle distillates (low formation of gasoline and gases) or of gasoline (low formation of gases) (Scheme 3):

Scheme 3

Heavy feeds $\longrightarrow$ Middle Distillates $\longrightarrow$ Gasoline $\longrightarrow$ Gases
β scission β scission β scission
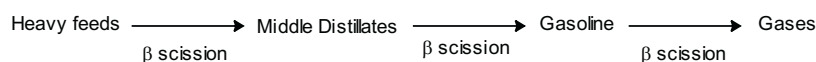
The mechanisms and kinetics of cracking and isomerization of olefinic intermediates on the acid sites can be specified from the distribution of the products of n-alkane transformation over ideal bifunctional catalysts [11,15]. The main conclusions are the following:

i) Branching of decenes occurs mainly through protonated cyclopropane intermediates (type B isomerization).

ii) The cracking products (C_3-C_7) result from β scission of bibranched decenes through mode B (which involves one tertiary and one secondary carbenium ion intermediates) or of tribranched decenes through mode A (two tertiary carbenium ion intermediates). The β scission of monobranched decenes (mode C, two secondary intermediates) and especially that of n-decenes (mode D, one secondary and one primary intermediates) are too slow to be considered.

iii) The values of rate constants for the main steps of alkene transformation are in the following order:

A cracking > B isomerization > B cracking > C cracking
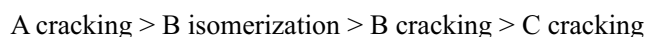
A cracking is approximately 20 times faster than branching (B isomerization), 50 times faster than B cracking and 10,000 times faster than C cracking [15].

2.2. Influence of the zeolite pore structure. n-Alkane hydroisomerization (and hydrocracking) through the classical bifunctional scheme (Fig. 1) should be particularly sensitive to diffusion limitations in the zeolite micropores. Indeed the branching of n-alkene intermediates causes an increase in both the molecular bulkiness and in the cracking reactivity. Thus, as was shown in Scheme 2 [15], the relative cracking rate constants (reference 10 for n-decane isomerization into monobranched isomers M) go from zero for n-decanes to 220 for tribranched isomers Tri (ε for M and 4 for bibranched isomers Bi).

As could be expected for this great sensitiveness to diffusion limitations, the characteristics of the diffusion path: size of the micropore apertures, mode of diffusion (mono, bi, tridirectional), crystallite size *etc.* have a significant effect on the catalytic behaviour. There are very few studies of n-alkane transformation over Pt small pore zeolites. Indeed with these zeolites, only linear cracking products can be observed in gas phase, because branched olefinic intermediates (isomers or cracking products)

are too bulky to desorb from the micropores; a fast deactivation can be observed due to the formation of bulky molecules (coke) which remain trapped in the micropores.

On the other hand, various Pt/zeolites with large or intermediate pore size were used for n-alkane transformation. However, the effect of nPt/nA was established only for n-heptane transformation over PtHFAU, PtHBEA, PtHMOR, PtHOFF and PtHMFI catalysts [31].

With PtHBEA and PtHMFI, the initial activity Ao first increases with nPt/nA and then above a certain value of nPt/nA remains constant as it was the case with PtHFAU samples. PtHMOR and PtHOFF behave differently: Ao passes through a maximum. Moreover, the maximum values of the turnover frequencies (Ao/nA) which are similar with PtHFAU, PtHBEA and PtHMFI are much smaller with PtHMOR and PtHOFF. This apparent low activity of the acid sites can be related to the high sensitiveness to pore blockage of mono (MOR) or quasi mono (OFF) dimensional systems: coke deposited during the first minutes reaction (before the first activity measurement) blocks the access of hydrocarbon molecules to the inner acid sites with consequently a very low apparent activity. Furthermore, the decrease in Ao observed for samples with high platinum content can be related to a blockage of part of the channels by platinum crystallites [31].

The product distribution depends very much on the zeolite pore structure:

- Whereas with all the catalysts, the maximum yield in isomers increases with nPt/nA, much lower values are found with monodimensional zeolites (MOR, OFF) and with the average pore size zeolite (MFI) than with the tridimensional large pore zeolites FAU and BEA. For nPt/nA $\geq$ 0.06, cracking becomes consecutive to isomerization on PtHFAU and PtHBEA, whereas on the other bifunctional catalysts cracking products appear as primary products whatever the value of nPt/nA.

- Another particularity of PtHMFI catalysts is the very low formation of bibranched isomers Bi. Therefore with these catalysts the parallel apparent formation of cracking products C and isomers I can be explained by a quasi complete cracking of the bulky and highly reactive bibranched alkenes during their slow migration in the narrow channels of MFI. With PtHMOR and PtHOFF, the explanation of the parallel scheme is different as suggested by values of monobranched/bibranched isomers (M/Bi) comparable to those found with PtHFAU and PtHBEA: the molecules of n-heptane which enter a mordenite channel would undergo several successive bifunctional transformations into M, Bi and Tri isomers then cracking products before desorbing from this channel (Tunnel shape selectivity [32]). The creation of mesopores by dealumination of MOR which makes the diffusion of molecules quasitridirectional [33] causes a significant increase in the maximum yield in isomers, confirming that the particular behaviour of PtHMOR samples results from the monodimensional pore system of this zeolite.

- Large differences can also be observed in the hydrocracking products. Thus, whereas with all the Pt/zeolite catalysts, the iso/nC_4 ratio increases with nPt/nA

then remains constant, this ratio is greater than 100 on PtHBEA and PtHMFI, equal to 30 on PtFAU, to 10 on PtHMOR and only to 0.3 on PtHOFF. In this latter case, the very low iso/nC_4 value suggests that cracking occurs for a large part in the gmelinite cages from which only linear products can desorb. On the other hand, the high values found on PtHBEA and PtHMFI were suggested to be due to a favourable matching of the transition states with the zeolite pores. Transition state selectivity was also proposed to explain the minima observed in the central hydrocracking of dodecane and tridecanes over PtHBEA samples [34].

Curiously, whereas zeolite characteristics such as average pore size (*e.g.* MFI) or monodimensional pore system have a very negative effect on isomerization selectivity, an exceptional high yield in isodecanes: 75% against 50% with a PtHFAU catalyst was found in n-decane transformation over PtHTON, *i.e.* with an average pore size monodimensional zeolite [16,17,34]. High selectivities to isomers and especially to monobranched isomers were obtained by using other monodimensional medium pore size molecular sieves. A Pt SAPO11 catalyst (SAPO11 is a monodimensional silico-aluminophosphate with pore apertures of 4.0×6.5 Å) is furthermore used for lowering the pour point of lubricants and middle distillate fuels through monobranching of long chain n-alkanes (isodewaxing) [35].

Obviously, the high isomer yield found with Pt/TON cannot be explained by a classical bifunctional mechanism with isomerization and cracking of alkene intermediates on the protonic sites of the zeolite micropores. Indeed the size of the TON pores (4.6×5.7 Å) is lower than the size of the MFI pores (5.1×5.5 Å and 5.3×5.6 Å), which should lead to stronger limitations in the diffusion of alkene intermediates and product molecules in the monodimensional pore system of this zeolite. Furthermore, a molecular modelling study concluded that the pores of TON can accommodate neither branched decane or decene molecules nor the protonated cyclopropane intermediates of branching, hence that isomerization could not occur (entirely) inside the TON micropores (16). Therefore, it was proposed that with PtTON catalysts, the isomerization of alkene intermediates formed by dehydrogenation of alkanes on Pt sites located on the outer surface of the zeolite crystallites occurred through **pore mouth catalysis**, hence was catalysed by protonic sites located on or near the outer surface [16,17,34]. This pore mouth catalysis was confirmed by a blockage of the access to the TON micropores by molecules of long monobranched chain alkanes trapped in these pores during the first minutes of reaction [36].

It should be specified that the branching of n-alkanes occurred preferentially near the end of the carbon chain, *viz*., at the C_2 and C_3 positions. Molecular models suggest that this branching would be catalysed by acid sites located in a half lobe at the pore entrance which is slightly larger than the channels. Alternatively, carbenium ions blocked near the entrance of the channels were proposed to be the active species, the branching occurring through an alkylation – isomerization-cracking mechanism [36]. Lastly, a **key lock mechanism** was proposed to explain that the second branching occurs at a distance of the first one close to the distance between the micropore apertures [17].

3. Ethylbenzene Isomerization

Paraxylene (pX), which is a chemical intermediate in the production of polyethyl-terephthalate (PET) fibers, resins and films is the most valuable xylene isomer (70% of the demand). Pure pX is mainly produced from transformation of the C_8 aromatic cuts. These cuts which result essentially from catalytic reforming contain approximately 20% of ethylbenzene (EB), the separation of which is too costly to be carried out and 80% of xylenes (X) in proportion close to thermodynamic equilibrium values (approximately 25% ortho, 50% meta and 25% para) [37–39]. Therefore, the production of pure pX requires a succession of chemical (interisomerization of xylenes plus EB isomerization) and physical (separation of pX generally by adsorption) steps (Fig. 3).
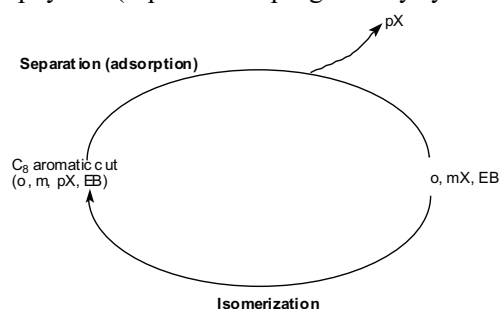

Figure 3. Production of p-xylene from the C_8 aromatic cuts: the aromatic loop.

Whereas xylene interisomerization is a typical acid reaction, ethylbenzene isomerization can occur only through bifunctional catalysis. Hence the isomerization of the C_8 aromatic cut must be carried out over bifunctional catalysts (Pt/MOR *etc*.). With these catalysts, side reactions can occur through bifunctional (reactions 1, 5), acid (reactions 2, 3) or metal (reaction 4) catalysis [5].

1. Hydrodealkylation of ethylbenzene into benzene and ethane.
2. Disproportionation of xylenes and of ethylbenzene.
3. Transalkylation between ethylbenzene and xylenes.
4. Hydrogenation of aromatics into naphthenes.
5. Hydrocracking of naphthenes.

3.1. Reaction scheme of ethylbenzene isomerization. The mechanism of ethylbenzene isomerization presented in Fig. 4 was firstly proposed by Weisz [4]. Like the scheme of alkane hydroisomerization, it comprises successive reaction steps on the metallic sites: hydrogenation of ethylbenzene into ethylcyclohexenes (only traces) and dehydrogenation of dimethylcyclohexenes into xylenes (steps 1 and 5) and on the acidic sites: rearrangement of ethylcyclohexenes into dimethylcyclohexenes (step 3) through methylethylcyclopentene intermediates:

Scheme 4
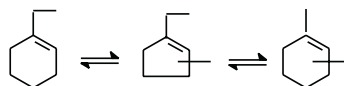
and physical steps (steps 2 and 4) *viz.*, diffusion of ethylcyclohexenes from Pt to acidic sites and of dimethylcyclohexenes from acidic to Pt sites.

When considering the reaction scheme of ethylbenzene isomerization (Fig. 4) and the side reactions, it can be concluded that like with n-alkane hydroisomerization, the catalytic properties of bifunctional Pt zeolite catalysts will depend: i) on the characteristics of the metallic and acid sites and especially of the balance between hydrogenating and acid functions and ii) on the characteristics of the zeolite pores. The influence of these parameters was quantitatively established over series of bifunctional catalysts constituted by intimate mixtures of well-dispersed Pt/Al_2O_3 (PtA) and of acidic zeolites: MOR, MFI and another medium pore size zeolite [28,40–43]. With all these bifunctional catalysts, ethylbenzene transformation was carried out under operating conditions close to those of the commercial processes, *viz.* = 400°C, 10 bar, H_2/ethylbenzene = 4.
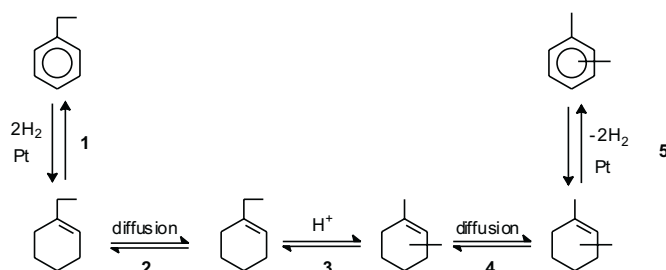

Figure 4. Bifunctional scheme of ethylbenzene isomerization.

3.2. Ethylbenzene transformation over PtA/MOR catalysts. Ethylbenzene transformation was investigated over a large number of PtA/MOR catalysts [42]. The catalysts differed by:
– the relative amounts of PtA and MOR components;
– the platinum content in PtA (0.5, 1.1, 2.3 wt %);
– the Si/Al ratio (x) in protonic mordenites (HMORx with $6.6 \leq x \leq 180$);
– the percentage y of exchange of HMOR10 by sodium (yNaHMOR with $y \leq 63$).

For all the bifunctional catalysts, nPt/n_{H+} was taken as representative of the metal/acid balance. It should be remarked that the PtA/MOR catalysts could differ not only by this balance, but also by other characteristics. Thus, the increase in the Si/Al ratio of the mordenite component causes not only a change in acidity (essentially a decrease in the protonic site concentration) but also in the mode of diffusion of organic molecules; indeed, dealumination creates a secondary porosity (mesopores) which transforms the monodimensional pore system of MOR into a quasi-tridimensional pore system [33]. The sodium exchange of HMOR10 has not only an effect on the concentration of protonic sites but also on their acid strength [43]. Therefore, the PtA/MOR samples were classified into three series:
– PtA/HMORx with x = 6.6 or 10, the protonic mordenites having no mesopores;
– PtA/HMORx with x $\geq$ 20, the protonic mordenites having mesopores;

– PtA/yNaHMOR in which there is a significant change in the strength of the protonic sites with introduction of the first sodium cations.

In each of the three series of catalysts, the effect of nPt/n_{H+} can be clearly specified since no significant change in porosity or in acid strength is expected. The effect of the other parameters will be discussed from the comparison of the behaviour of the different series of catalysts.

With all the catalysts, there is a relatively fast initial deactivation: decrease in activity of 30–50% during the first 10 hours reaction. Afterward, the catalysts present a good stability. No change in selectivity (the comparison between fresh and stabilized catalysts was of course made at similar conversions) can be observed. All the results which are discussed below were obtained over stabilized catalysts.

With all the catalysts, the apparent primary products resulted from 4 reactions: isomerization of ethylbenzene (EB) into xylenes (X), disproportionation into benzene and diethylbenzenes, deethylation and hydrogenation. It should be remarked that except for very low values of nPt/n_{H+}, the hydrogenation of C_8 aromatics into naphthenes is fast, making difficult an accurate determination of the hydrogenation activity. Moreover, these naphthenes which are recycled in the isomerization unit will not be considered in the estimation of selectivities.

3.2.1. Influence of the metal/acid balance. For the three series of bifunctional catalysts, the effect of nPt/n_{H+} on the isomerization activity Ai is the one expected from the bifunctional scheme (Fig. 4):

– For low values of nPt/n_{H+}, proportional increase of the turnover frequency TOF, *i.e.* the activity per protonic site (A_I/n_{H+}) with nPt/n_{H+}. The limiting step of isomerization is then the hydrogenation of EB into ethylcyclohexenes (step 1, Fig. 4).
– For high values of nPt/n_{H+}, constant value of TOF, the limiting step being then ethylcyclohexene rearrangement (step 3, Fig. 4).

Obviously, the values of TOF for the acidic side reactions: disproportionation (A_{dis}/n_{H+}) and dealkylation (A_{dealk}/n_{H+}) depend neither on the relative amounts of PtA and MOR components in the bifunctional catalysts nor on the Pt content of PtA but depend on the characteristics of the acid sites (par. 3.2.2).

For the three series of catalysts, the selectivity to isomers (estimated here at 35% EB conversion) increases with nPt/n_{H+}. This increase in isomerization selectivity occurs at the expense of disproportionation, of dealkylation and of the secondary reaction of naphthene cracking (*e.g.* PtA/HMOR10 samples in Fig. 5).

It should be remarked that the optimal (ideal) behaviour of the bifunctional PtA/HMOR catalysts in ethylbenzene isomerization: maximum value of the activity per acid site (TOF) and of the selectivity to xylenes, is obtained for very high values of nPt/n_{H+}: 0.75–1 and 4 with HMOR10 and HMOR with Si/Al > 30 respectively. These values of nPt/n_{H+} are 5 to 25 times higher than those required for obtaining the ideal behaviour of PtHFAU samples in n-decane hydroisomerization. These highest values are most likely related to the lower rate of the metallic step: aromatic hydrogenation is known to be more difficult than alkene hydrogenation or alkane dehydrogenation [44].
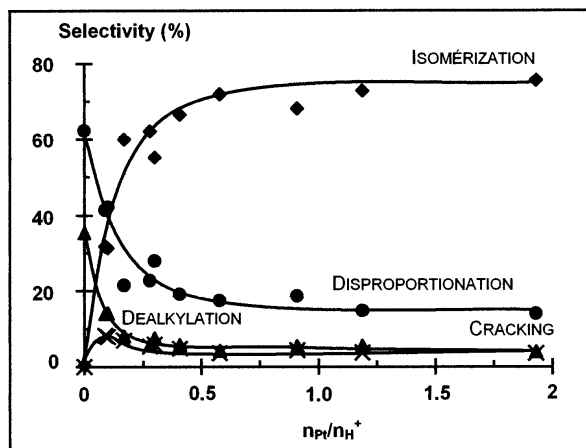
Figure 5. Ethylbenzene transformation over PtAl$_2$O$_3$/HMOR10 catalysts. Product distribution as a function of the metal/acid balance (nPt/nH$^+$) for an ethylbenzene conversion of 35%.

3.2.2. Influence of the characteristics of the acid sites. Whereas the TOF in isomerization is affected neither by the density of the protonic acid sites in the mordenite component nor by their strength, it is not the case for the TOF in disproportionation and in dealkylation. Thus, in each of the three series of catalysts, a proportionality was found between TOF in disproportionation and the concentration of protonic sites in the mordenite component. This proportionality suggests that disproportionation is a demanding reaction: two protonic acid sites would be necessary for its catalysis. This is not surprising when the complex mechanism of this acid reaction (6 successive steps [44]) is considered.

Furthermore, Na exchange which has no effect on the TOF in disproportionation causes a significant decrease of the TOF in dealkylation. This latter reaction which involves very unstable ethylcarbenium ions as intermediates is difficult to be catalyzed, hence occurs only on strong acid sites. The decrease in acid strength caused by Na exchange [43] is responsible for the highest isomerization selectivity of PtA/NaHMOR catalysts (Fig. 5).

3.2.3. Influence of the secondary porosity of the mordenite component. The secondary porosity has a significant positive effect on the values of TOF in isomerization, disproportionation and dealkylation [40–42,45,46]. Thus, when the mordenite component presents mesopores, the maximum values of TOF (*i.e.* at high values of nPt/n$_{H+}$) are 4–7 greater than in absence of mesopores. This suggests that in absence of mesopores, only the protonic sites of the crystallite shell can be active. The inner sites would not participe in isomerization because of a fast deposit of coke in the core of the zeolite crystallite. Indeed, during their diffusion in the monodimensional long channels of MOR, EB, X and olefinic intermediate may undergo condensation reactions leading to bulky products which remain trapped in the channels ("coke"). Diffusion limitations could also be responsible for these low values of TOF.

3.3. Ethylbenzene transformation over PtA/average pore size zeolites. Ethylbenzene isomerization was carried out over mixtures of PtA with HMFI or with a monodimensional average pore size zeolite [42]. PtA/HMFI catalysts are more active than PtA/HMOR catalysts but catalyze essentially EB hydrodealkylation into benzene and ethane [47,48]. Disproportionation is also observed (< 10% of the reaction products) but no isomerization. The mechanism of EB disproportionation is completely different from the one found on mordenite (through diphenylmethane intermediates). Here, disproportionation results from a deethylation-ethylation process: as demonstrated by the large effect of platinum on the product distribution [48]: the yield in disproportionation decreases significantly at the benefit of the yield in dealkylation owing to the rapid hydrogenation of ethylene, intermediate in the formation of diethylbenzene (Scheme 5).

Scheme 5
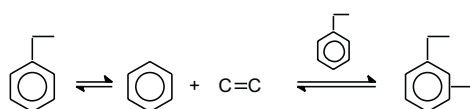
At least two proposals can be advanced to explain the absence of EB isomerization over PtA/HMFI catalysts:

– steric constraints on the isomerization of ethylcyclohexenes into dimethylcyclohexenes *via* ethylmethyl or trimethylcyclopentenes intermediates in the narrow pores of MFI;
– more pronounced inhibiting effect of aromatics on the adsorption of alkenes on the protonic sites or on their diffusion into the zeolite micropores.
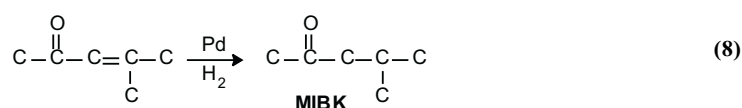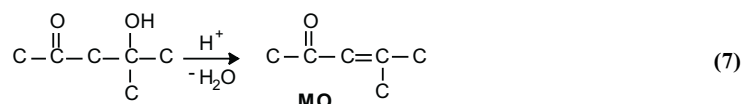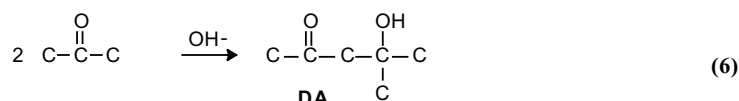
Curiously, whereas PtA/HMFI catalysts are not able to catalyze ethylbenzene isomerization into xylenes, this is not the case for mixtures of PtA and of a monodimensional medium pore zeolite [42]. The TOF values in isomerization are close to those found with PtA/HMOR catalysts and the selectivity higher. Again, this unexpected selectivity seems to be related to **a pore mouth catalysis** process on the stabilized catalysts [42].

4. "One pot" multistep synthesis of ketones

Bifunctional noble metal/zeolite catalysts could allow the "green" synthesis in one apparent step of functional compounds whose formation requires successive steps catalyzed by acid and metallic sites [7,8]. This multistep synthesis in one apparent step is obviously much less polluting and more economic than the process in successive chemical steps with intermediate steps of separation.

An important example deals with the synthesis of ketones such as methylisobutylketone from acetone, cyclohexylcyclohexanone from cyclohexanone, 1,3-diphenylbutan-1-one from acetophenone *etc*. Thus, methylisobutylketone (MIBK) which is used as a solvent for inks and lacquers was previously prepared from acetone

through a catalytic three step-process: base catalyzed production of diacetone alcohol (DA), acid dehydration of DA into mesityloxide MO then catalytic hydrogenation of MO on a Pd catalyst [49]:

$$2 \quad C-\overset{\overset{O}{\|}}{C}-C \quad \xrightarrow{OH^-} \quad C-\overset{\overset{O}{\|}}{C}-C-\overset{OH}{\underset{C}{\overset{|}{C}}}-C \qquad \textbf{(6)}$$

$$\textbf{DA}$$

$$C-\overset{\overset{O}{\|}}{C}-C-\overset{OH}{\underset{C}{\overset{|}{C}}}-C \quad \xrightarrow[-H_2O]{H^+} \quad C-\overset{\overset{O}{\|}}{C}-C=\overset{}{\underset{C}{\overset{|}{C}}}-C \qquad \textbf{(7)}$$

$$\textbf{MO}$$

$$C-\overset{\overset{O}{\|}}{C}-C=\overset{}{\underset{C}{\overset{|}{C}}}-C \quad \xrightarrow[H_2]{Pd} \quad C-\overset{\overset{O}{\|}}{C}-C-\overset{}{\underset{C}{\overset{|}{C}}}-C \qquad \textbf{(8)}$$

$$\textbf{MIBK}$$

Acetone aldolisation also occurs through acid catalysis as shown over a HMFI zeolite at 160°C: mesityloxide (MO) is the main reaction product, the aldolisation product being rapidly and irreversibly dehydrated [50]. Therefore, by associating an hydrogenation phase to the acid catalyst, it will be possible to synthesize MIBK in one apparent step.

The bifunctional reaction scheme (Fig. 6) shows that MIBK can be obtained without apparent formation of MO provided however that aldolisation (step 1) is the determining step *i.e.* that there are neither limitations by the diffusion of MO from the acid to the hydrogenating sites (step 3) nor by MO hydrogenation (step 4). Therefore, like for n-alkane and ethylbenzene isomerization, the hydrogenating/acid balance and the characteristics of the diffusion path, *i.e.* the pore structure in the case of zeolite as acid component should play a significant role in the catalytic properties of the bifunctional catalysts.
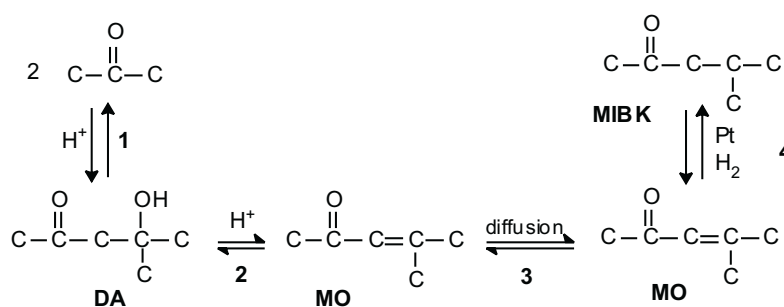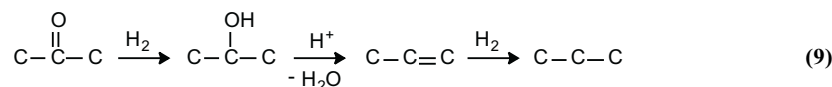

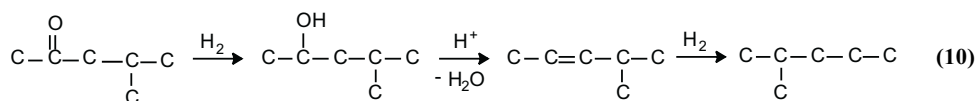**Figure 6.** Bifunctional scheme of acetone transformation into methylisobutylketone.

Like in ethylbenzene isomerization, various side products can be formed, here essentially through bifunctional catalysis [50,51]:

– Propane which results from the following transformations:

$$C-\overset{\overset{\text{O}}{\|}}{C}-C \xrightarrow{H_2} C-\overset{\overset{\text{OH}}{|}}{C}-C \xrightarrow[-H_2O]{H^+} C-C{=}C \xrightarrow{H_2} C-C-C \qquad (9)$$

The significance of propane production depends on the relative activity of the metallic sites for C=O and C=C hydrogenation. Therefore, palladium which is much more selective than platinum for the desired hydrogenation of the C=C double bond is generally chosen.

– 2-Methylpentane which can be formed either through acid dimerization of propene followed by hydrogenation or through the most likely following scheme:

$$C-\overset{\overset{\text{O}}{\|}}{C}-\underset{\underset{\text{C}}{|}}{C}-C \xrightarrow{H_2} C-\overset{\overset{\text{OH}}{|}}{C}-\underset{\underset{\text{C}}{|}}{C}-C \xrightarrow[-H_2O]{H^+} C-C{=}C-\underset{\underset{\text{C}}{|}}{C}-C \xrightarrow{H_2} C-C-\underset{\underset{\text{C}}{|}}{C}-C \qquad (10)$$

– Diisobutylketone DIBK (and other heavy ketones) which results from a bifunctional scheme similar to the one involved in MIBK formation:

$$(11)$$

DIBK
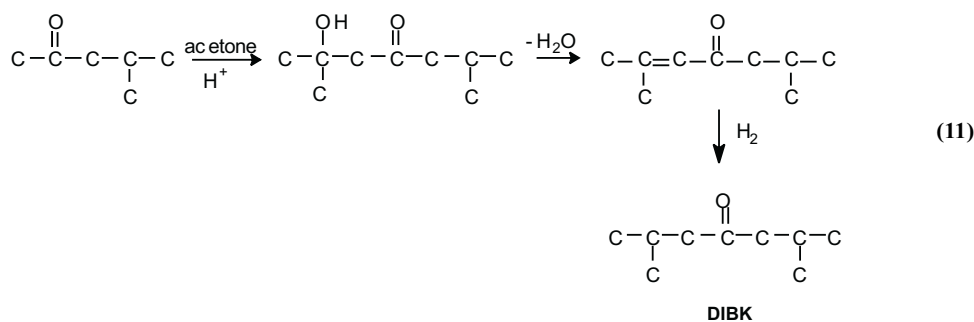
The significance of reactions 10 and 11 should depend mainly on the zeolite pore structure, an easy desorption of MIBK from the micropores and steric constraints near the acid sites on the formation of the bulky aldolisation intermediates being limiting factors. It should be remarked that bulky ketones trapped in the zeolite pores were shown to be mainly responsible for catalyst deactivation [51].

The effect of nPt/nA and nPd/nA on the activity, stability and selectivity of Pt and PdMFI catalysts for acetone transformation was established [51,52]. The bifunctional catalysts differed by the Si/Al ratio of the MFI component (which, with this zeolite, has no large effect on the path of diffusion of organic molecules) or/and by the Pt or Pd content. As expected from the bifunctional scheme, the turnover frequency TOF for MIBK formation (Ao/nA) increases with nPt/nA then remains constant above nPt/nA > 0.01 (Fig. 7). The limiting step is then acetone aldolisation on the acid sites. Inversely, TOF for MO formation which is high on HMFI decreases when nPt/nA increaes, remaining at a constant low value for nPt/nA > 0.01. (This low value corresponds to thermodynamic equilibrium between MO ($\approx$ 0.4%) and MIBK ($\approx$ 99.6%) under the operating conditions).

The residual activity estimated after 4 hours reaction, very low with HMFI (0.1) increases with nPt/nA remaining quasi constant (≈ 0.6) for nPt/nA > 0.01. This increase in stability was related to a decrease in the percentage of carbonaceous compounds (heavy ketonic compounds) trapped in the zeolite pores.

The selectivity to MIBK increases with nPt/nA becoming constant for nPt/nA > 0.01. Similar changes in TOF and residual activity were found with PdHMFI catalysts, the stability of PdHMFI catalysts being however lower than that of PtHMFI catalysts [52]. The other particularity of PdHMFI catalysts is their much higher selectivity to MIBK (Fig. 8 for Pd and PtHMFI samples with high values of nPt/nA).

For MIBK synthesis from acetone, no comparison of bifunctional catalysts with different zeolite structures was reported in the literature. However, the effect of the pore structure was shortly examined for the synthesis of cyclohexylcyclohexanone (a bulkiest ketone) from cyclohexanone [53]. Bifunctional catalysts containing zeolites with a tridimensional large pore system (FAU) were found more active and more se-
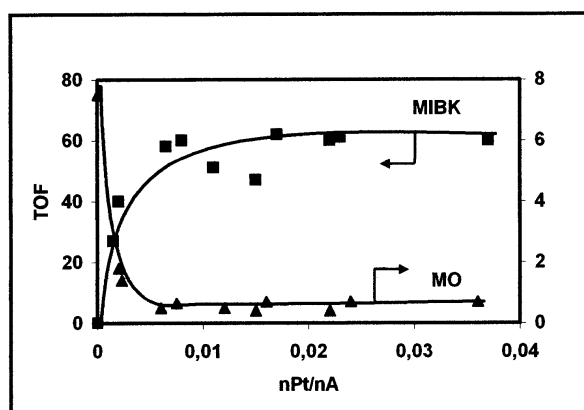

Figure 7. Acetone transformation into methylisobutylketone (MIBK) over PtHMFI catalysts. Turnover frequency values TOF (h^{-1}) for MIBK and MO (mesityloxide) formation versus the metal/acid balance (nPt/nA).
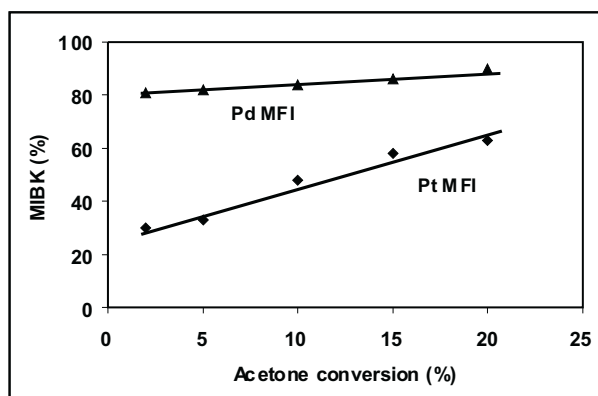

Figure 8. Acetone transformation into methylisobutylketone (MIBK) over Pt and Pd HMFI catalysts. Percentage of MIBK in the reaction products versus acetone conversion (%).

lective to cyclohexylcyclohexanone than those containing MOR (monodimensional large pore zeolite) or MFI (a tridimensional average pore size zeolite). The low cyclohexylcyclohexanone selectivity of MFI catalysts can be related both to steric constraints on the formation of the bulky bimolecular transition state of cyclohexanone aldolisation and to limitations in the desorption of cyclohexylcyclohexanone with therefore formation of bulky ketones. With MOR catalysts, desorption limitations are the main responsible for the low selectivity.

Conclusions

The three examples presented in this paper show the large benefit brought by the association in the same catalyst of hydrogenating sites with protonic acid sites:

– The stability is significantly improved. Thus, while deactivation by coking of acid zeolites is very fast, chosen Pt acid zeolites (with high values of the metal/acid balance) are very stable and even quasi perfectly stable.

– The selectivity can be directed to the desired products by an adequate choice of the metal/acid balance and of the characteristics of the zeolite pore system, *e.g.* selective transformation of long chain n-alkanes into monobranched isomers, selective ethylbenzene isomerization or selective methylisobutylketone formation.

– Reactions which cannot occur over acid catalysts such as ethylbenzene isomerization can be catalyzed by bifunctional metal/acid zeolite catalysts.

– The synthesis of products which requires several successive steps such as the synthesis of methylisobutylcetone from acetone can be carried out in one apparent step allowing the development of environmentally friendly and more economic processes.

The change of the catalytic properties (activity, stability, selectivity) with the physicochemical properties (concentration and strength of the protonic acid sites, balance between hydrogenating and acid functions, size and dimensionality of the pore system *etc.*) is well-known and well-understood. An exception however, the remarkable selectivity in n-alkane and ethylbenzene isomerization of bifunctional catalysts with a monodimensional average pore size zeolite remains to be explained; in particular the exact location of the reaction and the nature of active sites for the transformation of alkene intermediates have to be specified.

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