Transformation of acetophenone over Pd HFAU catalysts—reaction scheme

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Abstract

The transformation of acetophenone was carried out over a 0.5 wt.% Pd HFAU catalyst ($Si/Al = 17$) under the following conditions: flow reactor, 250°C, pressure of ketone and hydrogen equal to 0.8 and 0.2 bar, respectively. The reaction products were identified either by comparison in GC with reference compounds: benzene (B), ethylbenzene (EB), styrene (EB$^=$), cumene (IPB), isopropylbenzene (IPB$^=$) and benzoic acid (BA) or through GC/MS coupling: 1,3-diphenylbutane (DPB), 1,3-diphenylbutenes (DPB$^=$), 1,3-diphenylbutan-1-one (DPBO), 1,3-diphenylbut-2-ene-1-one (DPBO$^=$) and 2,4-diphenyl-3-methylpentenes (DPMP$^=$). These products are formed through three main reaction paths. DPBO$^=$ results from successive aldolisation of acetophenone and dehydration of the resulting alcohol over the protonic sites of the zeolite, DPBO from the hydrogenation of 1,3-diphenylbuten-1-one over the Pd sites (path 1). The formation of EB$^=$ involves hydrogenation of acetophenone followed by dehydration of the produced alcohol; EB results from EB$^=$ hydrogenation (path 2). DPB$^=$ can result from EB$^=$ dimerization (path 2) or from hydrogenation of DPBO followed by dehydration of the resulting alcohol (path 2). These reactions are similar to those observed during acetone and cyclohexanone transformation over bifunctional catalysts. In these reactions no alcohol intermediate is observed, which shows that alcohol dehydration is much faster than aldolisation and hydrogenation steps. The third reaction path which leads mainly to IPB, IPB$^=$ and BA, plays a significant role in acetophenone transformation whereas this path was very slow in acetone and cyclohexanone transformations. BA and IPB$^=$ result from acid cracking of DPBO$^=$, IPB from hydrogenation of IPB$^=$. IPB$^=$ undergoes also dimerization into DPMP$^=$ and IPB undergoes dealkylation into B over the protonic sites of the HFAU zeolite. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Acetophenone; Bifunctional catalyst; HFAU; Palladium

1. Introduction

Catalysts with redox and acid base/sites (i.e., bifunctional catalysts) are used in various industry commercial processes of refining and petrochemicals, reforming, hydroisomerization of C_5–C_6 alkanes, hydrocracking, isomerization of the C_8 aromatic cut [1–3]. The redox function is generally

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responsible for the formation of olefinic intermediates which are thermodynamically unstable under the operating conditions [1,2] through hydrogenation or dehydrogenation steps. The acid function is responsible for a rapid rearrangement and/or cracking of the olefinic intermediates. Chlorinated aluminas and protonic zeolites are generally used as the acid component, whereas noble metals or mixed sulfides of metals groups VI and VIII (Ni Mo, Ni W etc.) provide the redox function. Bifunctional catalysts present the advantages over monofunctional catalysts to allow transformations under milder conditions with better selectivity and stability. Thus hydrocracking operates at lower temperature (290–400°C) than catalytic cracking FCC (480–540°C), is more flexible allowing the selective production of middle distillates, of gasoline or even of gases. Moreover the deactivation of hydrocracking catalysts is much slower than in that of FCC catalysts [4].

Bifunctional catalysts can also be used for the synthesis of intermediates and fine chemicals [5,6] which requires generally various successive steps. These catalysts can perform several steps in one simple operation with consequently a decrease in the environmental problems very frequently associated with chemical transformations and product separation. This is in particular the case for the synthesis of methylisobutylketone (MIBK) from acetone. This ketone used as a solvent for inks and lacquers [7] can be prepared through three step process: base catalyzed production of diacetone alcohol by aldolisation of acetone, acid dehydration of diacetone alcohol into mesityloxide and hydrogenation of mesityloxide over a Pd catalyst. This three step synthesis can be obtained in one step, with a very low formation the intermediates diacetone alcohol and mesityloxide by using under hydrogenating conditions bifunctional Pd/acid catalysts such as Pd doped sulfonated resin [7,8] or Pd/HMFI [9–11]. Noble metal/HMFI catalysts can also be used for catalyzing the transformation of cyclohexanone into cyclohexylcyclohexanone [12,13]. The reaction scheme of the transformation of acetone and cyclohexanone over a Pt HMFI catalyst was established [12,14]. With both ketones the formation of the desired product is accompanied by that of hydrocarbon products resulting also from a bifunctional three step process: hydrogenation of the ketone followed by dehydration of the resulting alcohol into an alkene which is rapidly hydrogenated. This latter process is considerably slower when palladium, which is more selective for the hydrogenation of C=C bonds over the hydrogenation of C=0 bonds, is substituted for platinum.

The aim of this work was to establish the reaction scheme of acetophenone transformation over a bifunctional Pd zeolite catalyst. As the desired reaction product (1,3-diphenylbutan-1-one) is relatively bulky, a large pore zeolite HFAU was chosen as the acidic component. We show that in addition to the bifunctional reaction routes observed in the case of acetone and cyclohexanone transformation, there is another significant mode of transformation of acetophenone involving the acid cracking of its aldolisation products.

2. Experimental

HFAU ($Na_{0.08}H_{10.30}Al_{10.38}Si_{181.62}O_{384}$, $Si/Al = 17$) was supplied by IRMA, 0.5 Pd HFAU was prepared by ion exchange with $Pd(NH_3)_4Cl_2$ followed by calcination (6 h) under dry air flow at 500°C and reduction under hydrogen at 500°C during 6 h. The transformation of acetophenone was carried out in a flow reactor at 250°C with $P_{H2} = 0.2$ bar and $P_{acetophenone} = 0.8$ bar, WHSV (weight of reactant injected per weight of catalyst per hour) between 15 and 310 h^{-1}. The reaction products were condensed at the reactor outlet, then identified by a GC/MS coupling and analyzed by gas chromatography using a CP Sil 5 CB capillary column with 25 m of length, 0.15 mm of interior

diameter and 1.20 μm of internal phase. The experimental methods used to recover and to analyze the
heavy secondary products were the same as those used to analyze zeolitic coke [15].

3. Results and discussion

3.1. Identification of the reaction products and mode of formation

A chromatogram of the reaction products is given in Fig. 1. The following products: benzene (B),
ethylbenzene (EB), styrene (EB$^=$), cumene (IPB), isopropenylbenzene (IPB$^=$), benzoic acid (BA),
were identified by comparison in GC with reference compounds. The other products: 1,3-diphenyl-
butane (DPB), 1,3-diphenylbutenes (DPB$^=$), 1,3-diphenylbutan-1-one (DPBO), 1,3-diphenylbut-2-
ene-1-one (DPBO$^=$) and 2,4-diphenyl-3-methylpentenes (DPMP$^=$) were identified through GC-MS
coupling.

Various products result from reactions identical to those observed during acetone or cyclohexanone
transformation over bifunctional Pt or Pd zeolite catalysts [12–14].

Thus, DPBO$^=$ results from two successive steps catalyzed by the protonic acid sites: aldolisation
of acetophenone then dehydration of the resulting alcohol.

$$2 \; AP \xrightarrow{\;H^+\;} \quad \xrightarrow[\;-H_2O\;]{\;H^+\;} \quad DPBO^= \tag{1}$$
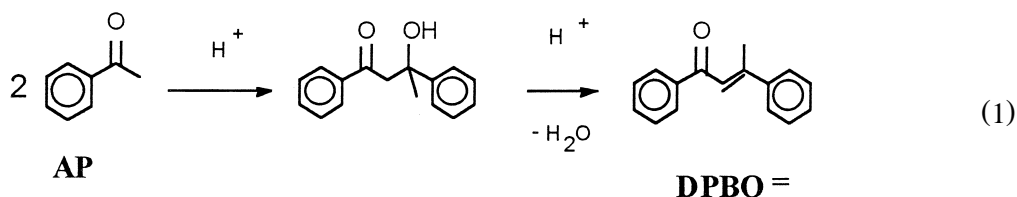
Therefore, DPBO$^=$ is equivalent to mesityloxide formed from acetone or to cyclohexenylcyclohex-
anone formed from cyclohexanone (Table 1). As was the case from these latter ketones the alcohol
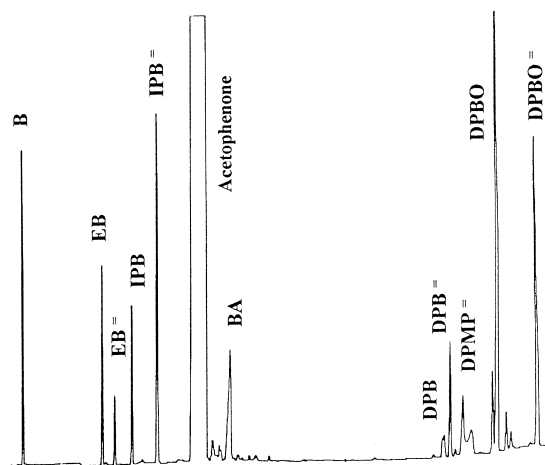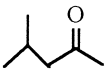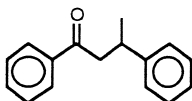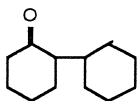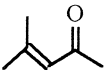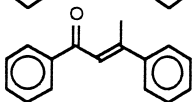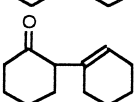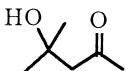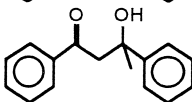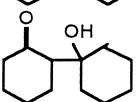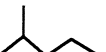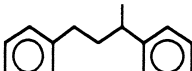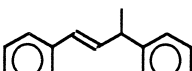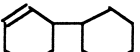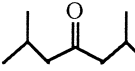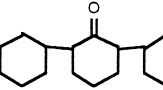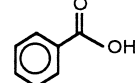
Fig. 1. Chromatogram of the products of acetophenone transformation over 0.5 Pd HFAU (17).

Table 1

Reaction products of acetone, acetophenone and cyclohexanone transformations over bifunctional Pt or Pd zeolite catalysts

Acetone	Acetophenone	Cyclohexanone
MIBK	DPBO	CHCHO
MO	DPBO=	CHCHO=
DA	DPBOH	CHCHOH
2 MP	DPB	BCH
--------	DPB=	BCH=
DIBK	--------	BCHCHO
IP	1-PE	CHOH
C3=	EB=	CH=
C3	EB	CH
--------	BA	--------
--------	IPB=	--------
--------	IPB	--------

intermediate is not observed, which means that alcohol dehydration is much faster than aldolisation. The mechanisms of aldolisation and dehydration have been previously described [12,14]. DPBO which is the equivalent of methylisobutylketone formed from acetone or of cyclohexylcyclohexanone formed from cyclohexanone (Table 1) results from the hydrogenation of the C=C double bond of DPBO$^=$ over the palladium sites.

Styrene (EB$^=$) which appears always in low amounts is the equivalent of propene observed only in traces [14] during acetone transformation and of cyclohexene [12] formed from cyclohexanone (Table 1). It results from the hydrogenation of acetophenone followed by the rapid dehydration of the alcohol produced.

(2)
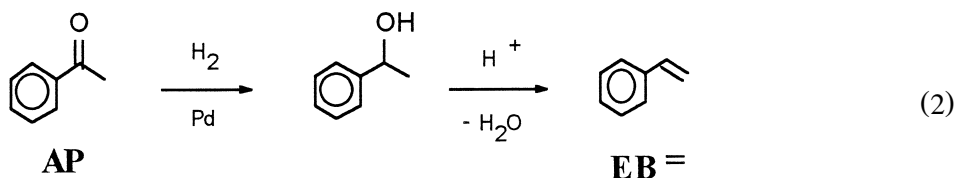
Again, no alcohol is observed, which indicates that alcohol dehydration is much faster than acetophenone hydrogenation. EB which is the equivalent of propane and of cyclohexane formed respectively from acetone and cyclohexanone transformation (Table 1) results from hydrogenation of EB$^=$.

DPB$^=$ which is the equivalent of methylpentenes, observed only in traces during acetone transformation and of cyclohexylcyclohexenes formed from cyclohexanone could result from the dimerization of styrene

(3)
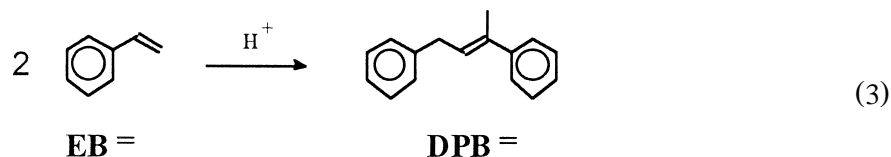
or from hydrogenation of DPBO followed by a rapid dehydration of the resulting alcohol

(4)
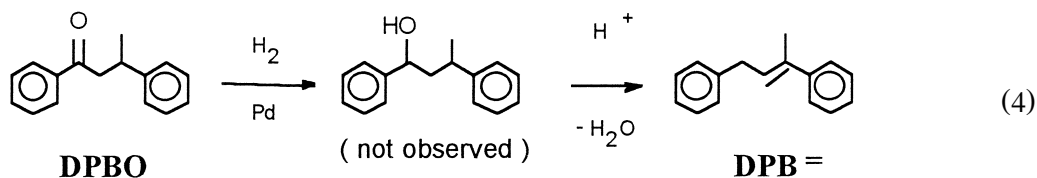
DPB which is the equivalent of 2-methylpentane or of cyclohexylcyclohexane results from DPB$^=$ hydrogenation.

Contrary to what is observed during acetone or cyclohexanone transformation (e.g., formation of diisobutylketone or of biscyclohexylcyclohexanone (Table 1) no product of condensation of DPBO with acetophenone is observed. This can be attributed to the difficulty in forming these very bulky products in the supercages of the FAU zeolite or in desorbing these products.

The other products which are observed: BA, IPB, IPB$^=$, B and DPMP$^=$ had no equivalent in acetone and cyclohexanone transformations over Pt MFI catalysts. Most likely BA, IPB$^=$ and DPMP$^=$ are formed through an acid mechanism. Indeed they are (with DPBO$^=$ at low conversion) the main products of acetophenone transformation over the HFAU 17 zeolite, this transformation being only 1.5 times slower than on 0.5 Pd HFAU 17 at 10 min reaction. BA and IPB$^=$ result most likely from the acid cracking of DPBO$^=$ or of the cetoalcohol formed by aldolisation of acetophenone (reaction 5). The acylium ion formed by their cracking would react with water produced by reactions 1, 2, 4 and 5 (reaction 6) with production of BA.

(5)

(6)
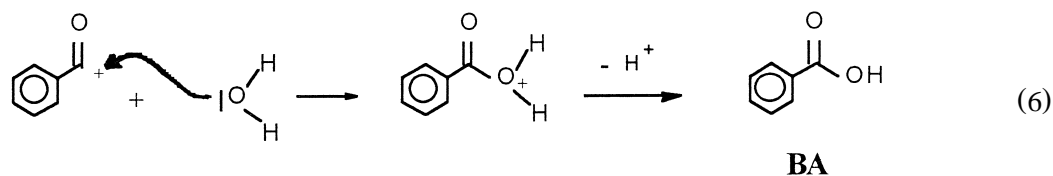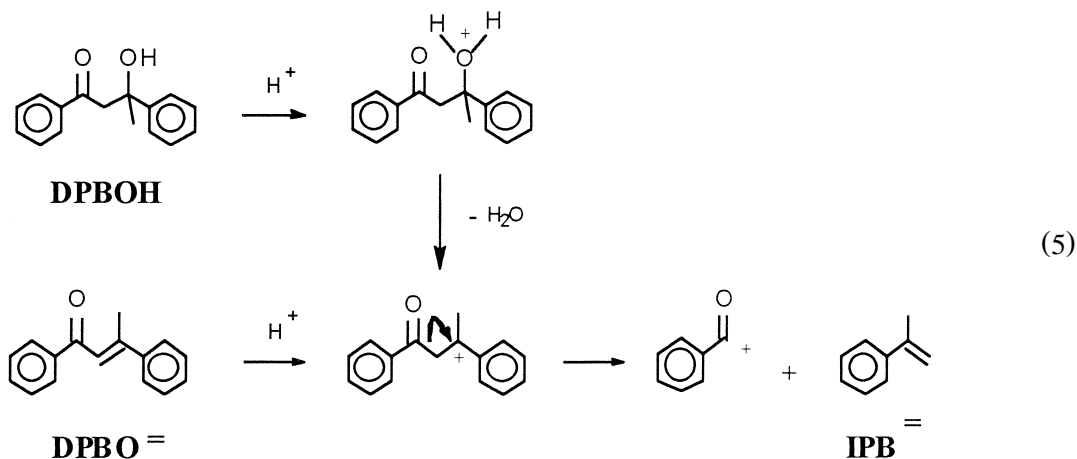
The high rate of these reactions can be related to the high stability of the carbocations involved: one tertiary carbenium ion and one acylium ion stabilized by mesomeric effect.

(7)
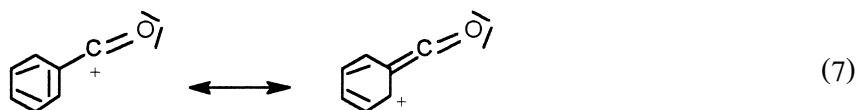
This stabilization does not exist with the acylium ion $(CH_3-C^+=O)$ resulting from acetone transformation, which explains that the equivalent of IPB$^=$ (and IPB) and of BA, i.e., isobutene (isobutane) and acetic acid are not observed during acetone transformation over Pt HMFI at 160°C [14]. However, these products are formed at higher temperatures e.g., 350°C [16–18] over purely acidic zeolites (HY, HZSM5). DPMP$^=$ is formed by dimerization of IPB$^=$ through an acid

mechanism. This reaction which involves only tertiary carbenium ion intermediates (reverse steps of A cracking [19]) should occur very rapidly. This is actually the case as shown by the large amount of DPMP$^=$ observed during acetophenone transformation over HFAU 17: 25 wt.% of the products at 10 min reaction (conversion of 20%) and 15% at 30 min (conversion of 5%). At least two peaks of DPMP$^=$ are observed, which indicates that dimerization is followed by isomerization through methyl shift.

$$(8)$$
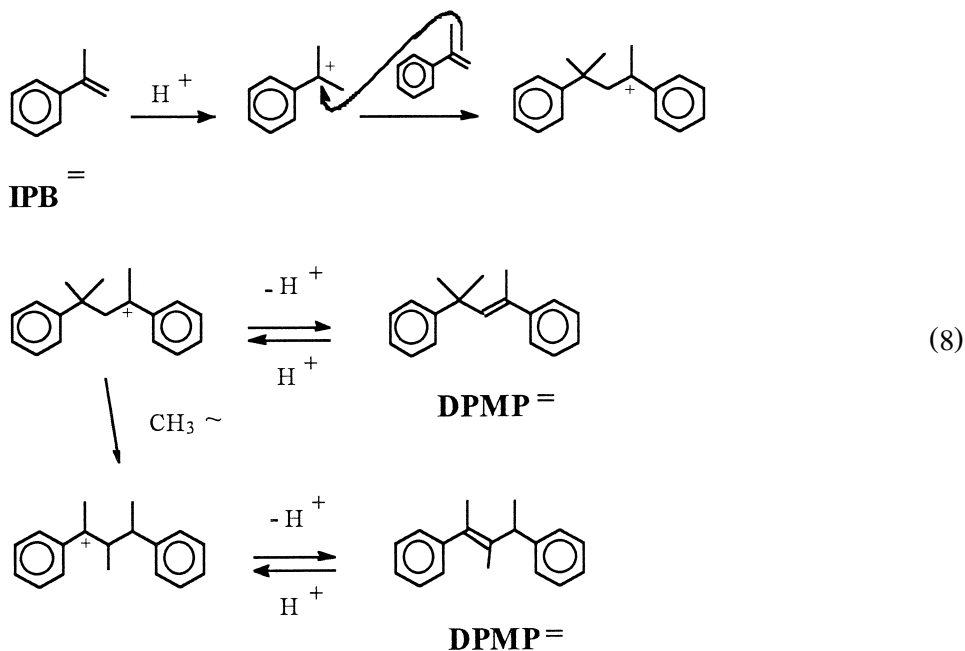
The formation of IPB and of B which are not observed with the HFAU 17 zeolite requires an hydrogenation step. IPB results from hydrogenation of IPB$^=$ and B from dealkylation of IPB through an acid mechanism.

$$(9)$$
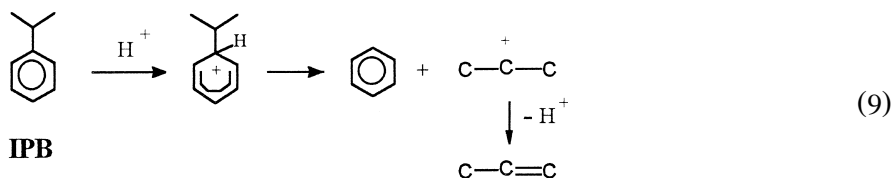
Propane formed by hydrogenation of propene is furthermore observed in the gaseous products.

The probable scheme of acetophenone transformation over 0.5 Pd HFAU 17 is indicated in Fig. 2. Acetophenone can undergo either acid aldolisation or hydrogenation. The resulting alcohols immediately dehydrated, do not appear in the products. The resulting olefinic products can undergo hydrogenation over the Pd sites, dimerization and cracking over the acid sites. Most of the reaction steps are similar to those implied in acetone or cyclohexanone transformation over bifunctional
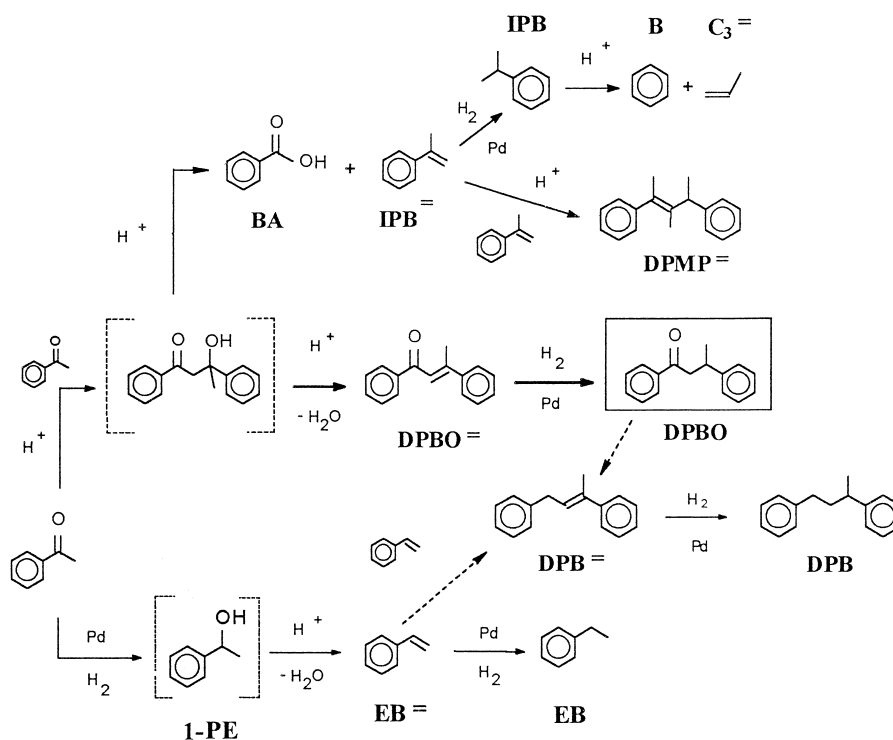
Fig. 2. Reaction scheme of acetophenone transformation over 0.5 Pd HFAU (17).

catalysts. However, a particular reaction is here observed, the acid cracking of the cetoalcohol resulting from acetophenone aldolisation or/and of the olefinic ketone ($DPBO^=$) produced by dehydration of this cetoalcohol. The appearance of this reaction is due to a large part to the high stability of the acylium ion intermediate even if the higher reaction temperature (250°C instead of 160°C with acetone and 200°C with cyclohexanone) can also play a role.

3.2. Influence of contact time

Fig. 3 shows for six values of the weight hourly space velocity WHSV (hence of the contact time) the change of acetophenone conversion X as a function of time-on-stream (TOS). Whatever the contact time there is at short TOS a rapid decrease of X followed by a slower one. The initial value of X (X_o) (at TOS = 10 min) is proportional to $1/\text{WHSV}$ hence to the contact time at least up to values of X_o of 30% (Fig. 4). From the slope of this straight line the initial activity of the catalyst (after 10 min reaction) was estimated to be equal to 9.3 mol h^{-1} g^{-1}.

The yield in the various products is plotted in Fig. 5 as a function of acetophenone conversion both on the fresh catalyst, i.e., at 10 min reaction and at longer time-on-stream. On the fresh as well as on the deactivated samples all the products except IPB, BA, B and DPB appear as primary products. This was expected for BA which needs for its formation water originating from acetophenone transformation. Furthermore as $IPB^=$ and $DPB^=$ appear as primary products the secondary formation of IPB and DPB indicates that hydrogenation of the corresponding alkenes is the limiting step of their formation. Finally the secondary formation of benzene was awaited since this product results from dealkylation of a secondary product (IPB).
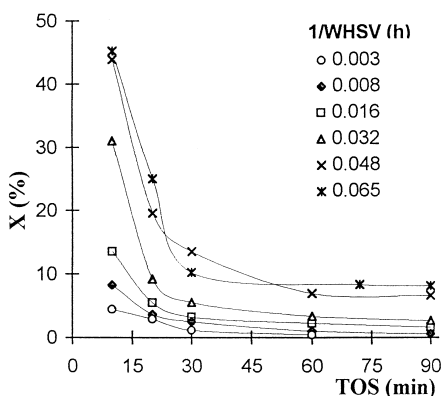
Fig. 3. Transformation of acetophenone over 0.5 Pd HFAU (17). Conversion of acetophenone X (%) vs time-on-stream (TOS) for six values of contact time (1/WHSV).

Contrary to what was found for acetone and cyclohexanone on all the bifunctional zeolite catalysts [12–14], the compounds resulting from aldolisation of acetophenone, dehydration (DPBO$^=$) and hydrogenation (DPBO) are formed only in low amounts: 17 wt.% of the products at 20% conversion on the fresh catalyst and 27% at 5% conversion. This is due to the high rate of cracking of the aldol and of DPBO$^=$ (reactions 5, 6). The corresponding products correspond to 78 wt.% at 20% conversion and to 68% at 5% conversion. As expected from ketone transformation over a bifunctional catalyst with Pd as hydrogenating agent the formation of ethylbenzene (and of traces of styrene) is relatively slow (5 wt.% of the products at 20 and 5% conversion). Indeed, palladium is not very active in the hydrogenation of C=0 bonds.

Whatever the contact time the ethylbenzene/styrene ratio (EB/EB$^=$) is much high than the cumene/isopropenylbenzene ratio (IPB/IPB$^=$) and than the 1,3-diphenylbutan-1-one/1,3-diphenyl-2ene-1-one ratio (DPBO/DPBO$^=$). This can be related to the lower degree of substitution of the double bond in styrene. Indeed the more substituted the olefinic compound the slower the hydrogenation.
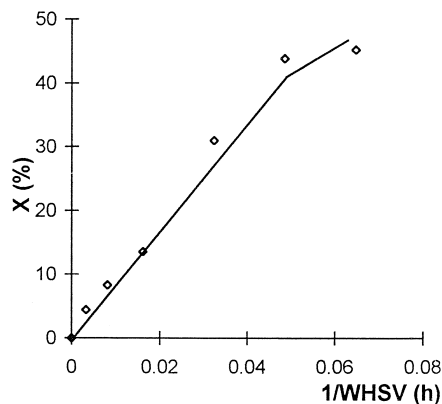

Fig. 4. Transformation of acetophenone over 0.5 Pd HFAU (17). Initial conversion X_o vs contact time (1/WHSV).

Deactivation has a slight effect on the product distribution. Thus for identical conversions there is with deactivation a small increase in DPBO and DPBO$^=$, in EB and EB$^=$ which are formed through bifunctional catalysis at the expense of IPB$^=$, BA and B which are formed through acid catalysis. This seems to indicate that the acid sites are more affected by deactivation than the metallic sites. This proposal is not in contradiction to the decrease with TOS in the (saturated/olefinic) compounds ratio shown in Fig. 6. Indeed this decrease is not due to a preferential deactivation of the metallic sites but to the decrease in conversion.

3.3. Origin of deactivation

Deactivation is most likely due to the retention in the pores of the zeolite of carbonaceous compounds. Indeed after 90 min a large amount of carbonaceous compounds (34 wt.% C) is retained on the catalyst after sweeping under hydrogen flow for 1 h. This corresponds to a conversion of acetophenone of approximately 10%.

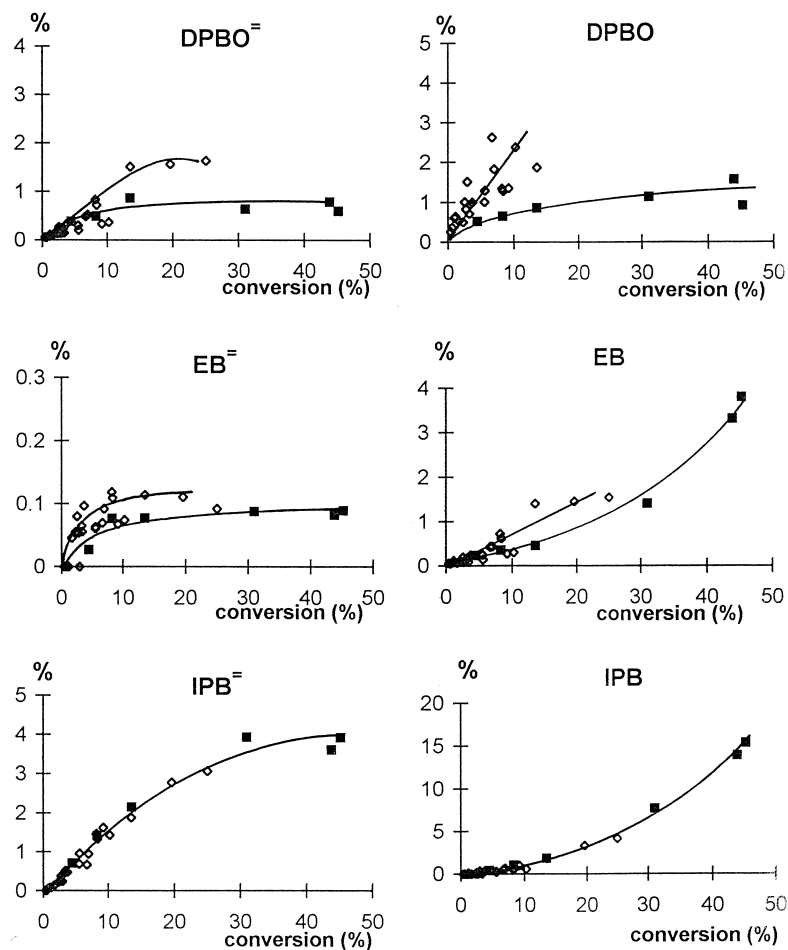Fig. 5. Yield of the reaction product (%) as a function of conversion: ■ initial yield on fresh catalysts, ◇ yield during catalyst deactivation.
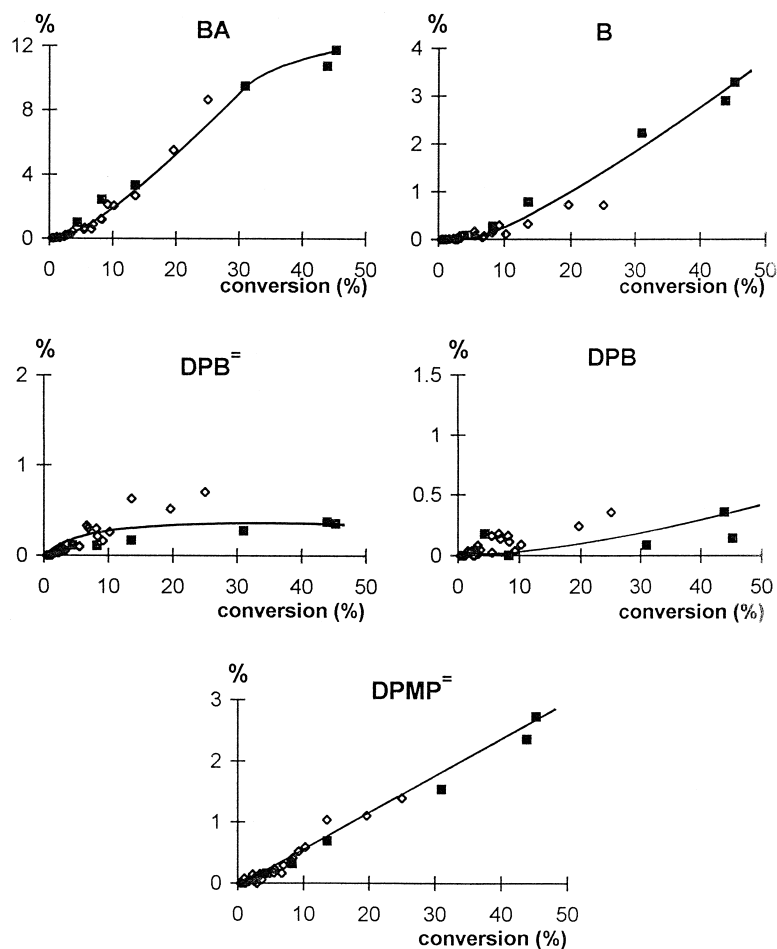
Fig. 5 (continued).

20% of these compounds are soluble in methylene chloride through a direct soxhlet treatment, hence are located on the outer surface of the crystallites or in supercages near this outer surface. They
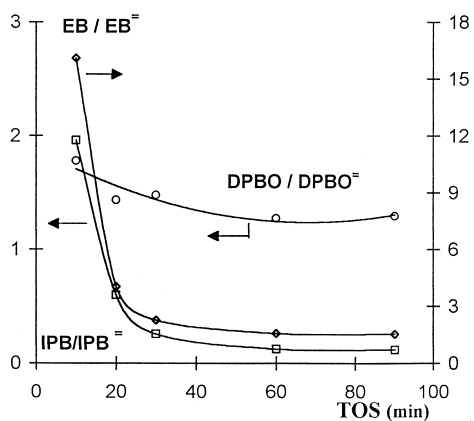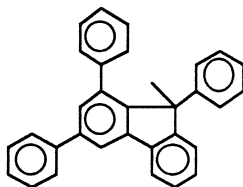

Fig. 6. Saturated/olefinic compounds ratio vs time-on-stream (TOS).

are constituted by approximately 40% of triphenylbenzene (mainly the 1,3,5-isomer), 30% of DPBO and 15% of $C_{32} H_{24}$ aromatic compounds having probably the following formula.


Small amounts of the reactant (AP: 7%) and of DPB$^=$ (8%) are also observed. Their retention on the zeolite can be related to their low volatility and to their relatively strong adsorption on the acid sites.

70% of the carbonaceous compounds can be dissolved in methylene chloride after dissolution of the zeolite in a HF solution, the remaining 15% being insoluble, hence probably constituted of very polyaromatic compounds. These polyaromatic compounds could result from the growth of coke molecules located in supercages near the outer surface of the crystallites with overflowing onto this surface, as was shown during *n*-heptane cracking over HFAU zeolites [20]. Part of them could also result from dehydrogenative coupling of polyaromatic species located in adjacent supercages [21]. The soluble compounds are constituted mainly by triphenylbenzene (40%) and by various other aromatic molecules with two or three aromatic rings (47%) such as:
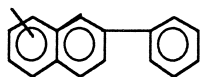
                    and
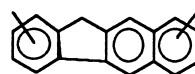
Small amounts of acetophenone (8%) and DPBO (5%) are also found. As these compounds cannot be recovered through the direct soxhlet treatment they are necessarily retained inside the supercages. Molecular modeling shows that the largest molecules (1,3,5-triphenylbenzene) can be accommodated in the supercages of HFAU zeolites (Fig. 7) but are sterically blocked in these cages. The retention of the other molecules which are much smaller is probably due to their blockage in the inner cages, the
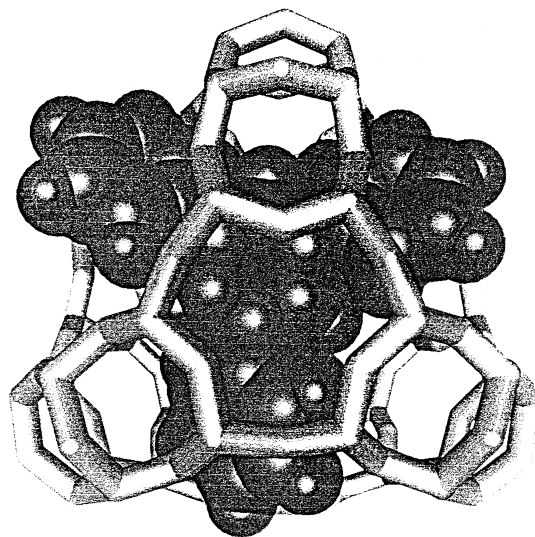

Fig. 7. Molecular modeling of 1, 3, 5 triphenylbenzene molecule located in the supercage of HFAU zeolite.

triphenylbenzene molecules which would be preferentially located in the outer part of the crystallites limiting or blocking their desorption. Indeed their size is smaller than the pore aperture (no trapping in supercages); their boiling point is not much higher than the reaction temperature and their polarity is low. The number of molecules of carbonaceous compounds was estimated to be close to the number of supercages of the HFAU zeolite (5×10^{20} g^{-1} for 4×10^{20} cages per gram). This means that most likely all the cages of the HFAU zeolite are occupied by these coke molecules.

1,3,5-Triphenylbenzene results most likely from the acid condensation of acetophenone. Indeed the synthesis of this compound can be carried out in HCl at 50°C [22]. The formation of triphenylbenzene occurs through condensation of three molecules of acetophenone under the enol form followed by rapid dehydration of the resulting trialcohol.
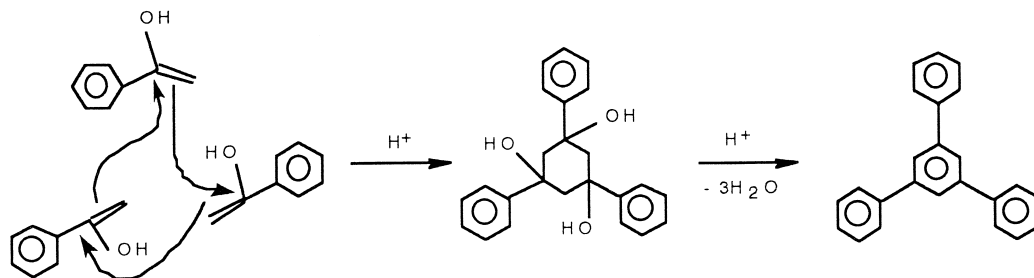
The formation of the $C_{32}H_{24}$ compound occurs through condensation of a 1,3,5-triphenylbenzene molecule and an other acetophenone molecule followed by rapid dehydration and cyclisation:

$C_{32}H_{24}$
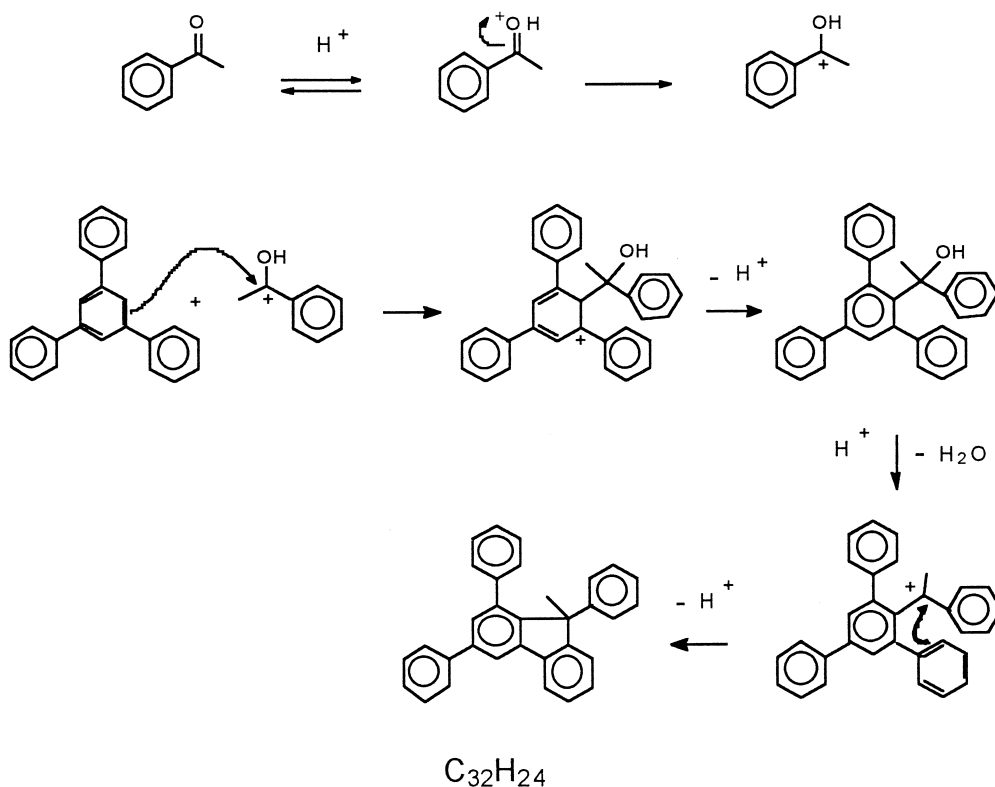
4. Conclusion

On 0.5 Pd HFAU 17 catalyst, acetophenone can be transformed into various compounds either through bifunctional catalysis or through purely acid catalysis. The bifunctional catalyzed transformations are those involved in the transformations of acetone and cyclohexanone over similar catalysts (i) successive aldolisation, dehydration and hydrogenation steps leading from acetophenone to DPBO. (ii) successive hydrogenation, dehydration and hydrogenation steps leading from acetophenone to EB. No alcohol intermediate is observed showing that like with acetone and cyclohexanone, alcohol dehydration is much faster than aldolisation and hydrogenation steps. The purely acid catalyzed transformation was not observed during acetone and cyclohexanone transformation. This transformation which leads to $IPB^=$ and BA involves successively acetophenone aldolisation, (eventually followed by dehydration of the cetoalcohol) and acid cracking of the dehydration product. For all the reactions there is a rapid deactivation of the catalysts due to the formation of bulky secondary reaction products, especially of 1,3,5-triphenylbenzene, and of more polyaromatic compounds inside the zeolite pores.

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