Effect of the metallic/acid site (nPt/nA) ratio on the transformation of acetone towards methyl isobutyl ketone

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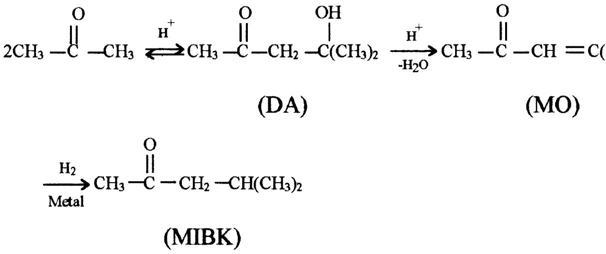
Received 5 November 1996; accepted 23 January 1997

Methyl isobutyl ketone (MIBK) was synthesized from acetone (Ac) and hydrogen over Pt-HZSM5 bifunctional catalysts. The reaction was carried out at 160°C, atmospheric pressure, and with a P_{H_2}/P_{Ac} molar ratio $= 0.33$, using a fixed bed and dynamic flow reactor. The results show that catalytic properties and coke formation largely depend on the ratio between the number of accessible hydro-dehydrogenation sites and the number of theoretical acidic sites (nPt/nA).

Keywords: acetone, methyl isobutyl ketone, HZSM5, platinum, bifunctional catalyst, coke

1. Introduction

4-methyl-2-pentanone or methyl isobutyl ketone (MIBK) is a very interesting product from the industrial point of view, because of its use as a solvent in the manufacturing of important finished products [1]. Industrially it is obtained from acetone, by means of a method which involves a number of successive stages; these are: (i) acetone aldolization to form diacetone alcohol (DA); (ii) DA dehydration to produce mesityl oxide (MO); and finally, (iii) hydrogenation of the olefin double bond of the MO to synthesize the MIBK [2]. The following general equation allows us to understand the process:



$$2CH_3-\overset{\overset{O}{\|}}{C}-CH_3 \overset{H^+}{\rightleftharpoons} \underset{(DA)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{OH}{|}}{C}(CH_3)_2} \xrightarrow[-H_2O]{H^+} \underset{(MO)}{CH_3-\overset{\overset{O}{\|}}{C}-CH=C(CH_3)_2}$$

$$\xrightarrow[Metal]{H_2} \underset{(MIBK)}{CH_3-\overset{\overset{O}{\|}}{C}-CH_2-CH(CH_3)_2} \qquad (1)$$

The synthesis through this process requires the use of highly polluting reactants, such as $Ba(OH)_2$, NaOH, H_3PO_4, and H_2SO_4 [2], which are used as catalysts in the different stages of the process. Moreover, this synthesis method should utilize some separation stages of intermediary reactants, DA and MO, which greatly contribute to environmental pollution.

Furthermore, the synthesis of this ketone may be carried out from propanone under hydrogen flux and using Pt-HZSM5 bifunctional catalysts. This method appears to be very attractive because it allows us to obtain MIBK without polluting stages such as those mentioned above.

This study is aimed at determining the effect of the nPt/nA ratio on catalytic properties (activity, stability, and selectivity) and on the formation of coke on these solids.

2. Experimental

An aluminosilicate of an MFI type zeolite with Si/Al ratio $= 41$ was synthesized by the method proposed by Guth and Caullet [3]. After calcination at 500°C under dry air, this solid was characterized by XRD, nitrogen adsorption at -196°C and by SEM. These techniques showed that this material has high crystallinity and purity. After NH_4^+ exchange and calcination the unit cell formula of the solid, determined by chemical analysis, was: $H_{2.00}Na_{0.30}Al_{2.30}Si_{93.70}O_{192}$. The number of theoretical protonic sites was also calculated at 2.1×10^{20} acidic sites per gram of solid. These sites represent the active acid centers of the catalyst, because in this kind of solids, most of the protonic sites are strong acidic sites [4].

From these H-zeolites, different bifunctional catalysts of the Pt-HZSM5(41) type were prepared, with platinum weight percentage ranging between 0 and 0.54 (table 1). Metal was introduced by cationic exchange of $Pt(NH_3)_4^{2+}$ in the presence of the competitive ion NH_4^+ with a $NH_4^+/Pt(NH_3)_4^{2+}$ ratio equal to 100 [5].

These catalysts were calcined under dry air at 300°C and then treated under hydrogen atmosphere at 500°C before the catalytic characterization, which was carried out using fixed bed and dynamic flow reactors. Platinum dispersion (D) was determined by TEM, estimated percentages of this metallic dispersion stage range between

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Table 1
Physicochemical characteristics of catalysts

Catalyst	Pt [a] (%)	A_H^0 [b] (mmol/(h g))	D [c] (%)	nPt/nA [d]
HZSM5(41)	–	–	–	–
0.03Pt-HZSM5(41)	0.03	1.3	40	0.0017
0.15Pt-HZSM5(41)	0.16	8.4	47	0.0110
0.31Pt-HZSM5(41)	0.31	12.1	35	0.0160
0.54Pt-HZSM5(41)	0.54	27.0	45	0.0357

[a] Percentage of plantinum on the catalysts.
[b] Initial acitivity for toluene hydrogenation.
[c] Dispersion of metallic phase.
[d] Accessible metallic centers / theoretical acidic sites ratio.

30 and 50% (table 1). Assuming that in these solids each structural aluminum atom generates a Brønsted acidic site, it was possible to determine the atomic ratio between the number of accessible platinum atoms per theoretical acidic site (nPt/nA) for all catalysts prepared (table 1). Hydrogenating activity of the catalysts was assessed using toluene hydrogenation ($T = 110$°C; $p = 1$ atm; $P_{H_2}/P_{\mathrm{Toluene}} = 9$) as a reaction model. Acetone transformation was carried out at 160°C, atmospheric pressure, P_{H_2}/P_{Ac} molar ratio equal to 0.33 and WWH (grams of acetone injected per grams of zeolite per hour) equal to 4.7 h^{-1}. These conditions were defined in previous studies [6–8]. The excellent co-relation between initial activity in toluene hydrogenation (A_H^0) and the number of accessible platinum atoms can be observed in table 1.

Characterization of coke contents (as %C) was carried out after 265 min of streaming, by means of an elemental analysis of the deactivated catalyst. In addition, an analysis of the nature of the carbon residue which deactivates the catalysts was carried out, using the method of the destruction of the zeolite structure with a 40 wt% HF solution. The coke was extracted with methylene chloride [9]. Coke was found to be soluble in CH_2Cl_2 in every case, which shows that these substances have low molecular weights.

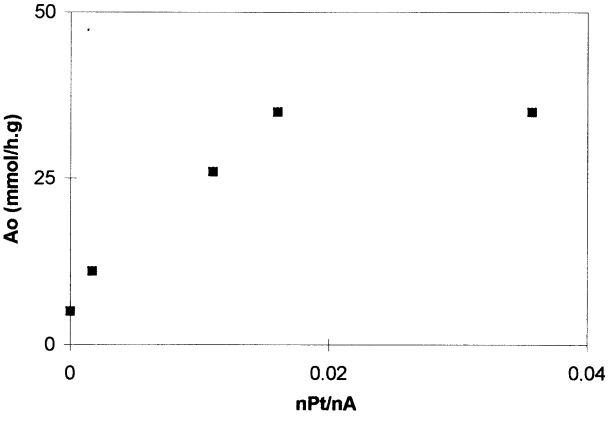


Figure 1. Initial global activity as a function of nPt/nA ratio of the catalysts.

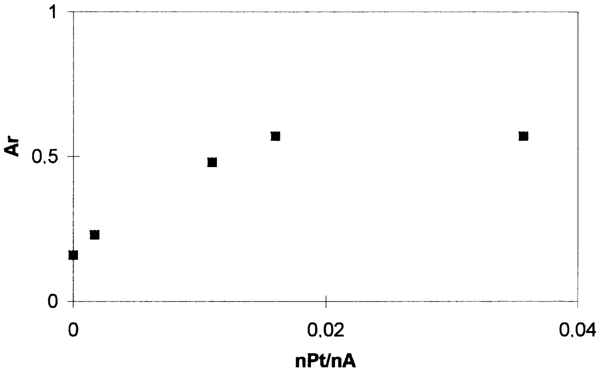


Figure 2. Residual activity as a function of nPt/nA ratio of the catalysts.

3. Results and discussion

The total initial activity in acetone transformation (A_0), the catalyst stability as well as the amount of coke deposited on the catalysts, largely depend on the platinum contents present in the zeolite support (figures 1–3).

Figure 1 shows A_0 variation as a function of nPt/nA. Initially an increase of A_0 is observed as nPt/nA increases, then it reaches a plateau for $n\mathrm{Pt}/n\mathrm{A} \geqslant 0.015$. This result clearly shows that acetone transformation occurs by means of a bifunctional mechanism. Therefore for catalysts with $n\mathrm{Pt}/n\mathrm{A} \leqslant 0.015$, the kinetically limiting step takes place over the hydrogenating centers. However, for solids with enough metallic sites ($n\mathrm{Pt}/n\mathrm{A} \geqslant 0.015$), the reaction limiting step takes place over the acidic function of the catalyst.

Residual activity (A_r) in acetone transformation, defined as the relation between the activity after 265 min of reaction, A_{265}, and the initial activity of the catalyst, A_0, obtained by extrapolation at $t = 0$ ($A_r = A_{265}/A_0$) as a function of nPt/nA is reported in figure 2. The amount of coke as a function of nPt/nA is reported in figure 3.

Figure 2 shows that A_r initially increases with the increase of nPt/nA and when $n\mathrm{Pt}/n\mathrm{A} \geqslant 0.015$, it reaches its maximum stability. In contrast, figure 3 shows that

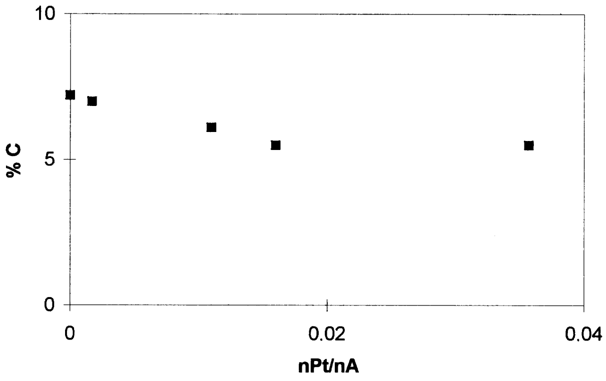
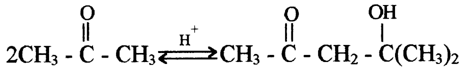


Figure 3. Coke (as %C) as a function of nPt/nA ratio of the catalysts.

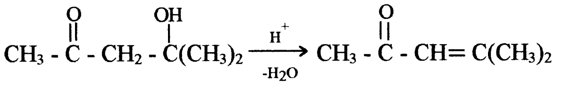
%C decreases as the *n*Pt/*n*A ratio increases and that from *n*Pt/*n*A$\geqslant$0.015 on, it remains constant at a minimum value.

These results show that once catalysts reach their optimum *n*Pt/*n*A ratio, the activity and the stability are the maximum and the coke formation the minimum. The activity loss on these solids is related to the amount of coke deposited, which certainly blocks the substrate access or covers the active centers necessary for the acetone transformation.

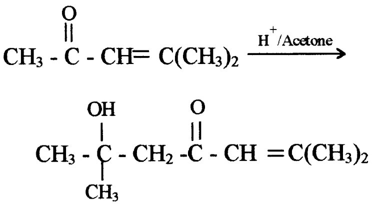
The nature of these carbon residues should vary considerably as *n*Pt/*n*A changes. For catalysts with *n*Pt/*n*A < 0.015, reactions which require only acid catalysis and lead to the formation of oxygenated carbon residues, such as isophorone, are favored. Formation of these products can be explained by means of the following reaction scheme:



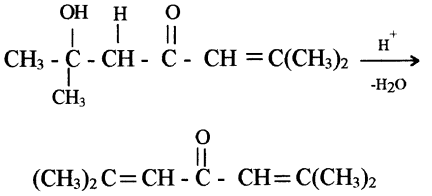
$$2CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightleftharpoons{H^+} CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{C}}(CH_3)_2 \qquad (2)$$



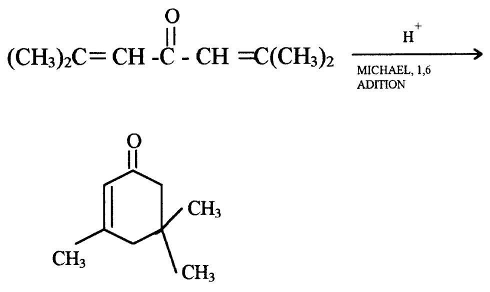
$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{OH}{\overset{|}{C}}(CH_3)_2 \xrightarrow[-H_2O]{H^+} CH_3-\overset{O}{\overset{\|}{C}}-CH=C(CH_3)_2 \qquad (3)$$



$$CH_3-\overset{O}{\overset{\|}{C}}-CH=C(CH_3)_2 \xrightarrow{H^+/\text{Acetone}} CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-CH_2-\overset{O}{\overset{\|}{C}}-CH=C(CH_3)_2 \qquad (4)$$



$$CH_3-\underset{CH_3}{\underset{|}{\overset{OH}{\overset{|}{C}}}}-\overset{H}{\overset{|}{CH}}-\overset{O}{\overset{\|}{C}}-CH=C(CH_3)_2 \xrightarrow[-H_2O]{H^+} (CH_3)_2C=CH-\overset{O}{\overset{\|}{C}}-CH=C(CH_3)_2 \qquad (5)$$

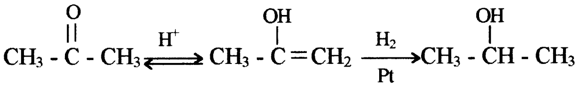


(6)

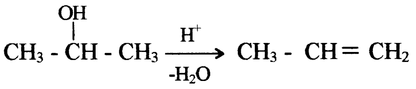
(Isophorone)

In contrast, when catalysts have a high *n*Pt/*n*A ratio (*n*Pt/*n*A$\geqslant$0.015), the reactions of acetone hydrogenation and intermediary reactants, such as propene, MO, phorone, etc. are favored. In these cases, the substances which would act as deactivating agents for these solids should be basically hydrocarbons of the polyalkylbenzene type (fundamentally formed by propene oligomerization reactions) and oxygen compounds as isophorone [10]. Using GC-SM coupling, it was demonstrated (by the analysis of the coke deposited during 265 min reaction over the catalyst with 0.54% Pt-HZSM-5(41)) that coke is formed mainly by isophorone ($T_{\text{boiling}} = 214°C$) and polyalkylbenzenes ($T_{\text{boiling}} > 200°C$). The following reaction schemes show the hydrogenation reactions and explain the formation of deactivating substances:

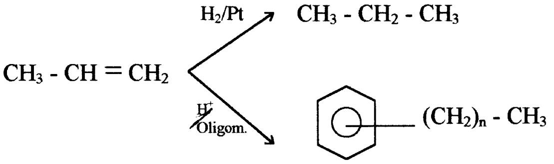
acetone hydrogenation



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3 \xrightleftharpoons{H^+} CH_3-\overset{OH}{\overset{|}{C}}=CH_2 \xrightarrow[Pt]{H_2} CH_3-\overset{OH}{\overset{|}{CH}}-CH_3 \qquad (7a)$$

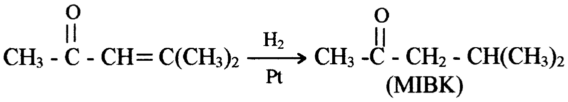


$$CH_3-\overset{OH}{\overset{|}{CH}}-CH_3 \xrightarrow[-H_2O]{H^+} CH_3-CH=CH_2 \qquad (7b)$$



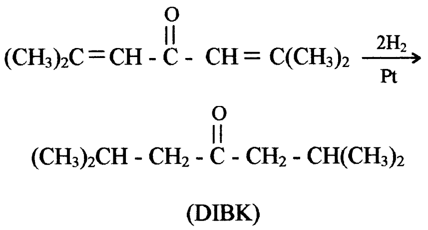
(7c)

mesityl oxide hydrogenation



$$CH_3-\overset{O}{\overset{\|}{C}}-CH=C(CH_3)_2 \xrightarrow[Pt]{H_2} \underset{\textbf{(MIBK)}}{CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH(CH_3)_2} \qquad (8)$$

phorone hydrogenation



$$(CH_3)_2C=CH-\overset{O}{\overset{\|}{C}}-CH=C(CH_3)_2 \xrightarrow[Pt]{2H_2} \underset{\textbf{(DIBK)}}{(CH_3)_2CH-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-CH(CH_3)_2} \qquad (9)$$

The distribution of the reaction products shows a clear dependence on the *n*Pt/*n*A ratio (table 2). Thus using H-zeolite (without platinum, HZSM5) as a catalyst, MO is basically generated as a main reaction product, accompanied by propene and MIBK traces, these two last substances being presumably formed by hydrogen transfer reactions. With platinum containing catalysts the products mainly formed are MIBK and propane, accompa-

Table 2
Selectivity of the catalysts (conversion = 10%)

Catalyst	*n*Pt/*n*A[a]	MIBK[b]	C_3[c]	2MP[d]	DIBK[e]	MO[f]
0.03Pt-HZSM5(41)	0.0017	8.0	1.0	0.30	0.20	0.50
0.16Pt-HZSM5(41)	0.0110	6.9	2.6	0.34	0.10	0.06
0.54Pt-HZSM5(41)	0.0357	5.0	4.4	0.40	0.11	0.05

[a] Accessible metallic centers/theoretical acid sites ratio.
[b] Methyl isobutyl ketone. [c] Propane. [d] 2-methyl pentane.
[e] Diisobutyl ketone. [f] Mesityl oxide.

nied by 2-methyl pentane (2MP), mesityl oxide (MO) and diisobutyl ketone (DIBK). Selectivity of these products varies as the number of hydro-dehydrogenating centers (*n*Pt) on the Pt-HZSM5(41) catalysts increases, because MO and Ac are more easily hydrogenated to achieve MIBK and C_3 formation [7]. All of the reaction products are formed by means of a bifunctional mechanism, except MO, which requires an acid catalysis to be formed from acetone.

4. Conclusions

The results obtained in the ketone transformation on bifunctional Pt-HZSM5(41) catalysts clearly show the dependence of catalytic properties on the metallic centers/theoretical acidic sites ratio ($n\mathrm{Pt}/n\mathrm{A}$). A_0 and A_r initially increase and then reach a constant value from $n\mathrm{Pt}/n\mathrm{A} \geqslant 0.015$ on. By contrast, the coke amount (as %C) decreases as $n\mathrm{Pt}/n\mathrm{A}$ increases, and then stabilizes at a minimum value from $n\mathrm{Pt}/n\mathrm{A} \geqslant 0.015$ on. This shows that activity, stability and coke amount deposited on the catalysts are a function of the $n\mathrm{Pt}/n\mathrm{A}$ ratio. Moreover, it is shown that ketone transformation into MIBK takes place by means of a bifunctional mechanism.

Acknowledgement

Financial support by the EC within the International Cooperation EC-ALA/MED countries (Contract CI1*CT94-0044) is gratefully acknowledged.

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