Acetone transformation into methyl isobutyl ketone over Pt/HMFI catalysts. IV. Effect of density and strength of the acidic sites

L. Melo [a,*], G. Giannetto [a], L. Cardozo [a], A. Llanos [b], L. García [a], P. Magnoux [c], M. Guisnet [c] and F. Alvarez [d]

[a] *Facultad de Ingeniería, Universidad Central de Venezuela, PO Box 48.057, Caracas 1041-A, Venezuela*
[b] *IUT Región Capital, Departamento de Química, Caracas, Venezuela*
[c] *Faculté de Science, Université de Poitiers, Poitiers, France*
[d] *Instituto de Superior Técnico, Lisbon, Portugal*

Received 6 May 1998; accepted 3 June 1999

Acetone transformation into methyl isobutyl ketone (MIBK) was studied using a fixed-bed dynamic reactor at 160 °C, 1 atm pressure and acetone/H_2 molar ratio $= 3$. The reaction was carried out over Pt/HMFI bifunctional catalysts, with 0.30 wt% of platinum which was supported over three aluminosilicates (Si/Al ratio $= 40$, 95 and 160) and a borosilicate (Si/B ratio $= 44$) with similar dispersion. The results show that catalytic properties depend greatly on density and strength of the acidic sites of the catalysts. Moreover, the limiting step of the MIBK synthesis reaction (aldolization of two acetone molecules) is carried out over the acidic sites of the aluminosilicates, but not over those of the borosilicate, which considerably affects reaction selectivity.

Keywords: acetone, MIBK, HZSM5, aluminosilicate, borosilicate, bifunctional catalyst, density and strength of acidic sites

1. Introduction

Acetone can react under acid or basic catalysis, generating a large number of aldolization products, usually with high volume and high molecular weight [1]. When acetone reacts over amorphous solids, either acid or base, the main reaction products obtained are cyclic ketones, such as isophorone and isoxilitones [2]. This is the result of the large size of the cavities in these solids. However, when acetone reacts over MFI type crystalline aluminosilicates at relatively low temperatures, the main product generated is mesityl oxide (MO) [3,4], an unsaturated α–β ketone, which is the most immediate intermediate for the synthesis of methyl isobutyl ketone (MIBK). This substance is very useful in industry as a solvent in the manufacturing of paints, lacquers, etc. [5]

MIBK synthesis is normally carried out in a process comprising three successive steps: (i) aldolization of the acetone molecules under acid or base catalysis, which permits the formation of the first intermediate, diacetone alcohol (DA); (ii) DA dehydration, by means of an acid catalysis which results in the formation of the unsaturated α–β ketone (MO); and (iii) selective hydrogenation of the double olefinic bond of MO, which allows MIBK to be obtained [3].

Recently MIBK has been obtained by means of a process with only one apparent step, using acetone under hydrogen atmosphere and bifunctional crystalline metal/aluminosilicates catalysts [6,7]. This produces a considerable simplification of the process, given the fact that the reaction product can be separated from the catalyst more easily and that less environmental pollution is produced.

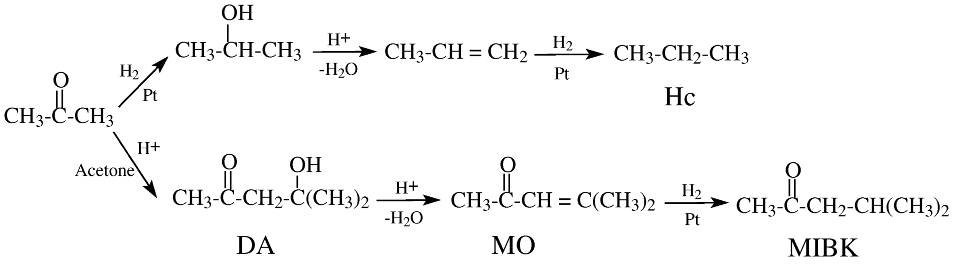
However, this method, that comprises the use of bifunctional catalysis, presents the following drawbacks:

(i) The presence of a parasite reaction, which leads to the formation of light hydrocarbons (Hc, basically propane), as shown in the reaction scheme (equation (1a)), proposed in a previous paper [8]. This propane formation results in a severe decrease of the MIBK formation selectivity.

(ii) The strong deactivation produced in these solids, as a consequence of working at a high acetone/H_2 molar ratio, which favors the presence of successive aldolization reactions resulting in the generation of carbonous residues in the cavities near the active centers of the solids. Since MIBK is a widely used solvent, which can be synthesized from acetone, in hydrogen atmosphere, over Pt/HMFI [7,8] bifunctional catalysts, it certainly represents a very interesting method. However, the fast deactivation of the solids used as catalysts is one of the major drawbacks of this method. In this regard, the purpose of our work is to elucidate how density and strength of the acidic sites of the catalyst influence its catalytic properties (activity, stability, and selectivity) as well as define the step which limits the synthesis of this important solvent. The results obtained show that both strength as well as density of acidic sites considerably effect catalytic properties of the solids.

---

[*] To whom correspondence should be addressed.



$$CH_3\text{-}CO\text{-}CH_3 \xrightarrow[Pt]{H_2} CH_3\text{-}CH(OH)\text{-}CH_3 \xrightarrow[-H_2O]{H^+} CH_3\text{-}CH=CH_2 \xrightarrow[Pt]{H_2} \underset{\text{Hc}}{CH_3\text{-}CH_2\text{-}CH_3} \quad (1a)$$

$$CH_3\text{-}CO\text{-}CH_3 \xrightarrow[\text{Acetone}]{H^+} \underset{\text{DA}}{CH_3\text{-}CO\text{-}CH_2\text{-}C(OH)(CH_3)_2} \xrightarrow[-H_2O]{H^+} \underset{\text{MO}}{CH_3\text{-}CO\text{-}CH=C(CH_3)_2} \xrightarrow[Pt]{H_2} \underset{\text{MIBK}}{CH_3\text{-}CO\text{-}CH_2\text{-}CH(CH_3)_2} \quad (1b)$$

Equation (1).

2. Experimental

Four MFI type solids were synthesized according to the method proposed by Guth et al. [9]. Three of them were aluminosilicates with variable aluminum concentration and the other was a borosilicate. Once calcined under dry air atmosphere, these solids were assessed by means of X-ray diffraction and nitrogen adsorption at −196 °C, which verified that they are highly pure and crystalline. Analysis by means of inductively coupled plasma (ICP) [10] shows that these solids have Si/Al ratios of 40, 95 and 160 for aluminosilicates and a Si/B ratio of 44 for the borosilicate. This last solid was obtained in a way that may ensure the absence of aluminum, therefore, its synthesis was effected using highly pure boric acid (Aldrich). The solid obtained was subjected to a rigorous elemental analysis by means of the ICP technique to determine its content of boron and silicon, and to verify the presence of aluminum traces, which was negative for this last element. Since the ICP method employed has few interference and the detection limits for aluminum and boron are 2 and 5 ppb, respectively [10], we can assume the absence of aluminum in the borosilicate.

Also, each one of these MFI type solids was assessed using TPD NH_3. This analysis established that the aluminosilicates desorb ammonia at temperatures over 450 °C, whereas this gas desorption does not exceed 200 °C for the borosilicate, as can be seen in the example in the ammonia desorption thermograms (figures 1 and 2) for H[Al]ZSM5 (Si/Al = 40) and H[B]ZSN5 (Si/B = 44), respectively. These results confirm those found using ICP, because if aluminum is found in the borosilicate this will show ammonium desorption at temperatures over 450 °C.

Once these solids were calcined, they were used as a support in the preparation of the bifunctional Pt/HMFI catalysts. Platinum was introduced by means of exchange with competition, using $Pt(NH_3)_4Cl_2$ as a precursor and NH_4^+ as a competing ion. A molar ratio equal to 200 ($nNH_4^+/nPt(NH_3)_4^{2+}$) was kept, which ensures a homogeneous exchange over the zeolite grain, as has been shown by Ribeiro et al. [11]. The exchange process with competition was carried out for 24 h, followed by dry evaporation at 50 °C. This let us ensure that $Pt(NH_3)_4^{2+}$ ion was exchanged and/or impregnated over the zeolite support, which was later confirmed through platinum chemical analysis using ICP (table 1).

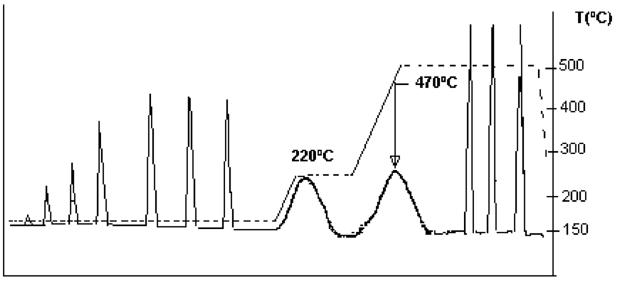


Figure 1. Thermogram of NH_3 desorption for H[Al]ZSM5 (Si/Al = 40) aluminosilicate.

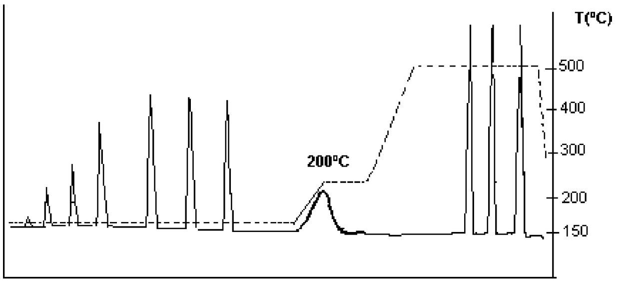


Figure 2. Thermogram of NH_3 desorption for H[B]ZSM5 (Si/Al = 44) borosilicate.

Table 1
Physicochemical characteristics of the catalysts.[a]

Catalyst	Si/M	Pt exp. (%)	D_{TEM} (%)	$D_{\text{H/Pt}}$ (%)	A_{H}^0 (mmol/h g)
0.30PtH[Al]ZSM5(40)	40	0.31	21	25	7.1
0.30PtH[Al]ZSM5(95)	95	0.29	23	22	7.0
0.30PtH[Al]ZSM5(160)	160	0.30	20	24	7.1
0.30PtH[B]ZSM5(44)	44	0.31	22	23	7.2

[a] Si/M: silica/structural metal atomic ratio; Pt exp.: percentage of platinum supported in each solid, experimentally determined; D_{TEM}: dispersion of platinum obtained by TEM; $D_{\text{H/Pt}}$: dispersion of platinum obtained by hydrogen chemisorption. A_{H}^0: total initial activity in toluene hydrogenation extrapolated at $t = 0$ min.

Catalysts were calcined in dry air atmosphere up to 300 °C and then reduced under hydrogen at 500 °C, according to well-established protocols [12]. Metallic phase dispersion of these solids was evaluated using transmission electronic microscopy (TEM), in a Jeol 100 CX II electronic microscope, and hydrogen chemisorption. A suspension of the solid in ethanol was prepared and then deposited over a copper grid, coated before with carbon film. Dispersion of the supported platinum phase was obtained as follows: random micrographs of the analyzed samples were taken and zones with 500–1000 metallic particles were selected.

These were considered spherical and, therefore, their diameter and frequency of appearance were determined. The average diameter ($\overline{d}$) of the disperse particles in the supports was then determined using the equation [13,14]

$$\overline{d} = \sum n_i d_i^3 \Big/ \sum n_i d_i^2, \qquad (2)$$

where (d_i) is the diameter of each metal particle and n_i the number of particle found with the same diameter in the selected sample. $\overline{d}$, determined in nanometer (nm), permitted us to determine metallic phase dispersion (D) using expression (3) proposed by Boudart et al. [15], which is an excellent approximation for transition metals:

$$D = 1/\,\overline{d}\ (\text{nm}). \qquad (3)$$

Results found are shown in table 1. The metallic phase of these catalysts was also assessed by means of hydrogen chemisorption. Both techniques show (table 1) that platinum dispersion of the solids prepared is almost 20%.

The hydrogenating activity of these Pt/HMFI catalysts was assessed using toluene hydrogenation [7] as a reaction model. This hydrogenation was carried out in a fixed-bed dynamic reactor at 110 °C, 1 atm pressure, H_2/toluene molar ratio = 4 and WHSV (grams of injected reagent per hour and per gram of catalyst) = 21.5 h^{-1}.

Acetone transformation reaction was carried out in a fixed-bed dynamic reactor at 160 °C, 1 atm pressure, acetone/H_2 molar ratio = 3 and WHSV between 9.5 and 28.4 h^{-1}.

The main products resulting from this reaction were methyl isobutyl ketone (MIBK) and propane (Hc). 2-methyl pentane (2MP), diisobutyl ketone (DIBK), and mesityl oxide (MO) are produced as minority products. Effluents from the reactor were injected on line into an HP-6890 chromatograph equipped with a phenyl–methyl siloxane type column, which allowed the determination of the composition of the mixture from the reactor at different reaction times and WHSVs.

3. Results and discussion

3.1. Toluene hydrogenation

The 0.30Pt/H[Al]ZSM5 catalysts (Si/Al ratio = 40, 95 and 160) as well as 0.30Pt/H[B]ZSM5 (Si/B ratio = 44) show a very similar activity in toluene hydrogenation, as can be seen in table 1. These results show that these solids have a very similar number of hydrogenating metallic centers (as shown by the dispersion measurements using TEM and chemisorption), because this reaction depends solely on the population of accessible metallic centers in the catalysts [3,7].

3.2. Effect of density of acidic sites

Acetone transformation was carried out over the platinum catalysts supported over MFI type aluminosilicates with Si/Al ratio of 40, 95 and 160. Figure 1 shows the evolution of conversion as a function of reaction time under standard conditions and WHSV = 19 h^{-1}. This figure also indicates that total initial activity decreases as the number of active acid centers of the catalyst decreases.

Since the initial step of the acetone transformation into MIBK is a bimolecular reaction (aldolization of two acetone molecules, equation (1b) and is catalyzed by acidic sites, a reaction mixture in the molecular ratio acetone/H_2 = 3, as the one used in this work, is expected to favor the formation of DA, MO and, finally, MIBK [3]. As a consequence, total transformation of acetone should occur mainly in this way. In this regard, the results reported in figure 3 are completely

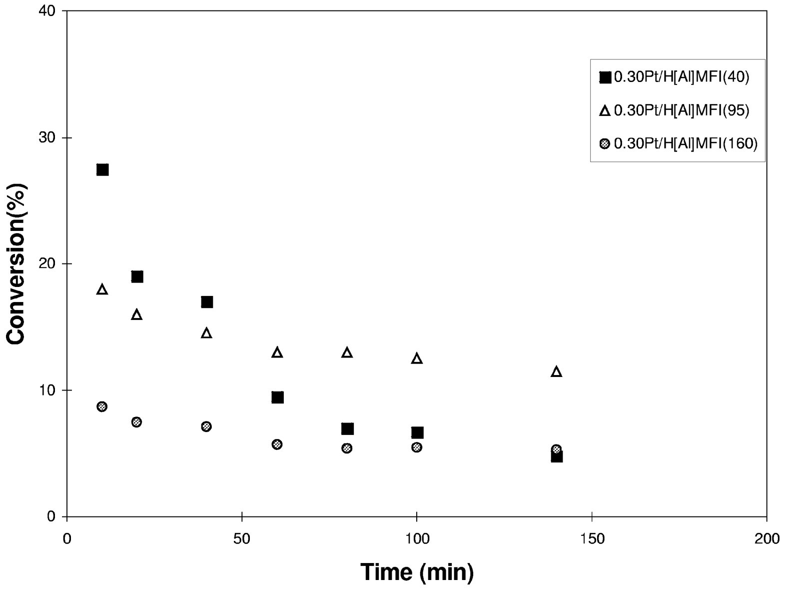


Figure 3. Evolution of acetone conversion as a function of reaction time for 0.30Pt/H[Al]ZSM5 (Si/Al = 40, 95 and 160) catalysts; T = 160 °C, acetone/H_2 molar ratio = 3 and WHSV = 19 h^{-1}.

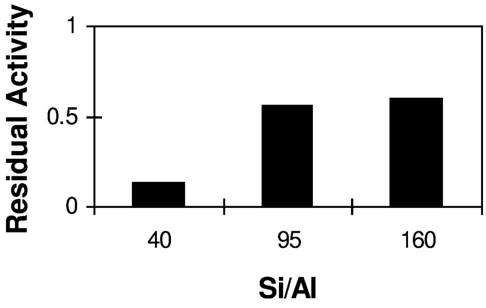


Figure 4. Residual activity as a function of the Si/Al ratio for 0.30Pt/H[Al]ZSM5 (Si/Al = 40, 95 and 160) catalysts; $T = 160\,^{\circ}$C, acetone/H_2 molar ratio = 3 and WHSV = 19 h^{-1}.

Table 2
Relationship of MIBK and Hc formation velocities and selectivity of the different products formed at 10% isoconversion, for all catalysts employed.

Catalyst	MIBK/Hc	MIBK	Hc	MO	2MP	DIBK
0.30PtH[Al]ZSM5(40)	10.6	8.4	0.8	0.4	0.3	0.1
0.30PtH[Al]ZSM5(95)	7.5	7.5	1.0	0.4	0.8	0.2
0.30PtH[Al]ZSM5(160)	4.3	6.5	1.5	0.4	1.4	0.2
0.30PtH[B]ZSM5(44)	0.3	2.0	7.5	0.3	0.2	–

logical, because in a series of catalysts like those used in this experiment (0.30Pt/H[Al]ZSM5 (Si/Al = 40, 95 and 160)), with similar number of metallic centers (table 1) and sites with the same acid strength, the catalyst with higher density in acidic sites is expected to show a higher total initial activity in acetone transformation, since this will be the catalyst producing the largest number of molecules of DA (bimolecular reaction), MO and, finally, MIBK.

Figure 4 shows that the catalytic stability of these solids, expressed as residual activity ($A_{\mathrm{r}} = A_t/A_0$, fraction of the initial activity remaining in the catalyst after a time t of 150 min of use under operation conditions) is directly proportional to their structural Si/Al ratio, which is a reasonable result, because the higher the density of the acidic sites, the higher the MO concentration generated over the surface of the solid. Assuming that these three catalysts (0.30Pt/H[Al]ZSM5 (Si/Al = 40, 95 and 160)) have a similar number of hydrogenating centers, a higher concentration of non-hydrogenated MO would remain over the solid with higher density of acidic sites. However, the fact that MO is one of the main precursors of coke in these solids [7] would explain why the highest and the lowest deactivation is produced over these catalysts 0.30Pt/H[Al]ZSM5 (Si/Al = 40) and 0.30Pt/H[Al]ZSM5 (Si/Al = 160), respectively.

Likewise, selectivity of these catalysts, expressed by means of the reaction rates ratio of MIBK and Hc formation (MIBK/Hc), at 10% isoconversion, decreases as density of acidic sites decreases, as shown in table 2.

It is obvious that selectivity for these bifunctional catalysts varies as the Si/Al ratio changes, because if the density of acidic sites is lower, it is less likely that the bimolecular aldolization reaction of two acetone molecules (equation (1b)) can take place, which results in the reduction of the concentration of the DA, MO and, of course, MIBK produced.

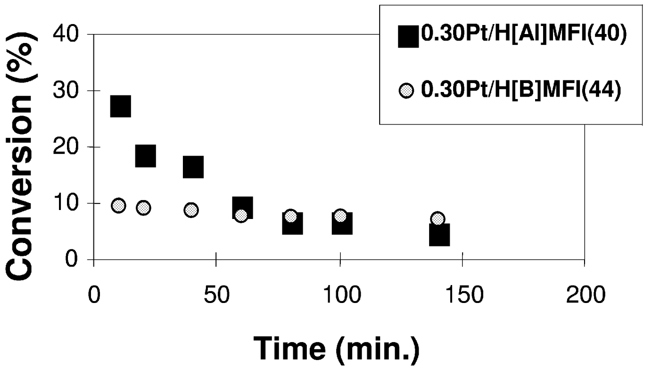


Figure 5. Evolution of acetone conversion as a function of reaction time for 0.30Pt/H[Al]ZSM5 (Si/Al = 40) and 0.30Pt/H[B]ZSM5 (Si/B = 44) catalysts; $T = 160\,^{\circ}$C, acetone/H_2 molar ratio = 3 and WHSV = 19 h^{-1}.

Hc production is practically invariable in these catalysts because the reaction limiting its formation seems to depend basically on the number of active metallic centers, which are very similar in the three catalysts (table 1). Since Hc concentration remains practically constant and that of MIBK decreases as the Si/Al ratio increases, the MIBK/Hc ratio is smaller when density of acidic sites in these catalysts is lower (table 2).

3.3. Effect of acid strength

Figure 5 shows the evolution of the acetone conversion as a function of the reaction time for 0.30Pt/H[Al]ZSM5 (Si/Al = 40) and 0.30Pt/H[B]ZSM5 (Si/B = 44) catalysts. As in the previous case, the reaction was carried out in a dynamic reactor under standard conditions and WHSV = 19 h^{-1}. The catalysts used have a similar number of metallic centers and of acidic sites.

Results reported in figure 5 show that total initial activity in acetone transformation over 0.30Pt/H[Al]ZSM5 (Si/Al = 40) is almost four times higher than total initial activity for 0.30Pt/H[B]ZSM5 (Si/B = 44). This figure also shows that catalytic stability of the 0.30Pt/H[B]ZSM5 (Si/B = 44) is five times higher than that of 0.30Pt/H[Al]ZSM5 (Si/Al = 40). These differences should be associated neither to density of acidic sites nor to porous structure of the supports, because these are similar in both catalysts. This catalytic behavior depends on the strength of acidic sites in each solid, which is higher in the aluminosilicate (Si/Al = 40) than in the borosilicate (Si/B = 44), as observed in the ammonia desorption thermograms (figures 1 and 2).

Table 2 shows (10% isoconversion) that the ratio of formation velocity of MIBK and Hc (MIBK/Hc) for the 0.30Pt/H[Al]ZSM5 (Si/Al = 40) catalyst is approximately 35 times higher than that obtained with the 0.30Pt/H[B]ZSM5 (Si/B = 44) catalyst.

Differences in the catalytic properties (activity, stability and selectivity) of these catalysts can be explained if we consider the strength in the acidic sites of each solid.

3.3.1. Activity

Both catalysts have the same number of metallic centers and similar density of acidic sites, therefore, the higher total initial activity obtained with the 0.30Pt/H[Al]ZSM5 (Si/Al = 40) catalyst can be attributed to the higher acid strength of the sites present in the aluminosilicate with respect to the borosilicate.

The acetone transformation over the 0.30Pt/H[Al]ZSM5 (40) catalyst can be expected to take place through two processes proposed in the reaction scheme (equations (1a) and (1b)). That is, through hydrogenation–dehydration–hydrogenation, which could lead to the formation of propane (equation (1a)) and the other process, which allows acetone transformation through aldolization–dehydration–hydrogenation, and will result in the formation of MIBK (equation (1b)). Both reactions would be perfectly feasible over this catalyst, because it has the active sites necessary to catalyze the acetone transformation through both processes; however, the most favored would be that resulting in the MIBK formation, because the acetone/H_2 molecular ratio of the reaction mixture is 3. The opposite can be observed over the 0.30Pt/H[B]ZSM5(44) catalyst, because acetone transformation through the process aldolization–dehydration–hydrogenation is not favored, due to the absence in the borosilicate of acidic sites with the strength necessary to catalyze the aldolization reaction. Therefore, activity in MIBK formation and total initial activity in acetone transformation are very low over this catalyst.

3.3.2. Stability

Catalytic stability for both catalysts has been estimated on the base of the residual activity (A_r). Figure 6 shows that A_r after 150 min reaction is approximately 0.14 and 0.80 for 0.30Pt/H[Al]ZSM5(40) and 0.30Pt/H[B]ZSM5(44), respectively. These results could be explained based on the capacity of each one of these solids to generate reaction intermediates which are not transformed into the final product of interest, as seems to be happening with the 0.30Pt/H[Al]ZSM5(40) catalyst. This solid, with density of very strong acidic sites, would be capable of catalyzing the aldolization reaction of two acetone molecules to produce the DA intermediate, which, by dehydration over the same acidic sites on which it is generated, would result in the formation of a high MO concentration over the catalytic surface. If the 0.30Pt/H[Al]ZSM5(40) catalyst does not possess the number of metallic centers enough to hydrogenate all of the MO produced (as should happen in the catalyst due to the low dispersion in its metallic phase), the remaining molecules of this unsaturated α–β ketone could continue to react with additional acetone molecules under acid catalysis, thus forming molecules with high volume and molecular weight, such as isophorone, which has been determined to be one of the main components of coke deactivating the medium-size pore aluminosilicates [7].

The phenomenon described before is not observed over the 0.30Pt/H[B]ZSM5(44) catalyst, because a very low concentration of DA, and, therefore, of MO, is produced over this catalyst. This hinders the formation of macromolecules and the early deactivation of the catalyst. However, after 150 min of reaction the catalyst loses 20% of its initial activity (figure 6). This deactivation cannot be attributed either to the formation of macromolecules through aldolization or to propene oligomerization, because the borosilicate does not have the sites with the acid strength required to catalyze these reactions (figure 2). This suggests that the loss of activity in this catalyst could be the result of the presence of water generated by dehydration of the intermediate alcohols in this process (basically isopropanol), which results in the formation of a step (probably a platinum oxide) inactive to the acetone hydrogenation reaction.

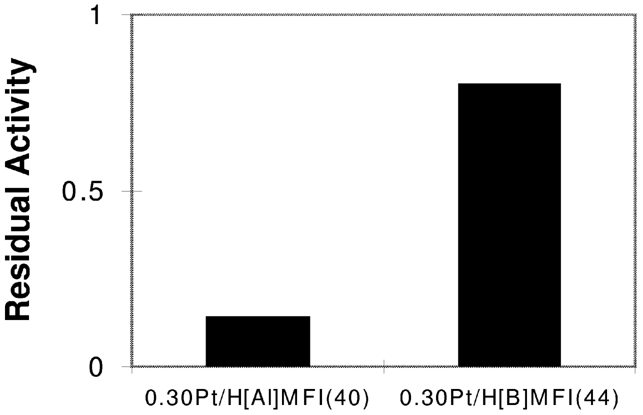


Figure 6. Residual activity for 0.30Pt/H[Al]ZSM5 (Si/Al = 40) and 0.30Pt/H[B]ZSM5 (Si/B = 44) catalysts; $T = 160\,^{\circ}\mathrm{C}$, acetone/$H_2$ molar ratio = 3 and WHSV = 19 h^{-1}.

3.3.3. Selectivity

Table 2 shows that, at 10% isoconversion, the 0.30Pt/H[Al]ZSM5(40) catalyst is much more selective to MIBK formation than to Hc (MIBK/Hc = 10.6). This higher selectivity towards MIBK is due to the fact that the platinum catalyst supported over aluminosilicate has sites with such an acid strength as would be appropriate to catalyze the aldolization step, which seems to require sites with an acid strength higher than the remaining steps needing acid catalysis in this process.

Moreover, the larger production of Hc (MIBK/Hc = 0.3) over the platinum catalyst supported over borosilicate (table 2) is explained, because there are no acidic sites over this solid with the strength required to catalyze the aldolization step. Therefore, most of the acetone molecules over the catalytic surface will not be aldolized, so that they could move from the acidic sites (weak), completely intact, towards the neighboring metallic centers, where they would be hydrogenated and converted into isopropanol. Since this is a secondary alcohol and is susceptible to be dehydrated over the weak acidic sites in the borosilicate, propene would be produced which then would be hydrogenated into propane over the metallic centers.

4. Conclusions

Total activity of acetone transformation under standard conditions, catalytic stability and selectivity of the reaction products depend mainly on the density of acidic sites present in the bifunctional catalysts of the 0.30Pt/H[Al]ZSM5 type with the same number of metallic centers.

The effect of the strength of the acidic sites is really important in the selectivity of the main reaction products (MIBK and Hc). It was found that for platinum catalysts supported over aluminosilicates, the selectively formed product is MIBK and over the platinum solid supported over borosilicate, light hydrocarbons (Hc) are the most favored.

Acknowledgement

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

References

[1] J.D. Roberts and M.C. Caserio, Chim. Org. Moderne (1977) 358.
[2] W.T. Reichle, J. Catal. 63 (1980) 295.
[3] L. Melo, Ph.D. thesis, Université de Poitiers, France (1994).
[4] A.I. Biaglow, J. Sepa, R.J. Gorte and D. White, J. Catal. 151 (1995) 373.
[5] W.F. Hoelderich, Stud. Surf. Sci. Catal. 41 (1988) 83.
[6] P.V. Chen, S.J. Chu, N.S. Chang, T.K. Chuang and L.Y. Chen, Stud. Surf. Sci. Catal. 46 (1989) 231.
[7] L. Melo, G. Giannetto, F. Alvarez, P. Magnoux and M. Guisnet, Catal. Lett. 44 (1997) 201.
[8] L. Melo, P. Magnoux, G. Giannetto, F. Alvarez and M. Guisnet, J. Mol. Catal. 124 (1997) 155.
[9] J.L. Guth and Ph. Caullet, J. Chim. Phys. 83 (1986) 155.
[10] R.M. Barnes, CRC Crit. Rev. Anal. Chem. (September 1978) 203.
[11] F. Ribeiro and C. Marcilly, Rev. Inst. Fr. Pétrol. XXXIV (1979) 405.
[12] G. Giannetto, G. Perot and M. Guisnet, Stud. Surf. Sci. Catal. 20 (1985) 265.
[13] T.E. White, Jr., Catal. Rev. 8 (1973) 117.
[14] G.N. Folefoc and J. Dwyer, J. Catal. 136 (1992) 43.
[15] H. Boudart and H.S. Hwuang, J. Catal. 39 (1975) 44.