

Transformation of acetone over a 0.4PtHMFI(60) catalyst. Reaction scheme

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Abstract

The transformation of acetone was carried out over a 0.4 wt% PtHMFI catalyst (Si/Al = 60) under the following conditions: flow reactor, 160°C, pressures of acetone and hydrogen equal to 0.75 and 0.25 bar, respectively. Methylisobutylketone, propane and traces of mesityloxy are observed as primary products while the other main products: 2-methylpentane and diisobutylketone result from secondary transformation of methylisobutylketone. The reactivity of the reaction products and of probable intermediates: diacetone alcohol, isopropanol and propene was compared to that of acetone, which allows us to establish the complete scheme of acetone transformation. Acetone is competitively transformed through bifunctional catalysis into methylisobutylketone and into propane. The limiting step of methylisobutylketone formation is acetone aldolisation over the acid sites of the catalyst while that of propane formation is acetone hydrogenation over platinum sites. Methylisobutylketone undergoes the same competitive bifunctional transformations leading to diisobutylketone (limiting step: acid coaldolisation of acetone and of methylisobutylketone) and to 2-methylpentane (limiting step: hydrogenation of methylisobutylketone). © 1997 Elsevier Science B.V.

1. Introduction

Methylisobutylketone (MIBK) is used as a solvent for inks and lacquers [1]. This ketone can be prepared from acetone through a catalytic three-step process: acid- or base-catalyzed production of diacetone alcohol (DA), acid dehydration of DA into mesityloxy (MO) followed by hydrogenation of MO over a noble metal catalyst [1]. All these steps are carried out at a relatively low temperature. Under these

conditions the first step is reversible but the other ones can be made irreversible. Therefore, it can be envisaged to prepare MIBK from acetone in one step, with a very low formation of diacetone alcohol and of mesityloxy by using under hydrogenating conditions bifunctional noble metal/acid catalysts such as Pd-doped sulfonated resin [1,2], Pt or Pd/HZSM5 [3–7], etc.

Unfortunately secondary reactions accompany the formation of methylisobutylketone over bifunctional metal/acid catalysts. In this paper the complete reaction scheme of acetone transformation over a 0.4 wt% PtHZSM5 catalyst

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with a Si/Al ratio of 60 was established (i) from the effect of contact time (or of acetone conversion) on the yields in the various products and (ii) from the comparison between the transformations of acetone, reaction products and probable intermediates.

2. Experimental

HZSM5 (Si/Al = 60) was prepared by the method proposed by Guth and Caullet [8], 0.4 PtHZSM5 was prepared by the method previously described [9]: exchange with $\text{Pt}(\text{NH}_3)_4^{2+}$ in competition with NH_4^+ , calcination under dry air flow at 300°C for 6 h, reduction under hydrogen flow at 500°C for 6 h. The transformation of acetone was carried out in a flow reactor at 160°C with $P_{\text{H}_2} = 0.25$ bar and $P_{\text{acetone}} = 0.75$ bar, WHSV (weight of reactant injected per weight of catalyst per h) between 2.4 h⁻¹ and 95 h⁻¹. The transformation of the reaction products and of the intermediates: propene, methylisobutylketone, mesityloxide, isopropanol and diacetone alcohol were carried out in a flow reactor at 160°C with $P_{\text{H}_2} = 0.25$ bar and P_{reactant} equal to 0.05 and 0.15 bar, WHSV = 22.9 to 28.4 h⁻¹.

Reaction products were analyzed on-line by gas chromatography with a CP Sil 5 CB capillary column. The experimental methods used to recover and to analyze the heavy secondary products were the same as those used to analyze zeolitic coke [10].

3. Results

3.1. Influence of contact time on acetone transformation

Under the standard conditions (160°C, $p_{\text{H}_2} = 0.25$ bar, $p_{\text{acetone}} = 0.75$ bar, WHSV (weight of reactant injected per weight of catalyst and per h) = 4.75 h⁻¹), acetone is transformed into methylisobutylketone (MIBK) and also leads to

propane (P), 2-methylpentane (2MP), diisobutylketone (DIBK) and to traces of mesityloxide (MO). The deactivation of the catalyst is relatively rapid particularly during the first hour of reaction. Thus after 4 h reaction the activity is approximately 2 times lower than the initial activity. This deactivation can be related to the formation of heavy secondary products: approximately 6.3 wt% on the catalyst after 4 h reaction, which corresponds to a conversion of acetone into these products of approximately 0.5%. These heavy products are blocked within the pores of the zeolite. Indeed only a small part of these compounds can be recovered in methylene chloride through a simple soxhlet treatment of the deactivated catalyst while all of them are recovered after dissolution of the zeolite in a hydrofluoric acid solution. IR spectroscopy shows bands characteristic of aromatic and of carbonylated compounds while GC-MS coupling indicates the presence of isophorone as a major component, accompanied by various polyalkylbenzenes (with 5 to 7 carbon atoms in the alkyl groups). All these compounds are retained in the zeolite pores because of their low volatility, of their adsorption on the acid sites and/or because their size is close to or greater than the size of the pore aperture. These compounds block the access of the reactant to the acid or to the platinum sites, hence causing a decrease in the catalyst activity.

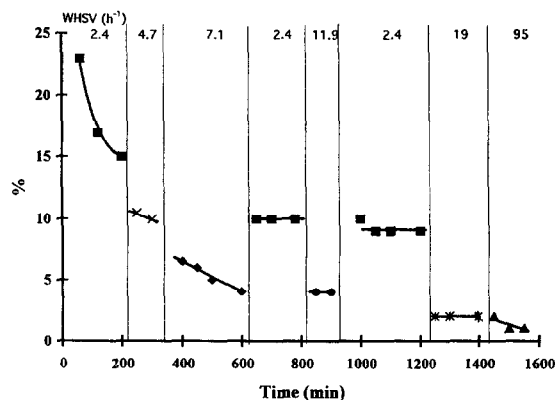


Fig. 1. Change in the yield in methylisobutylketone (MIBK) as a function of time-on-stream TOS (min) for various values of weight hour space velocity WHSV (h⁻¹).

The effect of contact time on the yields in the various products was established by the procedure shown in Fig. 1 on the example of MIBK. The values used were those deduced from the extrapolation at 800 min (i.e. after the rapid initial deactivation) of the curves giving the yields as a function of time-on-stream. Fig. 2 shows that MIBK, propane (P) and MO result apparently from a direct transformation of acetone (apparent primary products) while DIBK and 2MP are secondary products. The same conclusions can be drawn from the curves giving the yields as a function of acetone conversion (Fig. 3). Moreover these figures show that the catalyst selectivity does not depend on the

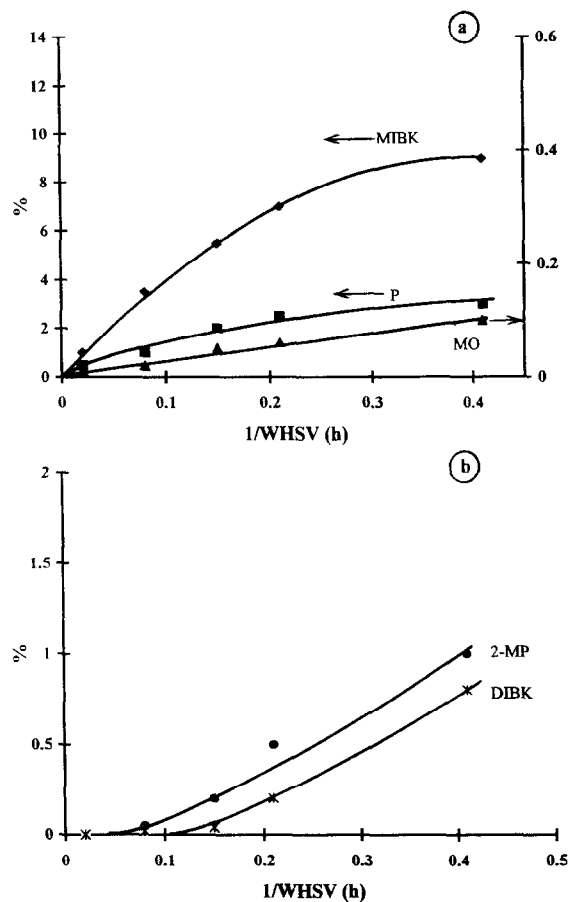


Fig. 2. Influence of contact time (taken as the reverse of WHSV, the weight hour space velocity) on the yields in the primary products (a) and in the secondary products (b).

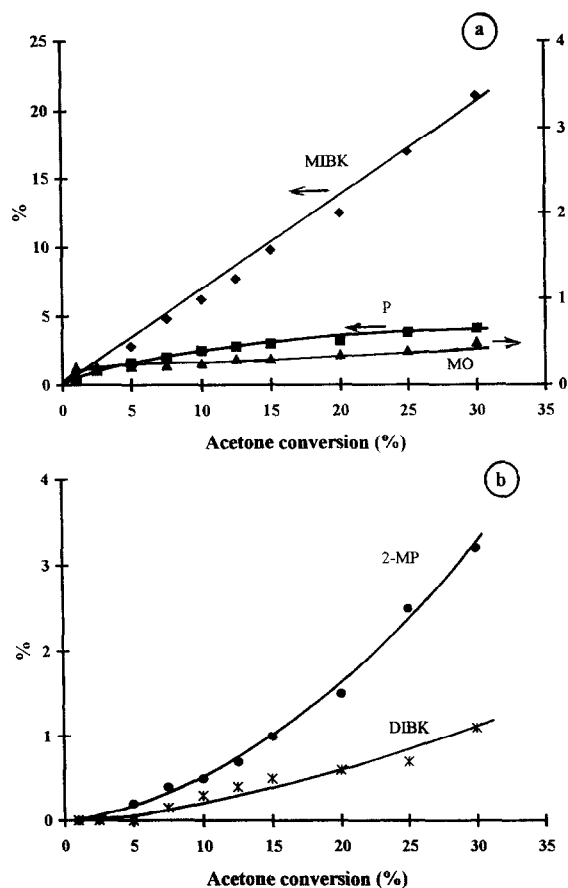


Fig. 3. Influence of acetone conversion on the yields in the primary products (a) and in the secondary products (b).

degree of deactivation. Indeed all the experimental values obtained, before or after the initial rapid deactivation, can be located on the same curves.

3.2. Transformation of various intermediates and products of acetone conversion

The transformation of MO, MIBK and of the probable reaction intermediates: diacetone alcohol, isopropanol and propene was compared to that of acetone through successive experiments on the same sample of catalyst. Two values of partial pressure comparable to the value attained by these compounds during acetone conversion: 0.05 and 0.15 bar were chosen, the hydrogen

pressure being kept at 0.25 bar and WHSV of acetone and the other compound between to 22.9 and 28.4 h⁻¹. The results obtained during the comparison of isopropanol and acetone transformations are given in Fig. 4. Fig. 4 shows that isopropanol transforms much more rapidly than acetone. Propane is the only product observed. This very high rate of isopropanol transformation into propane allows one to explain why isopropanol is not observed in the products of acetone transformation and why propane appears as a primary product.

Another interesting result is that isopropanol does not cause any supplementary deactivation of the catalyst (Fig. 4). The same is observed when propene or MIBK are used as reactants whereas in the case of diacetone alcohol and mesityloxyde a complete deactivation of the catalyst resulted.

The products of transformation of the various compounds are indicated below:

isopropanol → propane

propene → propane

diacetone alcohol → acetone > MO ≈ MIBK
 ≫ 2MP and DIBK

MO → MIBK ≫ acetone, 2MP, DIBK

MIBK → 2MP

Table 1 compares the rates of transformation of the various compounds to that of acetone. Isopropanol, propene, diacetone alcohol and MO are much more reactive than acetone (20 to 100

Table 1

Comparison of the conversion X_C of various compounds under two different conditions of partial pressure (X_{C_1} : $p = 0.05$ bar, X_{C_2} : $p = 0.15$ bar) to that of acetone (X_A) under standard conditions. The values are given in the order in which the experiments were carried out

Reactant	X_A	X_{C_1}	X_{C_2}	X_A
Isopropanol	0.05	0.98	0.05	1
Propene	0.05	1	0.05	1
Diacetone alcohol	0.05	0.99	—	0.90
MO	0.06	0.11	0.01	0.05
MIBK	0.06	0.01	0.04	0.01

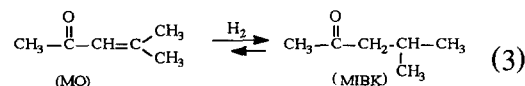
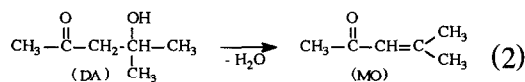
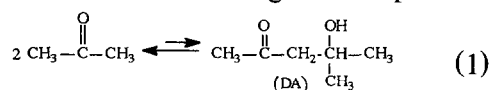
times more) while MIBK is approximately 6 times less reactive.

4. Discussion

4.1. Mode of formation of the products of acetone transformation

4.1.1. Mode of formation of MIBK

MIBK is an apparent primary product of acetone transformation (Figs. 2 and 3). Moreover, its formation from diacetone alcohol (DA) and from mesityloxyde (MO) is faster than from acetone. This confirms that the formation of this product involves the following three steps.



Acetone aldolisation (Eq. (1)) is the limiting step of MIBK formation. This step is equilibrated, the equilibrium being largely in favour of acetone: about 95% [11]. This explains the

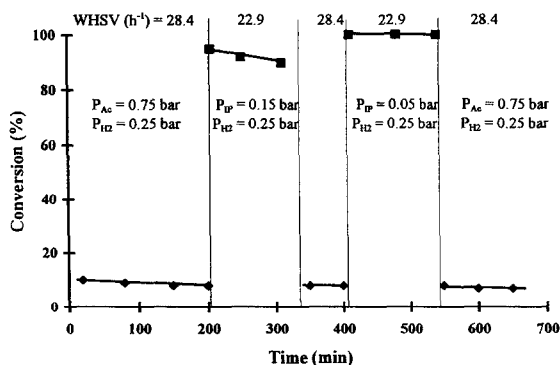
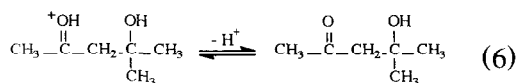
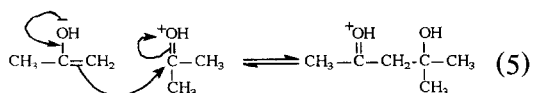
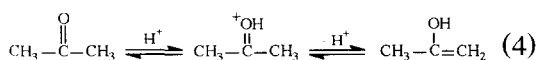


Fig. 4. Comparison of the reactivities of isopropanol (Ip) and of acetone (Ac) over a 0.4PtHZSM5(60) catalyst.

significant formation of acetone observed during DA transformation. However, under the operating conditions of acetone transformation the equilibrium of Eq. (1) is totally displaced towards the formation of MO by Eq. (2). Moreover, the thermodynamic equilibrium between MO and MIBK (Eq. (3)) which is in favour of MIBK is attained for acetone conversion above 5% (Fig. 5).

The mechanisms of the reactions involved in MIBK formation are well-known. The limiting reaction i.e. acetone aldolisation occurs through the following steps:



Protonation and deprotonation steps being generally rapid, Eq. (5) is most likely the limiting step of acetone aldolisation.

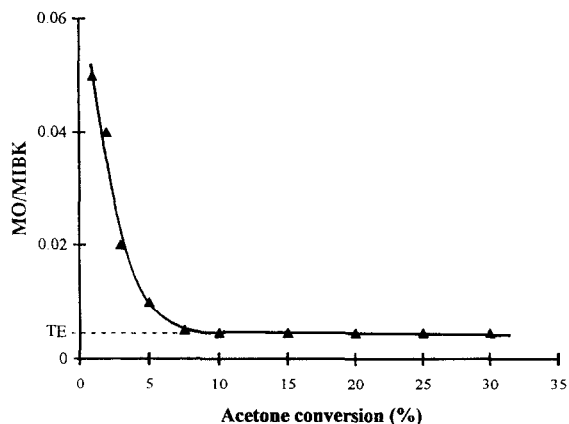
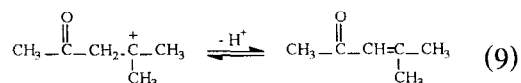
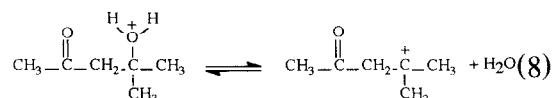
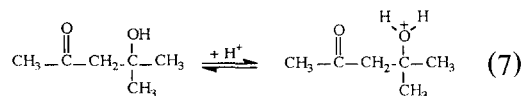


Fig. 5. Change in the ratio between the rates of formation of mesityl oxide and of methylisobutylketone (MO/MIBK) versus acetone conversion. TE: thermodynamic equilibrium ratio.

Dehydration of diacetone alcohol can be written as follows:

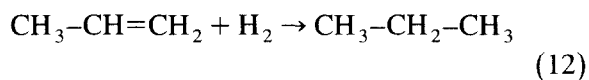
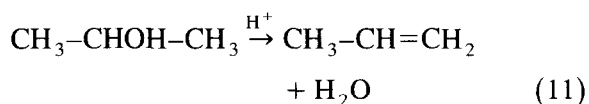
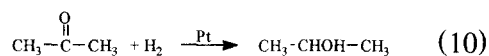


This acid reaction which involves the formation of a tertiary carbenium ion is known to be very rapid.

The hydrogenation of the C=C double bond of mesityl oxide occurs most probably through the Horviti Polanyi mechanism [12].

4.1.2. Mode of formation of hydrocarbons

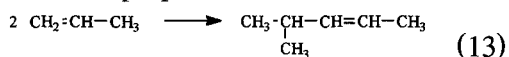
Propane results from the transformation of acetone through the following three steps catalyzed by platinum or by the acid sites.



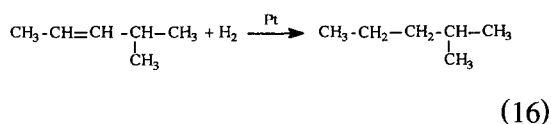
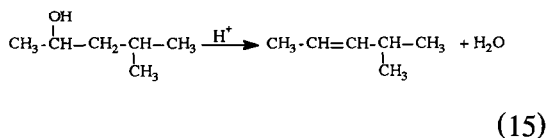
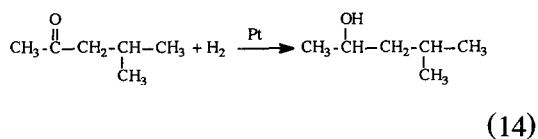
Eq. (10) is the limiting step of this process. Indeed isopropanol dehydration (Eq. (11)) is much faster than acetone transformation (Table 1) and no isopropanol is observed in the products of acetone transformation. Propene hydrogenation (Eq. (12)) is also much faster than acetone transformation (Table 1). Moreover, propene is not observed in the products of acetone and of isopropanol transformations, which

means that Eq. (12) is faster than Eqs. (10) and (11).

The very fast hydrogenation of propene allows us to explain that no 2-methylpentane (2MP) results from the transformation of this alkene. Under the operating conditions, the dimerization of propene



would be much slower than its hydrogenation (Eq. (12)). Therefore 2MP does not result from Eq. (13) followed by hydrogenation but from the secondary transformation of methylisobutylketone (MIBK) as shown in Section 3.2. The reaction scheme involves the same steps as the formation of propane from acetone: hydrogenation of the C=O bond (Eq. (14)), dehydration (Eq. (15)) followed by hydrogenation of the C=C bond (Eq. (16)).

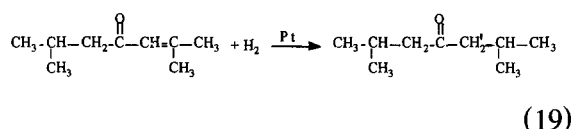
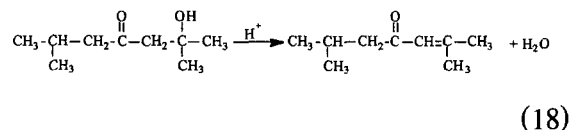
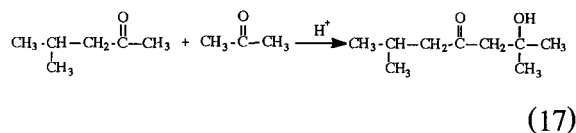


Similar to acetone transformation into propane, the limiting step is the hydrogenation of the C=O bond (Eq. (4)); indeed neither methylpentanol nor 2-methylpentenes are observed in the products.

4.1.3. Mode of formation of DIBK

DIBK is a secondary product of acetone transformation. Its formation can occur from aldolisation between mesityl oxide or MIBK and acetone followed by dehydration and hydrogenation of the C=C bond(s). Under the operating conditions, the concentration of MO is much

lower than that of MIBK and despite its greater reactivity (due to its stronger adsorption) DIBK should mainly result from the following reactions between MIBK and acetone.



Similar for the formation of MIBK, the limiting step of the formation of DIBK from MIBK is the aldolisation step (Eq. (17)): neither alcohol nor olefinic intermediates are observed in the reaction products.

4.2. Scheme of acetone transformation

The main reactions involved in acetone transformation are indicated in Fig. 6. Acetone undergoes competitive hydrogenation on the platinum sites and aldolisation on the acid sites, these reactions being the limiting steps of the formation of the main reaction products: MIBK and propane. This suggests that the greatest selectivity to MIBK could be obtained for catalysts having a small ratio between their hydrogenating and acid activities. This has been checked by using a series of PtHZSM5(41) catalysts with different platinum contents: the

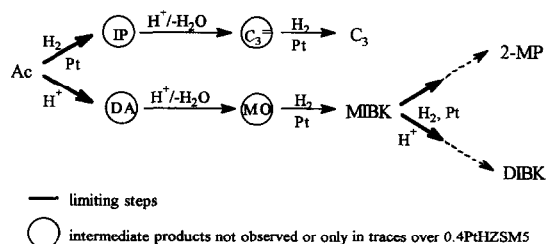


Fig. 6. Acetone transformation over Pt HZSM5. Reaction scheme.

lower the platinum content the greater the MIBK/propane formation ratio [13]. However platinum is necessary to hydrogenate mesityloxide into MIBK.

The desired reaction product MIBK undergoes competitive transformations into 2-methylpentane and into DIBK, the limiting step of 2MP formation being the hydrogenation of MIBK on the platinum sites and that of DIBK formation the acid aldolisation between acetone and MIBK. The lower the platinum content the greater the ratio between the amounts of DIBK and 2MP [13], thus agreeing with this theory.

5. Conclusion

Over a 0.4 wt% Pt HZSM5(60) catalyst acetone is transformed into various products. The main products: methylisobutylketone (MIBK) and propane are formed directly (primary products) while 2-methylpentane and diisobutylketone result from MIBK transformation (secondary products). The reaction scheme of acetone transformation was established from the kinetic nature of the products (primary or secondary) and from the study of the transformation of products and of probable intermediates: diacetone alcohol, mesityloxide, isopropanol and propene. It is shown that the limiting step of MIBK formation is the aldolisation of acetone, while that of propane is the hydrogenation of the C=O double bond. The formation of 2-methylpentane requires the same steps from MIBK as propane formation from acetone (the

limiting step being again the ketone hydrogenation). The formation of diisobutylketone involves the same steps as methylisobutylketone formation, the aldolisation step (between MIBK and acetone) also being the limiting step. From this reaction scheme it can be deduced that the initial selectivity to MIBK increases with increasing acid/hydrogenating activity ratio.

Acknowledgements

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