

THE CATALYTIC SYNTHESIS OF METHYL-ISOBUTYL KETONE FROM ACETONE. THE STUDY OF THE INFLUENCE OF ZINC ADDITION THROUGH IMPREGNATION ON THE BEHAVIOUR OF THE CATALYST Pd / Zn- H-ZSM 5

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abstract: Methyl-isobutyl –ketone (MIBK) was obtained in vapor phase, from acetone and hydrogen in a single step, using Pd/H-ZSM-5 as a catalyst. The experiments were performed in a continuous fixed bed reactor at 5 atm, 170 °C, hydrogen/acetone molar ratio measured at reactor outlet (MRHA) 0.4 and acetone WHSV 0.3 h⁻¹. Acetone conversions up to 50 % and MIBK yield up to 45 % were obtained. The experimental data showed that the presence of zinc oxide, in an amorphous form, decrease the Pd/Zn- H-ZMS-5 catalyst's activity in the process of reductive condensation of acetone. The selectivity for methyl-isobutyl ketone also presents a decrease when zinc in an amorphous form is added. This behavior is due probably to the decrease in the activity of the acid catalyst centers in the presence of zinc oxide in an amorphous form.

Introduction

Methyl-isobutyl –ketone is a chemical product of industrial interest obtained from acetone. It is mainly used as a solvent for polishes and dyes or for obtaining other chemical products (stabilizers, etc.) Due to its volatility, which is lower than that of acetone, MIBK is considered a solvent with higher performances.

The conventional technology of MIBK synthesis from acetone consists of a sequence of three steps and it has been the only one used until late 1960's. In this technological variant, acetone is condensed, in the first stage, to DAA (diacetonealcohol) in a basic catalysis in liquid phase. In the second stage, DAA is dehydrated to MO (mesityl oxide) with an acid catalyst such as the phosphoric or the sulphuric acid, and during the third stage MO is hydrogenated to MIBK. Recently, an one-stage process for manufacturing MIBK has been introduced, a process which uses bifunctional catalysts containing a metal (Pd usually) deposited on a solid acid support. The process presupposes the reversible condensation of

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acetone to MO on the acid centers and, in succession, the hydrogenation of MO to MIBK on the metallic centers.

An important number of studies have been published, which deal with the direct synthesis of MIBK from acetone and hydrogen on Pd-based catalysts deposited on ion-exchange resins [1], zeolites [2,3], zirconium phosphate [4] or niobic acid [5]. The direct synthesis of MIBK from acetone on catalysts of Ni deposited on magnesium oxide or alumina has been presented recently [6,7].

In this paper we present some of the results obtained in the research regarding the single-stage MIBK synthesis from acetone and hydrogen in the presence of a Pd catalyst deposited on a ZMS-5 zeolite in the form proton modified with zinc during the process of crystallization and of the same catalyst which also contains zinc oxide in an amorphous form at different concentrations.

Experimental

The tested catalyst is mainly made of palladium deposited on a H-ZMS-5 zeolite modified with zinc in the process of crystallization, made by ZECASIN S.A. The zeolite powder was bound in an amorphous alumina matrix, as extrudated composite pellets containing 30 % alumina. The catalytic pellets were dried and calcined at 550 °C and then impregnated with a water solution of palladium chloride, dried and calcined at 450 °C. To prevent the possible interactions of the acid centres with the metallic centres, the palladium chloride impregnation was performed on the surface area of the catalytic pellet by spraying. The activity of this catalyst remains virtually constant during the time of the experiment, according to the data presented in a previous paper [2].

Adding zinc oxide in different concentrations in the Pd catalyst deposited on an H-ZMS-5 zeolite modified with zinc in the crystallization process had the purpose of studying the influence of zinc oxide in an amorphous form on the activity of this catalyst in the process of acetone reductive condensation. Thus, to emphasize the fact that zinc oxide modifies its acidity in the presence of water only when it is in an amorphous form, catalysts containing amorphous zinc oxide were prepared, through the impregnation with a zinc salt of the Pd/Zn H-ZMS-5 catalyst, using different concentrations of this metal (3% and 5% respectively).

The deposit of zinc in an amorphous form was obtained through the impregnation of the catalyst with a water solution of zinc nitrate (the method of "filling the pores"), followed by drying and by calcination at 450 °C. The activation of the catalyst was made through the reduction in a stream of hydrogen at 180 °C. The reagents used in this experiment were analytically pure acetone and electrolytically pure hydrogen. The palladium content of the catalysts was determined through colorimetric methods applied to a water solution obtained by the dissolving of palladium. The specific surface area of the zeolite catalyst was determined through measurements of porosimetry with mercury and nitrogen absorption and the concentration of the acid centres of the zeolite catalyst was determined through the

method of programmed thermodesorption of ammonia (data presented in a previous paper [2]).

The experimental program of testing the bifunctional catalysts prepared according to the above described procedure was performed in a continuous fixed bed catalytic reactor. A mobile metallic jacket for thermocouple was also placed in the axis of the bed, in order to measure the reaction temperature. The process was carried out in isothermal conditions, the temperature being measured with a mobile thermocouple, the sheath of which was axially placed in the central zone of the catalyst layer. The composition of the reaction mixture was determined through gas chromatography on a HP 5890 chromatograph equipped with an HP - INNOWAX capillary column of 30 m in length and 0.25 mm in diameter.

Results and discussions

For the domain of variation of the reaction parameters within the experimental framework, the main reaction product was MIBK and the secondary products identified in small amounts diisobutyl ketone (DIBK), 2-methyl-pentane (2-MP), isopropyl-alcohol (iPA), diisopropyl-ether (DIPE), MO and traces of advanced condensation products.

The influence of the zinc content, added through impregnation, on the performances of the process is presented in figure 1.

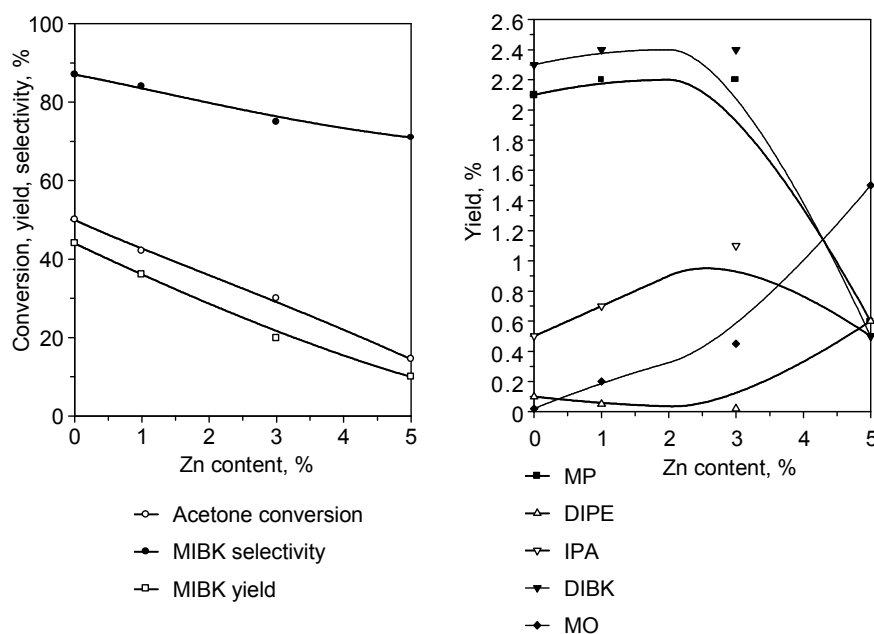


Fig.1. Influence of zinc content added by impregnation on the process performances
Catalyst 0.3% Pd/Zn-HZSM-5, $T=170^{\circ}\text{C}$, $P=5\text{ atm.}$, $WHSV=0.3\text{ h}^{-1}$, $MRHA=0.4$

One can notice a high decrease of acetone conversion in relation to the zinc content of the catalyst (added through impregnation) for the same values of the operating parameters. The selectivity for methyl-isobutyl ketone also presents a decrease when zinc in an amorphous form is added. The output in methyl-isobutyl presents a decrease directly proportional to the catalyst's zinc content added through impregnation.

Thus, increasing the catalyst's zinc content three times leads to a decrease in the methyl-isobutyl ketone output by half, and increasing the catalyst's zinc content five times leads to a five-time decrease in the methyl-isobutyl ketone output. The output in 2-metyl pentane and diisobutyl ketone is relatively constant when the catalyst's zinc content is increased up to 3 %, the increase in the catalyst's zinc content to 5 % triggering an important decrease in the output in these chemical compounds.

It should also be noted the formation of the mesityl oxide in the reaction product in the case of the catalyst promoted with amorphous zinc oxide. An increase in the content of the catalyst's zinc oxide (in an amorphous form) results in an increase in the mesityl oxide output.

The variation of the performances of acetone conversion process depending on the reaction time is presented in figure 2 for a 3 % zinc content in an amorphous form and in figure 3 for a 5 % zinc content in an amorphous form.

It can be seen that the activity of the Pd / Zn H – ZMS –5 catalyst impregnated with zinc oxide decreases in time, for the catalyst which contains 3 % Zn, as well as for the catalyst which contains 5 % Zn added through impregnation, decrease highlighted by the variation of acetone conversion in time. The selectivity for methyl-isobutyl ketone and the output in methyl-isobutyl-ketone also decrease in time.

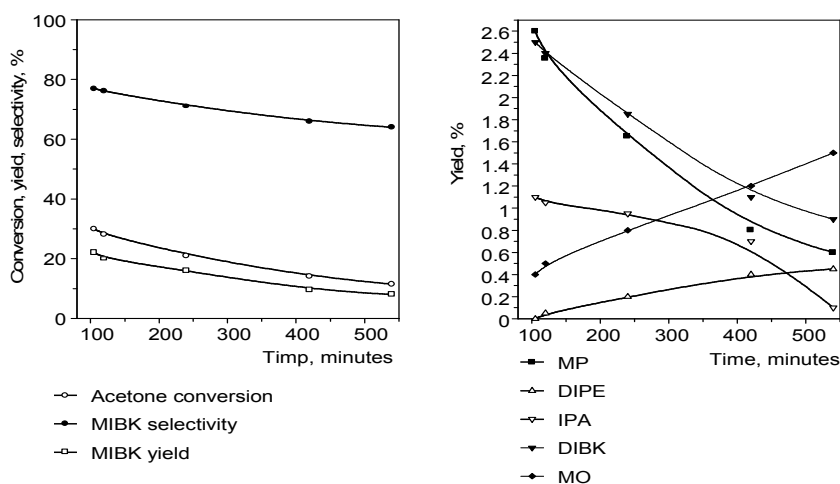


Fig.2. Variation of acetone conversion process performances vs. running time
Catalyst 0.3% Pd/Zn-HZSM-5 impregnated with 3% Zn
 $T=170^{\circ}\text{C}$, $P=5\text{ atm.}$, $WHSV=0.3\text{ h}^{-1}$, $MRHA=0.4$

The output in 2-methyl pentane also decreases in time, while the outputs in diisopropyl ether and isopropyl alcohol tend to remain constant in time. The output in diisobutyl ketone slowly decreases for the 5 % zinc catalyst and it presents a variation with a maximum point for the 3 % zinc catalyst.

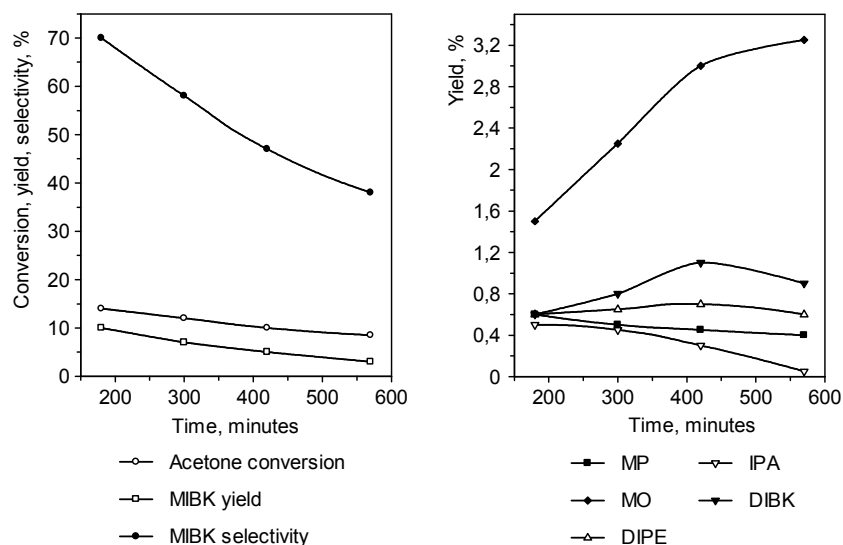


Fig.3. Variation of acetone conversion process performances vs. running time
Catalyst 0.3% Pd/Zn-HZSM-5 impregnated with 5% Zn
 $T=170^{\circ}\text{C}$, $P=5\text{ atm.}$, $WHSV=0.3\text{ h}^{-1}$, $MRHA=0.4$

The output in mesityl oxide increases with testing time, for the catalyst impregnated with 3 % zinc, as well as for the catalyst impregnated with 5 % zinc, output values in mesityl oxide being bigger for the catalyst containing 5 % zinc for the same amount of working time.

The decrease of acetone conversion in the case of the catalysts promoted with amorphous zinc oxide is due to the negative effect of amorphous zinc oxide on the metallic centers and probably on the acid centers as well. Thus, the presence of mesityl oxide in the reaction product, irrespective of the catalyst's zinc content, indicates a decrease in the activity of the metallic centers.

The scientific literature does not indicate any poisonous or deactivating effect of zinc on the palladium based catalysts used for hydrogenation (assertion also backed up by the behavior of the Pd/Zn H ZMS-5 catalyst on the reductive condensation of acetone). In these circumstances, the deactivation of the metallic centers in the presence of amorphous zinc oxide is probably due to the decrease in the desorption speed of the water formed in the reaction of acetone condensation in the presence of amorphous zinc oxide, water which negatively influences the palladium catalytic activity. Although the zinc oxide presents

certain acidity after calcinations, we did not notice any improvement in the activity of the catalyst's acid centers after zinc impregnation, improvement which would have determined an increase in the output in condensation products and implicitly in the acetone conversion. This behavior is probably due to the same reason, that is, the interaction between the reaction water and the amorphous zinc oxide. The decrease in the activity of the catalyst impregnated with amorphous zinc oxide in time, is probably due to the accumulation of water in the pores, due to its reduced desorption speed in the presence of zinc oxide.

Conclusions

The study of the influence of amorphous zinc addition on the activity of a bifunctional catalyst in the process of acetone reductive condensation was carried out through the impregnation with a zinc salt of a Pd catalyst deposited on a ZMS-5 zeolite in an acid form which contains zinc bound in a crystalline network.

The decrease in the Pd/Zn- H-ZMS-5 catalyst's activity in the presence of zinc oxide in an amorphous form in the process of reductive condensation of acetone is due to the decrease in the activity of the acid catalyst centers.

The variation in time of the performances of the catalysts containing zinc oxide in an amorphous form emphasized the fact that zinc oxide modifies its activity in the presence of water only when it is in an amorphous form.

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