

BIFUNCTIONAL CATALYSTS BASED ON ION-EXCHANGERS

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The consecutive condensation, dehydration and hydrogenation of acetone were studied in a trickle bed reactor. Purolite CT 275, a commercial cation exchange resin was used as a support for catalyst. The bifunctional catalysts based on ion-exchangers were prepared by the combined procedure of depositing-reduction of the active metal on the surface of ion-exchanger granules, using hydrogen as spraying gas. The operating parameters of the reaction system were pressure 30 atm, temperature of catalytic bed from 105 to 130°C, hourly space velocity of acetone: variable, from 0.4 to 2.4 h⁻¹, hydrogen/acetone molar ratio: variable, from 2 to 15, acetone conversions varying from 24 to 34 % and the methyl-isobutyl-ketone (MIBK) yield varied between 22 and 29%. The results indicated that the activity of metallic centers is considerably efficient even at high values of HSV, taking into account that mesityl oxide (MO) was not identified in the reaction product over the whole range of HSV checked in the test series.

Introduction

The catalysts based on ion-exchanging resins were normally used in some processes running in the conditions of acid or basic catalysis, as a support for enzymes and also in the peptides synthesis. The most catalysts based on acid-functionalized resins are of polystyrene-divinylbenzene sulfonate type, the synthesis of MTBE (methyl-tertbutyl-ether) being probably the most important process in which these catalysts are used.

Traditionally MIBK was manufactured from acetone using a three step process including acetone condensation to diacetone-alcohol (DAA), dehydration of the DAA to mesityl-oxide (MO), and the hydrogenation of the MO to MIBK (methyl-isobutyl ketone). The unfavorable equilibrium of the first two reactions complicated this process and the separate reaction steps made it an expensive process.

Numerous bifunctional catalysts have been reported for the one-step MIBK process from acetone. The combined synthesis was studied in the gas and liquid phase. The gas phase process have the advantage of atmospheric pressure conditions. Different metals on different acid-base supports were used [1-4]. Several patents can be found on the use of bifunctional catalysts for the one-step synthesis of MIBK in liquid phase using palladium as

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the active metal [5-10]. Various acidic and basic supports have been used, such as CaO-MgO-SrO-Al₂O₃, Nb₂O₅ etc.

There are relatively few literature informations referring to the preparation of bifunctional catalysts based on ion-exchangers, the most recommended method for palladium depositing being the impregnation by ionic exchange, without any further considerations about the influence of metal on the ion exchange capacity of resins.

As in the case of the oxidic type catalysts, the preparation of bifunctional catalysts based on ion-exchangers is performed in two steps:

- the impregnation step of the acid catalyst support (i.e. ion-exchanging resins) with an aqueous solution of the metallic precursor;
- the activation step by reducing the catalytic precursor to its metallic form.

For the preparation of bifunctional catalysts based on ion-exchangers, according to the earlier applied impregnating techniques [10], an ionic exchange method was used. The resin support was immersed into a solution containing a compound of the catalytic active element or the same solution was dropped on the support, under mixing and optionally heating. After the achievement of the equilibrium state, the excess of solvent was drawn out, the catalytic precursor was dried and finally activated by reduction.

Among the factors causing the degradation of polymers in the presence of metallic crystallites are important the following:

- the presence in the resin matrix of some functional groups having affinity for metallic crystallites (e.g. sulfonic group);
- a high concentration of the metal;
- a high local temperature value.

The main objective of the research study consisted in the preparation of ion-exchangers based bifunctional catalyst by a method which avoids the disposition of metallic catalytic centers in the neighborhood of the own acidic-basic centers of ion-exchangers, ensuring in this way an appropriate efficiency for both the activity of metallic function and of acidic-basic function and eliminating the possible interactions between the two functions. In this case, for the preparation of bifunctional catalysts a spraying method was used, consisting in the spraying of a solution containing a catalytic active component on dry-state ion-exchanger, continuously mixed by the circulation of the spraying gas.

The new and important feature of the method used in this work consists in using hydrogen as spraying gas and in maintaining an enough high impregnation temperature which allows a reduction of catalytic precursor to its metallic form just in the moment of its deposition on the resin support.

This improved method of preparation of bifunctional catalysts based on ion-exchangers has some important advantages:

- a good control of the thickness of metallic layer, avoiding the transport of reduced metal into the interior of the pores by the diffusion of the liquid phase (the metal being insoluble in this phase);

- a diminishing of the interactions between the two catalytic functions, the metallic one being disposed in the outer layer of the catalyst granule, and not in its core;
- a large distribution of the active component and of the dimensions of its crystallites.

The bifunctional catalysts based on ion-exchangers containing an acidic function and a metallic one are used successfully in various processes of organic synthesis, the reductive condensation of carbonylic compounds being an important application.

In this paper we present some results of a research study concerning the synthesis of methyl-isobutyl-ketone (MIBK) by a one-step process of reductive condensation of acetone in the presence of Pd/cation-exchanger as a bifunctional catalyst. The ion-exchanger used in these experiments was Purolite CT275, a macro porous and strongly acidic polymeric support, having a greater acid strength, a greater number of acidic centers and a greater thermal stability than the usual polymeric catalysts. Their unique structural features, as the high values of diameter and volume of pores, allow an easier access of the reactants to the acidic centers.

Due to the large distribution of pores size, the catalyst is less sensible to the depreciation caused by the accumulation of secondary products, having also good properties related to contraction and swelling and consequently an excellent physical and osmotic stability.

Experimental

The bifunctional catalysts based on ion-exchangers were prepared by the combined procedure of depositing-reduction of the active metal on the surface of ion-exchanger granules, using hydrogen as spraying gas. The impregnation of the polymeric support was achieved in a rotatory evaporating device, with a solution of tetrammine-palladium(II) chloride, $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, by heating (approximately at 80°C) and under a hydrogen flow (as spraying gas).

The reduction with hydrogen of the active component to the metallic state was observed by the changing in color (the granules impregnated in the outer layer with reduced Pd are black, while those impregnated under an air flow are gray). The distribution of the metallic component was established by electron microscopy, using a computer program which extracts numerical data from an image file of bitmap type. Thus, by a photographic device it was obtained a bitmap image file, a matrix, in which each point has an associated numerical value, as function of its color. For a black and white image file the associated values are only two, 0 or 1. The bitmap file was then vectorized giving the coordinates of all points of a certain value, as identified by electron microscopy. Knowing the number of points and the surface of the analyzed zone, it is possible to determinate the concentration of metal catalyst disposed in these zones (the „crown” or the outer layer and the core of the catalyst granule).

The data obtained for a catalyst granule prepared according the above described procedure are shown in Fig.7. The distribution of Pd in the catalyst 0,5% Pd/CT-275 demonstrates that 6,81% is found in the core, while in the „crown” of the granule is found 93,19% from the total Pd content (about 0,5%, determined separately by a colorimetric procedure). The

specific surface of ion-exchanger support is 20-35 m²/g and its total capacity of ionic exchange was 4,9 mequiv/g in dry-state.

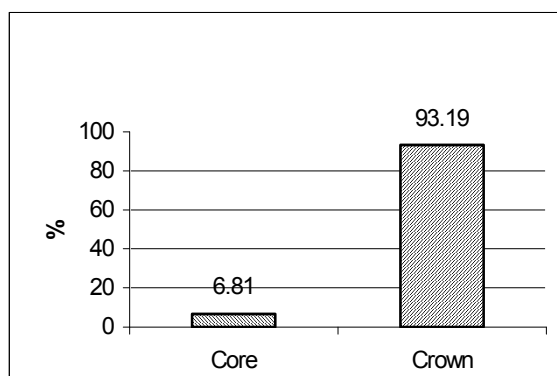


Fig.7. Distribution of Pd between the crown and the core of the catalyst granule

The experimental program of testing the bifunctional catalysts prepared according to the above described procedure was performed in a continuous fixed bed catalytic reactor, under isothermal conditions.

The studied reaction was the process of reductive condensation of acetone to methyl-isobutyl-ketone (MIBK) and the aim was to determine the influence of main parameters (temperature, hourly space velocity of acetone and hydrogen/acetone molar ratio) on the performances of the process.

The operating parameters of the reaction system were as follows:

- pressure: 30 atm (a constant value during the whole test);
- temperature of catalytic bed: variable, from 105 to 130°C;
- hourly space velocity of acetone: variable, from 0.4 to 2.4 h⁻¹;
- hydrogen/acetone molar ratio: variable, from 2 to 15.

The reactants used in these experiments were of analytical grade purity and hydrogen was of electrolytic purity.

The composition of effluent reaction mixture was determined by gas-chromatography, using a gas-chromatograph HP 5890 equipped with a capillary column HP-INNOWAX (30 m length, 0,25 mm diameter).

Results and discussions

MIBK was the main product in the reaction mixture, while 2-methyl-pentane (MP), iso-propyl alcohol, di-isobutyl-ketone (DIBK), mesityl oxide (MO) were identified in small amounts and high condensation products are found only as traces.

The chosen value of working pressure keeps the process in a gas-liquid-solid system and remain unchanged during the experiments, either for zero conversion or a final medium conversion (usually up 35%).

The reaction temperature consistently affects the performances of the process, as it is shown in Fig.1 and 2. Thus, the rising of temperature give higher values for the acetone conversion and the reaction yield to MIBK. In the case of 2-methyl-pentane, its abruptly rising yield is probably due to the hydrogenolysis favorable assisted by the metallic centers of the catalyst. The reaction product contains not even a small amounts of mesityl oxide, indicating also a high activity of metallic centers. The absence of DIBK in the reaction product demonstrates the presence of metallic centers only in the crown of catalyst granules. It is known, from other studies, that DIBK is a result of successive condensation-reduction processes occurred on the active acidic and metallic centers only if these are uniformly distributed in the whole granule core.

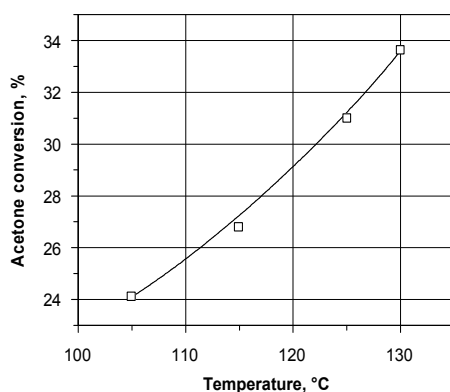


Fig.1. Variation of acetone conversion vs. reaction temperature

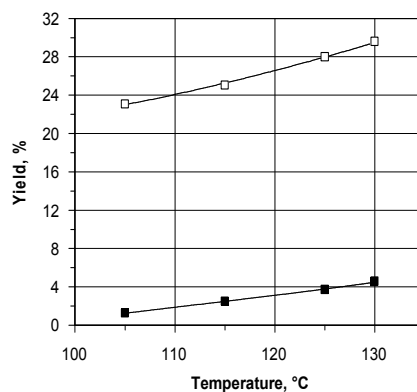


Fig.2. Variation of yield vs. reaction temperature

Experimental data concerning the influence of contact time and consequently the influence of hourly space velocity (HSV) are shown in Fig.3 and 4. The rising of HSV induces a decreasing of acetone conversion and of the yields values for MIBK and MP.

The activity of metallic centers is considerably efficient even at high values of HSV, taking into account that mesityl oxide (MO) was not identified in the reaction product over the whole range of HSV checked in the test series.

The influence of hydrogen/acetone molar ratio is shown in Fig.5 and 6, indicating a decreasing of acetone conversion and MIBK yield as the molar ratio increases. The rising of MP yield is probably due to a higher activity of metallic centers at raised values of hydrogen excess. On the whole studied variation of molar ratio the mesityl oxide (MO) was not analytically found in the reaction product, demonstrating a raised activity of the metallic centers.

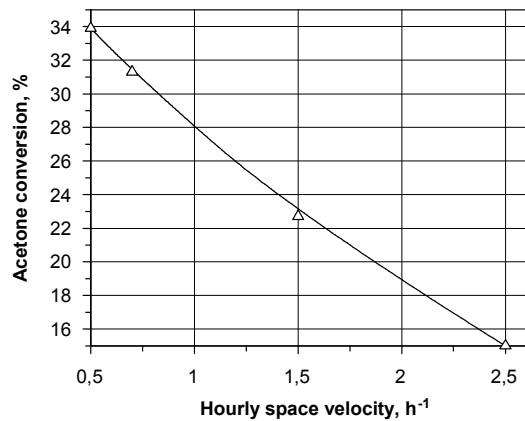


Fig.3. Variation of acetone conversion vs. hourly space velocity

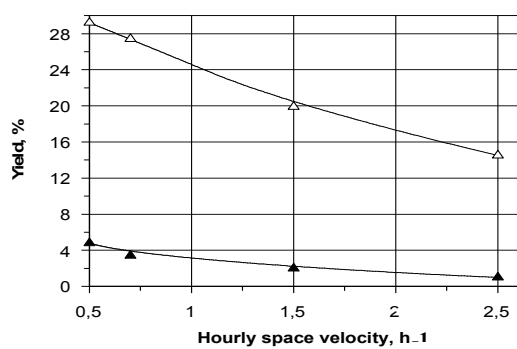


Fig.4. Variation of yield vs. hourly space velocity

—△— MIBK yield
—▲— MP yield

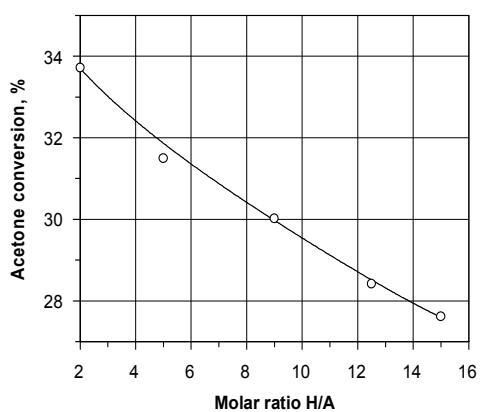


Fig. 5. Variation of acetone conversion vs. molar ratio hydrogen/acetone

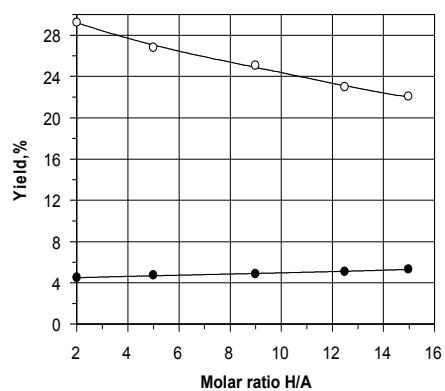


Fig. 6. Variation of yield vs. molar ratio hydrogen/acetone

—○— MIBK yield
—●— MP yield

From the experimental data presented and discussed above we can conclude that the bifunctional catalysts based on ion-exchangers and particularly the catalyst based on Pd

deposited on Purolite CT-275, prepared by the procedure described in this paper and tested in the process of reductive condensation of acetone, show a relatively high selectivity to methyl-isobutyl-ketone. The values of acetone conversion are similar with those obtained in the same process using the oxidic type of bifunctional catalysts. The absence of mesityl oxide in the reaction product proves a high and efficient activity of catalytic metallic centers.

Conclusions

The bifunctional catalyst, Pd / Purolite CT-275, prepared by the procedure described in this paper, showed high activity and selectivity for MIBK formation. The values of acetone conversion are similar with those obtained in the same process using the oxidic type of bifunctional catalysts. Furthermore, this catalyst is highly resistant to water in acetone. The activity of metallic centers is considerably efficient even at high values of HSV, taking into account that mesityl oxide (MO) was not identified in the reaction product over the whole range of HSV checked in the test series.

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