

## INFLUENCE OF THE Pd DISTRIBUTION IN A Pd /H-ZSM-5 CATALYST ON ACETONE CONVERSION TO METHYL ISOBUTYL KETONE

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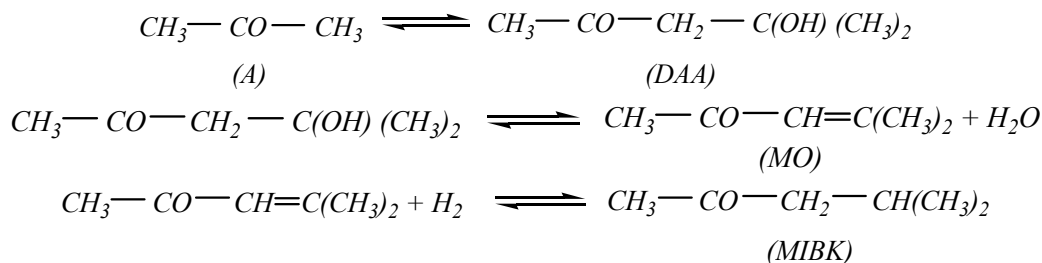
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Methylisobutyl ketone was obtained in vapor phase, from acetone and hydrogen in a single step, using Pd/H-ZSM-5 on an alumina matrix as a catalyst. The experiments were performed in a continuous fixed bed reactor at 5 atm, 130-170 °C, hydrogen/acetone molar ratio from 2.5 to 10 and acetone WHSV from 0.66 to 2.5 h<sup>-1</sup>. Acetone conversions up to 40% and MIBK yield up to 36% were obtained. Uniform and "egg-shell" type nonuniform distributions of Pd in the volume of catalyst pellet were tested. The results evidenced that the uniform Pd distribution catalyst provides better acetone conversions compared with a nonuniform distribution. This is explained by the strong limitation of acetone conversion to mesityl oxide in the Pd free zones of the pellet, due to the reversibility of the acetone condensation step.

### INTRODUCTION

Methyl isobutyl ketone (MIBK) is the most important product obtained from acetone. It is used mainly as a solvent for inks, paints and protective coating systems or as a reagent in dewaxing of mineral oils or as an intermediate in the synthesis of other chemical products (stabilizers, etc.). As a solvent, it is considered environmentally friendlier than acetone, due to its lower volatility.

MIBK is produced commercially from acetone, by a three-reaction process, including aldol condensation of acetone to diacetone alcohol (DAA) on basic or acidic catalysts, acid catalyzed dehydration of the DAA to mesityl oxide (MO), and selective MO hydrogenation to MIBK:



In modern technologies, the MIBK synthesis is performed in a single stage by direct transformation of acetone in the presence of hydrogen, on a bifunctional catalyst containing a metal (usually Pd) supported on a solid acid. The process involves the reversible condensation of acetone to mesityl oxide on the acid sites of solid catalyst and consecutive hydrogenation of MO to MIBK on the palladium surface. The reversibility of the acetone condensation step does not limit the overall process kinetics due to the irreversibility of the MO hydrogenation step. As a result of different secondary reactions, several by-products were also obtained in small concentrations.

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Numerous bifunctional catalysts have been tested in this process, based on ion-exchange resins,<sup>1,2</sup> zeolites,<sup>3,4,5</sup> zirconium phosphate,<sup>6</sup> aluminophosphate<sup>7</sup> or niobium oxide.<sup>8</sup> Compared with the ion-exchange resins, the inorganic solid acid catalysts present the advantage of a superior resistance to high temperatures and a better regenerability. In this work we studied the direct acetone conversion to MIBK on a Pd/H-ZSM-5 bi-functional catalyst. The influences of the Pd spatial distribution in the pellet, as well as of operating parameters on the acetone conversion and the MIBK yield were experimentally investigated.

## EXPERIMENTAL

A 25 mm inner diameter fixed bed reactor was used. The volume of catalyst bed used in all the experiments was 30 cm<sup>3</sup> (if not specified otherwise). The catalyst bed is supported on a 10 cm height layer of glass beads (3 mm in diameter) and the top part of the reactor was also filled with 3 mm diameter glass beads to ensure a good distribution of the fluid in the catalyst bed. A mobile metallic jacket for thermocouple was also placed in the axis of the bed, in order to measure the reaction temperature. Two wall heaters, connected to a temperature controller, were used to rise the reactor temperature.

The reagents used in the synthesis were high purity acetone (concentration 99.5%), and high purity hydrogen (concentration 99.99%). The zeolite used in the preparation of the catalyst was a H-ZSM-5 binded in an amorphous alumina matrix (70% wt zeolite and 30% alumina) as extrudated composite pellets. The catalyst pellets was calcined in air for 8 hours at 550 °C, then impregnated with Pd chloride, calcined in air for 6 hours at 450 °C and subsequently reduced in a stream of hydrogen at 180 °C.

Three spatial distributions of metallic Pd in the catalyst pellets were prepared and tested, the first one being an approximately uniform distribution of Pd in the volume of the pellet and the other two nonuniform, with Pd located in the vicinity of outer surface. The two nonuniform distributions differ only by the thickness of the layer containing the Pd. To be clearly distinguished, the thinner one will be called “egg-shell” type distribution and the thicker one “intermediary” distribution.

The uniform Pd distribution was realised by immersing the catalyst pellets in a liquid solution of palladium chloride under mixing a sufficiently long time (approximately one hour), whereas the nonuniform distributions were prepared by the pulverization of a liquid palladium chloride solution over a moving bed of catalyst pellets. The “egg shell” type distribution was realized by simultaneous pulverisation and reduction of Pd chloride (pulverisation in an atmosphere of hydrogen) whereas in the case of “intermediary” distribution, palladium chloride was reduced only after the pellets were impregnated with liquid solution (by pulverization). In the second case, the Pd chloride is penetrating with the liquid solution in a deeper layer inside the pellet. The pellets were subsequently dried in the oven at 450 °C. The activation of the tested catalysts was performed in the same operating conditions (temperature 275°C, 5 h activation time in a stream of hydrogen).

The amount of the deposited Pd (determined through the method of atomic adsorption) for all the prepared catalysts was about 0.25% (by weight). The spatial distribution of the palladium in the catalyst pellets was quantitatively determined from images obtained by scanning electron microscopy (HITACHI S2600N with EDAX spectrometer). The three Pd distributions we tested are presented in Figs. 1 to 3. The specific surface of the zeolite catalyst was 310 m<sup>2</sup>/g (determined by porosimetry measurements with nitrogen adsorption).

The reactor was operated at a pressure of 5 bar, reaction temperatures between 130-170 °C, hydrogen/acetone molar ratios from 2.5 to 10, and weight hourly space velocities (WHSV) between 0.66 and 2.5 h<sup>-1</sup>. Computations of liquid-vapor equilibrium for the system hydrogen-acetone-MIBK, at typical reaction mixture concentrations, indicated that the reaction mixture is completely evaporated in the selected working conditions. The duration of each experiment was 3 hours, counting from the moment the process parameters reached the steady-state values. After cooling and liquefaction, the reactor effluent was collected in a vessel, during the entire period of experiment. The composition of the liquid mixture so obtained was measured by chromatography only at the end of experiment. Consequently our results are based on time averaged reaction mixture composition measurements, during a 3 hours experiment. The polycondensation products trapped inside the porous structure of the catalyst pellets were recovered by extraction with methyl chloride. They nature was examined by infrared spectroscopy (FTIR Niolet Avatar 360).

## RESULTS AND DISCUSSION

The influence of the fluid-solid mass transfer (external diffusion) on the process kinetics was experimentally investigated by measuring the acetone conversion at different fluid velocities and constant fluid-solid contact time (constant catalyst volume to flowrate ratios). The results presented in Fig. 4 show that the influence of the external diffusion is negligible for volumetric flowrates of liquid acetone higher than 30 mL/h (superficial velocities of the reactant mixture at the entry in the catalyst bed, greater than 9 mm/s).

The internal diffusion influence on the process kinetics was investigated by measuring the acetone conversion on catalyst pellets having different classes of dimensions, in identical working conditions (same temperature, pressure and feed composition), at a sufficient high flowrate to make negligible the influence of the external mass transfer. Four classes of pellet dimensions, with uniform spatial distribution of Pd, were tested in this work: 1 mm, 2 mm, 2.5 mm and 5 mm, respectively.

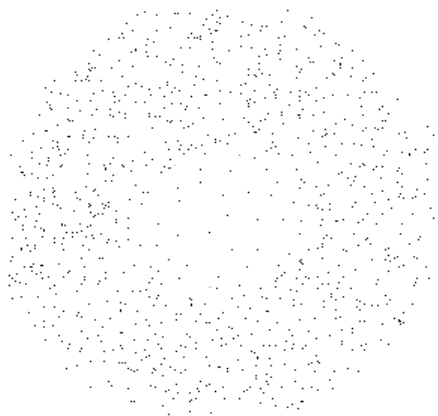


Fig. 1a – Spatial distribution image by electronic microscopy (uniform distribution).

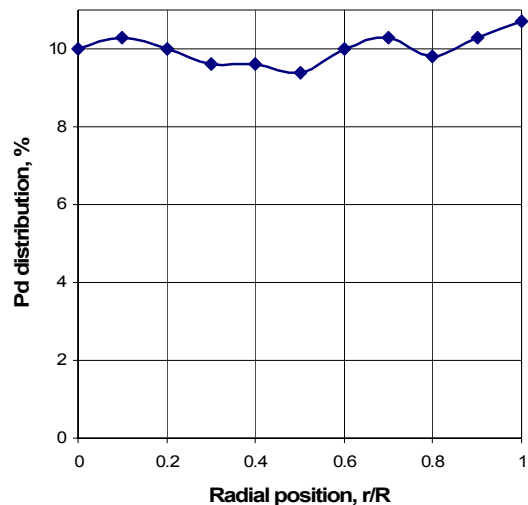


Fig. 1b – Pd distribution in the catalyst pellet (uniform distribution).



Fig. 2a – Spatial distribution image by electronic microscopy (intermediary distribution).

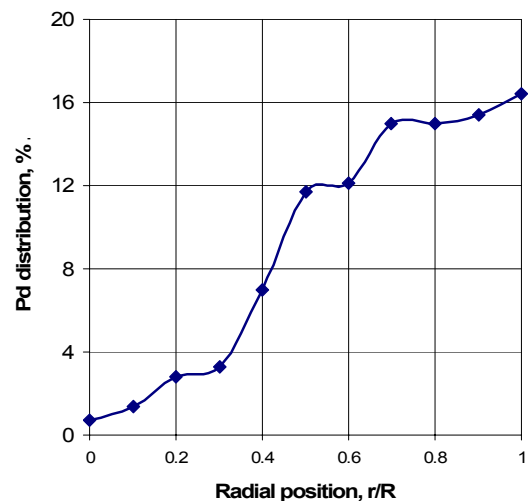


Fig. 2b – Pd distribution in the catalyst pellet (intermediary distribution).

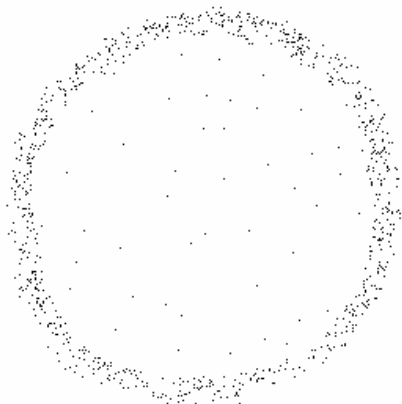


Fig. 3a – Spatial distribution image by electronic microscopy („egg shell” distribution).

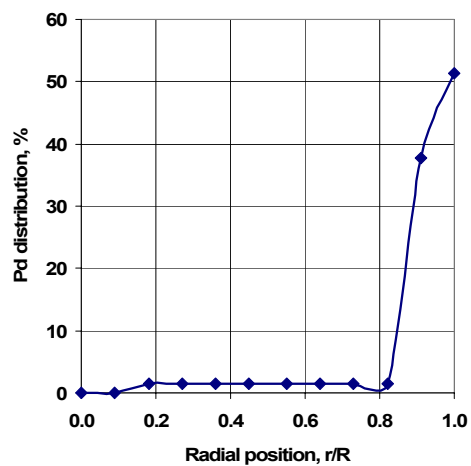


Fig. 3b – Pd distribution in the catalyst pellet („egg shell” distribution).

The dependence of the measured acetone conversion on the catalyst pellets dimension is represented in Fig. 5. From this diagram it can be concluded that, in the tested conditions, the influence of the internal diffusion could be neglected for pellet dimensions up to 2 mm.

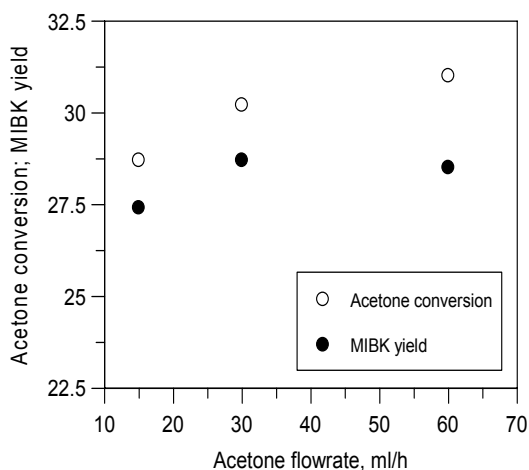


Fig. 4 – Acetone conversion and MIBK yield dependences on the liquid acetone flowrate; ( $T = 130\text{ }^{\circ}\text{C}$ ;  $p = 5\text{ bar}$ ; molar ratio, acetone:  $\text{H}_2 = 5:1$ ;  $d_p = 1\text{ mm}$ ).

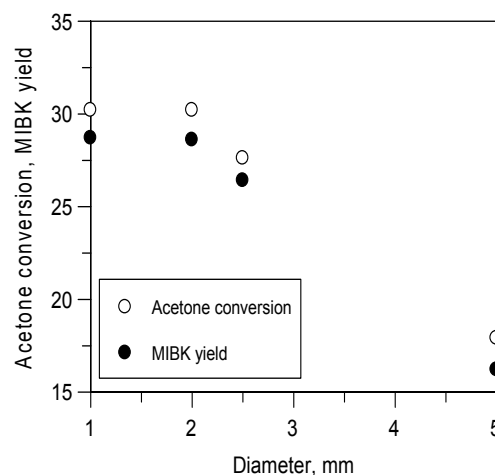


Fig. 5 – Acetone conversion and MIBK yield dependences on the catalyst pellet diameter; ( $T = 130\text{ }^{\circ}\text{C}$ ;  $p = 5\text{ bar}$ ; molar ratio, acetone:  $\text{H}_2 = 5:1$ ).

To investigate the effect of the Pd spatial distribution in the pellet, we performed several sets of experiments at different values of the main operating variables on the three types of distributions described above. The results are presented in Tables 1 and 2. The main observations that can be drawn from these tables are presented below.

The mesityl-oxyde is practically absent in the reaction mixture. This is due to the higher rate of MO hydrogenation step compared with the acetone condensation steps (palladium having a high catalytic activity in the hydrogenation of olefinic bonds).

The yield of the acetone transformation to MIBK on the catalyst with uniform Pd distribution is higher than in the case of the catalysts with nonuniform distribution of the metal. This behaviour is very probably explained by the reversibility of the first two reactions showed in Scheme (1). In the pellet regions where both acidic and metallic (Pd) centers are present, the MO product of the condensation reaction is irreversibly hydrogenated to MIBK, so that the reversibility of the condensation step is not limiting the overall kinetics. This hypothesis is supported by the facts that the kinetics of the hydrogenation step is much faster than the kinetics of the MO formation and the equilibrium conversion of acetone in the condensation reaction has relatively low values. Consequently, the hydrogenation of the olefinic bond of the mesityl oxide occurs as soon as this is formed, the MO concentration in the reaction mixture being stabilized at very low levels. However, in the regions where Pd is missing, the MO accumulates in the pores and the unfavourable influence of the condensation reversibility on the overall process kinetics prevails, so that lower acetone conversions and MIBK yields are obtained.

The nonuniform distribution of the Pd presents also the disadvantage of a faster catalyst deactivation. The high reactivity of the carbon-carbon double bond in mesityl oxide in the presence of an acid environment makes possible the occurrence of reactions of oligomerisation and advanced condensation leading to high molecular weight products which block the reactant access in the pores, diminishing the catalyst activity. So, the deactivation is favoured in the case of catalyst pellets with nonuniform distribution, which include internal zones free of palladium.

The effect of temperature on the yield in MIBK is depending on the type of Pd distribution. In the case of uniform distribution the increase of the temperature is beneficial, leading to an increase of the yield. However, in the case of the two nonuniform distributions we tested, the increase of temperature leads to the decrease of the acetone conversion and MIBK yield (recall that the conversion values are averaged values over a 3 h reaction time). The data in Table 2 show that the yield decrease with the temperature increase is

most pronounced in the case of “egg shell” distribution and slower in the case of intermediary distribution. This result permits to conclude that the increase of temperature is accelerating the deactivation kinetics in a stronger measure than the main reaction kinetics and the fact that the more extended the zone free of Pd, the faster the pellet deactivation intensity.

Table 1

Results with uniform spatial distribution of palladium								
Temperature (C <sup>0</sup> )	130	130	130	130	150	150	170	170
WHSV (h <sup>-1</sup> )	0,66	1	2	2,5	2,5	1	1	2,5
Molar ratios H <sub>2</sub> /A	5	5	5	5	5	5	5	5
Mass % of components								
Methyl-pentane	-	0,2	0,1	0,2	0,1	-	0,2	0,3
Acetone	57,2	68,4	72,7	83,2	78,3	67,8	63,0	74,6
Methyl isobutyl ketone	29,4	24,2	17,3	13,1	16,9	24,8	27,3	19,0
Water	10,3	6,3	9,4	3,2	4,3	6,1	7,8	5,7
Diisobutyl ketone	1,0	0,2	0,3	0,2	0,4	0,6	0,8	0,4
Rest	2,1	0,7	0,2	0,1	-	0,7	0,9	-
Acetone conversion (%)	39,6	30,2	22,4	15,8	20,6	30,8	34,9	23,5
Yield in MIBK* (%)	36,0	28,6	21,5	15,4	19,8	29,4	32,8	22,6

Table 2

Results with nonuniform spatial distribution of palladium									
Distributing of Pd	egg-shell distribution				crown distribution				
Temperature (C <sup>0</sup> )	130	130	150	170	130	130	130	150	170
WHSV (h <sup>-1</sup> )	1	2	1	1	1	1	1	1	1
Molar ratios H <sub>2</sub> /A	5	5	5	5	2,5	5	10	5	5
Mass % of components									
Methyl-pentane	-	-	-	0,3	0,1	-	-	-	0,2
Acetone	75,4	92,9	87,3	88,7	69,3	67,6	75,1	78,4	80,2
Methyl isobutyl ketone	16,3	5,0	9,0	7,1	22,8	21,6	19,1	16,7	14,8
Water	7,5	1,7	3,0	3,5	7,0	10,3	5,3	4,4	4,5
Diisobutyl ketone	0,4	-	-	-	0,7	0,4	0,5	0,4	0,2
Rest	0,4	0,4	0,7	0,4	0,1	0,1	-	0,1	0,1
Acetone conversion (%)	20,8	6,3	11,4	9,3	28,5	27,5	23,4	20,2	18,1
Yield in MIBK* (%)	19,8	5,8	10,6	8,4	27,3	26,8	22,7	19,6	17,6

\*MIBK- Methyl izobutyl ketone

The increase of hydrogen excess does not seem to reduce the deactivation intensity of the catalysts with nonuniform Pd distribution. Moreover, the catalytic performances slightly decrease once the molar ratio H<sub>2</sub>/acetone increases, due to the decrease of acetone concentration in the mixture.

As expected, the increase of the flowrate (increase of the WHSV) has a negative influence on the acetone conversion and on the yield in MIBK, irrespective of the type of Pd distribution, due to the diminution of the reagents-catalyst contact time. The effect is stronger in the case of nonuniform distribution of palladium, which is probably due to the slow kinetics of acetone condensation.

The increase of the diisobutyl-ketone concentration in the effluent is in direct relation with the increase of the contact time and the increase of temperature.

Infrared spectrum of the products that have been extracted from the used catalyst is presented in Fig. 6. It indicates the presence of a carbonyl coupled with an olefinic group (wave numbers 1600-1630 cm<sup>-1</sup>) and of isolated carbonyl group (wave numbers 1675-1690 cm<sup>-1</sup>), specific of the product of advanced condensation.<sup>9</sup> These products accumulate in time, blocking the acces of reactants to the acid centers of catalyst, decreasing its activity.

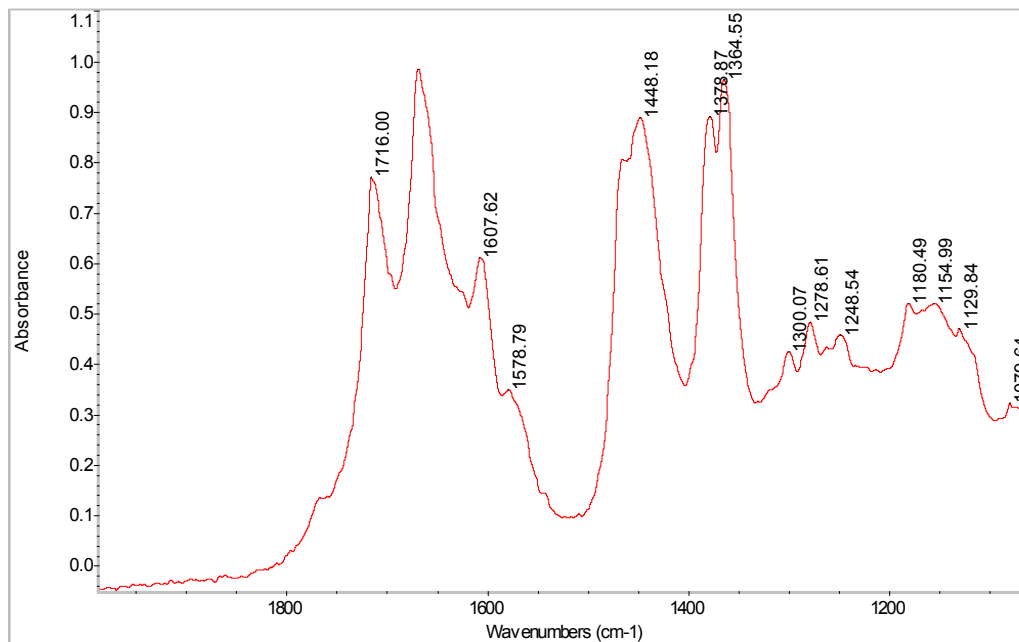


Fig. 6 – FTIR spectrum of high molecular weight products deposited on catalyst.

## CONCLUSIONS

The present study is evidencing the influence of the spatial distribution of Pd in the bifunctional Pd/H-ZSM-5-Al<sub>2</sub>O<sub>3</sub> catalyst for acetone conversion to MIBK, on the process performances. A nonuniform spatial distribution of Pd was found to be detrimental for both MIBK yield and deactivation.

The results also indicate a good activity of the bi-functional Pd/H-ZSM-5 catalyst for the one step conversion of acetone to MIBK with a rather good selectivity. The absence of MO among the reaction products indicate a high activity of the Pd in the hydrogenation of olefinic double bond.

The described experimental study also evidenced the working domains where the influences of internal and external diffusion steps on the acetone conversion kinetics can be neglected.

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