

Synthesis of Zn-B-P/Al/Al₂O₃-Acylation Catalyst Diethylamino M-Toluic Acid under Exposure to Radiation of Microwave Range

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Abstract— The paper presents the results of microwave synthesis of an active energy absorbing microwave radiation Zn-B-P-oxide catalyst supported on the surface of the fiber reinforced aluminum Al/γ-Al₂O₃-carrier to further intensification of the process of acylation diethylamine m-toluic acid diethylamide, m-toluic acid (DETA) under the effect of the microwave field.

Established the identity of the phase composition of the active mass of the samples formed under the action of microwave radiation (2450MHz) with the phase of the catalyst composition prepared by conventional heat treatment, which considering their more developed active surface also gives reason to expect a manifestation of higher catalytic efficiency.

Index Terms— Catalysis, acylation, m-toluic acid, diethylamine, diethyltoluamide, microwave, radiation

I. INTRODUCTION

Began in the middle of the last century, the use of new methods of heat treatment facilities in the food industry, medicine, agriculture, based on the absorption of the energy of microwave (MW) of the electromagnetic field in recent years continues to successfully spread in the area of high technology, as a preparation of heterogeneous catalysts and of the catalyst transitions stimulated by microwave radiation.

Possibility of effective implementation of heterogeneous catalytic reactions in a microwave field, along with the catalytic properties exhibited by solid contacts, is largely determined by sufficient amount of process heat generated by the transformation of the microwave energy in the treated technological environment. The maximum achievable dissipation of microwave energy in the amount of the catalyst charge is a prerequisite for efficient energy consumption

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during the process.

Earlier, in [1]–[3], we presented the results of microwave synthesis reinforced fine powder (PA-2) porous Al/γ-Al₂O₃ catalysts for vehicle damage type actively absorbing electromagnetic radiation of the microwave with a frequency 2450MHz, and capable of transforming the energy of the microwave field to heat sufficient to effectively heat the catalyst charge under dealkylation reactions of toluene with steam joint deep oxidation of carbon monoxide and n-butane, liquid phase oxidation of m-xylene.

Also in the works [4,5] proposed an effective way to direct heterogeneous catalytic acylation diethylamine m-toluic acid in the presence of a modified zinc oxide, boron phosphate-containing catalyst whose active composition was applied to the surface of γ-Al₂O₃ matrix.

The aim of this study is similar attempt microwave synthesis energy absorbing microwave radiation Zn-B-P-oxide catalyst on the surface of the reinforced aluminum Al/γ-Al₂O₃ - support for the further intensification of the process under the action of the microwave field.

II. EXPERIMENTAL PART

In accordance with the chosen optimum component composition Zn-B-P/γ-Al₂O₃ catalyst acylation diethylamine, characterized by high activity and selectivity diethyltoluamide [4] for the preparation of samples of absorbing microwave radiation, the Al/γ-Al₂O₃-carrier is impregnated (by incipient wetness) water boric acid, phosphoric acid and zinc nitrate appropriate concentrations, and after decanting the excess impregnating solution was sequentially subjected to drying and 24 acinations thermolysed in the microwave field. Massive samples B-P-Zn-oxide catalysts were prepared by evaporation of aqueous solutions of zinc nitrate, boric acid and phosphoric acid, followed by heat treatment of dry residue.

The experiments were performed at the facility, constructed on the basis of microwave brand EM-G5593V (Panasonic) with the volume of the cavity 23 liters. Heat treatment of the samples was carried out at an operating frequency of 2450 MHz with a maximum input power of the radiation generator 800 watts. The technical capabilities of the microwave oven allows for heat treatment as a normal sample electrically heated coil, so and programmed to vary the ratio of power of microwave and electric heating. To avoid overheating the sample in the cavity furnace installed capacity of the circulating flow of distilled water.

For X-ray diffraction patterns of the powders was applied to glass and instrumentation fixed with varnish, which has its own structural reflections. X-ray diffraction were obtained on an automated X-ray diffractometer DRON-3 with a graphite monochromator. The measurements were carried out on CuK α radiation in step-scan mode with a step $2\theta = 0,1^\circ$. The exposure time per point is 3 seconds. The treatment of diffraction patterns was performed using programs PHAN and PHAN (%) for the qualitative and quantitative X-ray analysis [6].

Studies were conducted on the surface acidity of the two detector installation of thermal desorption of ammonia, collected on the basis of a gas chromatograph brand LHM-8MD. Total surface acidity of the samples was evaluated on the assumption of single-center ammonia adsorption amount of chemisorbed molecules which desorption is substantially complete at a temperature rise in the catalyst column to 400-420 C. The total number of acid sites: N_Σ (units/m²) was calculated from the values of area under the desorption curve according to the formula:

$$N_\Sigma = \frac{6 \cdot 10^{23} \cdot \sum T_{max_i}}{22400 \cdot S_{ss} \cdot G} \quad (1)$$

where: $6 \cdot 10^{23}$ – Avogadro’s number; S_{ss} – specific surface area of catalyst (m²/g); G – weighed catalyst (g); $\sum T_{max_i}$ – the total area of the peaks in the thermal desorption curve (mm²) proportional to the amount of desorbed ammonia gas, V – (ml NTD). The number of moles of ammonia desorbed calculated as $V/22400$, where 22400 (ml) \approx volume of one mole of NH₃. Other necessary the calculations for this paper carried out using the software package OptimMe [7,8].

III. RESULTS AND DISCUSSION

Figure 1 shows the results of the influence of variable power microwave generator on the dynamics of changes in temperature of samples of Al/ γ -Al₂O₃ support, impregnated with aqueous solutions of zinc nitrate, boric and phosphoric acids, for different ratios of the active mass and the support, calculated as oxides. To compare the level of microwave absorption, and here presents data on heat treatment impregnated with a solution of metal nitrates samples reinforced aluminum γ -Al₂O₃-carrier.

It can be seen that at the minimum (in the investigated range) magnetron power value, ($W = 200$ W), all samples were initially wet, due to the high level of dielectric loss intensively absorb microwave radiation. Wherein the weight average temperature of the blend passes through a maximum and stabilized in 100-115°C until complete evaporation of the water. Notably, in case of reinforced samples carrier drying process proceeds with much greater intensity.

With increasing power of the emitter ($W = 400$ W) increasing the sample temperature to the active mass deposited on the surface of the reinforced microcrystalline aluminum carrier significantly outperformed growth temperature of the samples for unreinforced carrier, in the first case of thermolysis of zinc nitrate with a release of nitrogen oxides is observed even after 7-7.5 min. since the beginning of exposure in the temperature range 250-300°C. Further effects of microwave radiation at 800 W maximum power, leads to more rapid heating of the charge to a

temperature region 580-600°C that realizes the possibility of forming catalytically active phases: boron phosphate by the sequence of steps of dehydration of boric and phosphoric acids, as well as pyrophosphate and borate zinc [9]:

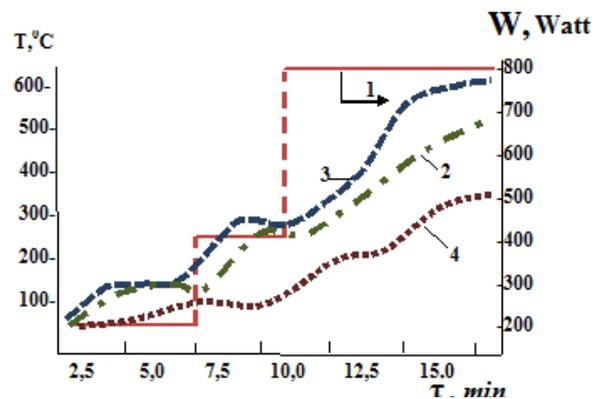
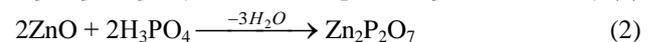


Figure 1. Effect of microwave power (1) on the dynamics of change of temperature samples Al/ γ -Al₂O₃-carrier impregnated with nitrate solutions of Zn, H₃BO₃ and H₃PO₄ in an amount of 10% (wt.) - (2) and 20% (wt.) - (3) based on oxides, and the sample reinforced γ -Al₂O₃-carrier impregnated with a solution of active ingredients in an amount of 20% (wt.) based on oxides - (4).



In contrast reinforced, reinforced samples γ -Al₂O₃-carrier, due to the relatively low dielectric loss, even after prolonged exposure to the maximum range studied magnetron power - 800W, are not capable of absorbing sufficient microwave energy to reach the transformation temperature of zinc oxide boric and phosphoric acids catalytically active phase.

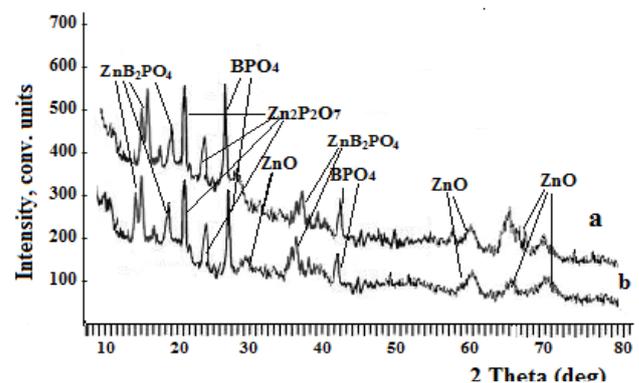


Fig.2. Diffraction patterns of samples of the active mass of the catalyst di-acylation reaction ethylamine m-toluic acid, prepared under the conditions of exposure to microwave radiation (a) and a conventional electrical heating (b). The

As is evident from the diffraction patterns of samples of the active mass of the catalyst acylation diethylamine m-toluic acid formed by heat treatment of precursors: Zn(NO₃)₂, H₃BO₃, H₃PO₄, taken in molar ratios (based on oxide) is 2:1:1 with microwave radiation (a) and conventional heating in an electric muffle (b) phase composition virtually identical.

Consequently, the thermal treatment of samples of potential catalysts for the acylation reaction of diethylamine of m-toluic acid in the microwave may carry out the formation of the active composition, phase composition identical phase composition of samples prepared by conventional heat treatment.

Table 1 compares the characteristics of the synthesized catalyst with the same composition of the active mass (molar ratio, based on the oxides ZnO, B₂O₃, P₂O₅, of 2: 1: 1) deposited on the surface of industrial γ -Al₂O₃-carrier A-1 (GOST 8136-76) and microcrystalline aluminum reinforced Al/ γ -Al₂O₃-carrier formed by heat treatment in the microwave.

It can be seen that the samples of catalyst, heat treatment which is carried out in the microwave, are characterized by a high surface area and porosity with a predominance of long-range 10-100 nm, which corresponds to the generally accepted ideas about the pores of average size.

Formation of Zn-B-P/ γ -Al₂O₃/Al samples with the above characteristics facilitates relatively short time of exposure in the microwave field, in contrast to the long time calcination Zn-B-P/ γ -Al₂O₃ catalyst under conventional heating in which possibly occurs coarsening crystallite size of the active mass, blocking the space inside the porous support matrix.

On education more developed active surface of the Zn-B-P-oxide catalysts supported on γ -Al₂O₃-reinforced carrier obtained under the effect of microwave radiation, as evidenced by the large number of acid sites, determined by the amount of ammonia desorbed.

Thus, these results suggest that the formation of Zn-B-P/ γ -Al₂O₃/Al-acylation catalyst diethylamine m-toluic acid chosen component composition using a heat treatment in a microwave field is acceptable for practical implementation, and from the point of view saving energy and time in synthesis favorably with conventional heat treatment processes.

The observed high thermal transformational capacity and the rate of heating of the catalyst charge, indicates the possibility of reaching a reaction temperature (400-450°C) due to the absorption of microwave energy radiation sufficient to carry out the process of acylation of diethylamine.

IV. CONCLUSION

Thus, these results suggest that the formation of Zn-B-P/ γ -Al₂O₃/Al-acylation catalyst diethylamine m-toluic acid chosen component composition using a heat treatment in a microwave field is acceptable for practical implementation, and from the point of view saving energy and time in synthesis favorably with conventional heat treatment processes.

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Table 1 Textural characteristics and acidity deposited Zn-B-P-oxide catalysts acylation diethylamine m-toluic acid.

The catalyst sample	Conditions of the heat treatment, °C/ time				S _{ss} , m ² /g	V _{pore} , cm ³ /g	Distribution of volume of pore size, nm			Acidity, N _Σ · 10 ¹⁹ , un/m ²
	Electric heating		Microwave radiation				5-10	10-10 ²	10 ² -10 ³	
	Drying	Baking	Drying	Baking						
Zn-B-P/ γ -Al ₂ O ₃ /Al	-	-	<u>100-120</u> 0,2	<u>450-470</u> 0,25	192	0,65	0,20	0,37	0,08	1,8
Zn-B-P/ γ -Al ₂ O ₃	<u>100-120</u> 2	<u>450-480</u> 4	-	-	175	0,53	0,16	0,26	0,11	1,2

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