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The Influence of Porous Structure and Acid-Base Properties of Active Aluminum Oxide on its Catalytic Activity in the Dehydratation of α-Phenylethanol

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Abstract

The influence of porous structure and surface acid-base properties of γ-Al_2O_3, prepared by means of aluminate-nitrate and electrochemical methods, on its catalytic activity in the process of α-phenylethanol dehydratation has been studied. It was shown, that activity of catalyst depends on the predominating diameter of pores. The methods of changing the porous structure of γ-Al_2O_3 with the purpose of increasing its catalytic activity were considered. Thermal or hydrothermal treatment of active aluminum oxide allows to obtain the porous structure, providing the maximum activity of catalyst in the process of α-phenylethanol dehydratation. It was also shown, that conversion of α-phenylethanol and selectivity are determined by the surface concentrations of Broensted and Lewis acid centers. The rate of catalyst deactivation (coke formation) is proportional to the concentration of base centers. The influence of content of sodium cations on the acid-base properties and activity of catalyst was determined. Purification of used γ-Al_2O_3 from sodium cations results in the catalyst, having the maximum catalytic activity.

INTRODUCTION

The catalytic dehydratation of alcohols is the basis of obtaining unsaturated hydrocarbons. At present time, the common opinion about mechanism of aromatic alcohols dehydratation on the surface of solid catalyst does not exist, despite the fact, that this reaction is known for more than 100 years. It is agreed, however, that the most effective catalyst for the process of dehydratation is active aluminum oxide (AAO) γ-Al_2O_3 [1–3].

It is known, that structural characteristics of AAO can vary, and depend on the method of synthesis of aluminum hydroxides, preceeding the oxides. It should be expected, that catalytic activity of AAO may change in the process of dehydratation, depending on the catalyst structure. Relationship of AAO structure with its catalytic activity in the reaction of α-phenylethanol dehydratation into styrene was practically not studied. The aim of present work is to investigate the influence of AAO structural characteristics on the conversion of α-phenylethanol and selectivity, and also to study the changes in porous structure and surface acid-base centers of AAO during dehydratation.

METHODS

The reaction of α-phenylethanol dehydratation was carried out in the flow isothermal reactor with volume 50 cm^3, in the temperature range 220–280 °C and volumetric feed rate of initial reagents $V = 1-4\ h^{-1}$. Heating of α-phenylethanol to working temperature was realized by superheated water steam with temperature 270–330 °C in the top part of reactor.

Water and initial reagent were introduced into the reactor at volumetric ratio of 1 : 1. Analysis of composition of final products of reaction was done by gas-liquid chromatography on the chromatograph Kristall 2000 with flame ionization detector.

Porous structure of the investigated of γ-Al_2O_3 samples was determined on the instrument ASAP-2400 Micrometrics by adsorption of nitrogen at low temperature. The measurement of each adsorption isotherm was carried out at 77 K, degassing – at 773 K to residual vacuum 30 mm Hg [4]. Distribution of pores was calculated based on the desorption isotherms using the method of Joiner and Halendu for cylindrical model of pores.

The acid-base properties of AAO surfaces were investigated by IR spectroscopy. The IR spectra were taken at adsorption temperature on the UR-20 spectrometer. Carbon monoxide and deuterochloroform were used as probe molecules for the determination of acid and base centers. Concentration of Lewis acid centers was calculated from the integral intensity of corresponding lines in the spectrum of adsorbed CO using the integral absorption coefficients from work [5].

RESULTS AND DISCUSSION

The porous structure of AAO samples was studied with the purpose to determine the influence of structural characteristics on catalytic activity of γ-Al_2O_3. The results are presented in Table 1. The reaction conditions, when incomplete conversion of α-phenylethanol was achieved (T = 220 °C, V = 4 h^{-1}) were selected in order to estimate the changes of catalytic activity. Results of catalytic tests presented in Table 2 indicate, that conducting the process at selected conditions allows to estimate the catalytic activity of sample by the change of α-phenylethanol conversion.

Analysis of resulting data (see Table 2) leads to the conclusion, that AAO catalytic activity depends on its porous structure. For example, catalyst showing the highest conversion of α-

TABLE 1

Porous structure characteristics of investigated samples of catalysts

Sample No.	S_{sp}, m^2/g	Pore volume, cm^3/g	Average pore diameter, Å	Distribution of pores by diameter, %		Maxima of pore distribution function, Å	Method of treatment
				≤100 Å	≥100 Å		
1	322	0.69	85	43	57	42, 87	Electrochemical
2	236	0.70	119	74	26	90	Aluminate-nitrate
3	216	0.68	126	62	38	95	»
4	215	0.65	120	70	30	93	»
5	197	0.77	155	20	80	87, 142	»
6	153	0.70	181	10	90	86, 150	Sample No. 4 after 5000 h of usage
7	173	0.69	160	22	78	73, 175	Aluminate-nitrate
8	244	0.70	115	32	68	42, 173	Aluminate-sulfate
9*	178	0.66	149	20	80	86, 160	Aluminate-nitrate
10**	159	0.74	187	12	88	174	»
11	153	0.70	163	4	96	152	Sample No. 6 after chemical wash cleaning
12	159	0.65	181	10	90	142	Sample No. 6 after electrochemical wash cleaning

*Sample No. 5 after hydrothermal treatment: pH 2.0, T = 130 °C, time – 10 h.

**Sample No. 5 after thermal treatment: T = 800 °C, time – 10 h.

TABLE 2

Changes in the catalysate composition during dehydratation of α-phenylethanol over the different samples of γ-Al_2O_3

Sample No.	Conversion, %	Catalysate composition, % mass				
		Styrene	Acetophenone	α-phenyl-ethanol	Σ light C_xH_y	Σ heavy C_xH_y
Initial raw material	–	0.039	14.747	78.361	3.872	2.008
1	50.92	42.963	15.325	38.211	1.582	1.920
2	61.59	52.074	14.215	29.788	1.072	1.937
3	63.31	53.025	14.973	28.914	0.803	1.751
4	66.20	56.949	16.210	23.990	1.280	1.571
5	69.57	58.615	15.604	23.695	0.769	1.316
6	35.85	31.054	15.972	50.269	1.359	1.346
7	57.57	53.837	15.308	28.012	1.169	1.674
8	50.37	43.357	14.497	38.642	0.762	2.170
9	80.39	67.854	14.044	15.265	0.425	1.900
10	64.81	56.061	14.354	26.399	1.169	1.674
11	75.28	64.372	14.248	19.371	0.503	1.506
12	75.12	63.369	14.945	19.496	0.463	1.727

Note. Experimental conditions: T = 220 °C, volumetric feed rate 4 h^{-1}, analysis was done after 3 h of reaction.

phenylethanol has the lowest value of specific surface area (S_{sp}) (sample No. 6). Sample No. 1, having the maximum value of S_{sp}, did not show a high catalytic activity. The increase of catalytic activity of γ-Al_2O_3 from 51 to 75 % is observed upon reduction of the value of S_{sp} from 322 to 153 m^2/g. It is normal, that the increase of average diameter of pores (85–185 Å) causes the reduction of S_{sp} value. As it follows from comparison of data in Tables 1 and 2, total volume of pores does not significantly influence the catalytic activity.

The examined catalyst samples, demonstrating high catalytic activity, all have only a small part of pores with diameter <100 Å (see Table 1). Therefore, it may be proposed, that dehydratation process is hampered in such micropores. In general, the parameter, correlating with the catalyst activity in dehydratation of α-phenylethanol, is the position of maximum of catalyst pore distribution function.

For samples No. 1 and 8, the bimodal distributions of pores with narrow maxima at 42 Å, indicating 8 and 7 % of pore volume, correspondingly, and wide maxima at 87 Å (40 % of pore volume) for sample No. 1 and at 173 Å (42 % of pore volume) for sample No. 8, are characteristic. For sample No. 7, the bimodal distribution of pores is also typical, but with two wide maxima at 73 Å (18 % of pore volume) and 175 Å (70 % of pore volume). The rest of samples are having the monomodal distributions of pores. Increase of catalytic activity for samples No. 1–6 is accompanied by the vanishing of maximum of pore distribution at 150 Å. Further increase of pore diameter leads to the reduction of catalytic activity. For example, samples No. 7 and 8, having the maxima of pore distribution at 175 and 173 Å, are showing catalytic activity at the levels of 57.6 and 50.4 %, respectively. By analyzing the data of Table 1, one can make a conclusion, that catalysts with maxima of pore distribution in the region of 150–170 Å are optimal ones to conduct the process of α-phenylethanol dehydratation into styrene.

It is known, that formation of the catalyst surface continues during all the technological stages of its preparation, and is determined by the technology of precipitation of hydroxide precursor.

Direct modification of the industrial catalysts is one of the variants of obtaining the aluminum oxides with necessary pore distributions. Increase of the diameter of catalyst pores may be accomplished via the processes of hydrothermal [6, 7] or thermal [8] treatment of catalysts with narrow pores.

Rehydratation of the AAO into metahydroxide with pseudoboehmite structure occurs at the initial stage of hydrothermal treatment. Then it is transformed into the boehmite, having large diameters of pores. This change of structure is caused by the processes of solution and precipitation [6, 9]. Further boehmite transforms into aluminum oxide due to the effect of pseudomorphism upon following thermal treatment (550 °C, 2 h); the porous structure of foregoing material remains unchanged (sample No. 9).

The lowering of dispersion of aluminum oxide crystallites is occuring under the conditions of thermal treatment at 750–900 °C due to the sintering of initial parts of oxide into larger aggregates. This leads to the lowering of S_{sp} and to the increase of pore diameters of material [8].

Structural characteristics of sample No. 5, modified by hydrothermal (sample No. 9) and thermal (sample No. 10) treatments, presented in Table 1 confirm, that vanishing of the maximum of pore distribution of catalyst at 142 Å and appearance of another one at 160 Å is occurring upon its hydrothermal treatment. When catalyst was subjected to hydrothermal treatment, this, probably, led to the rehydratation of initial AAO into the hydroxide with pseudoboehmite structure, with further crystallization to boehmite, for which a larger-pore structure and lower values of S_{sp} are characteristic [6, 9]. Thermal treatment of the same catalyst increases the diameter of pores up to 174 Å.

Results of catalytic tests of modified samples are presented in Table 2. It is obvious from these data, that catalyst subjected to hydrothermal treatment is demonstrating the increase of conversion of α-phenylethanol approximately from 70 to 80 %. At the same time, the increase of pore diameter to more than 170 Å upon thermal treatment leads to the lowering of conversion approximately from 70 to 65 %. It can be assumed, that it is necessary to use the AAO with lower diameter of pores, or to select the appropriate regime of treatment in order to achieve the required distribution of pores during the process of thermal treatment.

Structural characteristics and activity of AAO, which was used for 5000 h (sample No. 6), were studied with the goal to elucidate the reasons of catalyst deactivation in the process of α-phenylethanol dehydratation. The used sample within first 3 h under the same conditions when 66.20 % of α-phenylethanol conversion was achieved (sample No. 4), demonstrated significant lowering of conversion, despite the optimum distribution of pore diameters. This fact may indicate the decrease of concentration of active centers on the catalyst surface. The low activity of catalyst, which was used for 5000 h, probably was caused by the change of its acid-base properties, which were investigated by IR spectroscopy (Table 3).

The simultaneous presence of Broensted and Lewis acid centers (B- and L-centers), as well as base centers on the surface of AAO is possible. At the moment, common opinion about the nature of B-centers does not exist. It is considered, that B-centers appear as a result of dissociative adsorption of water on the surface of aluminum oxide [10]. L-centers are co-

TABLE 3

Acid-base properties of AAO samples

Sample No.	L-centers			Base centers					Na$_2$O content, % mass
	Electron affinity,	Concentration of centers		Proton affinity,	Concentration of centers		Σ concentration of centers		
	kJ/mol	μmol/g	μmol/m^2	kJ/mol	μmol/g	μmol/m^2	μmol/g	μmol/m^2	
4	33.0	314	1.46	910, 830	290, 310	1.35, 1.44	600	2.79	0.019
5	33.5	290	1.47	890, 825	130, 445	0.66, 2.26	575	2.92	0.020
6	33.0	300	1.85	910, 850	310, 380	1.91, 2.35	690	4.26	0.730

ordination-unsaturated cations of aluminum, formed due to the dehydratation of two neighboring OH groups. Oxygen anions also can be on the surface of aluminum oxide, and are the base centers.

As it follows from the data of Table 3, initial large- (sample No. 5) and small-pore (sample No. 4) catalysts are having similar concentrations and power of L-centers. The catalytic activity of these samples also differs insignificantly. During the deactivation of catalyst (sample No. 6), the increase of concentration of L-centers from 1.46 to 1.85 μmol/m^2 was observed, while the conversion of α-phenylethanol was reduced from 66.20 to 35.85 %. However, it will be proved further, that increase of the concentration of L-centers during the catalyst deactivation is not the cause of observed catalytic activity decrease.

The most of differences are observed in the main properties of samples. For example, large-pore sample 5 has the least strong (890 and 825 kJ/mol) base centers, and also has minimum concentration of the stronger centers (0.66 μmol/m^2). As it is obvious from the data of Table 3, substantial increase of the concentration of base centers from 2.79 to 4.26 μmol/m^2 is occurring during the usage of catalyst, simultaneously with the substitution of B-center protons by sodium cations, which content increases from 0.019 to 0.73 % mass, calculated as Na_2O for the initial (sample No. 4) and used (sample No. 6) catalysts, respectively. The reduction of power of acid centers, and increase of concentration and power of base centers are results of introducing the sodium cations into the aluminum oxide [11]. The increase of concentration of base centers for the same catalyst is leading to faster lowering of the yield of styrene. For example, the lowering of α-phenylethanol conversion by 3 % on the initial sample occurs in 20 h, while the same lowering on the used sample is observed in just 3 h. These facts are in accordance with the suggestion of authors of work [12], according to which the processes of oligomerization and polymerization on the surface of aluminum oxide, leading to the formation of supermolecular compounds (coke) and being the reasons of catalyst deactivation, are taking place only on the base centers.

Analyzing the collected data, one can make a conclusion that large-pore catalyst, not containing the sodium cations, must have the best working characteristics. The following methods of catalyst regeneration (sodium cation removal), chemical wash cleaning (sample No. 11) and electrochemical wash cleaning (sample No. 12), were considered, because the changes of structural characteristics under the influence of such regeneration media can be controlled. It was established, that wash cleaning from sodium cations does not influence the structural characteristics of catalyst, but the absence of sodium cations significantly improves its activity in the process of α-phenylethanol dehydratation.

Thus, investigation of the catalytic activity of these samples has demonstrated, that conversion of α-phenylethanol is increasing approximately from 36 % (for used sample) to 75 % (for wash cleaned samples) as a result of purification of used catalyst from sodium cations. This value is significantly lower for the fresh catalyst (sample No. 4). Content of the rest of reaction products in catalysate practically does not change. This fact allows to state, that selectivity of the catalytic reaction is preserved.

CONCLUSION

The influence of porous structure and surface acid-base properties of γ-Al_2O_3, prepared by means of aluminate-nitrate and electrochemical methods, on its catalytic activity in the process of α-phenylethanol dehydratation has been studied. It was shown, that activity of catalyst depends on the predominating diameter of pores. The methods of changing the porous structure of γ-Al_2O_3 with the purpose of increasing its catalytic activity were considered. Thermal or hydrothermal treatment of active aluminum oxide allows to obtain the porous structure, providing the maximum activity of catalyst in the process of α-phenylethanol dehydratation. It was also shown, that conversion of α-phenylethanol and selectivity are determined by the surface concentrations of Broensted and Lewis acid centers. The rate of catalyst deactivation (coke formation) is proportional to the concentration of base centers. The influence of content of sodium cations on the acid-base properties and activity of catalyst was determined. Purification of used γ-Al_2O_3 from sodium cations results in the catalyst, having the maximum catalytic activity.

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REFERENCES

1 R. Landau, New Petrochemical Processes and Perspectives of Development of Petroleum Chemistry, Khimiya, Moscow, 1970 (in Russian).
2 R. Landau, *Chem. Eng. News*, 45 (1967) 17.
3 Pat. 3526674 USA, U.S. Cl. 585/437.
4 S. J. Greg, K. S. W. Sing, Adsorption, Surface Area and Porosity, Mir, Moscow, 1984 (in Russian).
5 E. A. Paukshtis, Infrared Spectroscopy in the Heterogeneous and Acid-Base Catalysis, Nauka, Novosibirsk, 1992 (in Russian).
6 V. M. Chertov, V. I. Zelentsov, *Kolloid. zhurn.*, 1 (1973) 200.
7 I. E. Neimark, L. Kh. Freidlin, A. I. Rastrenenko, N. V. Borunova, *Izv. AN SSSR. Ser. khim.*, 7 (1956) 784.
8 T. S. Vinnikova, V. A. Dzis'ko, L. M. Kefeli, L. M. Plyasova, *Kinetika i kataliz*, 9 (1968) 1331.
9 V. I. Zelentsov, V. M. Chertov, *Kolloid. zhurn.*, 4 (1973) 805.
10 G. D. Chukin, *Zhurn. struktur. khimii*, 1 (1976) 122.
11 N. A. Prokudina, V. V. Chesnokov, E. A. Paukshtis, R. A. Buyanov, *Kinetika i kataliz*, 4 (1989) 949.
12 K. Tanabe, Solid Acids and Bases, Mir, Moscow, 1973 (in Russian).