

CATALYTIC REACTION MECHANISMS

Catalytic Dehydration of α -Phenylethanol on the Surface of Aluminum Oxides

R. G. Romanova, A. A. Lamberov, and I. G. Shmelev

Kazan State Technological University, Kazan, 420015 Tatarstan, Russia

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Abstract—The relationship between the acid–base properties of commercial and test samples of aluminum oxides and their catalytic activity in the dehydration of α -phenylethanol was studied. It was found that, in the dehydration of α -phenylethanol, the conversion of the alcohol and the yield of styrene on a catalyst depend on the concentrations of both Brønsted and Lewis acid sites. A hypothetical mechanism of the dehydration with the participation of coordinatively unsaturated aluminum atoms and bridging oxygen ions on the alumina surface was proposed.

INTRODUCTION

The dehydration of alcohols is fundamental for the industrial production of olefins; therefore, a study of this process is of both practical and theoretical interest. However, although the process of alcohol dehydration has long been in use, the mechanism of this reaction has remained open to questioning up to the present, particularly as applied to heterogeneous catalysis.

The dehydration of normal and isomeric aliphatic alcohols has been the most comprehensively studied. The reactions of compounds from this class in both liquid and gas phases have been studied in sufficient detail [1–5]. At the same time, the dehydration of aromatic alcohols, in particular, α -phenylethanol, has received little attention, although this process forms the basis of commercial styrene production and is of great practical importance.

One of the most efficient catalysts for alcohol dehydration is γ - Al_2O_3 . Because of the simultaneous presence of acid and base sites on its surface, the process can occur by at least two different mechanisms: (1) a synchronous mechanism with the participation of paired Lewis acid sites (LASs) and Lewis base sites and (2) a carbonium ion mechanism, when Brønsted acid sites (BASs) on the surface of alumina take part in the reaction. One or the other mechanism can occur depending on the process conditions (medium, temperature, pressure, etc.) and the nature of the dehydrated alcohol.

The aim of this study was to find the mechanism of the gas-phase reaction of α -phenylethanol dehydration on aluminum oxide. For this purpose, we examined the effects of the character and strength of acid–base sites at the catalyst surface on the catalyst activity and selectivity in styrene formation.

EXPERIMENTAL

Commercial and laboratory samples of aluminum oxides prepared by aluminate–nitrate and electrochemical [6, 7] technologies were taken for experiment (Table 1).

Phase analysis was performed on a DRON-3 M diffractometer ($\text{CuK}\alpha$ radiation with a Ni filter). Reference diffraction patterns of structurally different aluminum oxides (γ - Al_2O_3 and α - Al_2O_3) from ICSD were used for comparison with the data obtained.

The concentrations of sodium were determined by flame photometry.

Adsorption measurements for the determination of specific surface areas (S_{BET}), pore volumes (V_{BET}), and pore diameter distributions were performed by the thermal desorption of nitrogen on an ASAP-2400 unit. A catalyst sample (0.8–1.0 g) ground to a powder was taken for analysis and placed in an analyzer ampule. The adsorption–desorption isotherms were measured at 77 K, and outgassing to a residual vacuum of 10^{-4} Torr was performed at 377 K. In the calculations, the density of nitrogen in the normal liquid state was taken as being equal to 0.808 g/cm³, and the molecular cross-section area of nitrogen was set equal to 0.1620 nm². The pore volume and pore size distribution were measured with an accuracy of $\pm 13\%$; the specific surface area was measured to within $\pm 3\%$.

The acid–base properties of the catalyst surfaces were studied by IR spectroscopy.¹ Surface hydroxyl groups were studied by observing absorption bands due to OH vibrations in IR spectra. Lewis acid and base sites were characterized with the use of probe molecules of carbon monoxide and deuteriochloroform. The IR spectra were recorded at an adsorption temperature

¹ The experiments were performed at the Borskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk (head of laboratory: E.A. Paukshtis).

Table 1. Characterization of the test samples

Sample No.	Sample preparation technology*	$\omega^{**}(\text{Na}_2\text{O})$, wt %	S_{BET} , cm^2/g	V_{BET} , cm^3/g	Pore diameter (d) distribution, %		Pore distribution maximums, Å
					$d < 100$ Å	$d > 100$ Å	
1	1 c	0.010	7.53	0.0334	91.0	9.0	38, 70, 150
2	1 c	0.020	236	0.7059	74.0	26.0	94
3	1 c	0.020	216	0.6830	62.4	37.6	95
4	1 c	0.730	162	0.6946	12.0	88.0	140
5	2 l	0.023	292	0.4067	95.0	5.0	42, 56
6	2 l	0.021	323	0.6896	43.0	57.0	42, 87
7	1 c	0.020	173	0.6964	22.0	78.0	73, 175
8	1 c	0.020	197	0.7676	20.0	80.0	150
9	1 c	0.019	215	0.6794	70.0	30.0	93
10	1 l	0.023	256	0.8767	20.0	80.0	152

Note: c and l refer to commercial and laboratory samples, respectively.

* 1 and 2 refer to aluminate–nitrate and electrochemical [6, 7] technologies, respectively.

** Weight fraction of sodium oxide impurities in the catalyst sample.

on a Shimadzu 8300 Fourier spectrometer with a resolution of 4 cm^{-1} and a number of accumulated spectra of 50.

In this work, the concentrations of various sites were determined from IR spectra based on the Lambert–Bouguer–Beer law as applied to the absorption bands of adsorbed molecules (carbon monoxide for LASs and deuteriochloroform for the base sites) [8]. In the case of adsorbed probes, this law can be conveniently presented in the form

$$A = 10^{-3} A_0 C_s \rho,$$

where A is the apparent integrated absorbance of a band, A_0 is the integrated absorbance of the band for an adsorbate concentration of $1\text{ }\mu\text{mol/g}$ (or the total absorption coefficient), C_s is the concentration of the adsorbed probe ($\mu\text{mol/g}$), and ρ is the catalyst weight per 1 cm^2 of the light flux cross section (mg).

The value of $10^{-3} C_s \rho$ gives the number of micro-moles of the adsorbate per 1 cm^2 of the light flux cross-section. The concentration of LASs was determined from the integrated intensities of the corresponding bands in the spectrum of adsorbed CO with the use of the total absorption coefficients from [8]. These coefficients depend on the position of the absorption band of CO complexes in the range $2180\text{--}2240\text{ cm}^{-1}$. For aluminum oxides, this dependence is expressed by the equation $A_0 = 0.13(v_{\text{CO}} - 2130)$. The determination limit of sites was $0.2\text{ }\mu\text{mol/g}$. The strength of LASs was characterized by the heat of CO adsorption (Q_{CO} , kJ/mol), which was determined from the correlation equation [8] $Q_{\text{CO}} = 10.5 + 0.5(v_i(\text{CO}) - 2143)$, where $v_i(\text{CO})$ is the vibration frequency of CO adsorbed on the i th Lewis site. The relative intensities of absorption bands due to OH groups were determined by the internal normalization method after decomposing

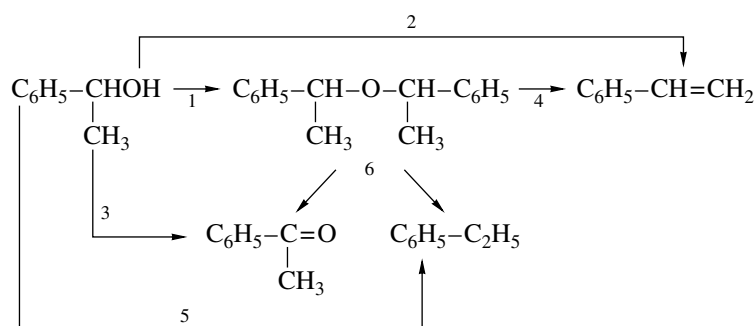
the spectra into Gaussian components. The surface OH groups were characterized by the vibration frequency $v(\text{OH})$ (cm^{-1}) and strength on a proton affinity (PA) scale (kJ/mol). In the determination of base sites, the spectra of a prepared sample were recorded in the regions $2000\text{--}2300$ and $3000\text{--}3900\text{ cm}^{-1}$ at room temperature. Next, the adsorption of CDCl_3 was performed at the same temperature and a saturation pressure of deuteriochloroform until the complete saturation of base sites, and the spectrum was measured after each adsorption of CDCl_3 . The concentration of base sites was determined from the integrated intensity of the bands $v(\text{CD})$ in complexes with base sites of different strengths. Absorption coefficients were taken from [8]. The strength of base sites was characterized using the scale of PA. The values of PA for the i th base site were determined from the correlation equation

$$\log \Delta v(\text{CD}) = 0.0066 \text{PA} - 4.36,$$

where $\Delta v(\text{CD})$ is the shift of the i th band of CD vibrations from the position $v(\text{CD})$ in the gas phase.

Tests for the catalytic activity of the catalysts obtained were performed in an isothermal flow reactor at $220\text{--}260^\circ\text{C}$ and in the presence of water vapor at a 1 : 1 volume ratio between water vapor and feed material. The process was performed with the use of real raw material containing from 78 to 85 wt % α -phenylethanol. The reaction was performed under the conditions of an incomplete conversion because only in this case can the activities of catalysts be compared. The feed and water space velocity was $0.5\text{--}5.4\text{ h}^{-1}$; the catalyst volume was 50 cm^3 .

The products of catalysis were analyzed on a Kristall-lyuks 4000 chromatograph with a thermal conductivity detector. A packed column with PEG 20000



Scheme 1. Possible transformations of α -phenylethanol.

poly(ethylene glycol) on Porokhrom was used. Components were identified based on the results of determinations by chromatography–mass spectrometry with the use of a Perkin-Elmer instrument.

RESULTS AND DISCUSSION

Scheme 1 illustrates possible α -phenylethanol reaction pathways in the presence of alumina, according to which styrene, diphenyldiethyl ether, acetophenone, and ethylbenzene can be reaction products. In this case, styrene can be formed both by the decomposition of diphenyldiethyl ether (path 1, 4) and by the direct dehydration of α -phenylethanol (path 2). Under certain conditions, the reactions of acetophenone and ethylbenzene formation from α -phenylethanol (paths 3 and 5) or diphenyldiethyl ether (path 6) can also occur in Scheme 1.

For practical purposes, we studied the dehydration of a raw material containing 78–85% α -phenylethanol on aluminum oxide over a temperature range from 220 to 300°C, which corresponds to the occurrence of a gas-phase process. A number of commercial and test samples of aluminum oxide with different structures and acid–base properties were taken as catalysts. Table 2 summarizes the compositions of the feed materials and the products of catalysis as determined by chromatography–mass spectrometry. It follows from these data that styrene was the main product of dehydration for all the samples tested except for sample 1. It can be seen in Table 2 that the process selectivity for styrene was 96–100% for samples 2–10; this suggests the predominant occurrence of the reaction of α -phenylethanol dehydration. The absence of diphenyldiethyl ether from the products of catalysis indicates that path 2 was predominant under the conditions chosen.

The main factors affecting the selectivity and activity of a catalyst in the reaction are its pore structure and the character of active sites on the surface. Because the process occurs in the gas phase, the pore size of the catalyst is responsible for the diffusion and mass-transfer processes of parent components and reaction products. In addition to the diffusion limitations, the catalyst pore size and surface provide an optimum distribution and accessibility of acid–base sites. Previously, we found

the effect of the surface characteristics of active alumina on its catalytic activity in the dehydration of α -phenylethanol and revealed the optimum pore structure, which improved the efficiency of the catalyst [9].

A comparison of the pore structure of test samples (Table 1) and the catalytic activity (Table 2) evidences that aluminum oxide with a small surface area (sample 1) does not participate in the process of dehydration. The identification of phase composition performed by X-ray diffraction analysis demonstrated that samples 2–10 belong to γ - Al_2O_3 with different degrees of perfection of their crystal structures, whereas sample 1 exhibits the structure of α - Al_2O_3 .

Thus, the experimental data indicate that the main factor responsible for the possibility of dehydration is the occurrence of catalytically active sites that are typical of low-temperature alumina modifications on the surface of aluminum oxide.

In accordance with the currently available models, the surface of γ - Al_2O_3 is a set of aluminum and oxygen atoms in different coordinations occupied by OH groups or water molecules at room temperature. Surface dehydroxylation results in the appearance of coordinatively unsaturated oxygen (Lewis base) and aluminum (Lewis acid) atoms [10]. Note that hydroxyl groups of different characters remained on the surface of γ - Al_2O_3 even after calcination at 773 K.

It follows from an analysis of the IR spectra of samples 2–10 in the region 3660–3800 cm^{-1} that all of them belong to γ - Al_2O_3 in terms of the hydroxyl cover. In this case, the spectra after calcination at 723–773 K exhibited a set of five absorption bands with maximums at 3800, 3770, 3730, 3690, and 3580–3620 cm^{-1} (Table 3). The above bands belong to the two types of OH groups [8]: terminal OH groups bound to an aluminum atom in the region 3800–3770 cm^{-1} and bridging OH groups arranged between two aluminum atoms with different coordinations in the range 3730–3620 cm^{-1} . Thus, the bands $\nu(\text{OH}) = 3800 \text{ cm}^{-1}$ and $\nu(\text{OH}) = 3770 \text{ cm}^{-1}$ belong to OH groups bound to aluminum ions in tetrahedral and octahedral coordinations, respectively. The bands $\nu(\text{OH}) = 3730 \text{ cm}^{-1}$ and $\nu(\text{OH}) = 3690 \text{ cm}^{-1}$ belong to OH groups bound to two aluminum atoms,

Table 2. Results of catalytic tests

Sample no.	Composition of the products of catalysis, wt %					Degree of α -phenylethanol conversion, %	w^{**} , (g styrene) (g Cat) ⁻¹ h ⁻¹	w^{**} , (g styrene) (m Cat) ⁻² h ⁻¹	Selectivity for styrene, %
	Σ light HCs*	styrene	acetophenone	α -phenylethanol	Σ heavy HCs				
1	0.872	4.639	14.247	77.861	2.008	0	0	0	0
2	1.072	52.074	14.215	29.788	1.937	61.59	3.37	0.0143	98.7
3	0.803	53.025	14.973	28.914	1.751	63.31	3.44	0.0159	98.9
4	1.359	33.315	15.972	48.009	1.346	38.34	2.04	0.0126	96.1
5	0.561	57.684	15.732	24.293	1.530	68.80	3.77	0.0129	99.0
6	1.582	42.963	15.325	38.211	1.956	50.92	2.73	0.0085	96.7
7	1.169	53.837	15.308	28.012	1.674	64.02	3.50	0.0202	98.7
8	0.769	58.615	15.604	23.295	1.316	69.57	3.84	0.0195	98.9
9	1.551	40.491	14.749	41.513	1.697	46.68	2.55	0.0119	98.6
10	0.770	58.642	15.586	23.295	1.346	70.04	3.82	0.0153	99.0

Note: Composition of the feed material (wt %): Σ light HCs, 0.872; styrene, 4.639; acetophenone, 14.247; α -phenylethanol, 77.861; and Σ heavy HCs, 2.008.

* HCs refers to hydrocarbons.

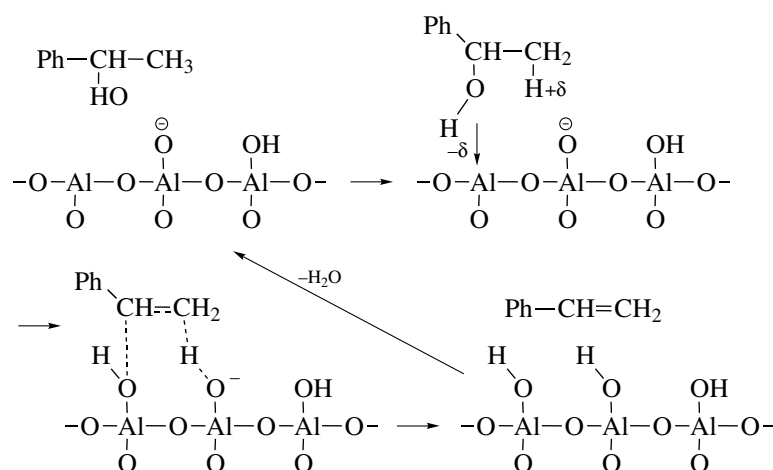
** w is the rate of styrene formation calculated as the ratio of the weight of styrene formed in the reaction to the weight of the catalyst or to the catalyst surface unit per hour.

Table 3. Positions and intensities of the absorption bands of hydroxyl groups in the IR spectra of test samples

Sample no.	Intensities (arb. u.) of absorption bands with maximums at $\nu(\text{OH})$, cm ⁻¹				
	3580–3620	3690	3730	3770	3800
2	22.3	28.1	26.3	14.2	2.3
3	31.3	35.3	23.0	14.9	2.7
4	8.7	18.1	23.0	15.6	2.0
5	19.3	21.8	20.7	11.5	2.4
6	28.5	31.0	22.5	9.2	1.4
7	25.8	27.4	21.0	11.8	1.5
8	28.2	26.5	20.1	11.7	0.5
9	21.6	23.3	23.0	12.1	2.6
10	28.0	27.0	27.0	12.1	7.0

which have either octahedral coordinations (PA = 1440 kJ/mol) or an octahedral and a tetrahedral coordination, respectively. According to the published data [8], hydroxyl groups on the surface of aluminum oxide exhibit different acidities, which are evaluated by the values of PA. Thus, OH groups having absorption bands with $\nu = 3620\text{--}3690$ cm⁻¹ are most strongly acidic, corresponding to PA = 1380–1410 kJ/mol. Bands at 3730–3710 and 3796–3756 cm⁻¹ exhibit medium (PA = 1410–1440 kJ/mol) and minimum (PA = 1440–1590 kJ/mol) acidities, respectively. Bridging

OH groups belong to proton acid sites (BASs). As can be seen from a comparison of the data in Tables 2 and 3, the catalytic activity is directly related to the intensity of the absorption bands due to OH groups at 3620 and 3690 cm⁻¹, which exhibit Brønsted acidity. Thus, for example, the relative intensities of absorption bands at 3580–3620 and 3690 cm⁻¹ in sample 4 were 8.7 and 18.1, respectively, which are more than twice as low as the relative intensities of the absorption bands of the other samples. This catalyst exhibited a low rate of styrene formation, as compared with samples having sim-



Scheme 2. Synchronous mechanism of α -phenylethanol dehydration.

ilar pore-size characteristics. Note that the sample is characterized by a higher sodium content (0.73 wt %); at the same time, it is well known that BASs are poisoned on the introduction of sodium into aluminum oxide because of the ion exchange of protons for alkali metal ions [11]. Thus, the above experimental data are indicative of the participation of BASs in the reaction of dehydration. However, generally, the Brønsted acidity of aluminum oxide is low [8]; therefore, it is expected that the Lewis and base sites of Al_2O_3 can also make a certain contribution to the reaction of catalytic dehydration.

Processes with the participation of Lewis sites are more difficult to study than reactions on Brønsted sites. In many cases, even the identification of adsorption sites is problematic. Only two structures can participate in the dehydration of alcohols: a donor–acceptor complex of an alcohol with a Lewis site and an alkoxide. However, it is still impossible to identify unambiguously which structure belongs to the intermediate. According to Paukshtis [8], the Lewis acidity of γ - Al_2O_3 is characterized by three types of acid sites dif-

ferent in strength with carbon monoxide adsorption energies equal to 30, 34, and 42 kJ/mol, respectively. Table 4 summarizes the positions of absorption bands in the spectra of carbon monoxide adsorbed on the samples and the strengths and concentrations of acid sites. It can be seen in Table 4 that the surface of the test aluminum oxides is nonuniform. The detected LASs characterized by an absorption band at 2188–2191 cm^{-1} in the IR spectrum belong to medium-strength sites. Chukin [10] interpreted them as aluminum cations on the defect faces of crystals. Sample 9 exhibited the weakest sites, whereas sample 10 exhibited the strongest sites; however, differences in the strength are not so great (2 kJ/mol). The highest concentration of sites was observed in sample 7 (2.14 $\mu\text{mol}/\text{m}^2$), and the lowest, in sample 9 (1.04 $\mu\text{mol}/\text{m}^2$). A comparison of the data in Table 4 with the catalytic activity (Table 2) demonstrated that, in the series of test samples with similar pore structures, the rate of styrene formation and the degree of α -phenylethanol conversion increased with the concentration of LASs.

A considerable amount of base sites also occurs on the surface of γ - Al_2O_3 . According to the published data [8, 10], each surface oxygen ion in aluminum oxide is a base site with a particular strength: strong base sites are bridging oxygen ions, whereas weak base sites are interpreted as the oxygen of OH groups. The base properties of aluminum oxide were evaluated from the spectra of adsorbed deuteriochloroform. Table 5 summarizes the strengths and concentrations of base sites. According to Table 5, the test samples exhibited two types of base sites: (1) strong sites characterized by the band $\nu(\text{CD}) = 2200\text{--}2225\text{ cm}^{-1}$, which corresponds to $\text{PA} = 890\text{--}910\text{ kJ/mol}$ according to Paukshtis [8], and (2) weak sites with $\nu(\text{CD}) = 2250\text{ cm}^{-1}$ and $\text{PA} = 825\text{--}850\text{ kJ/mol}$. Actually, the spectra of deuteriochloroform complexes with aluminum oxide exhibited other bands in the region $\nu(\text{CD}) = 2230\text{--}2235\text{ cm}^{-1}$. These bands are indicative of a wide variety of base sites related to alu-

Table 4. Characterization of the aprotic acidity of samples

Sample no.	$\nu(\text{CO})$, cm^{-1}	Q_{CO} , kJ/mol^{-1}	N , $\mu\text{mol/g}$	N , $\mu\text{mol}/\text{m}^2$
2	2191	34.5	275	1.17
3	2192	35	269	1.25
4	2188	33	300	1.85
5	2190	34	323	1.11
6	2190	34	336	1.04
7	2190	34	370	2.14
8	2189	33.5	290	1.47
9	2188	33	314	1.46
10	2190	35	418	1.63

Table 5. Characterization of the base sites of test samples

Sample No.	ν (CD), cm^{-1}	Site strength, kJ/mol	N		ΣN	
			$\mu\text{mol/g}$	$\mu\text{mol/m}^2$	$\mu\text{mol/g}$	$\mu\text{mol/m}^2$
2	2220	910	360	1.53	920	3.90
	2250	830	560	2.37		
3	2225	890	360	1.67	870	4.03
	2250	830	510	2.36		
4	2220	910	310	1.91	690	4.26
	2245	850	380	2.35		
5	2220	910	360	1.23	750	2.57
	2250	830	390	1.34		
6	2225	900	440	1.36	1065	3.30
	2250	830	625	1.94		
7	2218	911	320	1.85	680	3.93
	2247	843	260	1.50		
8	2225	890	130	0.66	575	2.92
	2252	825	445	2.26		
9	2220	910	290	1.35	600	2.79
	2250	830	310	1.44		
10	2220	910	161	0.63	293	1.15
	2250	820	132	0.52		

minum atoms in octahedral, tetrahedral, and other states. However, it is practically impossible to distinguish and assign these bands experimentally. Note that the amount of weak base sites detected in the test samples was much greater than that of strong base sites. Sample 4 exhibited a maximum concentration of base sites. As can be seen in Table 1, the concentration of impurity sodium cations in this sample was much higher than those in the other aluminum oxides, and it was equal to 0.73 wt %. In this case, an increase in the number of base sites was likely due to an increase in the number of oxygen ions, which exhibit electron-acceptor properties, upon the replacement of BASs by sodium ions. A minimum amount of base sites was detected in sample 10. An analysis of data on the catalytic activity and base properties of the samples demonstrated that the concentration of base sites in aluminum oxide has no effect on the degree of α -phenylethanol conversion and on the rate of styrene formation. Taking into account that, as a rule, the total number of base sites is greater than the total number of LASs, we can believe that the dehydration of α -phenylethanol occurs on paired sites—coordinatively unsaturated aluminum atoms and oxygen ions—in accordance with Scheme 2.

Thus, the studies of the acid–base properties and the catalytic activity of alumina samples demonstrated that both Brønsted and Lewis acid sites participate in the dehydration of α -phenylethanol. The found relationship between the catalytic activity and the amount of aprotic sites on the surface of alumina suggests that the reaction of α -phenylethanol dehydration occurs by a synchronous mechanism with the participation of coordinatively unsaturated aluminum atoms and bridging oxygen ions.

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