Effect of Phosphorus–Oxygen Compounds on Structural, Acidic, and Catalytic Properties of γ-Alumina in the Acetic Acid Ammonolysis Reaction

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Abstract—The effect of a promoter on the acidic and catalytic properties of aluminum oxide in the reaction of acetic acid ammonolysis has been studied. It has been shown that the promotion of γ -Al₂O₃ with phosphorus–oxygen compounds results in a change in the porous structure, an increase in the concentration of acid sites, and site strength redistribution, thereby enhancing the activity and selectivity of the catalyst. The change in the acid properties of γ -Al₂O₃ surface has a significant effect on the second stage of the process, the dehydration of acetamide.

Keywords: acetic acid ammonolysis, acetonitrile, phosphorus–oxygen compounds, acetamide **DOI:** 10.1134/S0965544114050041

Acetonitrile is an important intermediate in organic, pharmaceutical, and petrochemical syntheses [1]. It is also widely used as a solvent and a component in extractive and azeotropic distillation of hydrocarbons in petrochemical processes [2] and as a mobile phase in high-performance liquid chromatography [3]. Today, acetonitrile is mainly produced as a byproduct in the ammonolysis of propylene to acrylonitrile [4], but acetonitrile obtained in this process contains hydrocyanic acid as an impurity, which demands additional and rather significant costs for its purification and use in subsequent target transformations. The processes under development for manufacturing of acetonitrile by ammonolysis of paraffins [5] and olefins [6] are also characterized by the formation of hydrocyanic acid as a byproduct in addition to a low yield of the desired product. However, in the case of acetonitrile production by ammonolysis of acetic acid [7, 8] or alcohols [9, 10], it is possible to avoid the formation of hydrogen cvanide and, hence, make these processes promising in terms of reduced operating costs for the separation and purification of the final product acetonitrile. In the studies on the ammonolysis of oxygen-containing compounds [7-10], alumina promoted with phosphoric acid [7] or modified with Co, Ni [9], or Cu [10] metals, or SO_4^{2-}/ZrO_2 [8] is

used as the base catalyst. The alumina modification reported in [7-10] was performed in order to reduce the reaction temperature, enhance the yield of the desired product, and increase the catalyst on-stream time.

The aim of this work was to reveal the effect of the amount of the added promoter (oxygen compounds of phosphorus) on the structural, acidic, and catalytic properties of γ -Al₂O₃ in the reactions of acetic acid ammonolysis and dehydration of the intermediate product acetamide.

EXPERIMENTAL

The experiments were performed in a flow steel (12Ch18N10T grade) riser reactor with preheating the reaction mixture to the reaction temperature [11], the acetic acid and acetamide feed space velocity of 1.05 h^{-1} at molar ratios of NH₃: CH₃COOH = 2 : 1 and NH₃: CH₃CONH₂ = 1 : 1.

The starting γ -Al₂O₃ (A-64 grade) was promoted with phosphoric acid to have 2 or 4 wt% on a P₂O₅ basis and then calcined for 4 h in an air stream at T =400°C and for 5 h in a nitrogen stream at T = 500°C.

The products were analyzed on a Chromatec-Kristall 5000.1 chromatograph with two thermal conductivity detectors. Conditions of the analysis: helium carrier gas; flow rate, 0.0012 m³/h; column temperature, 180°C; a column 2 m in length with Separon SDA sorbent for detecting ammonia, hydrocyanic acid, water, acetonitrile, acetone, ammonium acetate, and acetamide; a 3 m long column packed with Carbosieve S-II for detecting ammonia, carbon monoxide, and carbon dioxide. Thermal studies of the cocked catalysts were conducted using a Netzsch STA-449 synchronous TG–DTA/DSC thermal analyzer (Germany); temperature rise rate, 10°C/min in

No.	Sample	$S_{\rm sp},$ m ² /g	Pore volume 17–3000 Å, cm ³ /g	Pore size, Å	Micropore volume $3.3-5.4 \text{ Å}, \text{ cm}^3/\text{g}$	CP, wt %	Yield of acetonitrile, %
1	γ -Al ₂ O ₃	171	0.660	130-113	0.0051	_	73.3
2	$2\% P_2O_5/\gamma$ -Al $_2O_3$	150	0.629	145-119	0.0090	_	95.6
3	$4\% P_2O_5/\gamma$ -Al ₂ O ₃	129	0.573	160-124	0.0122	_	98.5
4	γ -Al ₂ O ₃	156	0.614	120-109	—	5.04	56.5
5	$2\% P_2O_5/\gamma$ -Al $_2O_3$	137	0.587	148-121	0.0092	2.52	92.1
6	$4\% P_2O_5/\gamma \text{-}Al_2O_3$	120	0.569	173-128	0.0125	2.14	96.3

Table 1. Effect of γ -Al₂O₃ promotion on the porosity parameters and catalytic properties at $T = 360^{\circ}$ C and an acetic acid space velocity of 1.05 h⁻¹. Freshly prepared catalysts, nos. 1–3; catalysts after 120 h of operation, nos. 4–6

an air stream. The parameters of the porous structure and the specific surface area of the samples were determined carried out on a Micromeritics TriStar II 3020 porosity analyzer (USA). An ammonia temperatureprogrammed desorption (TPD) study was performed on a Micromeritics ChemiSorb 2750 instrument (USA) at an ammonia adsorption temperature of 100° C and a heating rate of 10° C/min. The acidic properties of the surface of catalyst samples were determined using titration in a nonaqueous medium with an indicator [12]. The amount of acid sites was found by titration with a benzylamine solution (C =0.01 N) of a suspension in dry dimethylformamide of the powdered catalyst with a pre-adsorbed indicator. The quantity of benzylamine spent for titration corresponds to the number of acid sites $(\mu mol/g)$ with an acid strength greater than or equal to the pK_a of the indicator used. For adsorption, the following indicators were used: methyl red ($pK_a = 4.8$), *p*-dimethylaminoazobenzene (p K_a =3.3), 2-amino-5-azotoluene $(pK_a = 2.0)$, brilliant green $(pK_a = 1.3)$, and crystal violet (p $K_a = 0.8$).

RESULTS AND DISCUSSION

The reaction of acetonitrile synthesis from acetic acid and ammonia is an equilibrium two-stage processes involving the formation of acetamide as an intermediate product [7, 13]:

1.
$$NH_3 + CH_3COOH \Leftrightarrow CH_3CONH_2 + H_2O$$
,
 $\Delta H = -2.18 \text{ kJ/mol}$,
2. $CH_3CONH_2 \Leftrightarrow CH_3CN + H_2O$,
 $\Delta H = 84.37 \text{ kJ/mol}$.

The intermediate formation reaction is slightly exothermic; the equilibrium constant K_p is greater than 1 in the temperature range of 250–450°C. Acetamide dehydration reaction (2) is endothermic, the equilibrium constant becomes higher than 1 at a temperature above 320°C.

The promotion of γ -Al₂O₃ with 2 or 4 wt % phosphoric acid (in terms of P₂O₅) results in a decrease in the specific surface area and pore volume of the catalyst (Table 1). The average pore size is also increased by

modifying the starting γ -Al₂O₃; at the same time, the micropore volume increases with an increase in the amount of P_2O_5 in comparison with the initial alumina sample. After 120 h on-stream at $T = 360^{\circ}$ C for all samples of the catalysts the formation of condensation products (CP) was observed: the maximum amount for unpromoted γ -Al₂O₃ and an amount smaller by a factor of 2 or 2.4 for the sample promoted with 2 or 4% P_2O_5 , respectively. For all of the cocked samples, a decrease in the specific surface area and pore volume is observed as compared with the freshly prepared samples (Table 1): micropores are completely plugged with condensation products in the case of unpromoted $4\% P_2 O_5 / \gamma - Al_2 O_3$ and remain intact in the case of the promoted samples. According to the data in Table 1, the yield of acetonitrile in the case of the freshly prepared samples is higher for the promoted catalysts and the yield of the desired product varies slightly after 120 h on-stream for the 2% and 4% P_2O_5/γ -Al₂O₃ systems, unlike the case of unpromoted alumina.

According to Fig. 1, ammonia desorption from the surface of all the catalysts is characterized by one peak with $T_{\text{max}} = 220^{\circ}$ C and close activation energies of desorption, 49.1–50.2 kJ/mol. The areas of the ammonia TPD peaks increase after the promotion of γ -Al₂O₃ with phosphoric acid, thereby indicating an increase in the concentration of acid sites on the surface of the promoted alumina (Fig. 1, Table 2). It is impossible to differentiate surface acid sites by their strength from the ammonia TPD spectra.

According to the indicator titration data (Table 2), the promotion of γ -Al₂O₃ with phosphoric acid in addition to increasing the total concentration of acid sites alters the acid strength distribution of the sites; i.e., the concentration of strong acid sites with the Hammett acidity function of H_o < 2.0 decreases and that of acid sites of a medium strength with $3.3 \ge H_o >$ 2.0 significantly increases. Phosphoric acid in alumina modified with phosphorus compounds is adsorbed on low-coordination-number aluminum ions (Lewis acid sites) to form Brönsted acid sites. In this case, polyphosphate structures are likely to be formed on the surface of the contact catalysts during the calcination of the promoted samples [14]. The concentration of

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Fig. 1. Spectra of ammonia thermal-programmed desorption from the surface of the catalysts (1) γ -Al₂O₃, (2) 2% P₂O₅/ γ -Al₂O₃. and (3) 4% P₂O₅/ γ -Al₂O₃.

acid sites measured by the indicator method is underestimated in comparison with the ammonia temperature-programmed desorption data (Table 2). This difference is due to the fact that the large size of indicator molecules as compared with ammonia hinders their adsorption in alumina pores, whose size is equal to or smaller than that the indicator molecule. A decrease in the concentration of strong acid sites on the catalyst surface with the addition of P_2O_5 , which sites presumably mediate the decomposition and decarboxylation of adsorbed acetic acid, leads to a decrease in the amount of CP during acetic acid ammonolysis (Table 1). Thus, along with changes in the structural characteristics of the surface, catalyst operation for 120 h leads to a decrease in the concentration of acid sites; a significant decrease in the concentration of acid sites, especially strong sites, is observed for unpromoted γ -Al₂O₃ (Table 2; no. 1, 4). In the case of the promoted catalysts (Table 2), a decrease in the concentration of acid sites with the Hammett acidity function of $4.8 \ge H_0 > 2.0$ is insignificant, whereas the concentration of sites with the acidity of $2.0 \ge H_0 > 1.3$ decreases noticeably. For all the catalysts after operation in the reaction mixture, acid sites with $1.3 \ge H_{o}$ were not detected by indicator titration, probably, because of their blocking with CP (Table 2). At the same time, an increase in the concentration of medium-strength acid sites for the freshly prepared catalysts significantly increases the acetic acid conversion accompanied by enhancement of the selectivity for acetonitrile, especially, at low temperatures of $350-360^{\circ}$ C for $2\% P_2 O_5 / \gamma$ -Al₂O₃ as compared with unpromoted γ -Al₂O₃ (Fig. 2). For the 4% $P_2 O_5 / \gamma$ -Al₂O₃ catalyst, the concentration of medium strength acid sites increases (Table 2), thereby slightly improving the conversion of CH₃COOH compared with the 2% $P_2 O_5 / \gamma$ -Al₂O₃ system, but the selectivity for acetonitrile is higher than 90% at low temperatures, $350-360^{\circ}$ C, in this case (Fig. 2).

These findings suggest that the Brönsted acid sites of medium strength are responsible for the occurrence of reaction (2), the dehydration of acetamide to acetonitrile (scheme). Thus, when acetamide and ammonia are used as a feedstock under conditions identical to ammonolysis of acetic acid, along with the desired acetamide dehydration reaction, reverse reaction (1) (see Scheme) of the hydrolysis of acetamide produced

	Catalyst	Acid sites concentration							
No.		µmol NH3	benzylamine, µmol						
			$4.8 \ge H_0 > 3.3$	$3.3 \ge H_0 > 2.0$	$2.0 \ge H_0 > 1.3$	$1.3 \ge H_0 > 0.8$	$0.8 \ge H_0$	total quantity	
1	γ-Al ₂ O ₃	220.6	81.0	12.7	57.2	0.7	4.5	155.9	
2	$2\% P_2O_5/\gamma\text{-}Al_2O_3$	305.9	88.5	53.1	22.2	0.5	3.0	167.3	
3	$4\% P_2O_5/\gamma \text{-}Al_2O_3$	355.7	60.1	99.7	16.0	0.2	—	176.0	
4	γ -Al ₂ O ₃	122.9	51.0	6.5	27.5	—	—	85.0	
5	$2\% P_2O_5/\gamma\text{-}Al_2O_3$	272.5	86.2	49.6	12.4	—	—	148.2	
6	$4\% \ P_2O_5/\gamma\text{-}Al_2O_3$	327.6	59.2	93.8	6.1	_	_	159.1	

Table 2. Concentration of acid sites per gram of the catalyst according to NH_3 TPD and indicator adsorption data. Acid strength distribution of the sites, according to adsorption of indicators. H_0 is the Hammett acidity function. Freshly prepared catalysts: nos. 1–3; catalysts after 120 h of operation: nos. 4–6



Fig. 2. Dependence of the selectivity for acetonitrile (solid lines) and the acetic acid conversion (dashed lines) from the reactor temperature over the (1) γ -Al₂O₃, (2) 2% P₂O₅/ γ -Al₂O₃ and (3) 4% P₂O₅/ γ -Al₂O₃ catalysts.

in reaction (2) proceeds on unpromoted γ -Al₂O₃ at $T = 360^{\circ}$ C to give ammonium acetate (Table 3).

An increase in the reactor temperature to 380° C, in accordance with the thermodynamic equilibrium [13], facilitates the conversion of acetamide and reduces the selectivity for ammonium acetate. Increasing the concentration of Brönsted acid sites in the case of the $2\%P_2O_5/\gamma$ -Al₂O₃ catalyst leads to a significant increase in the conversion of CH₃CONH₂ and significantly reduces the rate of the reverse reaction of acetamide hydrolysis to ammonium acetate. For the $4\%P_2O_5/\gamma$ -Al₂O₃ sample, an increase in the concentration of Brönsted acid sites on the catalyst surface makes it possible to achieve 100% conversion of acetamide with the complete inhibition of the hydrolysis reaction to have the 100% selectivity for acetonitrile (Table 3).

The foregoing suggests that the promotion of γ -Al₂O₃ with phosphoric acid leads to a decrease in the

specific surface area and the volume of meso- and macropores of the catalyst; at the same time, the promotion contributes to an increase in the micropore volume. The addition of phosphorus-oxygen compounds to γ -Al₂O₃ can decrease the concentration of strong acid surface sites, at which the irreversible adsorption of acetic acid take place followed by its decomposition and formation of byproducts, mainly CO₂ and acetone (decarboxylation reaction), as well as condensation products, which lower the catalyst activity and shorten the on-stream time. At the same time, the promotion of γ -Al₂O₃ with phosphoric acid lead to an increase in the concentration of medium-strength Brönsted acid sites, which mediate the dehydration reaction of the intermediate acetamide to acetonitrile, thereby significantly enhancing the conversion of acetic acid and the yield of the desired product acetonitrile in the ammonolysis reaction.

Catalyst	T, °C	K, %	Selectivity for acetonitrile, %	Selectivity for ammonium acetate, %	Yield of acetonitrile, %
γ-Al ₂ O ₃	360	92.0	97.4	2.5	89.6
	380	98.0	99.5	0.5	97.6
$2\% P_2O_5/\gamma$ -Al ₂ O ₃	360	98.3	99.5	0.5	97.7
	380	99.4	99.4	0.2	98.8
$4\% P_2O_5/\gamma$ -Al ₂ O ₃	360	99.9	100	—	99.9
	380	100	100	_	100

Table 3. Effect of temperature and amount of the promoter on the acetamide dehydration reaction (reaction mixture, acetamide : ammonia = 1 : 1 molar ratio; acetamide space velocity, $1.05 h^{-1}$)

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