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CHEMICAL KINETICS AND CATALYSIS

Catalytic Conversion of Isopropanol on a Heteropoly Acid-η-Aluminum Oxide System

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Abstract—The results from catalytic conversion of isopropanol on a heteropoly acid– η -aluminum oxide system are discussed. It is established that modification increases its activity and selectivity toward oxygen-containing products. Based on a comparative analysis of reaction products, it is shown that the active sites of unmodified η -aluminum oxide consist only of strong Lewis acid sites (LASes) and strong Lewis basic sites (LBSes), represented predominantly by Brønsted basic sites (BBSes) after modification with a heteropoly acid. The synthesized systems are characterized via X-ray diffraction, scanning electron microscopy, elemental analysis, and IR spectroscopy. The set of obtained results shows that the Keggin structure decomposes as it interacts with the basic oxide to form heteropoly anions. Due to their negative charge, these interact with the electron-accepting Lewis acid sites to form a surface–ligand complex. This then begins to act as a new Brønsted base, due to its uncompensated negative charge.

Keywords: isopropanol, η-aluminum oxide, heteropoly acid, catalysis **DOI:** 10.1134/S0036024420010082

INTRODUCTION

Due to their set of valuable properties, heteropoly acids (HPAs) are used as heterogeneous catalysts of oxidative and acid-catalyzed reactions, and as bifunctional catalysts that have oxidative and acidic properties simultaneously [1-5]. Because of the small specific surface areas $(1-5 \text{ m}^2/\text{g})$ of these catalysts, however, their use in heterogeneous catalysis is often limited. There have been works in which heteropoly acids were deposited onto different supports (SiO₂, Al₂O₃, ZrO₂, TiO₂), allowing compositions of new catalysts to be proposed, particularly for the deep hydrotreatment of straight-run and secondary diesel fractions and heavy vacuum gasoil, the selective hydrotreatment of catalytic cracking gasolines, plant oil, and diesel fractions, the isomerization of nalkanes, and the synthesis of oxygen-containing compounds (OCCs) [6-10].

In connection with the prospects for using heteropoly acids in heterogeneous catalysis, the question naturally arises of immobilizing them on the surfaces of other usually used supports (e.g., η -aluminum oxide) with subsequent study of their catalytic activity. A great many original works and reviews have been devoted to different aspects of the industrial use of aluminum oxide [11–19]. Being thermally stable, easily regenerable, and highly adsorptive, aluminum oxide has found the most extensive application as an adsorbent, a support, and a component of the most widely used catalysts. It is also employed in different oil refining and petrochemical processes (e.g., reforming, hydrotreatment, and hydrocracking). The most widely used modifications are γ -, η -, θ -, and χ -aluminum oxides, since they have developed surfaces and differ in their catalytic properties. Despite the numerous studies of aluminum oxide that have been performed, this question in many cases remains in the focus of attention.

It is therefore of undoubted interest to study specific features of the effect modifying η -aluminum oxide with a heteropoly acid has on its catalytic properties in the process of isopropanol conversion. The selection of the η -Al₂O₃ polymorph as an object of study is due to it having the largest specific surface area [20], which is greatest in the η -Al₂O₃ > γ -Al₂O₃ > $(\chi + \gamma)$ -Al₂O₃ > δ -Al₂O₃ > θ -Al₂O₃ > κ -Al₂O₃ > α -Al₂O₃ series of aluminum oxides and is one of the most important factors in modifying with a heteropoly acid.

EXPERIMENTAL

The HPA on η -Al₂O₃ catalyst with a specific composition was prepared by impregnating aluminum



Fig. 1. (Color online) Effect of process time τ on conversion γ of isopropanol in the presence of η -Al₂O₃ at temperatures of (*1*) 150, (*2*) 200, and (*3*) 250°C. Dashed lines are the corresponding trends at temperatures of (*I*') 150, (*2*) 200, and (*3*') 250°C.

oxide (dried at 200°C for 3 h) with a HPA solution in aqueous ammonia (HPA on η -Al₂O₃). The compounds used in the process were

(1) bayerite (calcined for 3 h at 300°C to form η -Al₂O₃);

(2) aqueous ammonia (GOST 3760-79; ammonia content, no less than 10 wt %; concentration, 90–100 g NH_3/L);

(3) phosphomolybdic heteropolyacid (HPA) $H_7[P(Mo_2O_7)_6] \cdot H_2O$; and

(4) isopropanol (GOST 9805-84).

The catalytic properties of the initial and modified η -Al₂O₃ were studied in a flow reactor in the temperature range of 150–250°C at a feedstock hourly space velocity of 75 h⁻¹.

The feedstock and liquid reaction products were analyzed via chromatography on a CHROM 5 chromatograph equipped with a flame ionization detector and a column packed with polyethylene glycol (17%) on CELITE C-22. Gaseous reaction products were analyzed on a CHROM 5 chromatograph equipped with a thermal conductivity detector. The sorbent was diethylene glycol *n*-butyrate supported on Inza brick INZ-600. The chromatograms of the obtained catalyzate were analyzed quantitatively via absolute calibration and internal normalization.

The infrared spectra were recorded on a Thermo-Scientific Nicolet IS 10 spectrometer in the 400 to 4000 cm^{-1} range of wavenumbers at a resolution of 4.0 cm^{-1} .

X-ray diffraction analysis was performed on a RIGAKU SC-70 diffractometer in the $3^{\circ}-60^{\circ}$ range of angles at an angular scanning rate of 10 deg/min using Cu*K* radiation (40 kV, 15 mA).

The surface morphology and elemental composition of samples were studied via scanning electron microscopy (SEM) on a JEOL JSM-6610 LV microscope that had a lattice resolution of 0.14 nm and a built-in EDS Genesis 4000 EDX analyzer, using a Si(Li) detector at an accelerating voltage of 100 kV. Samples for scanning electron microscopy were fixed on carbon-coated copper grids. The statistical diameter of the particles was measured by analyzing SEM micrographs of each sample.

RESULTS AND DISCUSSION

Catalytic Properties

Isopropanol was chosen as a model feedstock because the mechanisms of its dehydration and dehydrogenation are thoroughly studied, and there are a great volume of accumulated practical data, and the possibility of testing the effect the chemical composition of the modifier had on the course of the reaction [21-24].

The results on the change in the conversion of isopropanol in the presence of η -Al₂O₃ at different process temperatures and times are presented in Fig. 1. As can be seen, η -Al₂O₃ began to display catalytic activity at 150°C: maximum alcohol conversion was 36.2%. Raising the temperature to 200°C led to a 7% increase in alcohol conversion (up to 43.1%). The maximum feedstock conversion of 51.8% was observed at a temperature of 250°C.

As can be seen from the data presented in Fig. 1, a specific feature of the effect the process time and rest breaks had on the parameters of the process was observed at all three experimental temperatures. Every time the process was started, activation of the catalyst took 2 h. After repeated activation, the initial parameters were lower than those observed earlier. These were reached again after 2 h of operation, and the catalyst returned to its steady-state level.

It should be noted that the catalytic activity exhibited by η -Al₂O₃ for long periods changed in different ways, depending on the process temperature. At a temperature of 150°C, the conversion of alcohol fell abruptly after 8 h of operation, but its catalytic activity at higher temperatures remained the same for 14–15 h.

With η -Al₂O₃, the conversion of isopropanol followed two paths (Fig. 2): dehydration to propylene via mechanism *E*1 and to diisopropyl ether via the mechanism of $S_N 2\beta$ substitution (the latter is typical of basic oxides. Their yield is due to the predominance of one path or another of the two competing processes, and thus the nature of the acid sites on the catalyst's surface. The highest yield of diisopropyl ether was observed at a temperature of 250°C in the 3 to 9 h period of η -Al₂O₃ catalyst operation.



Fig. 2. (Color online) Effect of process time on the yield of diisopropyl ether (histograms) and propylene (solid lines) in the presence of η -Al₂O₃ at temperatures of (*I*) 150, (*2*) 200, and (*3*) 250°C.

Dependences illustrating the effect process time has on the conversion of isopropanol in the presence of modified HPA/ η -Al₂O₃ catalysts are shown in Fig. 3. The obtained results indicate that the presence of HPA had an inconclusive effect on the catalyst's activity. The sample with the low HPA content (5%) is characterized by low conversion of alcohol, but the picture is reversed abruptly when the content of HPA in the catalyst is raised to 7–10%. The maximum feedstock conversion is observed with for the sample with 10% HPA and reaches 56%. The abrupt drop in alcohol conversion in the presence of the sample of 13% HPA was likely due to its fast deactivation.



Fig. 3. Effect of process time on the conversion of isopropanol in the presence of HPA/ η -Al₂O₃-catalysts with HPA contents of (1) 5, (2) 7, (3) 10, and (4) 13%. Dashed lines are the corresponding trends at HPA contents of (1') 5, (2') 7, (3') 10, and (4') 13%. The process temperature is 230°C.

Also noteworthy is the stability of catalytic properties during the process, though a period of activation similar to the one mentioned above for the unmodified analogs was also observed here. In addition, the modified samples of 5, 7, 10, and 13% HPA exhibited high selectivity toward oxygen-containing products (Table 1). The selectivity of the sample of 7% HPA is 3.5 times higher than for the unmodified sample. Another characteristic feature of the HPA effect is the presence of acetone in the reaction products. (No acetone was formed in the presence of the initial sample.)

The nature of the formed products indicates that the active sites of unmodified aluminum oxide are exclusively Lewis sites: strong Lewis acid sites and strong Lewis basic sites, which are responsible for the high content of propylene (the *E*1 mechanism; in light of the low process temperatures, the contribution from the formation of propylene from ether can be ignored) and ether (the $S_N 2$ mechanism), respectively. Considering the high ratio of propylene to the overall yield of oxygen-containing compounds, we may assume that strong Lewis sites are in the majority on the η -Al₂O₃ surface, which is in good agreement with the literature data [13, 19, 25].

To make it easier to consider the contribution from Lewis acid sites and basic sites (both Lewis and Brønsted), let us consider the ratio of reaction products that form on them:





Fig. 4. (Color online) X-ray diffraction pattern of (a) initial η -Al₂O₃ and (b) modified η -Al₂O₃ + 7% HPA.

A comparative analysis of the reaction products formed in the presence of the modified samples shows that the introduction of 5% HPA results in an abrupt increase in the yield of acetone (the maximum acetone : ether ratio and one of the highest propylene/OCC ratios). In contrast, the sample of 7% HPA with the highest yield of OCCs has the lowest propylene/OCC ratio. The active sites of the latter are thus predominantly basic; according to the acetone : ether ratio, these sites are Brønsted basic sites. It should be noted that the predominance of acetone over ether is typical of all the modified samples and strongly differs from the unmodified sample. Raising the HPA content to 10 and then to 13% was accompanied by a contribution from Lewis acid sites and a drop in the contribution from basic sites. Despite the apparent inconsistency, similar results are possible if we assume HPA loses its structure after being sorbed on η -Al₂O₃.

Phase Composition

According to the results of X-ray diffraction analysis, the studied samples were poorly crystallized (i.e., predominantly X-ray amorphous) and consisted of η -, χ , and γ -polymorphs (Fig. 4a). This can be explained by the background of the precursor sample (bayerite) and the temperature of its calcination. These data are in good agreement with the results in [8–11], according to which the nature of initial aluminum hydroxide (amorphous aluminum hydroxide, pseudoboehmite, boehmite, bayerite, gibbsite) has a crucial effect on the formation of metastable aluminum oxide polymorphs (γ -, η -, χ -, and θ -Al₂O₃) upon thermal treatment.

It is clearly seen that the X-ray diffraction pattern of unmodified alumina contains three strongly smeared halos in the 2θ regions of $15^{\circ}-30^{\circ}$ and $35^{\circ} 50^{\circ}$, which correspond to the most intense reflections at diffraction angles 2θ of 32.4° and 42.67° and can be

Catalyst	<i>K</i> _{conv} , %	τ, h	S _{OCCs} , %	$lpha_{ m acetone}$, vol %	α_{ether} , vol %	Ratio	
						C ₃ H ₆ /OCCs	$C_{3}H_{6}O/C_{6}H_{14}O$
η -Al ₂ O ₃ (without HPA)	42	8	14.9	—	6.25	5.72	_
η -Al ₂ O ₃ + 5% HPA	44.6	7	46.6	16.3	4.5	1.44	3.62
η -Al ₂ O ₃ + 7% HPA	50.1	11	52.1	17.4	8.7	0.92	2.0
η -Al ₂ O ₃ + 10% HPA	54.3	3	40.1	14.5	7.3	1.49	1.99
η -Al ₂ O ₃ + 13% HPA	59.2	1	28.5	10.2	6.7	2.50	1.52

Table 1. Relationship between catalyst composition, process parameters, and the ratio of reaction products*

* The given alcohol conversions and process times τ correspond to the highest yield of OCCs for a particular sample; $T = 200^{\circ}$ C.

Peak no.	2θ, deg	$d, \mathrm{\AA}$	h, counts/s	<i>l</i> , deg	$I_{\rm integr}$, counts deg	w _{integr} , deg	CSR, Å					
Initial η-Al ₂ O ₃												
1	19.2	4.61	111	6.0 (7)	710 (130)	6 (3)	112.1					
2	32.40	2.76	457.86	2.063	811.10	1.7715	330.8					
3	37.53	2.39	408 (58)	2.06 (17)	1309 (56)	3.2 (6)	126.2					
4	39.311	2.29	409.091	2.063	725.33	1.7730	121.7					
5	42.67	2.12	460.956	2.063	817.70	1.7739	—					
6	45.66	1.99	394 (57)	1.66 (9)	763 (39)	1.9 (4)	74.3					
Modified η -Al ₂ O ₃ + 7% HPA												
1	12.94	6.834	317.927	2.479	1030.71	3.24198						
2	19.80	4.478	382.586	2.479	1240.78	3.24314	94.3					
3	31.83	2.809	364.316	2.479	1182.75	3.24648	330.6					
4	37.55 (8)	2.393 (5)	553 (68)	4.3 (3)	4674 (595)	8 (2)	103.6					
5	39.40	2.284	463.848	2.479	1507.3	3.24955	100.8					
6	42.56 (7)	2.123 (3)	198 (41)	1.0 (3)	376 (115)	1.9 (10)						
7	45.64 (6)	1.986 (3)	562 (68)	2.48 (17)	2651 (270)	4.7 (11)	69.9					
8	48.73	1.867	314.618	2.47952	1023.94	3.25455						
9	58.95	1.565	357.932	2.47952	1167.55	3.26193						

Table 2. Effect of modification on the structural characteristics of the η -Al₂O₃ samples*

* 2θ is the angle characterizing the position of the peak, *d* is the interplanar distance, *h* is height, *l* is the full width at half maximum, *I* is intensity, and *w* is width.

classified as reflections typical of γ - and η -aluminum oxide polymorphs, respectively.

In the X-ray diffraction pattern of the HPA modified sample (Fig. 4b), we can see new peaks at 2θ angles of 12.9° , 48.73° , and 58.96° , which can be attributed to molybdenum hydr(oxide) against the background of the remaining X-ray amorphous phases.

No phosphorus peaks are observed in the X-diffraction pattern, due probably to either its small amount (4.65 wt %) or its penetration into aluminum oxide. The height and integral intensity of the reflections at 19.8°, 37.55°, 39.4°, and 46.64° grow by 2-3.4 times as a result of an increase in the relative η -Al₂O₃ content against the background of a drop in the other aluminum oxide phases (Table 2). The reason for these changes could be the conditions under which the modified sample was prepared, particularly the additional stage of calcination. Also noteworthy is the change in the interplanar distances and the broadening of reflections at 2 θ angles of 19.8°, 37.55°, 39.4°, and 45.6° (the characteristic width grew by 20-110%) in the modified sample. The partial phase transition was thus accompanied by appreciable dispersion of the initial phase, as is confirmed by the reduction of the coherent scattering region (CSR) (Table 2), and possibly the emergence of microstrains in this structure.

Surface Morphology

Electron micrographs of the initial and modified aluminum oxides are shown in Fig. 5. As can be seen, the surface of the unmodified sample appears to consist of closely packed coarse agglomerates (Fig. 5a), but the morphology and size of these formations changed after the introduction of 7% HPA; i.e., they were destroyed and then represented by two types (see the particle size distribution curve). In the overwhelming majority of cases, these were highly dispersed nearly spherical particles, their aggregates that were more than 50 μ m in size (the formation of finely dispersed particles is in good agreement with the results from X-ray diffraction), and a small number of aggregates that were micrometers in size (Figs. 5b-5d), respectively. Their loose packing ensures a larger surface area, which is a necessary condition for the effective use of HPAs in heterogeneous catalysis.

X-ray mapping performed in addition to SEM (Figs. 6a-6d) and semi-quantitative EDX analysis (Fig. 6e) showed that the contents of molybdenum and phosphorus after modifying aluminum oxide with HPA were 4.65 and 0.2 wt %, and they were uniformly distributed over the sample volume.

IR spectroscopic studies were performed ex situ (Fig. 7) for two types of aluminum oxide: unmodified and HPA-modified η -Al₂O₃ samples. Without exception, our aluminum oxide samples had two common features.





Fig. 5. (Color online) SEM micrographs of (a) initial η -Al₂O₃ and (b–e) modified η -Al₂O₃ + 7% HPA, (b) general view, (c, d) structure of individual particles, (e) particle size distribution histogram.

(1) The presence of a low-intensity vibrational mode (a transverse optical phonon) with a maximum at 450 cm⁻¹, testifying to the formation of O–Al bond stretching vibrations typical of crystalline aluminum oxide, according to the literature data [13, 26–29].

(2) IR spectra with a solitary intense peak at 1632 cm^{-1} , which belongs to the molecular water O–H bond bending vibrations $\delta(H_2O)$ and is split. The intensity of the latter is higher for the modified samples.

Subsequent comparative analysis showed that the four studied samples had several differences.

(1) In the initial (prior to catalytic experiments) aluminum oxide (Fig. 7a), the surface OH groups were predominantly bridging OH– located between two aluminum atoms, the coordination numbers of which were 1 and 2, as is indicated by the bands at 3742 cm^{-1} (the groups are linked to two octahedral aluminum ions; the authors of [30] gave a proton affinity of PA = 1410-1440 kJ/mol, which testifies to its characteristic medium acidity) and 3813 cm^{-1} (high-frequency OH groups were linked to tetrahedral aluminum ions; according to the same authors, PA = 1440-1590 kJ/mol, so these hydroxyl groups had the lowest acidity), respectively. These bands completely disap-



Fig. 6. (Color online) (a–d) Element distribution maps and (e) EDX analysis of η -Al₂O₃ + 7% HPA.



Fig. 7. IR spectra of η -Al₂O₃: initial (a) before and (b) after catalysis, modified η -Al₂O₃ + 7% HPA (c) before and (d) after catalysis, and (e) initial modifier (phosphomolybdic heteropoly acid).

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peared for this sample after catalytic experiments, due probably to such surface transformations as the formation and liberation of water molecules and the formation of Lewis acid (Al^{3+}) and basic (O^{2-}) sites (the results for the catalytic conversion of isopropanol on unmodified aluminum oxide agree with this model when Lewis sites predominate). The modified samples had no such bands, showing indirectly that η -Al₂O₃ contains aluminum vacancies randomly distributed between the tetrahedral and octahedral positions.

(2) The spectrum of the unmodified sample after catalytic process (Fig. 7b) was characterized by the emergence of a transmission band at 1533.41 cm⁻¹, which is indicative of surface carbonate groups coordinated to Al^{3+} . It is likely that these groups, being strongly adsorbed during the process, block active sites and are responsible for the rapid drop in the catalytic activity of this sample.

(3) For all four aluminum oxide samples, the region of $3100-3700 \text{ cm}^{-1}$, which corresponds to the absorption of O–H bond stretching vibrations, contained a broad intense absorption band with a maximum at 3416 cm⁻¹ (for the unmodified samples) and bands shifted toward the 3404 and 3385 cm⁻¹ region of lower frequencies (for the modified samples; Figs. 7c and 7d), due probably to the presence of the modifier. Also conspicuous was a drop in intensity for the modified samples, indicative of modifier–support interaction;

(4) The bands at 462.84, 494.65, 550.82, 802.88, 896.42, 965.65, 1060.03, 1124.55, and 1167.45 cm⁻¹, observed when the initial HPA was used as a modifier (Fig. 7e), disappeared after deposition onto aluminum oxide, testifying to the lack of a Keggin structure on the samples' surfaces.

The considered data indicate that the evolution of active sites in the HPA/aluminum oxide system proceeds according to a specific mechanism.

(I) The oxide surfaces contain mainly LASes (coordinatively unsaturated aluminum atoms Al^{3+}) and LBSes (coordinatively unsaturated oxygen atoms O^{2-}); the bridging and terminal hydroxide groups, which do not exhibit catalytic activity but were detected by studying the results from IR studies, indicate a certain number of ABSes that, according to the Knözinger–Ratnasamy model (currently recognized as the one most complete and with the best correspondence to the current level of knowledge about aluminum oxide [28, 29]) have the structure



(II) At the stage of modification with HPA, there is interaction (possibly multipoint dissociative HPA adsorption) between its cations and the hydroxy groups (dehydration) of ABSes, with their conversion into LASes (the bands of the bridging and terminal hydroxide groups disappeared in the IR spectra of the modified samples).

(III) Surface LASes interact with the heteropoly anion to form surface complexes. Since the highest electron density is concentrated in the heteropoly anions on the oxygen atoms of corner M-O-Mgroups, the formation of bonds with LASes proceeds through the oxygen atoms of this group.

(IV) Since η -Al₂O₃ is predominantly characterized by weak LASes, the charge of the heteropoly anion is only partially compensated for, and the surface complex exhibits the properties of BBSes, which are acceptors of hydrogen, as has been observed in catalytic studies.

CONCLUSIONS

Considering the obtained data and the results on the catalytic activity of the HPA/ η -Al₂O₃ system in the conversion of isopropanol, we may assume that the interaction between a Keggin structure and the basic oxide destroys the latter's structure with the formation of heteropoly anions. Being negatively charged, they interact with surface electron-accepting centers (LASes). According to the results in [19, 27, 30, 31], the concentration of weak LASes on a surface of n- Al_2O_3 is several times higher than the content of strong and medium sites (there are almost none of the latter). so the interaction of the heteropoly anions likely occurs with weak acid sites, which cannot completely compensate for its negative charge. As our data indicate, this results in the formation of a negatively charged surface-ligand complex that subsequently acts as a hydrogen acceptor.

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