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Dehydration of Glycerol to Acrolein over Sulfated Iron Oxide Catalysts

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Abstract—The problem of disposal of glycerol, the main waste product in the production of biodiesel, has been explored. It has been shown that cheap catalysts on the basis of iron(III) oxide can be use for mediating the transformation of glycerol to acrolein—an important intermediate product of industrial organic synthesis. The influence of external factors on the process of dehydration of glycerol to acrolein has been examined.

Keywords: disposal of glycerol, acrolein, iron(III) oxide, acid catalysis

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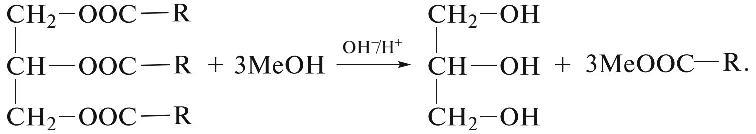
As is known, the main process for production of biodiesel [1] includes transesterification of vegetable oils with methanol over a base or acid catalysts as the key step [2]. The resulting methyl esters of fatty acids represent biodiesel. The byproduct glycerol is formed in significant amounts, namely, about 100 kg of glycerol per ton of biodiesel.



$$\begin{array}{l} CH_2{-}OOC{-}R \\ | \\ CH{-}OOC{-}R \\ | \\ CH_2{-}OOC{-}R \end{array} + 3MeOH \xrightarrow{OH^-/H^+} \begin{array}{l} CH_2{-}OH \\ | \\ CH{-}OH \\ | \\ CH_2{-}OH \end{array} + 3MeOOC{-}R.$$

The main obstacle restraining wide use of biodiesel is the need for the withdrawal of significant areas from the agricultural use and a high cost [3]. Because of this, it is important to use all the products formed in the process of production of biodiesel, in particular, glycerol, fullest possible. However, the amount of glycerol obtained as the waste in the production of biodiesel many times exceeds the demand for it. Accordingly, the development of chemical processes utilizing glycerol as feedstock becomes a relevant task.

One of the most valuable substances synthesized from glycerol, acrolein, is an important intermediate product of modern chemical industry [4]. Acrylic acid and its nitrile and esters required for the production of various plastics and polymer fibers as well as essential amino acid D,L-methionine used as a feed additive and its analogue, 2-hydroxy-4-methylthiobutyric acid (hydroxy analogue of methionine, HAM), are obtained from it.

Many works are devoted to the investigation of the methods of transformation of glycerol to acrolein [5–11]. Various acid catalysts are used for the execution of this reaction. However, good yields of acrolein are generally achieved either under harsh conditions (high pressure and temperature) or using catalysts containing relatively scarce elements (zirconium, tungsten, etc.). At the same time, as has been noted above, not simply the development of the ways for disposal of glycerol, but the search for cheaper methods of its disposal is of the greatest relevance. Therefore, the researchers face the task of maximally reducing the cost of each stage of the glycerol processing scheme, in particular, searching for the cheapest catalysts for this processing.

The conversion of glycerol to acrolein occurs over acid catalysts. One of the cheapest and abundant acid catalyst is iron(III) oxide additionally treated with an acid, e.g., sulfuric acid [12]. In this work, we studied the applicability of several such catalysts to the dehydration reaction of glycerol to acrolein.

EXPERIMENTAL

Synthesis of Iron(III) Oxide

A 16.9-g portion of $FeCl_3 \cdot 6H_2O$ was dissolved in 50 mL of distilled water with constant stirring using a magnetic stirrer. Then a solution of 15.75 g of $NaHCO_3$ in 190 mL of H_2O was added dropwise from a dropping funnel. After this, the precipitate was aged by boiling for 1.5 h and left overnight. The precipitate was rinsed with distilled water six times and centrifuged at 10000 rpm. The obtained sample was dried in an oven for 5 h at 200°C. After this, the catalyst was ground to a powder in a mortar. The fine powder fraction was separated by means of sedimentation in distilled water.

Synthesis of Nickel(II) Oxide

An 18-g portion of $NiCl_2 \cdot 6H_2O$ was dissolved in 50 mL of distilled water with constant stirring using an electrical stirrer. Then a solution of 11 g of NaOH in 25 mL of H_2O was added dropwise using a dropping funnel. The mixture was continuously stirred for 1 h and left overnight. To purify the precipitate from salts, it was rinsed with distilled water five times and centrifuged at 10000 rpm. The obtained sample was dried in an oven for 6 h at 230°C. After this, the catalyst was ground to a powder in a mortar. The fine powder fraction was separated by means of sedimentation in distilled water.

Characterization

The specific surface area of the samples was determined on a Sorbtometr-M instrument via thermal desorption of nitrogen. To calculate the specific surface area, the Brunauer–Emmett–Teller (BET) equation was used.

The crystal structure of the initial support and prepared catalysts was determined via X-ray diffraction analysis (XRD) on a DRON-3M instrument (cobalt K_α radiation, having a wavelength of 0.179021 nm).

The acid properties of the samples were studied via temperature programmed desorption of ammonia (TPD NH_3) on a Unisit USGA-101 sorption analyzer. The sample was calcined in a dried helium flow at 400 or 600°C and then cooled to 60°C. The adsorption of ammonia was performed for 30 min at 60°C; ammonia was diluted with nitrogen in a ratio of 1 : 1. Physisorbed ammonia was removed by flushing with dry helium at 100°C for 1 h. The experiments on TPD NH_3 were performed in the temperature range of 60 to 800°C in a dry helium stream (at a flow rate of 30 mL/min). The heating rate was 8°C/min.

Determination of the total pore volume by the drop method. Distilled water was added dropwise to a finely powdered precipitate using a pipette while shaking the sample and achieving the destruction of the initially formed lumps of the wet support. The addition continued until the lumps of the support stopped to be destroyed by shaking, which gave the evidence of the complete saturation of the pores with water. The pore volume was judged by the added volume of water.

Catalyst Preparation

Samples of the $Fe_2O_3 \cdot H_2SO_4$ catalyst were obtained on the basis of iron oxide supports (S_{sp} = 53 m^2/g and V_{pore} = 0.6 mL/g; S_{sp} = 364 m^2/g and V_{pore} = 0.83 mL/g) (Tables 1 and 2) by mixing a weighed portion of the oxide with the diluted acid. The concentration of the acid was chosen in such a way that the volume of the added acid would correspond to the pore volume of the taken amount of the oxide. After this, the catalyst was dried for 2 h at 160°C, then heated at a rate of 5°C/min to the corresponding temperature, and held at this temperature for the required time.

Another set of $Fe_2O_3 \cdot H_2SO_4$ catalysts was prepared on the basis of the iron oxide support with S_{sp} = 364 m^2/g and V_{pore} = 0.83 mL/g (Table 2).

$NiO \cdot H_2SO_4$ dehydration catalysts were prepared on the basis of a nickel oxide support (S_{sp} = 150 m^2/g and V_{pore} = 0.8 mL/g) (Table 3). The catalyst preparation procedure was the same as in the case of iron oxide supports.

Glycerol Dehydration Procedure

Glycerol was added to a catalyst in a flask; the catalyst : glycerol weight ratio was 1 : 20. Then this mixture was distilled in a Claisen flask, and the distillate was collected. Solid resin was left in the flask after distillation.

Gas Chromatographic Analysis

The analysis was performed on a Kristall-Lyuks gas chromatograph equipped with a flame ionization detector. A capillary column with a length of 20 m and an internal diameter of 0.22 mm was used. The FFAP stationary phase (polyethylene glycol esterified by nitroterephthalic acid) was used. The stationary-phase film thickness was 0.25 μm. The carrier gas was helium. For the first 2 min, the elution was carried out at 30°C, and then the column was heated to 200°C at a rate of 20°/min. The duration of one analysis was 15 min.

The obtained products were analyzed in the form of 10% solutions in ethanol. For quantitative measurements, a model mixture consisting of 80 wt % ethanol, 10 wt % glycerol, and 10 wt % acrolein was injected into the chromatograph with a microsyringe. To determine the characteristics of hydroxyacetone, a 10% solution of hydroxyacetone in ethanol was used. The retention times of glycerol, hydroxyacetone, and acrolein were determined by the obtained chromatograms, as well as the relative sensitivity of the detector to glycerol, hydroxyacetone, and acrolein in comparison with ethanol. The sensitivity of the detector to acrolein, hydroxyacetone, or glycerol was 0.67, 1.5, or 1.6 of the sensitivity to ethanol.

Table 1. Conditions of preparation of the catalysts on the basis of iron oxide with a specific surface area of 53 m^2/g

Sample no.	Number of acid molecules per 1 nm^2 of surface	Calcination temperature, °C	Calcination time, h
1	10	200	6
2	10	400	6
3	10	600	6
4	5	200	2
5	5	200	4
6	5	200	6
7	5	400	2
8	5	400	4
9	5	400	6
10	5	600	2
11	5	600	4
12	5	600	6
13	3	200	6
14	3	400	6
15	3	600	6

Table 2. Conditions of preparation of the catalysts on the basis of iron oxide with a specific surface area of 364 m^2/g

Sample no.	Number of acid molecules per 1 nm^2 of surface	Calcination temperature, °C	Calcination time, h	Catalyst mass, mg
1	3	200	2	120
2	3	600	6	120
3	3	200	2	20
4	3	600	6	20
5	6	200	2	120
6	6	200	2	20

Table 3. Conditions of preparation of the catalysts on the basis of nickel oxide

Sample no.	Number of acid molecules per 1 nm^2 of surface	Calcination temperature, °C	Calcination time, h
1	3.0	400	6
2	3.0	600	6
3	1.5	400	6
4	1.5	600	6

RESULTS AND DISCUSSION

Dehydration over Iron Oxide Catalysts

According to the XRD data, all the studied samples are pure hematite (α-Fe_2O_3), no other phases have been detected in any of the cases.

The influence of the specific surface area of catalysts on the dehydration reaction. To study the character of the influence of the specific surface area of the catalyst on the occurrence of the dehydration reaction, two support samples of with specific surface areas of 53 and 364 m^2/g were prepared.

It has been found that the activity and selectivity of the samples with a high specific surface area is noticeably higher, and the yield of acrolein can reach 21% under otherwise equal conditions. However, it should be noted that the synthesis of the iron oxide samples with such a high value of the specific surface area (364 m^2/g) is distinguished by low reproducibil-

Table 4. The influence of the amount of acid on the results of dehydration of glycerol (iron oxide catalysts, S_{sp} of 53 m^2/g)*

Number of acid molecules per 1 nm^2 of surface	Catalyst calcination temperature, °C	Y_d, %	Y_a, %	Y_h, %
10	200	77.0	2.3	0.3
10	400	51.0	7.8	1.1
10	600	65.0	0.2	0.3
5	200	32.0	6.2	0.3
5	400	38.0	3.2	0
5	600	68.0	2.5	0.3
3	200	17.0	0.2	0.2
3	400	16.0	0.2	0.1
3	600	20.0	0.2	0.1

* Y_d is the yield of the distillate, Y_a is the yield of acrolein, and Y_h is the yield of hydroxyacetone.

Table 5. The influence of the temperature and time of calcination of the iron oxide catalysts on the results of dehydration of glycerol*

Calcination temperature, °C	Calcination time, h	Y_d, %	Y_a, %	Y_h, %
200	2	74.0	2.7	0.4
200	4	54.0	0.2	0.2
200	6	32.0	6.2	0.3
400	2	49.0	8.1	1.4
400	4	54.0	11	2.3
400	6	38.0	3.2	0
600	2	28.0	4.5	1.2
600	4	21.0	7.5	0.1
600	6	680	2.5	0.3

* Y_d is the yield of the distillate, Y_a is the yield of acrolein, and Y_h is the yield of hydroxyacetone.

ity. Because of this, we cannot recommend such supports for the glycerol dehydration reaction until reproducible synthesis methods of them are developed. Further discussion will only concern the samples with a specific surface area of 53 m^2/g, which are characterized by high reproducibility.

The influence of the amount of acid supported on the catalysts on the yield of acrolein. To find out this influence, a series of samples with the number of acid molecules per 1 nm^2 of the surface from three to ten was synthesized. The obtained catalysts were tested in the dehydration reaction; the results are presented in Table 4. The time of calcination of the samples was 6 h.

As is seen from the table, samples with the formal surface concentration of the acid of five molecules per 1 nm^2 possess the best properties in almost all the cases. Samples with a lower concentration of the acid turned out to be almost inactive in all the cases, apparently, due to the too low acidity. Regarding the samples with a higher acidity, the yield of the distillate is also higher in this case, but it mainly contains the acrolein oligomerization products. Because of this, further discussion will only concern the samples with the surface concentration of the acid of five molecules per 1 nm^2 of the support surface.

The influence of the catalyst calcining temperature and time. The results of the dehydration reaction over the catalysts prepared under different conditions are presented in Table 5.

It has been found as a result of the studies that the dependence of the activity and selectivity of the catalyst on the temperature of calcination passes through a maximum, i.e., the yield of both the distillate and acrolein increases. The highest yield is observed at a calcination temperature of 400°C. For this temperature, the dependence of the catalyst activity and selectivity also passes through a maximum. The investigation of the catalysts using the ammonia TPD method shows that the best yields are achieved for the catalysts with a high relative concentration of strong acid sites. The yields over the samples with a high relative concentration of weak acid sites are low. This difference is apparently due to the fact that the dehydration of glyc-

Table 6. The influence of the temperature and time of calcination of the catalysts based on the nickel oxide support (S_{sp} = 150 m^2/g and V_{pore} = 0.8 mL/g) on the results of dehydration of glycerol*

Number of acid molecules per 1 nm^2	Calcination temperature, °C	Calcination time, h	Y_d, %	Y_a, %	Y_h, %
3.0	400	6	30.0	2.7	0.2
3.0	600	6	31.0	6.9	0.6
1.5	400	6	33.0	4.0	0.4
1.5	600	6	50.0	4.9	0.5

* Y_d is the yield of the distillate, Y_a is the yield of acrolein, and Y_h is the yield of hydroxyacetone.

erol requires quite strong acid sites [4]; however, the side reactions (of the polymerization type) may well be accelerated by weak acid sites.

It has also been found that the presence of iron sulfate on the surface of the catalyst is very important as well. This compound was not detected by XRD; however, it can be assumed that the decomposition of this compound is responsible for the peak in the TPD spectra at temperatures of about 600°C. The yields of the desired product (as well as hydroxyacetone) over the catalysts free from iron sulfate are extremely low despite the presence of a sufficient number of strong acid sites in the sample.

To explain this effect, it can be assumed that the active sites of the catalyst are Brønsted sites, and iron sulfate acts as a Lewis acid in this case forming donor—acceptor complexes with the glycerol molecule. Apparently for steric reasons., iron sulfate complexes with the terminal OH groups of glycerol molecules are predominantly formed. This structure facilitates the production of acrolein because its formation results from the protonation of a glycerol molecule by the middle hydroxyl, which remains free in such complexes. Note that glycerol is a stronger Lewis base than acrolein. Because of this the formation of the complexes of glycerol with Lewis acid sites should preclude the adsorption of acrolein on the catalyst surface and, hence, impede the undesirable side reactions with the participation of acrolein. To verify this assumption, samples on the basis of nickel oxide were prepared and studied (see below).

It should also be noted that the yields of hydroxyacetone over our samples are quite low—they are always lower than the yields of acrolein. Probably, this is associated with the instability of hydroxyacetone in an acidic medium; it can condense according to the aldol—crotonic type acting as both the carbonyl and methylene components. Acrolein, however, can only act as the carbonyl component in this reaction; hence, it requires third-party molecules for the condensation by this route.

Thus, the formation of acid sites with the required strength on the surface requires the calcination of the samples, however, not very severe.

Dehydration over Nickel-Containing Catalysts

According to the XRD data, all the studied samples are pure bunsenite (α-NiO), no other phases were detected in any of the cases.

The influence of the acid concentration and calcination temperature on the catalyst activity and selectivity. To study the influence of the concentration of the acid on the dehydration reaction, two series of catalysts with the amount of the acid of 3 and 1.5 molecules on the surface were prepared (Table 6). The catalyst with the amount of the acid on the surface of 3 g/nm^2 turned out to be much more selective for acrolein. It has also been found that increasing the concentration of the acid in the catalyst composition leads to a sharp decrease in the distillate yield. The samples of the distillate obtained in this case were not subjected to chromatographic analysis in view of their small amount.

To reveal the influence of the specified factors on the occurrence of the reaction, two sets of experiments were performed (see Table 6), one set at 400°C and the other at 600°C. It was found in these experiments that the activity and selectivity of the catalyst increases with an increase in the calcination temperature.

It was very important to get an answer to the question about the role of Lewis acid sites on the surface. As has been mentioned above, the presence of iron sulfate on the surface is the prerequisite for the occurrence of the desired reaction over the iron oxide catalysts. This fact can be explained by the assumption that iron sulfate acts as a Lewis acid in this case (see above). To verify this assumption, catalysts on the basis of nickel oxide doped with sulfuric acid were studied using TPD of ammonia. Nickel is a chemical analogue of iron; these elements are very close in their chemical properties. However, nickel is the most stable in the divalent rather than the trivalent state, in contrast to iron. The radius of the Ni^{2+} ion is larger than the radius of the Fe^{3+} ion (0.069 versus 0.064 nm), and the charge is smaller. Hence, nickel(II) sulfate is a noticeably weaker Lewis acid than iron(III) sulfate.

It has been found that the number and strength of acid sites on the nickel oxide catalysts are approximately the same as those of the iron oxide catalysts.

However, the yields of acrolein and hydroxyacetone over these catalysts are noticeably lower than in the case of the iron oxide catalysts. Thus, it can be concluded that the presence of Lewis acid sites on the surface of the catalyst in addition to strong Brønsted acid sites is indeed the prerequisite for the successful occurrence of the reaction. In addition, it has been shown that the yield of acrolein is higher for the sample containing a greater number of strong acid sites (calcination at 600°C), which is in agreement with the results obtained for the iron oxide catalysts.

In summary, sulfated iron(III) oxide exhibits activity in the dehydration reaction of glycerol. The yield of acrolein over the reproducibly obtained samples is about 11 wt %. It can be increased by increasing the specific surface area of the catalyst. However, there is the problem of low reproducibility of the synthesis of iron oxide samples with a high specific surface area. This difficulty is due to the fact that the texture of iron oxide depends on a great number of synthesis parameters the influence of which has been little studied.

It has been found that increasing the concentration of the acid on the surface leads to a growth in the activity of the catalyst in the glycerol dehydration reaction; however, the selectivity for the desired product drops in this case. It has been shown that the presence of strong acid sites (apparently, of the Brønsted type) on the catalyst surface is important for the dehydration of glycerol to acrolein, whereas the presence of weak acid sites leads to a decrease in the selectivity of the catalysts. The formation of strong acid sites on the surface requires the calcination of the catalyst.

The presence of iron sulfate on the surface of iron oxide catalysts leads to an increase in the product yield. In its absence, the selectivity of the catalysts is extremely low despite the presence of strong acid sites.

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