Esterification of Oleic Acid with Glycerol in the Presence of Sulfated Iron Oxide Catalyst

F.S. Guner*, A. Sirkecioglu, S. Yılmaz, A.T. Erciyes, and A. Erdem-Senatalar

Istanbul Technical University, Chemical Engineering Department, 80626 Maslak, Istanbul, Turkey

ABSTRACT: Esterification of oleic acid with glycerol was investigated in view of the reaction kinetics, using "superacidic" sulfated iron oxide catalysts. A series of different sulfate contents were prepared and characterized by a multitude of techniques prior to their use as catalysts. The sulfated iron oxide reaction was carried out with equivalent amounts of reactants in the temperature range of 180–240°C. Effects of the sulfate content and the catalyst amount on reaction kinetics at different temperatures were evaluated.
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KEY WORDS: Esterification, glycerol, kinetics, oleic acid, sulfated iron oxide, superacidity.

The esterification reaction between fatty acids and polyhydric alcohols is an industrially important tool for obtaining desired polyhydric esters. Free acids, obtained by splitting triglycerides, are fractionated with respect to molecular weight or degree of unsaturation and then reesterified with glycerol. Thus, a synthetic oil with improved properties may be produced. Other widely used fatty acid esters are the partial glycerides. These can be produced by direct esterification as well. A considerable amount of work has been done on the esterification of fatty acids with glycerol (1–7). In most of these studies, either with (8–21) or without catalyst (6,8,18,22,23), the conditions necessary to obtain specified partial glycerides in high yield and to reach lower acid values in a reasonable time period were determined. The reaction was also investigated by several researchers with respect to its kinetics. Feuge et al. (8) studied catalyzed and uncatalyzed esterification of glycerol with peanut oil fatty acids at temperatures from 166 to 241°C and found the reaction to be second-order (8). However, stannous chloride- and zinc chloride-catalyzed reactions showed a deviation from second-order kinetics. The kinetics of the esterification of glycerol with soapstock fatty acids (24), lauric acid (25), and palmitic acid (26) were studied. Additionally, Dunlop and Heckles (21) included glycerol in their study on the catalyzed esterification of oleic acid with various glycols (21). Hartman (22) studied the esterification kinetics of some saturated and unsaturated fatty acids with glycerol at 180°C with and without a cosolvent. In fact, the use of

a cosolvent was suggested by several workers to force the formation of partial glycerides in high yield (9,22,27,28). In this connection, a simple laboratory method for the esterification of fatty acids with glycerol in the presence of pyridine was developed previously in this laboratory (29). In that study, the optimal conditions for mono- and diglyceride production in high yields were determined. As an extension of this study, the effect of pyridine on the esterification kinetics was investigated (30).

In the present study, the kinetics of the esterification of oleic acid with glycerol were investigated by using sulfated iron oxide as catalyst. Sulfated metal oxides have been studied in coal liquefaction processes (31–33) and acid-catalyzed reactions (34–36). Due to their unusual properties, the most important one being their so-called "superacidity," sulfate-promoted iron oxides seemed to be worth investigating in the reaction between glycerol and oleic acid. For this purpose, the reaction was carried out at different temperatures in the 180–240°C range with equivalent amounts of reactants, and the kinetics for each case were determined. Additionally, the effects of the catalyst amount and sulfate content on the reaction kinetics were investigated. The obtained results were evaluated in view of the catalytic behavior of sulfated iron oxide at different conditions by considering the nature of the acidic centers present on the catalyst surface.

EXPERIMENTAL PROCEDURES

Materials. Oleic acid was of analytical grade from Merck (Darmstadt, Germany) with an acid value of 200 and an iodine value of 92. Other reagents, including glycerol, ferric alum, and urea, were also of analytical grade from Merck.

Preparation of catalyst. A series of sulfated iron oxide catalysts of different sulfate content were prepared according to the homogeneous precipitation method, detailed previously (32). Appropriate amounts of ferric alum and urea were dissolved in distilled water with stirring at room temperature. The solution was heated to 90°C and kept at this temperature for 2 h. The ammonium hydroxide formed *in situ* during the heating period caused iron oxyhydroxide, FeOOH, to precipitate. The mixture was cooled to room temperature, and the resulting precipitate was separated and washed with distilled water until no sulfate ion was observed in the washings. The

precipitate was dried in an oven at 110°C for 24 h. Dried precipitate was then calcined at 500°C for 3 h to convert the oxyhydroxide into the stable oxides. The sulfated iron oxides thus obtained were stored dry and heated again to 450°C for 1 h prior to their use as catalyst in the reaction.

Characterization of the catalysts. Detailed characterization was carried out on a sulfated iron oxide catalyst with a sulfate content of 5.10% by weight to aid in understanding the amount and nature of the acid sites and to relate these to the sulfate content determined thermogravimetrically. Other catalyst samples were only characterized for their sulfate contents by thermogravimetric analysis (TGA).

Conductometric titration and temperature-programmed desorption of ammonia (NH_3-TPD) were used for the characterization of the acid catalytic centers: 0.1-mL portions of 0.1 N NaOH solution were used in the former method to titrate the catalyst suspension prepared by dispersing the catalyst in double-distilled water. The acid site concentration was calculated from the alkali consumption that corresponded to the turning points of the titration curve.

A Shimadzu (Tokyo, Japan) TGA-50 thermogravimetric analyzer was used for NH_3-TPD analysis. Initially, the sample was activated by heating to 450°C with a heating rate of 10°C/min under a nitrogen flow of 45 mL/min. Activation was carried out at this temperature for one hour. The sample was then cooled, and NH_3 adsorption was carried out at 30°C. For the desorption of physically bound and weakly chemisorbed ammonia, the sample was heated to 170°C and flushed at this temperature for 1 h with a nitrogen flow of 45 mL/min. The temperature was then raised to 400°C at a rate of 10°C/min and kept at this value for 1 h for complete removal of the strongly chemisorbed ammonia. The concentration of strong acid sites was calculated from the weight loss that took place in the temperature range of 170–400°C.

The sulfate content was determined by both TGA and gravimetric methods. In the first method, the sample was heated to 800°C with a heating rate of 20°C/min under a nitrogen flow of 50 mL/min. The sulfate content was determined from the weight loss recorded within the heating period. For the gravimetric determination, sulfated iron oxide was dissolved in HCl solution, and the sulfate was precipitated as $BaSO_4$ with $BaCl_2$ solution. Sulfate percentage was calculated from the weight of $BaSO_4$ precipitate.

The presence and nature of the sulfate groups were also confirmed by infrared (IR) spectroscopy in Mattson 1000 FTIR equipment (Mattson Instruments, Madison, WI) in the wavenumber range of 400–4000 cm^{-1}. For this purpose, the catalyst sample was homogeneously mixed with KBr, which had been dried at 110°C, at a ratio of 1:300, and the mixture was pressed into wafers under a pressure of 10 kg/cm^2.

The specific Brunauer-Emmett-Teller (BET) surface area of the catalyst was determined by nitrogen adsorption at −196°C. A constant-volume adsorption system was used for this purpose. The sample was heated under a vacuum of 10^{-4} mbar to 400°C at a rate of 2°C/min and was activated at this temperature for 1 h prior to the adsorption experiment.

Scanning electron micrographs were taken with a JEOL-JSM-T330 scanning microscope (JEOL Ltd., Tokyo, Japan). Samples were coated with carbon in a JEOL-JEF-4X vacuum evaporator. Finally, a D-MAX 1000, Rigaku (Tokyo, Japan) X-ray diffractometer (XRD) was used to obtain the XRD patterns in the 5–50° 2θ range with CuKα radiation, at 50 kV and 20 mA. A scan rate of 1°/min was used.

Set-up and procedure of esterification reaction. The esterification reaction was carried out in a four-necked flask, equipped with a stirrer, a thermometer, an air condenser, and an inert gas (nitrogen) inlet tube.

In the reaction, glycerol and oleic acid were used in equivalent proportions. Oleic acid was placed into the reaction flask and heated under agitation to the reaction temperature. A given amount of sulfated iron oxide catalyst was initially added to the oleic acid. Glycerol was heated separately to the reaction temperature and then added to the reaction flask. The stirring rate was adjusted to 200 rpm, and nitrogen was passed over the surface of the reaction mixture at a rate of 200 mL/min to provide an inert atmosphere and to remove water. Samples were withdrawn at predetermined time intervals and cooled immediately by immersion into cold water. Acid values of the samples were determined (37). The oleic acid concentration was expressed in terms of weight percentage as determined from the acid value and equivalent weight of the acid. A correction for loss of water was applied to each sample. Each experiment was carried out twice to check for the reproducibility of the results.

RESULTS AND DISCUSSION

The sulfate contents of the four catalyst samples prepared in this study were determined thermogravimetrically to be 2.44, 3.47, 5.10, and 7.62% by weight. The weight loss due to the sulfate groups took place above 500°C with the temperature program employed. The sample with 7.62% sulfate was also analyzed gravimetrically and, from the weight of the $BaSO_4$ precipitate, its sulfate content was determined to be 7.20%. The values obtained by both methods are sufficiently close to each other.

Detailed characterization of the sample with 5.10% sulfate was carried out as explained in the previous section. The amounts of strong and weak acid sites were determined to be 0.484 and 0.668 mmole/g catalyst, respectively, from the conductometric titration. This sample was calculated to contain 0.531 mmole/g catalyst of strong acid sites, assuming that each sulfate group is associated with a strong site. The presence of sites of different strength was also evident in the TPD of ammonia. The concentration of strong acid sites determined by this method, from the amount of ammonia desorbed in the temperature range of 170–400°C, was 0.647 mmole/g catalyst. The fact that this value is slightly higher may be related to the tailing of the lower temperature peak, due to the continuing desorption of ammonia adsorbed on weaker sites, under the temperature program applied. Accurate quantitation of the weak acid sites was not possible by NH_3-TDP be-
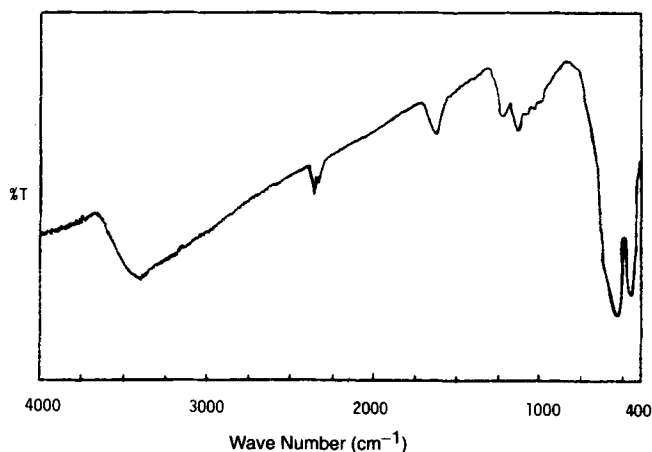
FIG. 1. Infrared spectra of the sulfated iron oxide catalyst.

FIG. 3. Rate of sulfated iron oxide-catalyzed esterification of glycerol with oleic acid at 180°C: ■, 0.3% catalyst with 5.10% sulfate, r^2 (coefficient of determination) = 0.9972; +, 0.3% catalyst with 3.47% sulfate, r^2 = 0.9964; and □, 0.9% catalyst with 3.47% sulfate, r^2 = 0.9991.

cause it was difficult to separate the weakly chemisorbed ammonia from the amount physically adsorbed on the catalyst surface.

The infrared spectrum of the catalyst, shown in Figure 1, contained absorption bands at 1219, 1137, 1080, 1038, 1000, and 920 cm^{-1} wavenumbers, indicating a chelating bidentate complex structure for the sulfate groups with the metal ions, as was also observed previously (36).

The sample was concluded to be highly amorphous from the XRD analysis. The SEM micrographs, given in Figure 2, show aggregates in the size range of 1–6 μm, which consist of much smaller particles, with sizes below about 100 nm. The BET surface area of the sample was determined to be 98 m^2/g catalyst from the nitrogen adsorption isotherm.

For kinetic evaluation, experimental data were correlated by the integral method. A differential rate equation, based on the disappearance of the functional groups, assuming that the reaction is irreversible under the applied conditioning, was constructed for this purpose and solved. A second-order rate equation showed the best fit to the experimental data for all
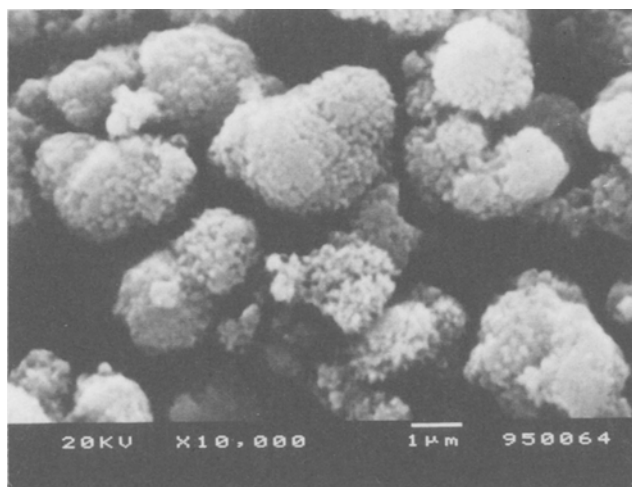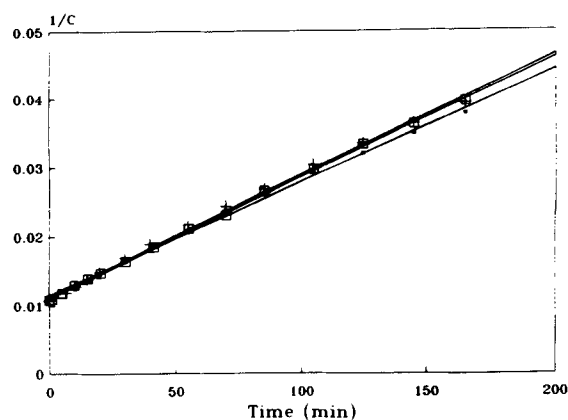
experiments with sulfated iron oxide catalyst. The straight lines fitted to the data for the reactions at 180, 200, 220, and 240°C are shown in Figures 3–6. The rate constants calculated from the slopes of the lines are given in Table 1, together with the corresponding reaction conditions.

Several other catalysts that had been tested for the same reaction previously in our laboratory, such as lead oxide, zinc chloride, cobalt chloride, and tin chloride, all yielded second-order kinetics. Aluminum chloride and potassium hydroxide were not active at 180 and 200°C. At 220°C, where they were active, similar second-order kinetics was apparent for the reaction (38). The data from those experiments are given in Table 2 for comparison, together with the data from uncatalyzed experiments.

The uncatalyzed esterification reaction between glycerol and oleic acid follows third-order kinetics, similar to the esterification reaction between castor oil and oleic acid (38,39). In the case of the latter, we have observed the order of the catalyzed reaction to change with the catalyst used and with the
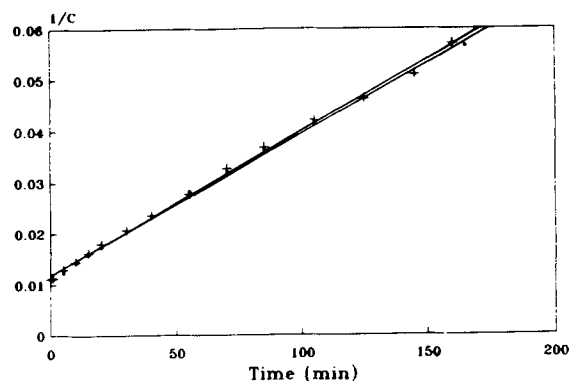

FIG. 2. SEM micrograph for the sulfated iron oxide catalyst.

FIG. 4. Rate of sulfated iron oxide-catalyzed esterification of glycerol with oleic acid at 200°C: ■, 0.3% catalyst with 5.10% sulfate, r^2 (coefficient of determination) = 0.9976; and +, 0.1% catalyst with 2.44% sulfate, r^2 = 0.9975.
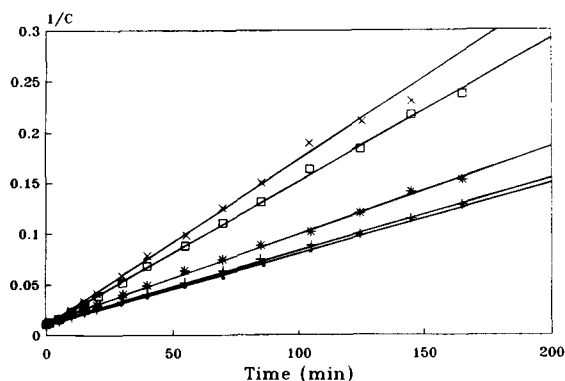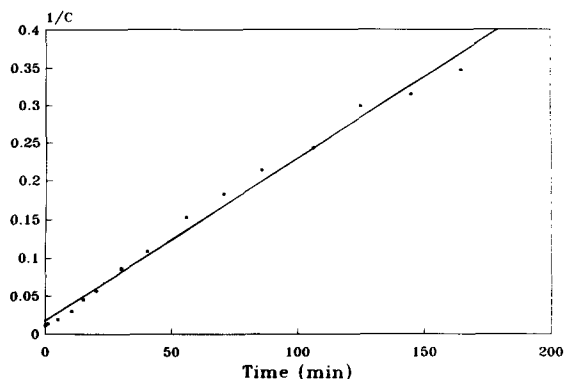
FIG. 5. Rate of sulfated iron oxide-catalyzed esterification of glycerol with oleic acid at 220°C: ■, 0.1% catalyst with 5.10% sulfate, r^2 (coefficient of determination) = 0.9986; +, 0.3% catalyst with 5.10% sulfate, r^2 = 0.9989; *, 0.9% catalyst with 5.10% sulfate, r^2 = 0.9984; □, 0.3% catalyst with 7.62% sulfate, r^2 = 0.9990; and ×, 0.9% catalyst with 7.62% sulfate, r^2 = 0.9960.

TABLE 1
Rate Constant for the Esterification Reaction of Glycerol with Oleic Acid in the Presence of Sulfated Iron Oxide Catalyst

Temperature (°C)	Amount of catalyst (%)	Sulfate content of the catalyst (%)	Reaction order	Rate constant, k, $(wt\%)^{-1}$ $(min)^{-1}$
180	0.3	5.10	2	1.6334×10^{-4}
	0.3	3.47	2	1.7489×10^{-4}
	0.9	3.47	2	1.7516×10^{-4}
200	0.3	5.10	2	2.7556×10^{-4}
	0.1	2.44	2	2.8097×10^{-4}
220	0.1	5.10	2	6.9700×10^{-4}
	0.3	5.10	2	7.1428×10^{-4}
	0.9	5.10	2	8.6466×10^{-4}
	0.3	7.62	2	1.4051×10^{-3}
	0.9	7.62	2	1.6220×10^{-3}
240	0.3	7.62	2	2.1292×10^{-3}

temperature (39). This observation was interpreted by investigating the reaction mechanism, and a kinetic expression was proposed and shown to explain the changes in the apparent order (40). No such change of order was observed for the catalyzed reaction between glycerol and oleic acid under the applied conditions in the present study.

Table 1 shows that the amount of iron oxide catalyst, and its sulfate content did not have an observable effect on the reaction rate at 180 and 200°C. Additionally, only a small increase was observed in the rate constants at 200°C, compared to those at 180°C. On the other hand, at 220°C, the rate constant increased both with the catalyst amount and with the sulfate content. The rate constant at 220°C acquired values considerably greater than those calculated for the reactions at 180 and 200°C.

For interpretation of these results, both the nature of the catalyst and the possible reaction mechanism with the catalyst should be considered together. It is well known that any reaction with a heterogeneous catalyst proceeds over a se-

quence of steps, including diffusion of the reactant(s) to the catalyst surface; adsorption of the reactant(s) on the surface; reaction on the surface; desorption; and diffusion of the product(s) from the surface. Any one or a combination of these steps may be slow and, therefore, rate-limiting.

As mentioned previously, two kinds of acidic centers were observed to be present on the sulfated iron oxide catalyst, and the ammonia desorption temperature from the strong acidic sites was found to be considerably higher than that from the weaker sites. The observed increase in the rate of reaction and its dependence on the concentration of the strong acid sites at higher temperatures can be explained by the expectation that the catalyst should exhibit the same kind of behavior during the reaction and in the step of product desorption from the surface. This implies that, in order to force the strong acidic sites to catalytic activity, reaction temperature should be high enough for rapid desorption from these sites, and hence for their regeneration to take place at a sufficient rate. This condition was fulfilled at 220°C in this study, where the rate was observed to increase with the sulfate content of the catalyst which, in turn, is a measure of the concentration of strong sites.

FIG. 6. Rate of sulfated iron oxide-catalyzed esterification of glycerol with oleic acid at 240°C: 0.3% catalyst with 7.62% sulfate, r^2 (coefficient of determination) = 0.9904.

TABLE 2
Rate Constant and Activation Energies for the Esterification Reaction of Glycerol and Oleic Acid

Catalyst used in the reaction	Rate constant, k^a, $(wt\%)^{-1}$ $(min)^{-1}$			Activation energy, E, kcal/mole
	180°C	200°C	220°C	
Lead oxide	1.45×10^{-4}	2.74×10^{-4}	6.16×10^{-4}	15.95
Zinc chloride	2.03×10^{-4}	5.10×10^{-4}	1.12×10^{-4}	18.84
Cobalt chloride	1.51×10^{-4}	3.42×10^{-4}	7.51×10^{-4}	17.69
Tin chloride	3.77×10^{-4}	8.49×10^{-4}	2.05×10^{-3}	18.7
None	2.06×10^{-6}	6.79×10^{-6}	1.40×10^{-5}	21.32

^{a}The units of the rate constant for the uncatalyzed reactions are $(wt\%)^{-2}$ $(min)^{-1}$.

From the Arrhenius plot of the data at 180, 200, and 220°C, the energy of activation was found to be 16.29 kcal/mol for the reaction with iron oxide catalyst of 5.10% sulfate content. This value was 21.32 kcal/mol for the uncatalyzed reaction, as shown in Table 2. The activation energy of 16.29 kcal/mol may not have a predictive power for the rates of iron oxide-catalyzed reactions at temperatures outside the employed range because of the change that took place in the behavior of the strong sites in the 200–220°C region.

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