Methoxylation of Methyl Oleate in the Presence of Dealuminated Y Faujasites in Their Protonic Form

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ABSTRACT: Methoxylation of methyl oleate into methyl methoxy stearate was carried out in a batch reactor at temperatures ranging from 150 to 190°C in the presence of dealuminated H-Y faujasites as catalysts. In the presence of an excess of methanol, the H-Y faujasite with a Si/Al ratio of 15 was shown to achieve the title reaction with a yield of methyl methoxy stearate that does not exceed 40% because of the parallel formation, at comparable rates, of methyl oleate isomers identified as methyl elaidate, methyl *trans*-vaccenate, and methyl *cis*-vaccenate. Isomerization reactions were confirmed to occur rapidly in an independent manner. FFA are also present in small amounts owing to the *in situ* dehydration of methanol and subsequent hydrolysis of the esters. Finally, starting from pure oleic acid leads to results similar to those obtained with methyl oleate as the starting material.

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KEY WORDS: Lubricants, methyl oleate, methoxylation, zeolites.

Rapeseed and sunflower oils are raw materials that easily can be developed for the lubricant market after chemical transformation. Indeed, vegetable oils are known to be excellent and completely biodegradable lubricants (1,2). However, their poor thermal stability and poor oxidation and corrosion resistance strongly limit their use. One of the main reasons for this instability is the presence of unsaturations on the alkyl chains. Vegetable oils can be modified by taking advantage of the reactivity of this double bond system. Indeed, methyl oleate derived from rapeseed or sunflower oil can be methoxylated into methyl methoxy stearate in the presence of strong acid catalysts (Scheme 1). Three methods have been proposed to obtain satisfactory yields of methoxylated products. The first is the direct addition of methanol to the double bond of methyl oleate using the methoxy mercuration–demercuration method (3,4). The second, more recent, method is the methoxylation of methyl linoleate using a 50 wt% BF_3-MeOH complex and yielding 56% of monomethoxy and 22% of dimethoxy adducts (5). Finally, in a more conventional approach with sulfuric acid as catalyst, methanol was shown to alkoxylate soybean oil, but with a low yield, 21% (6).

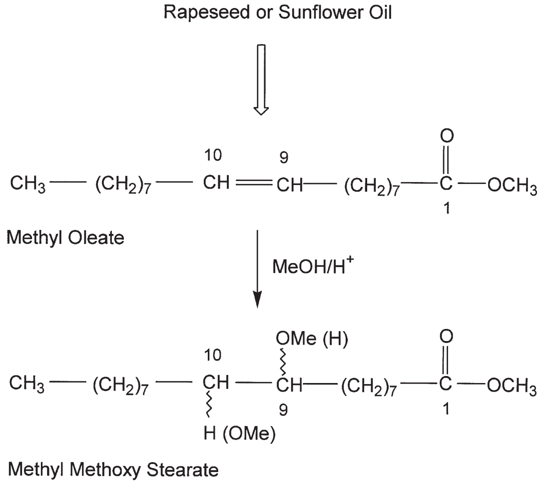
It is well known that zeolites and related materials can contribute to the development of environmentally friendly processes (7–9). Indeed, there is continuing interest in the application of micro- and mesoporous materials as catalysts in the synthesis of bulk and fine chemicals because of their tunable acidic properties, shape selectivity properties, ease of separation from the reaction medium, and recyclability.

The objective of the present work was to add methanol to the double bond of methyl oleate in the presence of a series of dealuminated large-pore zeolites in order to avoid diffusional limitations expected to occur with small or medium pore-size zeolites.

EXPERIMENTAL PROCEDURES

Reactants. Methyl oleate (purity 83%) was kindly provided by Stéarinerie Dubois (Ciron, France). Pure methyl oleate, methyl elaidate, methyl *trans*-vaccenate, methyl *cis*-vaccenate, and methanol, all with a purity >99 %, were from Aldrich (Lyon, France) and used without further purification.

Catalysts. Dealuminated Y faujasites in their protonic form were obtained from Zeolyst International (Valley Forge, PA).



SCHEME 1

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Except where otherwise mentioned, they were calcined at 773 K (1 K min^{-1}) under flowing air (200 mL min^{-1}) for 6 h.

Procedure. Experiments were carried out in a 0.1-L magnetically stirred autoclave (Autoclave Engineers type Magne-Drive), operating in a batch mode and equipped with a system for sampling of liquid during the course of the reaction without stopping the agitation. The procedure was typically as follows: methyl oleate (0.074 mol), freshly activated catalyst (1.2 g), and methanol (variable amount) were poured in the autoclave. After it had been purged with nitrogen, the temperature was increased to 453 K and the agitation speed was 1000 rpm to avoid external diffusion limitations. Zero time was taken to be when the temperature reached 323 K.

Analyses. Samples were periodically withdrawn and analyzed by GC on a Hewlett-Packard 6890 gas chromatograph equipped with an FID and an HP5-capillary column (30 m × 0.32 mm, 0.25-μm film thickness, hydrogen as carrier gas), 423 K for 30 min, 423 to 463 K at 5 K min^{-1}. Reaction products were identified by comparison with authentic samples and GC–MS analysis. Methyl heptadecanoate was used as external standard. FFA were titrated with ethanolic KOH, with phenolphthalein as colored indicator.

Kinetics. The initial reaction rates were deduced from the experimental plots of concentrations vs. time by curve-fitting using the Origin Graph software or from the determination of the slope at the origin. Experimental errors are estimated to ±10 %.

RESULTS AND DISCUSSION

Catalyst screening. Experiments were performed over a series of dealuminated Y faujasites that differ in their acidic properties and that have a suitable hydrophilic/hydrophobic balance to allow adsorption of both methyl oleate and methanol. Figure 1 illustrates the reaction network for methoxylation of methyl oleate at 458 K in the presence of the most acidic H-Y faujasite with a Si/Al ratio of 15 (denoted later as HY15), and for a methanol to methyl oleate molar ratio of 7. From this figure, one may immediately observe that the HY15 catalyst is active up to nearly complete consumption of methyl oleate over a 24-h period. However, the concentration in methoxy methyl stearate reaches a maximum at about 2 h, followed by a continuous decrease, which corresponds to the formation of oleic acid owing to the *in situ* dehydration of methanol and subsequent hydrolysis of the ester.

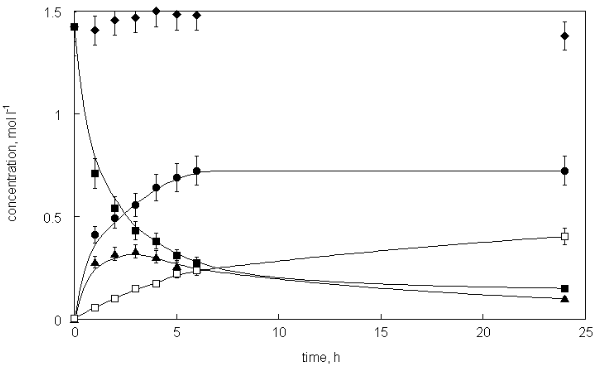

FIG. 1. Catalyst screening for the methoxylation of methyl oleate over HY15 (1.2 g), methyl oleate (0.074 mol), methanol (0.544 mol), 458 K, 1000 rpm, 1.7 MPa; methyl oleate (■), methyl methoxy stearate (●), isomers (▲), mass balance (◆), and FFA (□). Error bars represent an error of ± 10%

In parallel, an important amount of methyl oleate isomers is formed. This is not completely unexpected since the literature already mentioned isomerization of FA and/or fatty esters over zeolites and/or related materials (10–14).

Identification of methoxy methyl stearate. The reaction of methyl oleate with methanol in the presence of Y faujasites was followed by GC–MS analysis. Methyl 9- and 10-methoxy stearates were identified through their mass spectra. According to the literature (5), the fragmentations take place at the α-position, followed by successive loss of methanol as illustrated in Figure 2. Identification of methyl methoxy stearate was also confirmed by ^{1}H and ^{13}C NMR.

Identification of methyl oleate isomers. Isomerization of methyl oleate was performed in the absence of methanol (Fig. 3). Three isomers were identified by comparison of the experimental retention times with those of methyl elaidate and *cis*- and *trans*-methyl vaccenates, which were expected to result from the *cis-trans* isomerization of the double bond on carbon 9 or from the shift of the double bond to the carbon 11 position. As one can see in Figure 3, methyl *cis*-vaccenate is formed more rapidly than methyl elaidate and methyl *trans*-vaccenate. However, methyl elaidate tends to be isomerized into methyl vaccenates as observed for its methyl oleate *cis*-isomer.

To evaluate the influence of the isomerization of methyl oleate on the methoxylation reaction, methoxylation of pure samples of methyl oleate and methyl elaidate was performed under the same experimental conditions. In spite of its *trans* double-bond stereochemistry, methyl elaidate behaves as its *cis* isomer methyl oleate, leading to the formation of methyl methoxy stearate with approximately the same yield (34–38%), and at comparable reaction rates.

Influence of dealumination of Y faujasites. As illustrated in Figure 4, the initial rates of disappearance of methyl oleate and appearance of reaction products over a series of dealuminated Y faujasites pass through a maximum for a Si/Al ratio of 15, which corresponds to a balance between the number and the strength of the acidic sites, as usually observed.

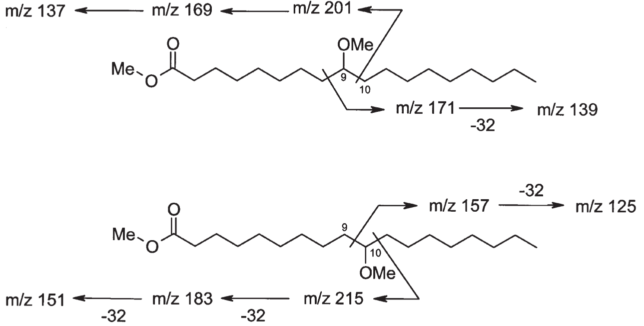

FIG. 2. Principal fragmentations for methyl 9- and 10-methoxy stearates.

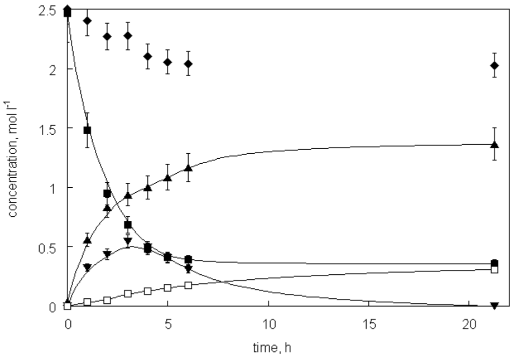

FIG. 3. Isomerization of methyl oleate over HY15 (1.2 g), in the absence of methanol; methyl oleate (0.074 mol), 458 K, 1000 rpm, 1.7 MPa; methyl oleate (■), methyl elaidate (▼), *cis*- (▲) and *trans*- (□ ≤) methyl vaccenates, mass balance (◆). Error bars represent an error of ± 10%.

Influence of the weight of catalyst. As shown in Figure 5 in the plot of the initial reaction rates as a function of the catalyst weight, an apparent kinetic first order is observed. As often observed in heterogeneous catalysis (15), a saturation phenomenon occurs at high coverage of the catalyst, and a nearly zero order is observed. Under the experimental conditions used, yields of methyl methoxy stearate are close to 30% after 3 h of reaction for catalyst amounts exceeding 1.8 g.

Influence of the reaction temperature. Activation energies have been calculated from the plots of the logarithms of the initial rates vs. the reciprocal of temperature (Fig. 6). The values obtained are higher than the limit values generally accepted for external diffusion limitation, i.e. around 40 kJ mol^{-1} (15). The value of the activation energy calculated for the disappearance of methyl oleate is 94 kJ mol^{-1}, and the values for the formation of the isomers of methyl oleate and methyl methoxy stearate are 162 and 85 kJ mol^{-1}, respectively. A point worth noting is that the selectivity in methyl methoxy stearate becomes more important than the formation of the isomers of methyl oleate at low temperature because of the differences in the activation energies of both reactions. However, this is to the detriment of the global activity.

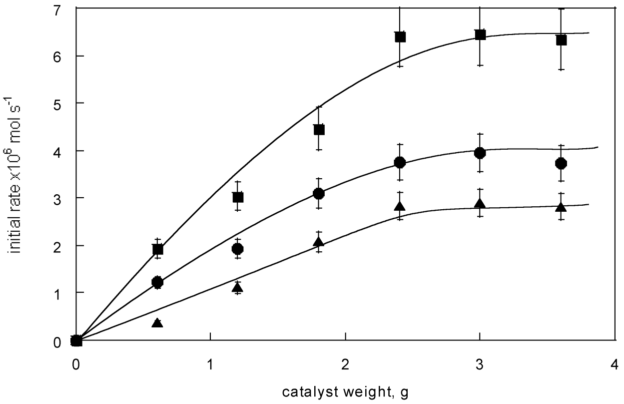

FIG. 5. Effect of catalyst weight on the initial rates of disappearance of methyl oleate and appearance of reaction products; methyl oleate (0.074 mol), methanol (1.088 mol), HY15 (1.2 g), 458 K, 1000 rpm, 2.5 MPa; methyl oleate (■), methyl methoxy stearate (●), isomers (▲). Error bars represent an error of ± 10%.

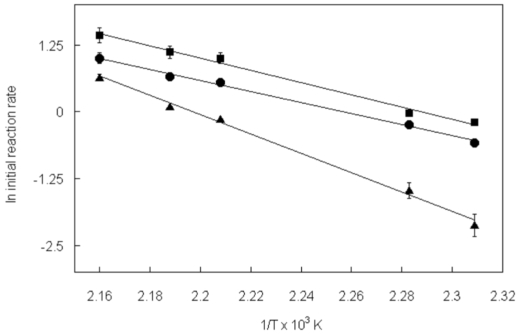

FIG. 6. Effect of temperature on the initial rates of disappearance of methyl oleate and appearance of reaction products; methyl oleate (0.074 mol), methanol (1.088 mol), HY15 (1.2 g), 458 K, 1000 rpm, 2.5 MPa; methyl oleate (■), methyl methoxy stearate (●), isomers (▲). Error bars represent an error of ± 10%.

Influence of the methyl oleate/methanol molar ratio. Initial reaction rates vs. the methyl oleate to methanol molar ratio are given in Figure 7. The total volume of the reaction mixture is kept constant at 75 mL in order to have the same catalyst con-

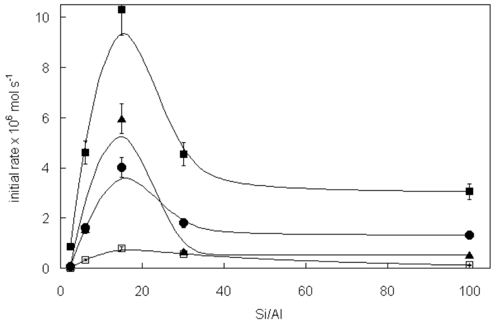

FIG. 4. Effect of dealumination of Y faujasites on the initial rates of disappearance of methyl oleate and appearance of reaction products; methyl oleate (0.074 mol), methanol (0.544 mol), catalyst (1.2 g), 458 K, 1000 rpm, 1.7 MPa; methyl oleate (■), methyl methoxy stearate (●), isomers (▲), FFA (□). Error bars represent an error of ± 10%.

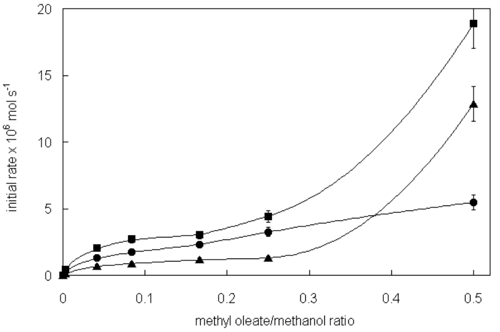

FIG. 7. Effect of methyl oleate/methanol molar ratio on the initial rates of disappearance of methyl oleate and appearance of reaction products; total volume methyl oleate + methanol = 75 mL, HY15 (1.2 g), 458 K, 1000 rpm, 2.5 MPa; methyl oleate (■), methyl methoxy stearate (●), isomers (▲). Error bars represent an error of ± 10%.

centration. As methanol is both reactant and solvent for this reaction, it is not surprising to obtain a nonconventional evolution of initial rates and yields vs. the methyl oleate/methanol molar ratio. The first observation is the spectacular increase of the initial reaction rates at low methanol content, but to the detriment of the yield in methyl methoxy stearate. The relatively linear increase of the yield in methyl methoxy stearate, from 11% for a molar excess in methanol of 2 to 40% for a large excess of methanol, is linked to the increase of methyl oleate concentration in the reaction mixture allowing the methyl oleate to occupy most of the catalytic sites, then leading first to isomerization reactions and then to the degradation of methyl methoxy stearate. In other words, yields are low because methanol is less adsorbed for high methyl oleate concentrations. On the other hand, when methanol is in large excess, the initial reaction rates are lower, but with a significant increase in methyl methoxy stearate yield.

Oleic acid as starting material. For practical reasons it could be interesting to use the oleic acid resulting from the hydrolysis of crude rapeseed or sunflower oil directly. Experiments were then conducted under operating conditions close to those used for the addition of methanol to methyl oleate, i.e., 0.074 mol of oleic acid, 1.088 mol of methanol, 1.2 g of HY15 catalyst; 458 K; 1000 rpm, 2.2 MPa. The concentrations in reactant and products are plotted against reaction time in Figure 8. From this figure, one may immediately see that oleic acid is nearly totally converted into methyl oleate within the first hour. Then, the reaction proceeds as was already observed when methyl oleate is the starting material, i.e., through the parallel formation of methyl oleate isomers, methyl methoxy stearate (30% yield after 6 h), and free oleic acid.

Methoxylation of methyl elaidate and methyl linoleate. In another series of experiments under the following operating conditions, pure fatty ester (2 g), methanol (72 mL), HY15 catalyst (1.2 g), 458 K, 1000 rpm, 2.6 MPa, methoxylation of methyl oleate was compared with methoxylation of its *trans* isomer, methyl elaidate, and methoxylation of methyl linoleate with two unsaturations. As illustrated in Figure 9, methoxylation of methyl oleate initially yields methyl methoxy stearate as the major product. At complete methyl oleate conversion after 22 h, nearly similar amounts of methyl methoxy stearate and methyl oleate isomers are formed. By comparison with the methoxylation of crude methyl oleate (Fig. 1), no formation of FFA is observed. Although methyl oleate and its *trans* isomer, methyl elaidate, are methoxylated at nearly similar initial reaction rates within a ±10% experimental error, methoxylation of methyl elaidate seems to reach an equilibrium after 6 h, with methyl methoxy stearate as the major reaction product, even after 22 h (Fig. 10). Finally, methoxylation of methyl linoleate, with two unsaturations, was carried out under similar experimental conditions as above. As illustrated in Figure 11, the initial rate of methoxylation is similar to that of both methyl oleate and methyl elaidate. However, it was not really expected that the formation of a dimethoxylated adduct would be more rapid than the formation of a mono-methoxylated adduct with a nearly quantitative mass balance up to a reaction time of 6 to 8 h.

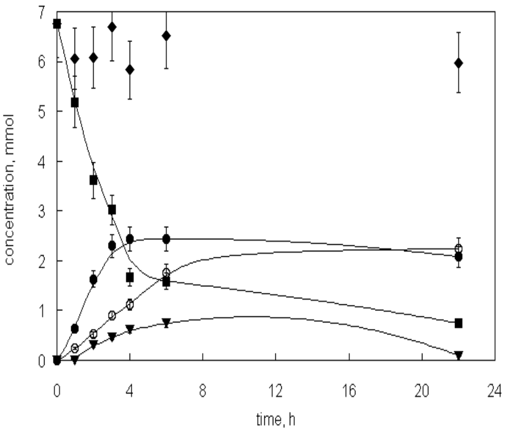

FIG. 9. Reaction of methyl oleate with methanol; methyl oleate (2 g), methanol (72 mL), HY15 (1.2 g), 458 K, 1000 rpm, 2.6 MPa; methyl oleate (■), methyl methoxy stearate (●), methyl elaidate (▼), other isomers (○), mass balance (◆). Error bars represent an error of ± 10%.

Thus, the acid-catalyzed methoxylation of methyl oleate into methyl methoxy stearate is easily achieved in the presence

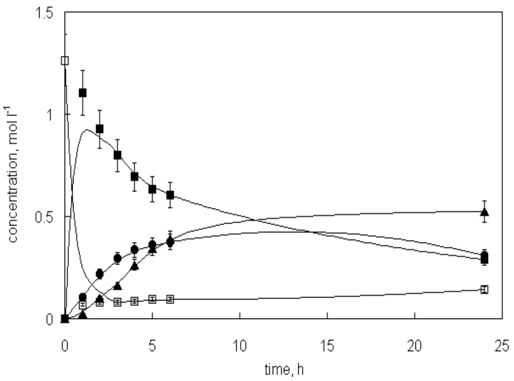

FIG. 8. Reaction of oleic acid with methanol; oleic acid (0.074 mol), methanol (1.088 mol), HY15 (1.2 g), 458 K, 1000 rpm, 2.2 MPa; methyl oleate (■), methyl methoxy stearate (●), isomers (▲), FFA (□). Error bars represent an error of ± 10%.

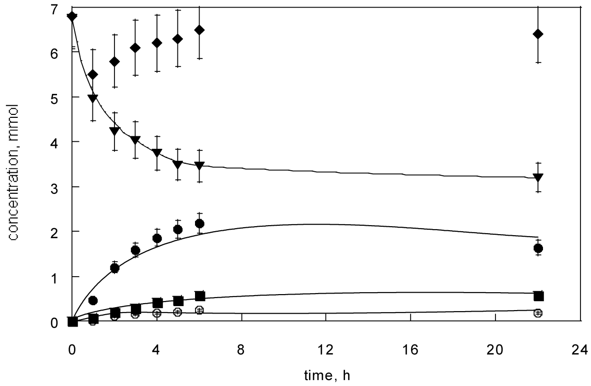

FIG. 10. Reaction of methyl elaidate with methanol; methyl elaidate (2 g), methanol (72 mL), HY15 (1.2 g), 458 K, 1000 rpm, 2.6 MPa; methyl elaidate (▼), methyl methoxy stearate (●), methyl oleate (■), other isomers (○), mass balance (◆). Error bars represent an error of ± 10%.

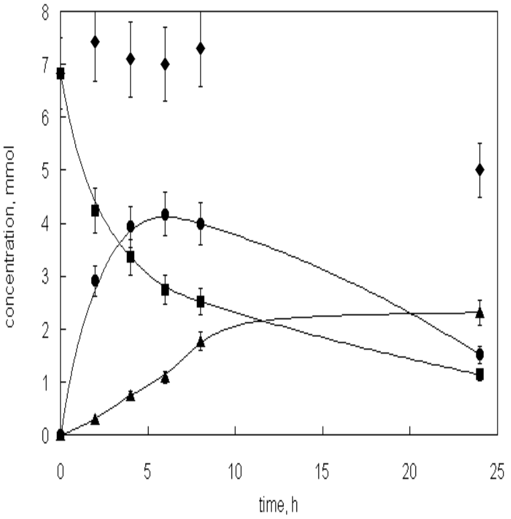

FIG. 11. Reaction of methyl linoleate with methanol; methyl linoleate (2 g), methanol (72 mL), HY15 (1.2 g), 458 K, 1000 rpm, 2.6 MPa; methyl linoleate (■), monomethoxylated adduct (▲), dimethoxylated adduct (●), mass balance (◆). Error bars represent an error of ± 10%.

of dealuminated Y faujasites in their protonic form as catalysts. Under optimized operating conditions of catalyst, temperature, and methanol to methyl oleate molar ratio, the yield in methyl methoxy stearate does not exceed 40% due to the parallel acid-catalyzed formation, at comparable rates, of methyl oleate isomers. Starting from pure oleic acid leads to results similar to those obtained with methyl oleate as the starting material.

ACKNOWLEDGMENTS

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