



Flash pyrolysis of model compounds adsorbed on catalyst surface: A method for screening catalysts for cracking of fatty molecules



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ABSTRACT

The aim of this study is to compare the flash pyrolysis of model fatty compounds, that were either pure or adsorbed on different solid catalysts and to use this information for the selection of catalytic materials for renewable fuel production. Myristic acid adsorbed on ZSM-5-type catalysts, methyl oleate adsorbed on γ -alumina, and oleic acid adsorbed on SAPO5-type solids were processed by flash pyrolysis at 650 °C under a helium flow. The main products formed during the decomposition reaction were analyzed on line by gas chromatography/mass spectrometry (GC-MS). In every case, the presence and the nature of the catalysts induced modifications in the type, amount and distribution of the products. Flash pyrolysis of triglycerides and related compounds adsorbed on catalysts may be used as a screening test reaction for the following purposes: (i) to characterize properties of catalysts, and (ii) to confirm the presence of even minute amounts of products, especially primary reaction intermediates.

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1. Introduction

The pyrolysis of fatty compounds has been shown to be useful in the formation of potential fuels and chemicals, and a review on this subject has recently been published [1]. The main conclusions of the recent review are that pyrolysis is able to form highly deoxygenated molecules, such as alkanes, alkenes and aromatics that can be added directly to petroleum fuels.

The pyrolysis of fatty compounds can be slow and fast, with fast pyrolysis leading to lighter compounds. Pyrolysis can also be conducted either with or without a catalyst, and at temperatures ranging from 300 to 800 °C. A higher amount of light products, including gases and compounds with a high degree of deoxygenation, generally results from pyrolysis at higher temperatures or in the presence of catalysts [2–4].

The nature of the fatty compounds also has a significant influence on the composition of the products. Thermal pyrolysis of crude triglycerides and fatty residues at 400–500 °C leads to rather complex liquid products and only moderate yields of deoxygenated compounds [5,6]. Generally, distillation separates those

compounds in fractions compatible with either the gasoline or diesel fraction [2,4–7]. Catalytic pyrolysis also produces a complex liquid mixture, with the surface properties of the catalyst affecting the mixture composition. Acidic catalysts with strong Bronsted sites favor the formation of aromatics and polyaromatics [8], whereas catalysts with moderate or no acidity are able to direct pyrolysis toward the formation of linear saturated and unsaturated hydrocarbons [8,9]. The use of metallic catalysts, such as palladium supported on activated carbon, was shown to produce high amounts of n-C17 alkanes during the thermal decomposition of stearic acid in the presence of n-dodecane at 300 °C under a helium atmosphere [10]. Finally, basic catalysts have also been tested for pyrolysis. These catalysts are generally less efficient for deoxygenation and ketones, and aldehydes are formed. Linear hydrocarbons similar to those obtained when using poorly acidic catalysts are also produced [9,11].

Cracking of fatty model molecules has provided more knowledge of the decomposition mechanisms of triglycerides. Lappi and Alen [3] have decomposed fatty acid sodium salts at temperatures between 450 and 750 °C. Important differences in the product distribution were observed when varying the pyrolysis conditions and the degree of saturation of the fatty acid moiety. Linear saturated and unsaturated hydrocarbons were favored when sodium stearate was pyrolyzed. Lappi and Alen [3] presented strong evidence of decarboxylation and decarbonylation

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followed by dehydration to explain their results. Maher et al. [12] studied the pyrolysis of stearic acid and proposed a mechanism consistent with the deoxygenation reactions cited by Lappi and Alen. Benson et al. [13] built a special set-up where micro amounts of pure fatty acids were injected on a catalyst bed that was connected to on-line gas chromatography with flame ionization detector (GC-FID) and gas chromatography/mass spectrometry (GC-MS) analytical systems. A general mechanism of transformation was proposed. That investigation also showed that the nature of the catalyst has a strong influence on the product distribution. In the great majority of works using catalysts in the decomposition of fatty compounds, the reaction conditions also enabled purely thermal decomposition as well as conversion of the primary products formed.

In the present work, flash pyrolysis of very small amounts of fatty compounds adsorbed on different catalysts has been used as a “pseudo-catalytic test reaction”. This method favors catalytic decomposition over pure thermal decomposition that allows the observation of important differences between catalysts and reacting molecules. The on-line analysis also seems useful for observing primary intermediate compounds during the decomposition of fatty molecules and thus possible reaction steps can be identified.

2. Experimental

2.1. Materials

Fatty acids such as myristic (MA) (Merck) and oleic (OA) (Nuclear) acids, and methyl oleate (MO) (Sigma–Aldrich) were used as model fatty reagents.

2.2. Preparation of the catalysts

- ZSM-5 zeolite: the H form was prepared from $\text{NH}_4\text{ZSM-5}$ (Zeolyst) by thermal treatment at 550°C , under air for 3 h. The Na form was obtained after 3 successive exchanges with an aqueous solution of NaNO_3 (VETEC). At the end of each exchange, the solid phase was separated by filtration and dried at 120°C before being submitted to an additional exchange process. The final exchanged solid was heated at 550°C under air for 3 h.
- γ -Alumina (support of HDT catalysts in extruded form, $S_{\text{BET}} = 210 \text{ m}^2 \text{ g}^{-1}$): the alumina was first manually ground and impregnated with distilled water before drying at 120°C , followed by a heat treatment at 600°C . The impregnation with water was performed to have a true reference support when working with alumina-supported active phases prepared by impregnation via aqueous solutions of precursor salts.
- SAPO-5: SAPO-5 was prepared with the molar composition $0.35\text{SiO}_2 : \text{P}_2\text{O}_5 : \text{Al}_2\text{O}_3 : 1.4(\text{C}_2\text{H}_5)_3\text{N} : 0.072\text{CTMABr} : 4.40\text{hexanol} : 40\text{H}_2\text{O}$, in a two-phase medium, following the previously described methodology [14,15]. The final solid was dried at 110°C and heat treated at 450°C for one hour (heating rate of $10^\circ\text{C min}^{-1}$) under a nitrogen flow of 100 mL min^{-1} . Then, nitrogen was changed for synthetic air and the solid was heated at 550°C (heating rate of $10^\circ\text{C min}^{-1}$) for 5 h.
- NiMo/SAPO-5: This material was prepared by wet impregnation of the SAPO-5 powder with a solution of ammonium heptamolybdate in 21 vol% of H_2O_2 at pH 2 to obtain 5 wt% MoO_3 . The solid was dried at 120°C and calcined in an air flow at 450°C (5°C min^{-1}) for 1 h. The Ni was impregnated using nickel nitrate to obtain 3 wt% NiO. Calcination was carried out using the same conditions as for Mo/SAPO-5.

2.3. Addition of fatty compounds onto the catalysts

Fatty compounds were adsorbed on the powdered form of the solid catalysts. Before adsorption, the catalyst was heat treated at 150 – 200°C to remove most of the adsorbed water. The liquid fatty compounds (oleic acid and methyl oleate) were added to the catalyst by adding micro amounts of organic material, up to 0.1 g per gram of catalyst, under constant manual mixing. Myristic acid, in solid form, was introduced by mechanical co-grinding and followed by a heat treatment at a temperature slightly higher than the fusion temperature, with manual mixing. In the majority of the cases, the preceding process introduced about 10 wt% of organic compound on the solid material, which always maintained its initial powder form. The final materials can be considered as catalysts “impregnated” with fatty organic molecules.

2.4. Characterization of the adsorbed species

To verify the amount of adsorbed organic material on the catalysts and observe its release from the catalysts, thermogravimetric analysis (TG and DTG) were performed for some of the “impregnated” catalysts, using Perkin Elmer STA 6000 equipment, under 20 mL min^{-1} of nitrogen flow. In this case, the system composed by 0.002 g organic fraction “impregnated” in 0.02 g of catalyst was heat treated from room temperature up to 650°C , at a heating rate of $10^\circ\text{C min}^{-1}$. For a comparison experiment, 0.002 g of pure organic compound was also submitted to the TG/DTG experiment, under the same conditions.

2.5. Pyrolysis experiments

Flash pyrolysis was carried out under helium flow in a Pyroprobe 5200 (CDS Analytical) micro-pyrolyzer at 650°C and a estimated heating rate of $1000^\circ\text{C min}^{-1}$ coupled to a Shimadzu QP 2010 Plus GC-MS (Py-GC/MS). The sample was maintained at 650°C for 0.25 min. The GC injector operated in split mode (1:150). A DB-5MS column ($30 \text{ m} \times 0.25 \text{ mm} \times 0.25 \mu\text{m}$) was used for separation of the products. The helium flow rate through the column was 1.0 mL min^{-1} . The temperature of the column oven was ramped from 45 to 240°C at a rate of 4°C min^{-1} and the injector temperature was maintained at 250°C . The GC-MS interface temperature was 290°C , the ion source temperature was 250°C and m/z was analyzed in the range of 45–400. Approximately 0.1 mg of fatty compound/catalyst was used. The helium flow rate through the sample was 150 mL min^{-1} . The peaks from GC-MS were identified by comparison of their mass spectrometry fragmentation patterns with data from the NIST library. Identification of the majority of products was based on a probability match equal or higher than 90%. The identification of products was also supported by literature data [1–3,5].

3. Results and discussion

3.1. Pyrolysis of myristic acid adsorbed on ZSM-5 type material

Fig. 1 shows thermogravimetric curves obtained when heating pure myristic acid (MA) and MA adsorbed on NaZSM-5 (MA/NaZSM-5) and HZSM-5 (MA/HZSM-5) catalysts. For pure myristic acid, a single weight loss with a maximum rate at 230°C was observed. Under flash pyrolysis conditions, the experiment with pure myristic acid did not allow the detection of significant amount of low molecular weight products due to myristic acid decomposition. Only untransformed myristic acid was observed by GC-MS (Fig. 2). This suggests that pure myristic acid in the TG experiment leaves the sample holder without an important chemical transformation. The TG/DTG thermogram of myristic acid

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