



# Fatty acid methyl esters into nitriles: Acid–base properties for enhanced catalysts<sup>☆</sup>



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## ABSTRACT

Fatty nitriles have lately become of interest in the frame of biofuels or for the valorization of the oil part of biomass as fine chemicals such as polymers. The production of long-chain fatty nitriles by direct reaction of esters with ammonia has however not been academically extensively studied, although several catalysts were developed and published in patents. Acid–base features are implicitly considered as leading the catalysis of this reaction, but no direct correlation was investigated with any nature or number of acidic or basic sites. The present study aims at understanding which sites are responsible of this reaction and thus how to design better catalysts. Strong acidity correlates at 300 °C for ester conversion and nitrile yield, suggesting a common nature of the reaction among all kinds of catalysts. An upper strength limit, over which undesirable side-products appear, was evaluated, and the factors influencing the production of N-methyl amide were analyzed.

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## 1. Introduction

Nitriles are platform molecules that are useful in medicine as well as in polymer chemistry. Besides, in the frame of renewable energy resources, the valorization of non-edible biomass into biofuels and fine chemicals has become a major field of research, and the conversion of the oil part of biomass, that is, triglycerides, into fatty esters and nitriles has been envisaged for biofuel production [1,2]. Nitriles have a high energy density which makes them attractive to be investigated as aviation fuels, even though the possibility of NO<sub>x</sub> exhaust has to be cared about. Their use as fine chemicals however brings the necessity of controlling the chain's nature, especially regarding the unsaturations. Indeed, the nature of commonly used catalysts and also, and perhaps mainly, the high working temperature of the nitrilation processes are the source of isomerization and several side-reactions, such as Piria, Diels–Alder, or peroxidation in  $\alpha$  position of the unsaturations (Fig. 1). Thus, in order to produce higher added value nitriles with control over the fatty chain, we can aim at reducing the operating temperature or the contact time with the catalyst, which can be achieved in a gas-phase reactor.

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The nitrilation of fatty acids or esters by direct reaction with ammonia is mainly performed via two processes: first the batch one, where the acid reactant is in liquid phase and the nitrile remains in the reactor; second the gas-phase continuous one, where the acid is vaporized prior to a catalytic bed, through which it is passing together with ammonia. While the gas-phase process (few seconds contact time) consumes energy for the vaporization of the reactant and then could lead to modification of the carbon chain in the evaporation chamber before the catalytic bed, the batch liquid-phase process needs few hours of reaction at high temperature, where side-reactions are likely to happen, especially with unsaturated chains. Thus, the gas-phase process is usually more adapted to short carbon chains ( $C \leq 12$ ) and to unsaturated carbon chains, since the contact time with the catalyst is short, whereas the liquid-phase process is more adapted to long carbon chains ( $C \geq 12$ ) and especially saturated chains. A previous study focused on the liquid-phase batch process [3], and the scope of the present study is the transformation of shorter chain fatty esters (C12:0) in a gas-phase continuous process in the attempt of decreasing the working temperature lower than the state-of-the-art. Investigations on mono-unsaturated material are under progress and will not be addressed in the present article.

Catalyzed direct reaction of acids with ammonia in gas phase for the production of nitrile was first reported in 1916 by Van Epps and Reid [4], using alumina and thoria and operating at 500 °C for a 85% yield in acetonitrile, while no reaction was occurring when starting from the ethyl ester. However, in 1918, Mailhe [5] performed the conversion of ethyl acetate into acetonitrile with the

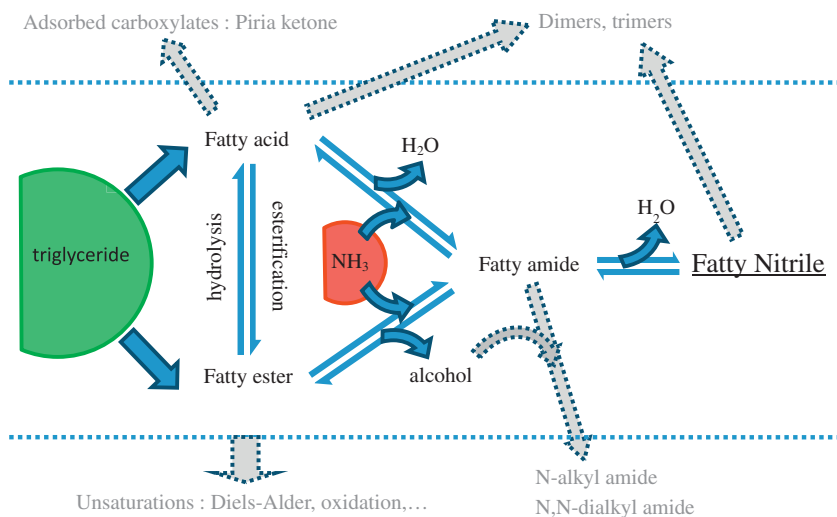


Fig. 1. Reaction scheme of the conversion of fatty esters into nitriles by direct reaction with ammonia, with the possible side-reaction.

same catalysts and same temperature. Then in 1931, Mitchell and Reid [6] performed a more extensive study with silica gel at 400–575 °C (optimum at 500 °C) on a large variety of acids and esters. The catalyst was stable for reactions with acids, whereas with esters it was rapidly fouled, probably due to the formation of aldehyde from the produced alcohol. Besides, such as described by Ralston et al. in 1935–1936 [7], some “cracking” is occurring above 400 °C on the long-chain acids and esters. Ralston et al. present high-temperature pyrolysis on alumina bed at 400–600 °C as a way of producing shorter nitriles and hydrocarbons out of long-chain compounds, preventing the formation of heavy side-products such as polymers or resins; however, further stages of separation and purification are then needed. Afterward, most advances are recorded in the patent literature, such as Wortz in 1940 [8], reporting the preparation of long-chain ( $C \geq 8$ ) aliphatic nitriles from acids of the same chain length and at 425–450 °C, in contradiction with Ralston’s earlier statements. Several metal oxide dehydrating catalysts are presented and the ratio of ammonia to acid is of 2.5. Above 450 °C, cracking is reported, while below 425 °C, severe decrease in conversion is observed. Then in 1992, Akikubo and Takaoka [9] reported the conversion at lower temperature, that is, “200–400 °C,” of fatty acids or esters of carbon chain length from 6 to 22. Conversion of methyl laurate at 1–3 g/h, performed at 300 °C on several catalysts (mean residence time of 4–13 s), is given as an example, displaying good results for oxides of Zr, Ta, Ga, In, Sc, Nb, Hf, Fe, Zn and Sn, and bad results with oxides of Si, Mn, V and W; no results were disclosed at significantly lower temperature. However, high acid strength is pointed out as a source of side-reactions, and oxides of zirconium or potassium, as well as alkali impregnated alumina, appeared to display less of these drawbacks. The main problem with starting from an ester is the handling of the produced alcohol, not only because it may foul the catalyst, but also because it induces side-products. Takaoka et al. reported in 1998 [10] a series of zirconia-based catalysts in order to reduce the amount of such side-products, especially N-methyl-amide. Multivalent metal cations (Al, Sb, Zn, Ce, V, Nb, Ta, Cr, Mn, Fe, Co, Ni, and lanthanides) showing no strong acidity were impregnated at around 0.4 wt% on zirconia, performing a 96% conversion of methyl laurate at 1 g/h at 300 °C, displaying low amounts of N-methyl-amide in the heavy fraction and of methylamine in the lighter fraction (water, methanol, ammonia). Lately, solutions to overcome the question of methylated side-products follow the pathway of ammoxidation of alcohols, recently performed at “240–290 °C” using both dehydrating and dehydrogenating catalysts mixed in a catalytic bed [11], and lauryl alcohol

conversion is presented to reach 98% at 300 °C, with a 94% yield of laurionitrile for about 4 g/h of reactant. Recent academic literature is quite scarcer concerning these issues; however, Bizhanov et al. [12] reported in 1985 a kinetic study of the nitrilation at 300 °C of mixtures of aliphatic acids of 10–22 carbon chain length. By using alumina catalyst, they obtained almost full conversion at 40 min contact time and observed zero order kinetics for the formation of amide and nitrile with  $123.3 \text{ mmol s}^{-1}$  and  $97.7 \text{ mmol s}^{-1}$ , respectively. Although the choice of esters as starting reactants can be the source of fouling or pollution of the product, their comparatively higher vapor pressure is of high interest (about twice larger at 250 °C). Furthermore, some biomass sources are more easily transformed into esters than into acids; thus, the overall conversion of triglycerides into fatty nitriles can become more interesting via esters.

## 2. Experimental

Commercial zinc oxide (Sigma–Aldrich),  $\gamma$ -alumina (DEGUSSA), niobium oxide (STARCK), zirconia (Norpro St-Gobain), zeolite H-MFI Si/Al 28 (Sud Chemie AG), faujasite HY with a 5.1:1 mol ratio of  $\text{SiO}_2/\text{Al}_2\text{O}_3$  (Alfa Aesar), tungsten oxide (Fluka), bentonite (KSF/O Sud Chemie), titanium dioxide (Degussa P25), phosphotungstic acid on  $\text{TiO}_2$ , phosphated zirconia (Norpro St-Gobain),  $\text{H}_3\text{PO}_4/\text{SiO}_2$  (Johnson Matthey), silica–alumina Siralox 30 and Siralox 40–450 (SASOL), hydrotalcites (Mg/Al = 3 [13] and Norpro St-Gobain), hydroxyapatites (Fluidinova 1.66 reference nanoXIM.HAp402 [14] and Ca/P = 1.66 calcined at 400 °C following Lamonier et al. procedure [15]), magnesium oxide (MERCK),  $\text{Cs}_{3.0}\text{PW}_{12}\text{O}_{40}$  (from Lefebvre et al. [16]) and  $\text{Cs}_{2.5}\text{H}_{1.5}\text{SiW}_{12}\text{O}_{40}$  (Nippon-Kokan Kabushiki Kaisha), boron oxide (STREM), iron (III) oxide hydrated (Aldrich), aluminum fluoride 55% (from Brunet et al. [17]) were used. Zinc–indium mixed oxides and  $\gamma$ -alumina were prepared and characterized in a previous article [18]. Tungstated zirconia “16% $\text{WO}_x/\text{ZrO}_2$ ” was prepared by calcination of commercial tungstated zirconium hydroxide (MEL Chemicals) and “24% $\text{WO}_x/\text{ZrO}_2$ ” as well as every  $\text{M}/\text{ZrO}_2$  ( $\text{M} = \text{Al, Fe, Co, Zn}$ , each at 0.4 wt%) was prepared by incipient wetness impregnation [19]. Boron-containing alumina’s preparation was performed by Dubois and Fujieda [20].

Lauric acid methyl ester (98%, Sigma–Aldrich) was used as reactant in this study. Reference material for GC–FID and GC–MS was dodecanenitrile (99%, Sigma–Aldrich), dodecanamide (>98%, TCI), and dodecanoic acid (98%, Alfa Aesar).

The specific surface area (BET: Brunauer–Emmet–Teller) was determined by nitrogen adsorption at 77 K on an ASAP 2020

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