



# Selective Synthesis of Fatty Alcohols over Mild Reaction Conditions via Non-Catalytic Liquid-Phase Fatty Acid Methyl Esters' Reduction <sup>†</sup>

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**Abstract:** The upgrading of fatty alcohols synthesis from natural fatty acid methyl esters' reduction using alumina-supported NaBH<sub>4</sub> without H<sub>2</sub> supply was investigated. It was possible to synthesize fatty alcohols efficiently with high yields. By using pure NaBH<sub>4</sub> or alumina-supported NaBH<sub>4</sub> and methanol as co-reactants, 100% selectivity towards fatty alcohols was achieved. The purpose of supporting the metal hydride is to increase its stability and ensure the recovery of the product at the end of the reaction. A high final fatty alcohol yield was obtained when alumina-supported NaBH<sub>4</sub> was used. The use of more than stoichiometric amounts of methanol and NaBH<sub>4</sub> is important to produce alkoxyborohydride anions that act as better reducing species than NaBH<sub>4</sub>. The reaction conditions effect was investigated and the role of short carbon chain alcohol structure was explained. The effect of fatty acid methyl ester structure was also examined. Saturated fatty acid methyl esters (methyl laurate, methyl myristate) with short carbon chains can be easily reduced using NaBH<sub>4</sub>/Al<sub>2</sub>O<sub>3</sub> and methanol, thus obtaining high conversion and selectable fuel alcohol. Unsaturated fatty acid methyl ester (methyl oleate) with longer carbon shows steric hindrance, which is not suitable for the interaction of esters and reduces the surface area, meaning that the conversion of fatty acid methyl ester is lower.

**Keywords:** fatty alcohols; reduction reaction; fatty acid methyl esters



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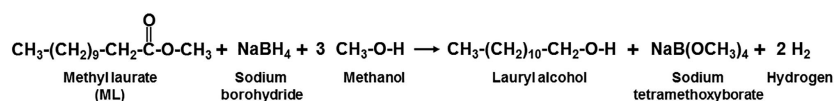
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## 1. Introduction

Industrially, natural fatty alcohols (FOLs) are synthesized by the conversion of fatty acid methyl esters (FAMES) and fatty acids (FAs) via catalytic hydrogenation reaction. In these processes severe reaction conditions are used that involve high temperatures (473–573 K), high pressures of H<sub>2</sub> (20–30 MPa), and solid catalysts based mainly on chromium, such as Cu-Cr [1] and Zn-Cr [2,3], which resulted in their being selective to FOL, but these Cr-based catalysts are not environmentally friendly. Because of this environmental issue, research studies have used catalyst solids of Ru-Sn/Al<sub>2</sub>O<sub>3</sub> [4], Pt/TiO<sub>2</sub> [5], Re-Sn bimetallic solids deposited on ZrO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> [6] under similar industrial conditions.

In this work, we propose an alternative route for the synthesis of FOL via hydrogen and hydride transfer reduction. Lauryl (LA), myristil (MA) and oleyl alcohols (OA) were synthesized in non-catalytic reactions from methyl laurate (ML), myristate (MM) and oleate (MO), respectively, using a metal hydride (NaBH<sub>4</sub>) as H<sup>−</sup> donor and an alcohol (methanol) as the H<sup>+</sup> donor. FOL were synthesized from ML, MM and MO in a methanol/THF solvent mix. The stoichiometry involved in the FAME reduction reaction is shown in Scheme 1.

We used pure  $\text{NaBH}_4$  and alumina-supported  $\text{NaBH}_4$ . The aim of supporting the metal hydride was to increase its stability and achieve the full recovery of the solid in which it is transformed during the reduction reaction without a catalyst.



**Scheme 1.** Stoichiometry of FOL synthesis reaction using FAME, methanol and sodium borhydride.

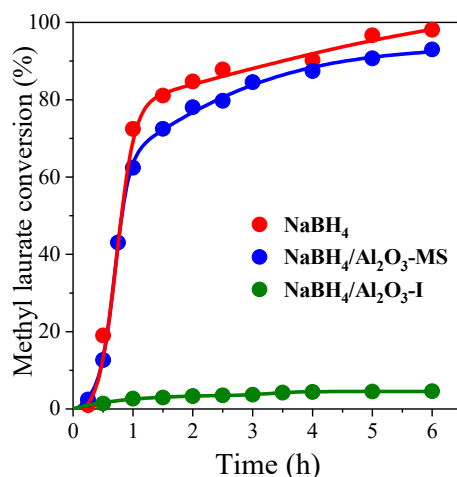
## 2. Materials and Methods

Characteristic reduction reactions of FAME with methanol and either pure  $\text{NaBH}_4$  or alumina-supported  $\text{NaBH}_4$  were carried out at 323 K under atmospheric pressure in a semi-batch glass reactor, firstly loading the reactor with a solution of FAME/THF = 0.024 (molar ratio). The reaction was permanently exposed to an  $\text{N}_2$  gas stream and the mixture was heated to the reaction temperature under magnetic stirring at 700 rpm.  $\text{NaBH}_4$  (0.7 g) was added in the reactor with a molar FAME/ $\text{NaBH}_4$  ratio of 0.36. After that, methanol (5 mL) was added over a period of 1 h, reaching a molar alcohol/ $\text{NaBH}_4$  ratio of 6.0. During the experiments of 6 h, samples were extracted from the reactor and analyzed by gas chromatography.

## 3. Results

### 3.1. Effect of Supporting $\text{NaBH}_4$

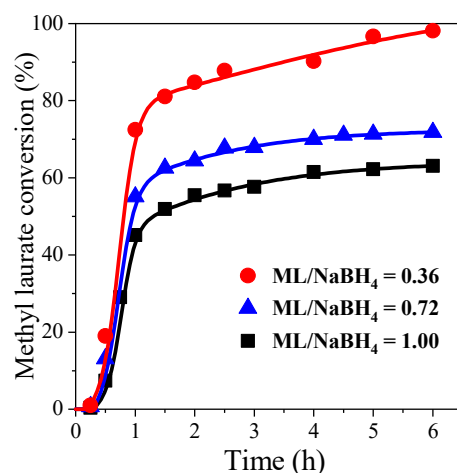
Two processes were used to load  $\text{NaBH}_4$  among other products to reduce waste during the FAME reduction. In this way,  $\text{NaBH}_4$  was supported on  $\text{Al}_2\text{O}_3$  to obtain 50% as a weight-reducing agent in the final product. Firstly, the mixture ( $\text{NaBH}_4/\text{Al}_2\text{O}_3$ -MS) was prepared in a mortar just before being used in the reaction. In another preparation, alumina ( $\text{NaBH}_4/\text{Al}_2\text{O}_3$ -I) was impregnated with  $\text{NaBH}_4$  using a small amount of water. The samples were dried in an oven at 323 K. The amount of  $\text{NaBH}_4$  added to the reactor in these experiments was 0.7 g, that is, it was preserved compared to the experiments performed with unsupported hydride. Due that the selectivity to FOL in all experiments was 100%, a final LA yield ( $Y_{\text{LA}}$ ) of 93% was obtained using a mixture of  $\text{NaBH}_4$  and  $\text{Al}_2\text{O}_3$  ( $\text{NaBH}_4/\text{Al}_2\text{O}_3$ -MS) (Figure 1). This  $Y_{\text{LA}}$  value is slightly lower than that obtained using pure  $\text{NaBH}_4$  ( $Y_{\text{LA}} = 98\%$ ). The slight decrease in final LA can be attributed to the loss in the metal hydride's freedom to interact with other reactants during the reduction reaction. On the other hand, when  $\text{NaBH}_4/\text{Al}_2\text{O}_3$ -I was used as the reducing agent, FAME did not decrease and the final  $Y_{\text{LA}}$  was close to 4.5% (Figure 1). As a result, mechanical mixing is the most suitable method to obtain  $\text{NaBH}_4$  attached to alumina, since the highest FOL yield values are obtained during the FAME reduction. Thus, this reducing solid was selected to perform the reaction optimization.



**Figure 1.** Effect of supporting  $\text{NaBH}_4$ .

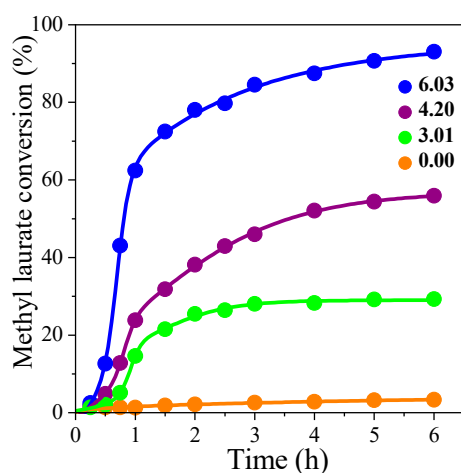
### 3.2. Effects of Varying $\text{NaBH}_4$ and Methanol Amounts

Experiments were carried out at 323K, using pure  $\text{NaBH}_4$  to reduce the FAME, with a methanol/ $\text{NaBH}_4$  molar ratio of 6.0 and FAME/ $\text{NaBH}_4$  molar ratios of 0.36, 0.72, and 1.00. As shown in Figure 2, the best results were obtained by using an excess of  $\text{NaBH}_4$  relative to the stoichiometric ratio of 1:1 (see equation in Scheme 1). Additionally, the higher the reducing agent amount, the higher the final  $Y_{\text{LA}}$  value. Therefore, reducing the ML/ $\text{NaBH}_4$  molar ratio from the stoichiometric ratio (1.00) to 0.36 increased the final FOL yield from 63% to 98%. At the end of the 6 h run in Fig. 2, the reaction liquid mixture was rich in LA and contained residues consisting mainly of  $\text{NaBH}_4$  and sodium tetramethoxyborate  $\text{Na}[\text{B}(\text{OCH}_3)_4]$ .



**Figure 2.** Effect of varying ML/ $\text{NaBH}_4$  molar ratio.

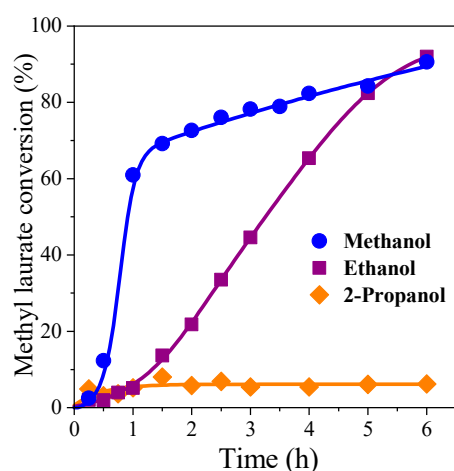
Other experiments were performed at 323 K using  $\text{NaBH}_4/\text{Al}_2\text{O}_3\text{-MS}$  as the reducing agent, and the methanol/ $\text{NaBH}_4$  molar ratio varied between 0.0 (experiments without methanol) and 6.0. While there was no decrease in FAME when the experiments were carried out without methanol, the conversion of ML increased with the increase in the methanol/ $\text{NaBH}_4$  ratio in the experiments with methanol. Assuming that the selectivity of FOL is 100% in all experiments, the final LA yield reaches a maximum ( $Y_{\text{LA}} = 93\%$ ) when the methanol/ $\text{NaBH}_4$  molar ratio is 6.0. When a lower molar ratio is used, not only will the final LA results be lower, but the FAME conversion rate will also be slower; this can be determined by observing the slope of the change history versus time curve in Figure 3. In fact, when using the stoichiometric molar ratio of methanol/ $\text{NaBH}_4$ , the final  $Y_{\text{LA}}$  value is only 29%, while when the methanol/ $\text{NaBH}_4$  molar ratio is 4.2, the final  $Y_{\text{LA}}$  value can be increased to 54%. These results show that the presence of methanol is very important and must be in excess for the reduction of FAME to FOL (methanol/ $\text{NaBH}_4$  molar ratio = 6.0). The need for more methanol can be explained by the fact that, in addition to the interaction with FAME during reduction, methanol also participates in other reactions in which methanol decomposes to form  $\text{H}_2$  in the presence of  $\text{NaBH}_4$ . In the methanol decomposition of  $\text{NaBH}_4$ , methanol is converted to  $\text{H}_2$  and  $\text{NaBH}_4$  is converted to  $\text{Na}[\text{B}(\text{OCH}_3)_4]$ .



**Figure 3.** Effect of varying methanol/ $\text{NaBH}_4$  molar ratio.

### 3.3. Effect of the Structure of Short-Carbon-Chain Alcohol and FAME

Experiments were carried out at 323 K using  $\text{NaBH}_4/\text{Al}_2\text{O}_3\text{-MS}$  as the reducing agent and ethanol/ $\text{NaBH}_4$  and ML/ $\text{NaBH}_4$  molar ratios of 6.0 and 0.36, respectively. The results are shown in Figure 4. ML changes at the end of the 6 h study were similar to the decrease obtained with methanol and ethanol (Figure 4), with  $X_{\text{ML}}$  values increasing from 91% to 93%. However, in experiments with ethanol, ML conversion was slower; this can be calculated from the first slope test of the ML transformation compared to the reaction time curve in Figure 4. On the other hand, ML was not converted when 2-propanol was used as the  $\text{H}^+$  donor ( $X_{\text{ML}} = 6.2\%$ ). The length and complexity of reducing species difficult, due to the steric hindrance introduced, the interaction with  $\text{NaBH}_4$ . In fact, the ethoxide and isopropoxide anions are larger than the methoxide anion. Therefore, problems arise in the incorporation into the borohydride structure and the simultaneous removal of the H-anion. When ethanol and 2-propanol are used, LA selectivity is lower and ethyl laurate and isopropyl laurate are produced. The selectivity of FOL is 100% when methanol is used. In summary, ML can be modified by reduction reaction to obtain the desired FOL and LA, especially when methanol is used as a short carbon chain alcohol, and the final LA yield reaches 93%. As the length and complexity of the alcohol carbon chain increase, the final FOL yield becomes lower because the steric hindrance introduced by the alcohol cannot support the occurrence of reduction. In fact, final LA yield results of 28.2% and 5.1% were obtained using only ethanol and 2-propanol, respectively.



**Figure 4.** Effect of short carbon chain alcohol structure.

The evolution of FAME conversion as a function of time using different FAMEs are shown in Figure 5. As can be seen, the final FAME conversion results were similar using ML and MM; they ranged from 90.8 to 93.0%. On the contrary, MO final conversion barely reached 34.5%. Additionally, the reaction is slower when MO is used. These results indicate that the reduction in FAMEs with short carbon chains can be easily promoted using  $\text{NaBH}_4/\text{Al}_2\text{O}_3$ -MS and methanol as co-reactants. On the contrary, the presence of unsaturation and elongation in the FAME carbon chain indicates steric hindrance, which is unfavorable for the interaction of the ester and reduces its surface area. As expected, the FOLs obtained with ML and MM, LA and myristyl alcohol, respectively, are saturated FOLs, and FOL selectivities of 100% were achieved in both cases. Using methyl oleate as raw material leads only to oleyl alcohol, i.e., unsaturated FOL with 100% selectivity. These results indicate that  $\text{NaBH}_4/\text{Al}_2\text{O}_3$ -MS contributes to the selective reduction in the  $\text{C}=\text{O}$  bond, preserving the  $\text{C}=\text{C}$  bond of MO.

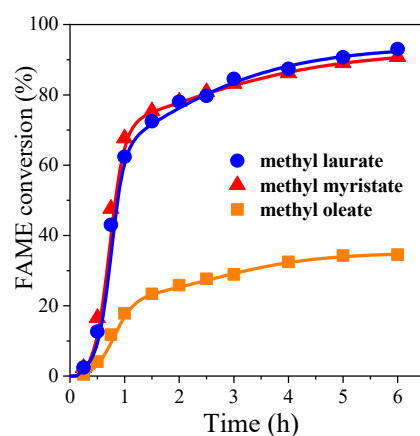


Figure 5. Effect of FAME structure.

#### 4. Conclusions

LA synthesis can be performed non-catalytically using alumina-supported  $\text{NaBH}_4$  and unsupported  $\text{NaBH}_4$  from ML and methanol with selectivities to FOL of 100%. Final FOL yields up to 93% were obtained. Soft reactions, i.e., heat and pressure, were used and the  $\text{H}_2$  gas state is not achieved.

Increasing the length and complexity of the short carbon chain alcohol results in decreased FOL production due to the emergence of steric hindrance. Therefore, when methanol is used as the short-carbon-chain alcohol, ML can be converted to LA via the reduction reaction, and the final FOL yield reaches 93%. The final FOL yield was lower when ethanol and 2-propanol were used.

On the other hand, FAME structure also affects FOL synthesis. The reduction of short carbon chain FAMEs such as ML and MM is easy using  $\text{NaBH}_4/\text{Al}_2\text{O}_3$  and methanol as co-reactants are used.

Unsaturated FAME, such as methyl oleate, with longer carbons introduces steric hindrance which disfavors the interaction between ester and solid surface of  $\text{NaBH}_4$ . Using methyl oleate to initiate FAME resulted in only oleyl alcohol, i.e., no saturated FOL was obtained. These results indicate that  $\text{NaBH}_4/\text{Al}_2\text{O}_3$  helps to selectively reduce the  $\text{C}=\text{O}$  bond and protect the  $\text{C}=\text{C}$  bond of the methyl crude acid ester.

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