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Selectively synthesis of fatty alcohols over mild reaction conditions via non-catalytic liquid-phase fatty acid methyl esters reduction

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Abstract: The upgrading of fatty alcohols synthesis from natural fatty acid methyl esters reduction using alumina-supported $NaBH_4$ without H_2 supply was investigated. It was possible to synthesize fatty alcohols with high yields. Pure $NaBH_4$ or alumina-supported $NaBH_4$ and methanol were used as co-reactants and 100% fatty alcohols selectivities were achieved. The aim of supporting the metal hydride was to increase its stability and achieve the full recovery of the solid at the end of reaction. When alumina-supported $NaBH_4$ was used, final fatty alcohol high yields were achieved. The use of methanol and $NaBH_4$ in amounts higher than stoichiometric is important to generate alkoxyborohydride anions which act as better reducing species than $NaBH_4$. The reaction conditions effect was investigated and the role of short carbon chain alcohol structure was elucidated. The effect of fatty acid methyl ester structure was also studied. Fatty acid methyl esters with shorter carbon chain length and without unsaturation (methyl laurate, methyl myristate) were easily reduced using $NaBH_4/Al_2O_3$ and methanol reaching high conversions and fatty alcohol selectivities. Unsaturated fatty acid methyl ester with longer carbon chain (methyl oleate) introduced steric hindrance which disfavoured interaction between ester and reducing solid surface and fatty acid methyl ester conversion was noticeably lower.

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

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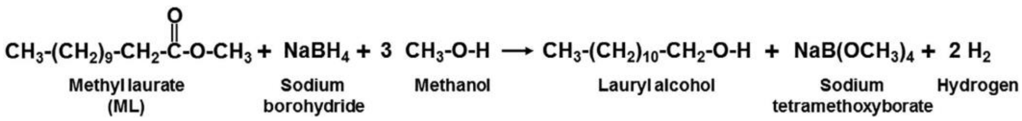
1. Introduction

Industrially, natural FOL are synthetized by conversion of fatty acid methyl esters (FAME) and fatty acids (FA) via catalytic hydrogenation reaction. In these processes severe reaction conditions are used that involve high temperatures (473-573 K), high pressures of H_2 (20-30 MPa), and solid catalysts based mainly on chromium, such as Cu-Cr [1] and Zn-Cr [2,3], which resulted selective to FOL but these Cr-based catalysts are not environmentally friendly. Because of this environmental issue, research studies have used catalysts solids of Ru-Sn/Al_2O_3 [4] , Pt/TiO_2 [5], Re─Sn bimetallic solids deposited on ZrO_2 and Al_2O_3 [6] with similar conditions of the industry.

In this work, we propose an alternative route for the synthesis of FOL by 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 oleyl (MO), respectively, using a metal hydride ($NaBH_4$) as H^- donor and an alcohol (methanol) as H^+ donor. FOL were synthesized from ML, MM and MO in a methanol/THF solvent mix, using $NaBH_4$ pure or supporting on alumina. The stoichiometry involved in the FAME reduction reaction is shown in Scheme 1.We used pure $NaBH_4$ and alumina-supported $NaBH_4$. 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 noncatalytic reduction reaction.



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

2. Materials and Methods

Characteristic reduction reactions of FAME with methanol and pure $NaBH_4$ or alumina-supported $NaBH_4$ were carried out at 323 K and atmospheric pressure in a semi-batch fournecked glass reactor, firstly loading the reactor with a solution FAME/THF = 0.024 (molar ratio). The reaction was permanently exposed to an inert gas stream (N_2) and the mixture was heated up to the reaction temperature under magnetic stirring (700 rpm). 0.7 g of $NaBH_4$ was added so that the molar ratio FAME/$NaBH_4$ in the reactor was 0.36. After that, a volume of 5 mL of methanol was added over a period of 1 hour reaching a molar ratio alcohol/$NaBH_4$ = 6.0. During the 6-hour experiments, samples were extracted from the reactor and analyzed by gas crhromatography.

3. Results

3.1. Effect of supporting $NaBH_4$

Two processes were performed to load $NaBH_4$ among other products to reduce waste during FAME reduction. In this way, $NaBH_4$ is supported on Al_2O_3 to obtain 50% by weight reducing agent in the final product. Firstly, the mixture ($NaBH_4/Al_2O_3$-MS) was prepared in a mortar just before being used in the reaction. In another preparation, alumina ($NaBH_4/Al_2O_3$-I) is impregnated with $NaBH_4$ using a small amount of water. The samples were dried in an oven at 323 K. The amount of $NaBH_4$ added to the reactor in these experiments was 0.7 g, that is, it was preserved compared to the experiments performed with unsupported hydride. A final LA yield (Y_{LA}) of 93% was obtained using a mixture of $NaBH_4$ and Al_2O_3 ($NaBH_4/Al_2O_3$-MS) (Figure 1). This Y_{LA} value is slightly lower than that obtained with $NaBH_4$ and without charge (Y_{LA} = 98%). The slight decrease in final LA can be attributed to the loss of freedom of the metal hydride to interact with other reactants during the reduction reaction. On the other hand, when $NaBH_4/Al_2O_3$-I was used as the reducing agent, FAME did not decrease and the final Y_{LA} was close to 4.5% (Fig. 1). As a result, mechanical mixing is the most suitable method to obtain $NaBH_4$ attached to alumina, since the highest FOL yield values are obtained during FAME reduction. Thus, this reducing solid was selected to perform the reaction optimization.

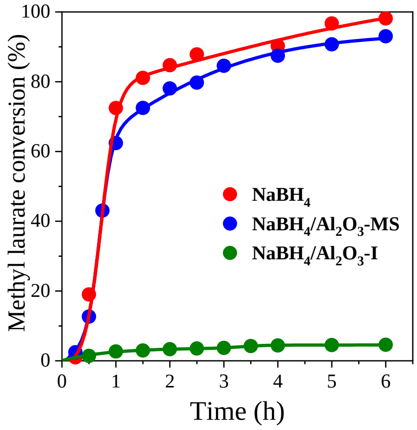


Figure 1. Effect of supporting $NaBH_4$.

3.2. Effect of varying NaBH4, metanol amount

Experiments were carried out at 323 K using pure $NaBH_4$ as reducing solid, a molar ratio methanol/ $NaBH_4$ of 6.0 and FAME/$NaBH_4$ molar ratios of 0.36, 0.72 and 1.00. As can be seen in Fig. 2, the best results were obtained working with an excess of $NaBH_4$ with respect to the stoichiometric ratio 1:1 (see equation of Scheme 1). In addition, the higher the excess of the reducing agent, the higher the final yield to LA. Thus, the final FOL yield increases from 63% to 98% by decreasing the ML/$NaBH_4$ molar ratio from the stoichiometric ratio (1.00) to 0.36. At the end of the 6-hour run of Fig. 2, the liquid reaction mixtures are enriched in LA and they contain a solid residue composed mainly of $NaBH_4$ and sodium tetramethoxyborate, $Na[B(OCH_3)_4]$.

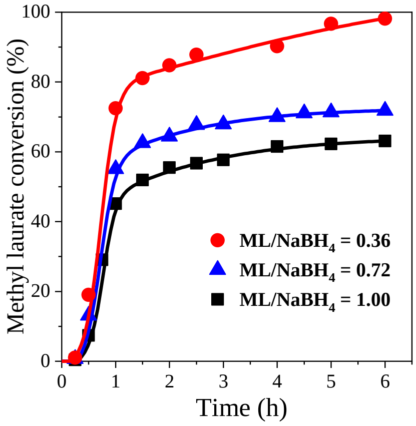


Figure 2. Effect of varying ML/$NaBH_4$ ratio.

Experiments were performed at 323 K using $NaBH_4/Al_2O_3$-MS as the reducing agent, and the methanol/NaBH4 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/NaBH4 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_{LA} = 93%) when the methanol/$NaBH_4$ molar ratio is 6.0. When a lower molar 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/$NaBH_4$, the final YLA value is only 29%, while when the methanol/NaBH4 molar ratio is 4.2, the final YLA 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/$NaBH_4$ 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 H_2 in the presence of $NaBH_4$. Methanol decomposition of $NaBH_4$ in which methanol is converted to H_2 and $NaBH_4$ is converted to $Na[B(OCH_3)_4]$.

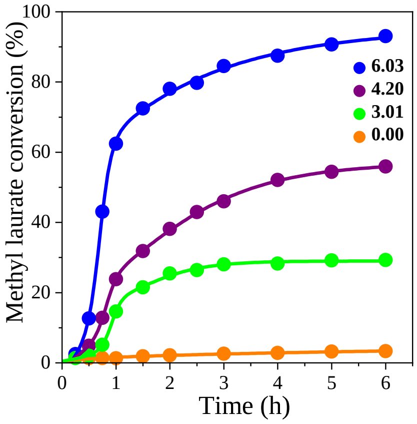


Figure 3. Effect of varying methanol/$NaBH_4$ ratio.

3.3. Effect of structure of short Carbon Chain Alcohol and FAME structure

These experiments were carried out at 323 K using $NaBH_4$/Al_2O_3-MS as reducing solid and molar ratios alcohol/$NaBH_4$ and ML/$NaBH_4$ of 6.0 and 0.36, respectively. Results obtained are shown in Fig. 4. ML conversions at the end of 6 h-run result similar for reduction reaction carried out using methanol and ethanol (Fig. 4) where X_{ML} values between 91 and 93% were achieved. However, during experiment carried out using ethanol the ML conversion is noticeably slower, as can be deduced from the analysis of initial slopes of ML conversion vs. reaction time curves in Fig. 4. On the other hand, when 2-propanol is used as H^+ donor ML is practically not converted (X_{ML} = 6.2%). The explanation for results of Fig. Figure 4 shows the structure of the short chain alcohol used. In fact, the length and complexity of species reduction make the design of species reduction difficult due to the steric hindrance introduced by species reduction. 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 low 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 circuit, and the final LA yield reaches 93%. As the length and complexity of the alcohol carbon fiber increases, the final FOL yield becomes lower because the steric hindrance introduced by the alcohol cannot support the occurrence of reduction. In fact, final LA results of 28.2% and 5.1% were obtained using only ethanol and 2-propanol, respectively.

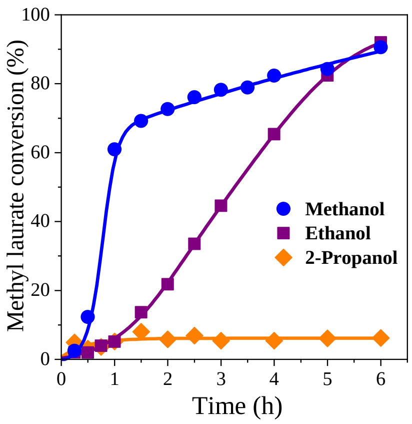


Figure 4. Effect of alcohol structure.

The evolution of FAME conversion as a function of time using different FAME are shown in Fig. 5. As can be seen in Fig. 5, the final FAME conversion resulted similar when ML and MM are used and varied between 90.8 and 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 of weak FAMEs with short carbon chains can be easily promoted using $NaBH_4/Al_2O_3$-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, were saturated FOLs, and 100% selection was achieved in both cases. Using methyl oleate to initiate FAME leads to obtaining only oleyl alcohol, i.e., unsaturated FOL with 100% selectivity. These results indicate that $NaBH_4/Al_2O_3$-MS contributes to the selective reduction of the C=O bond, preserving the C=C bond of MO.

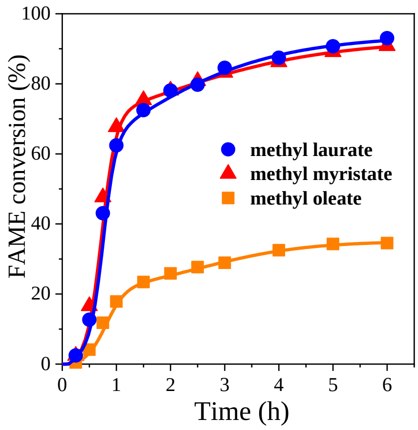


Figure 5. Effect of FAME structure.

4. Conclusions

LA synthesis can be performed non-catalytically using alumina-supported $NaBH_4$ and unsupported $NaBH_4$ from ML and methanol with 100% selectivity and final yields up to 93%. Soft reactions, i.e., heat and pressure, are used and the H_2 gas state is not achieved.

Increasing the length and complexity of the alcohol carbon chain results in decreased drug 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 by 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, the FAME structure also affects FOL synthesis. Reduction of long-carbon deficient FAMEs such as ML and MM is easy using $NaBH_4/Al_2O_3$ and methanol as co-reactants.

Unsaturated FAME,methyl oleate, with longer carbons will show steric interference which is not necessary for the interaction of the ester and reduces the product surface. Using methyl oleate to initiate FAME resulted in only oleyl alcohol, i.e., no FOL. These results indicate that $NaBH_4$/Al2O_3 helps to selectively reduce the C=O bond and protect the C=C bond of the methyl crude acid ester.

Supplementary Materials: “Not applicable”

Author Contributions: For research articles with several authors, a short paragraph specifying their individual contributions must be provided. The following statements should be used “Conceptualization, V.K.D and C.A.F.; methodology, V.K.D.; formal analysis, V.K.D. and A.V.O.; investigation, A.V.O.; resources, V.K.D.; writing—original draft preparation, A.V.O.; writing—review and editing, V.K.D. and C.A.F.; visualization, V.K.D.; supervision, V.K.D. and C.AF.; project administration, V.K.D.; All authors have read and agreed to the published version of the manuscript.”

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