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"Selective synthesis of a valuable unsaturated fatty alcohol via catalytic and non-catalytic liquid-phase methyl oleate reduction"

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Abstract

The upgrading of oleyl alcohol synthesis via methyl oleate reduction using $NaBH_4$ without H_2 supply was investigated. It was possible to synthesize selectively the valuable unsaturated fatty alcohol with high yields. Non-catalytic and catalytic experiments were developed trying to improve the low final oleyl alcohol yield previously obtained. The effect of reaction temperature, methyl oleate/$NaBH_4$ molar ratio and properties of different catalysts on final oleyl alcohol yield was analyzed. Thus, alumina-supported metal (M) catalysts (M = Fe, Ce, Mo) were synthesized by impregnation at incipient wetness. The M/Al_2O_3 catalysts were characterized in their chemical, textural, structural and acid-base properties using ICP, N_2 physisorption, XRD and NH_3 and CO_2 TPD. During non-catalytic methyl oleate reduction final methyl oleate conversion and oleyl alcohol yield of 94% were obtained using a methyl oleate/$NaBH_4$ molar ratio of 0.11 at 333 K. Catalytic activity of M/Al_2O_3 solids did not correlate with basic site number but increased as acid site number and ionic potential of M cations increase. This suggests that cations with high acid site number and polarizing power are the ones that promote the polarization of the ester C=O and anion $[BH_4]^-$ bonds favoring de methyl oleate conversion. In addition, the reaction mechanism for fatty acid methyl ester reduction was investigated from a theoretical approach using Density Functional Theory method at B3LYP/6-31++G(d,p) computational level. Results obtained during theoretical calculations confirmed that the formation of reducing alcoxyborohydride species is energetically favored and allowed to understand the events at microscopic level involved in the reaction mechanism.

Keywords: **methyl oleate; oleyl alcohol; sodium borohydride; reduction reaction mechanism; DFT calculations**

1. Introduction

Natural fatty alcohols (FOL) are linear, monohydric, saturated or unsaturated carbon compounds and have carbon chains between C6-C22. These fatty alcohols are obtained from renewable sources such as animal or vegetable fats, waxes and oils. Fatty alcohols, due to their amphiphilic character (combination of nonpolar carbon chain with polar hydroxyl group), exhibit surface and interface activity, which allows their use in emulsions and microemulsions [Noweck, 2011], favoring their use in personal care and cosmetic industries taking part in the formulation of liquid soaps, shampoos, conditioners, skin emollients, emulsifiers and densifiers of creams and lotions. Thus, fatty alcohols are employed in ionic and non-ionic surfactant production [Sad et al., 2007]. In particular, fatty alcohol sulfates and fatty alcohol ether sulfates belong to the group of anionic surfactants. In addition, fatty alcohol polyglycolethers and fatty alcohol ethoxilates are the first non-ionic surfactants manufactured in technical scale, being the ethoxilates compounds better low-foaming surfactants than the former. Alkyl polyglucosides are manufactured from fatty alcohols and sugar molecules following various procedures. These FOL-derived surfactants are surface active agents which have wide industrial applications as cleaning agents and detergents.

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 [Miya, 1981] and Zn-Cr [Rieke et al., 1997; Rieke et al., 1997], which resulted selective to FOL but is harmful to the environment due to the pollution generated by the final disposal of Cr. Due that, in recent years research has been directed at studying catalysts with similar catalytic activities, which are more efficient and generate less

75 pollution, mainly using catalysts based on noble metals. In fact, when using Ru-Sn/Al_2O_3
76 bimetallic catalysts, a high FOL selectivity is obtained by hydrogenation of methyl laurate
77 using milder reaction conditions (523 K, 5.6 MPa of H_2) [Toba et al., 1999]. In addition,
78 other authors using a similar Ru-Sn/Al_2O_3 catalyst, obtained stearyl alcohol (saturated
79 alcohol) with final yields up to 96% by hydrogenation of C=C and C=O bonds of methyl
80 oleate under severe reaction conditions (553 K, 10 MPa of H_2) [Tahara et al., 1996]. On
81 the other hand, when hydrogenating fatty acids (decanoic acid) over Re_2O_7, low
82 conversions and moderate selectivities to 1-decanol are achieved using 403 K and 10 MPa
83 of H_2 [Yoshino et al., 1990]. There are excellent results in the synthesis of FOL via
84 hydrogenation of FAME or FA, however, expensive noble metal-based catalysts and high
85 temperatures and H_2 pressures are required.

86 On the other hand, FAME reductions using mild reaction conditions via hydrogen and
87 hydride transfer in the liquid phase and without supplying gaseous H_2 have been studied
88 using homogeneous catalysis and there is practically no information related to the use of
89 heterogeneous catalysis in these reaction processes. In this sense, different authors have
90 demonstrated that metal hydrides are efficient carbonyl compounds reducing agents in
91 presence of alcohols of short carbon chain [Soai et al., 1982; Soai et al., 1984; Brown et
92 al., 1982; Rajeswara Rao et al., 1987; Xu et al., 2010]. Brown et al. [Brown et al., 1982]
93 studied the conversion of ethyl caproate and ethyl benzoate using $NaBH_4$, $LiAlH_4$ and
94 $Ca(BH_4)_2$ and alcohols such as ethanol and 2-propanol. In addition, Soai et al. [Soai et al.,
95 1982; Soai et al., 1984] investigated the esters and lactones reduction employing $NaBH_4$
96 and different solvent mixtures (tert-butanol/methanol, tetrahydrofuran/methanol).
97 Rajeswara et al. [Rajeswara Rao et al., 1987] and Xu et al. [Xu et al., 2010] investigated
98 the synthesis of FOL from FAME using $NaBH_4$ or $LiAlH_4$ and methanol achieving final

99 FOL yields between 35-96%. Thus, high ester conversions and alcohol selectivities have
100 been obtained in all these studies.

101 In addition, in a previous work [Vallejo Orrego et al., 2020] we managed to selectively
102 synthesize different FOL during non-catalytic experiments using mild reaction conditions
103 via hydrogen transfer and hydride without supplying H_2 gas. These results allowed us to
104 determine the role played by the hydride donor (metal hydride) and the hydrogen donors
105 (short carbon chain alcohols) in the fatty acid methyl ester reduction. Particularly, we
106 investigated the effect of fatty acid methyl ester structure using methyl laurate (ML),
107 methyl myristate (MM) and methyl oleate (MO). Experiments were carried out at 323 K
108 employing molar ratios methanol/$NaBH_4$ and FAME/$NaBH_4$ of 6.0 and 0.36,
109 respectively, and $NaBH_4/Al_2O_3$ as reducing solid. Results obtained in that reaction
110 conditions showed that final ML and MM conversions varied between 90.8 and 93.0%
111 while MO final conversion resulted significantly lower (34.5%).

112 Taking into account these previous results, in the present work we report on results
113 obtained during the upgrading of oleyl alcohol synthesis via methyl oleate reduction using
114 $NaBH_4$ as reducing agent without H_2 supply. Our goal is to continue the research related
115 to the synthesis of oleyl alcohol by carrying out non-catalytic and catalytic experiments
116 trying to improve the low final FOL yield previously obtained. Thus, catalysts based on
117 different M metals (M = Fe, Ce, Mo) supported on γ-Al_2O_3 were synthesized,
118 characterized, and tested in the MO liquid phase reduction reaction. The effect of reaction
119 conditions and the presence of different catalysts on final oleyl alcohol yield were
120 analyzed. In addition, the mechanism of reaction steps involved in non-catalytic reduction
121 of methyl oleate with $NaBH_4$ was investigated from a theoretical approach using density
122 functional theory (DFT) method at B3LYP/6-31++G(d,p) computational level.
123

2. Materials and experimental procedures

2.1. Chemicals and solid materials

The commercial fatty acid methyl ester, methyl oleate (Sigma-Aldrich, 99%) was used without further purification. Fatty alcohol, oleyl alcohol (Sigma-Aldrich, ≥ 99%) was employed for identification purpose. Methanol (Cicarelli, 99.8%) was used without any purification.

The external standard n-hexadecane (Sigma-Aldrich, 99%) and the solvent tetrahydrofuran, THF (Biopack, ≥ 99%) were used during tests.

Sodium borohydride, $NaBH_4$ (analytical grade) was purchased from Biopack.

2.2. Catalyst synthesis

Alumina-supported metal catalysts (MO_x/Al_2O_3, with M = Ce, Fe, Mo), containing around 8.0 wt.% of metal were prepared by incipient wetness impregnation of commercial γ-Al_2O_3 Cyanamid Ketjen CK 300 with aqueous solutions of different metal precursors. Metal precursors used were $Ce(NO_3)_3.6H_2O$ (Fluka, ≥ 99%), $Fe(NO_3)_3.9H_2O$ (Anedra, 99%) and $Na_2MoO_4.2H_2O$ (Merck, 98%), respectively. The catalyst precursors were thermally treated in flowing air at 673 K during 5 h with the exception of the one containing molybdenum that was treated at 773 K. Catalysts were denoted as *x*MAl, where *x* is the metal content expressed in wt.%.

The γ-Al_2O_3 pellets were crushed and sieved retaining particles between 180-480μm. The powdered alumina was thermally treated at 773 K in flowing air for 5 h to remove adsorbed water before the impregnation procedures.

2.3. Catalyst characterization

148 BET surface areas (SA) of catalysts were measured by N_2 physisorption at 77 K using
149 an Autosorb Quantachrome 1-C sorptometer. After calcination, the chemical content of
150 metal was analyzed by inductively coupled plasma (ICP-OES).
151 The structural properties of solid materials were analyzed by X-Ray Diffraction (XRD)
152 technique using a Shimadzu XD-D1 instrument with nickel filtered Cu Kα radiations
153 between 10 and 80°.
154 Total acid site number (n_a, μmol/g) were determined by TPD of NH_3 preadsorbed at
155 373 K. Samples were thermally treated in Heat the corresponding calcination temperature
156 and then exposed to a 1.11% NH_3/He flow at 373 K during 30 min to enable surface
157 saturation. Weakly adsorbed NH_3 was removed by flushing with He. The temperature
158 was then increased at a rate of 10 K/min from 373 K to 593 K and kept constant for 1 h.
159 NH_3 concentration in the reactor effluent was monitored by a mass spectrometer (MS)
160 detector in a Baltzers Omnistar unit.
161 Total basic site number (n_b, μmol/g) were measured by temperature-programmed
162 desorption (TPD) of CO_2 preadsorbed at room temperature. Samples were pretreated in
163 situ in a N_2 flow at 773 K, cooled to room temperature, and then exposed to a flowing
164 mixture of 3% of CO_2/N_2 until surface saturation was achieved (5 min). Weakly adsorbed
165 CO_2 was removed by flushing in N_2. Finally, the temperature was increased to 773 K at
166 a ramp rate of 10 K/min. Desorbed CO_2 was converted in CH_4 on a methanation catalyst
167 (Ni/Kieselghur), then analyzed using a flame ionization detector (FID).
168
169 ***2.4. Experimental procedure for methyl oleate reduction***
170 Typical non-catalytic and catalytic reduction reactions of methyl oleate (MO) with
171 methanol and pure $NaBH_4$ and *x*MAl catalyst-supported $NaBH_4$ were carried out.
172 Reaction temperatures between 308 K and 333 K and atmospheric pressure were used in

a semi batch four-necked glass reactor. A solution of MO in tetrahydrofuran (THF) solvent with FAME/THF = 0.017 (molar ratio) was firstly loaded in the reactor. The reactor was permanently exposed to an inert gas stream (flowing N_2). The reaction mixture was warmed up to the reaction temperature. Magnetic stirring (700 rpm) was used. The absence of solubilization problems of MO in the THF solvent under the reaction conditions used was evidenced in the experiments. Thus, a single phase was observed once all the reactants were added to the reactor at the reaction temperatures used.

During typical catalytic test an amount of 0.7 g of sodium borohydride ($NaBH_4$) was added so that the molar ratio FAME/$NaBH_4$ in the reactor was 0.28. After that, a volume of 5 mL of methanol was added over a period of 1 h reaching a molar ratio alcohol/$NaBH_4$=6.0. During the 6-hour experiments, 11 samples of ≈ 0.2 mL were extracted from the reactor.

Product of reaction was identified using a Thermo Scientific Trace 1300 GC with a Thermo Scientific TR-5MS capillary column coupled to a Thermo Scientific ISQ QD MS unit. The analysis and quantification of reactants and product concentrations (C_j) were done using a 7890A Agilent Technologies GC equipped with a FID detector and a Supelcowax-10 30M capillary column. Response factors were calculated using solutions containing weighted amounts of the different reactants (FAME, short carbon chain alcohols) and products (FOL) and the standard (n-hexadecane) were injected in the GC.

Methyl oleate conversion (X_{MO}^t) was calculated as:

$$X_{MO}^t\ (\%) = \frac{n_{MO}^0 - n_{MO}^t}{n_{MO}^0} \cdot 100 \qquad \text{(Eq. 1)}$$

where n_{MO}^0 are the moles of methyl oleate initially loaded to reactor and n_{MO}^t are the moles of MO at the reaction time *t*. Selectivities to products *j* (S_j^t) classically defined as shown in Equation 2:

$$S_j^t(\%) = \frac{n_j^t}{n_{MO}^0 - n_{MO}^t} \cdot 100 \quad \text{(Eq. 2)}$$

were calculated in practice according to Equation 3:

$$S_j^t\ (\%) = \frac{C_j^t}{\sum C_j^t} \cdot 100 \quad \text{(Eq. 3)}$$

since $\frac{n_{MO}^0 - n_{MO}^t}{Volume} = \sum C_j^t$. In Equation 3, C_j^t is the concentration of product *j* at reaction time *t*.

Product yields (Y_j^t) were calculated according to Equation 4:

$$Y_j^t\ (\%) = \frac{X_{MO}^t(\%)\ S_j^t(\%)}{100} \quad \text{(Eq. 4)}$$

The initial methyl oleate conversion rate (r^0_{MO}, mol/hg_{cat}) was calculated from the initial slope of the X_{MO} vs. time curve after multiplication by n^0_{MO}/W, according to:

$$r_{MO}^0 = \left[\frac{\mathrm{d}\, X_{MO}}{\mathrm{d}\,(\frac{tW}{n_{MO}^0})}\right]_{\frac{tW}{n_{MO}^0} = 0} \quad \text{(Eq. 5)}$$

where n^0_{MO} is the number of moles of methyl oleate in the reactor at t = 0 and W the catalyst load.

2.5. Computational details for theoretical study of FOL synthesis mechanism

Density functional theory (DFT) molecular orbital calculations were performed using the B3LYP/6-31++G(d,p) level theory [Lee et al.,1988] with Gaussian 09 software package [Frisch et al., 2016]. An initial conformational optimization was performed for the reactants, products and transition state (TS) geometries to obtain the lowest energy conformation.

The theoretical study of the reaction mechanism was carried out, optimizing the reactants, products, transition states and intermediate states. Looking for the transition states, the frequencies of the optimized structures were calculated in order to verify that one of them is negative. We confirmed that all the reactants, intermediates, and products have no imaginary frequencies whereas each transition state has only one imaginary frequency. Energies values presented and discussed in this work are Gibbs free energies, because Gibbs free energies include thermal correction to the electronic energies, as well as the entropic factor.

For modeling purposes, a shorter saturated methyl ester, methyl acetate, was used as FAME. Each reaction mechanism step that was studied is composed of reactants, transition state, intermediate state and products. We treated the reaction in the gas phase and all thermochemical parameters were calculated at 298 K and 1 atm.

3. Results and discussion

3.1. Catalyst characterization

Pure Al_2O_3 and *x*MAl catalysts were characterized in their chemical, textural, structural and acid-base properties. Results obtained are presented in Table 1. The chemical analysis, carried out by ICP, shows that catalyst metal loadings vary between 7.0 and 8.9 wt.%, which are close to the desired nominal content (8.0 wt.%). All catalytic solids exhibit surface areas (*SA*) lower than that of the alumina support (230 m^2/g) and vary between 53 and 173 m^2/g. This result suggests a pore blockage produced by metallic species added during impregnation preparation method.

Structural properties of the solids were analyzed by XRD technique and the results obtained for all samples investigated are shown in Figure 1. The XRD analysis of 7.7FeAl and 7.0CeAl catalysts, showed signals attributable to incipient crystalline phases of Fe_2O_3

243 (JCPDS-ICDD 34-192), $AlFeO_4$ (JCPDS-ICDD 84-2153) and CeO_2 (JCPDS-ICDD 81-
244 792), respectively, in addition to the amorphous phase of the γ-Al_2O_3 support. On the
245 other hand, diffractogram of 8.9MoAl do not show crystalline phases of Mo incorporated
246 on the γ-Al_2O_3 during impregnation, suggesting that the Mo species are dispersed on the
247 surface of the support even with contents close to 8.9 wt.%.

248 The surface acid and basic properties of the *x*MAl samples were investigated by CO_2
249 TPD and NH_3 TPD techniques, respectively. The desorption profiles of both probe
250 molecules are shown in Figure 2. The CO_2 TPD profiles (Figure 2A) show that most
251 solids exhibit a single desorption peak centered at low temperature (360-400 K). This
252 result suggests that their basicity is weak. The number of total basic sites (n_b, μmol/g)
253 was determined by integration of the CO_2 desorption profiles and are presented in Table
254 1. As can be seen, the n_b value of the γ-Al_2O_3 support is low (19 μmol/g), in agreement
255 with previously reported results [i Díez et al., 2003]. On the other hand, as expected, the
256 promotion of the support with metal cations with recognized Lewis acid properties, in
257 general decreases the basic properties of the solids (Table 1). In effect, in all cases n_b
258 values of *x*MAl are lower than that of alumina varying from 1 to 16 μmol/g.

259 On the other hand, the NH_3 TPD profiles (Figure 2B) exhibit a broad desorption peak
260 between 500-900 K indicates the presence of acid species that adsorb NH_3 with different
261 binding energies. Al_2O_3 support exhibits two peaks at 480 and 615 K, corresponding to
262 weak and strong acid sites, respectively. Solids 7.7FeAl and 7.0CeAl also exhibit two
263 desorption peaks at 585 and 833 K. These results suggest that *x*MAl catalytic solids
264 exhibit strong acidity. The total acid site number (n_a, μmol/g) was determined by
265 integration of the NH_3 desorption profiles and are presented in Table 1. All the solids
266 showed n_a values higher than that of the support (24 μmol/g).

267 The acid properties of Lewis nature of the solids caused by incorporation of M^{n+}

cations, were theoretically evaluated considering the ionic potential *q/r* (Table 1). This parameter, defined as the quotient between the charge and the radius of each of the cations [Bernal et al., 2008], takes the lowest value for 7.0CeAl sample and the highest for 8.9MoAl catalyst. Evidence that this parameter allows visualizing the acidity of the catalysts is its relationship with the n_a values. In fact, in Figure 3 it can be seen that n_a increases monotonically with *q/r*.

In summary, observing in Table 1 the results obtained during the characterization of the acid-base properties and data taken from literature for 8.9MoAl [Inmanee et al., 2017], results evident that within the series of *x*MAl catalysts investigated, 8.9MoAl exhibits the highest Lewis acidity.

3.2. Non-catalytic reduction of methyl oleate using pure $NaBH_4$

In a previous work [Vallejo Orrego et al., 2020] we demonstrated that fatty alcohol (FOL) synthesis can be performed through non-catalytic fatty acid methyl ester (FAME) reduction experiments without H_2 supply. Through these experiments it was possible to elucidate the roles of $NaBH_4$ and methanol in FAME reduction. Both reactants allow forming alkoxyborohydride species which are better reducing agents than $NaBH_4$. We also postulated a mechanism for methyl laurate reduction and which is shown adapted for any FAME in Scheme 1. The effect of FAME structure was also investigated in this previous work employing methyl laurate (ML), methyl myristate (MM) and methyl oleate (MO). Results obtained showed that the lowest final FAME conversion was achieved using MO which barely reached 34.5%. As expected, the only FOL obtained from ML and MM were lauryl alcohol and myristyl alcohol, respectively; i.e., the saturated FOL, reaching in both cases selectivities of 100%. Surprisingly, using methyl oleate as starting FAME oleyl alcohol was exclusively obtained, i.e., the selectivity towards unsaturated

293 FOL was 100%. This result allowed us to conclude that $NaBH_4/Al_2O_3$ contributes to the
294 selective reduction of C=O bond preserving C=C bond of MO.

295 In this work, the experiments are focused on optimization of the MO reduction reaction
296 using $NaBH_4$ as reducing agent (hydride donor) and methanol (proton donor). The MO
297 reduction reaction is shown in Scheme 2 where the stoichiometric ratio involved is
298 depicted. Our goal was to improve the low final MO conversion (X_{FAME}) and FOL yield
299 (Y_{FOL}) values obtained using MO as the starting FAME in our previous work [**¡Error!**
300 **Marcador no definido.** Vallejo Orrego et al., 2020].

301 The effect of reaction temperature on MO conversion and FOL yield was firstly
302 investigated. These experiments were carried out using typical methanol/$NaBH_4$ and
303 FAME/$NaBH_4$ molar ratios of 6.0 and 0.28, respectively. Figure 4 shows the MO
304 conversion evolution with reaction time obtained at 308, 320 and 333 K. In all
305 experiments, selectivity towards unsaturated FOL (oleyl alcohol) was 100%. Results
306 from Figure 4 and Table 2 show an increase of final methyl oleate conversion (X_{MO}) and
307 final oleyl alcohol yield (Y_{OA}) as reaction temperature increases from 308 to 333 K. In
308 effect, the X_{MO} values reached at end of reaction (6 h) were 31.9, 40.2 and 58.6%,
309 respectively (Table 2). Reaction temperature can not be increased above 333 K working
310 at atmospheric pressure due that the boiling temperature of methanol co-reactant (338 K).

311 From the analysis of reaction temperature effect can be concluded that 333 K is the
312 most appropriate temperature to carried out MO reduction and it was adopted to perform
313 optimization of experimental conditions.

314 After optimizing the reaction temperature, the effect of MO/$NaBH_4$ molar ratio was
315 investigated. During these experiments pure $NaBH_4$, a molar ratio methanol/$NaBH_4$ of
316 6.0, MO/$NaBH_4$ molar ratios of 0.11, 0.28 and 0.72 and a reaction temperature of 333 K
317 were used. The evolution of MO conversion with reaction time for each MO/$NaBH_4$

318 molar ratio is shown in Figure 5. The oleyl alcohol (S_{OA}) was the only product observed
319 in all experiments. The best results were obtained working with an excess of $NaBH_4$
320 respect to the stoichiometric ratio 1:1 indicated in the reaction pathway of Scheme 2.
321 Results from Figure 5 also show that the higher the excess of the reducing agent, the
322 higher the final OA yield. In fact, results from Table 2 show that the final FOL yield
323 increases from 21.4% to 93.9% by decreasing the MO/$NaBH_4$ molar ratio from the 0.72
324 to 0.11.

325 In a previous work, we obtained similar results during reaction condition optimization
326 using methyl laurate (ML) as starting FAME [Vallejo Orrego et al., 2020] and in all
327 experiments. In those experiments, the selectivity toward FOL was 100% and ML
328 conversions at 6 h of reaction were 72, 78, and 98%, respectively.

329 The conversion of methyl oleate to fatty alcohols was previously studied. In most of
330 these works the reaction strategy is the catalytic hydrogenation using high pressures of
331 gaseous H_2 (0.1 and 8 MPa) and high temperatures (473-563 K). Thus, in some of them
332 expensive catalysts involving noble metals such as Ru-Sn/Al_2O_3 [Echeverri et al., 2011;
333 Pouilloux et al., 1996; Narasimhan et al., 1989; Mazzieri et al., 2010], Ru-Ge/Al_2O_3
334 [Sánchez et al., 2013] have been employed. Final yields toward unsaturated alcohol (oleyl
335 alcohol) were generally low and varied between 12 and 60% being the saturated FAME
336 (methyl stearate) and saturated alcohol (stearyl alcohol) the main products obtained.
337 Other authors used mono and bimetallic catalysts based in no-noble metals supported on
338 different oxides, such as Co/ZnO, Sn/ZnO, Co/Al_2O_3, Co-Sn/Al_2O_3, Co-Sn/ZnO, Co-
339 Sn/SiO_2 [Pouilloux et al., 1998; Pouilloux et al., 2000; De Oliveira et al., 2001; De
340 Oliveira et al., 2012]. Using these catalysts, MO hydrogenation yields mainly heavy esters
341 (oleyl oleate) being the yields toward oleyl alcohol low (11-51%).

Different authors investigated metal hydrides as effective reducing agents of C=O compounds using short carbon chain alcohols [Soai et al., 1982; Soai et al., 1984; Brown et al., 1982; Rajeswara Rao et al., 1987; Xu et al., 2010], but the raw materials to be reduced in these cases were ethyl caproate and ethyl benzoate [Brown et al., 1982] using different metal hydrides or esters and lactones using $NaBH_4$ [Soai et al., 1982; Soai et al., 1984]. However, very few works are known in the open literature that have investigated methyl oleate (MO) reduction using metal hydrides as reducing agents. In effect, McKee et al. [McKee et al., 2019] and Xin et al. [Xin et al., 2021] investigated MO reduction using cobalt chloride/sodium borohydride and Ni-La-B systems, respectively, but these studies lead methyl stearate as main product (reduction of C=C bond) and not produce the most value product (unsaturated alcohol). The best result during methyl oleate reduction to the corresponding unsaturated FOL (oleyl alcohol, OA) using $NaBH_4$ or $LiAlH_4$ and methanol was obtained by Rajeswara Rao et al. [Rajeswara Rao et al., 1987], reaching a final yield toward oleyl alcohol of 72%. However, in these works authors do not investigate fully the effect that different reaction conditions have on oleyl alcohol selectivity and yield during MO reduction. Here, we achieved promising results during the reduction reaction of methyl oleate to the unsaturated fatty alcohol (oleyl alcohol) making for the first time, a huge effort in analyzing the effect of reaction conditions during optimization of OA synthesis through non-catalytic MO reduction.

3.3. Methyl oleate reduction using $NaBH_4$ supported on xMAl catalysts.

In previous paragraphs the optimization of reaction conditions during oleyl alcohol (OA) synthesis from methyl oleate (MO) using $NaBH_4$ and without supplying H_2 gas was described. However, despite the high MO conversion values obtained at the end of the reaction in experiments carried out at 333 K and whit a molar ratio MO/$NaBH_4$ of 0.11,

initial FAME conversion values were low, as we could be concluded analyzing the slopes at the origin of the conversion vs. time curves of Figures 4 and 5.

Previously, a mechanism for the reduction of FAME in using $NaBH_4$ and methanol as co-reactants was proposed [Vallejo Orrego et al., 2020]. Briefly, the initial stage of mechanism consists in the formation of the reducing species: alkoxyborohydride anions. The second stage involves the successive steps that allow the interaction between the reducing species and the FAME, leading to the formation of FOL. FAME (MO) conversion to FOL (OA) requires reducing species that allow the reduction of the C=O carbonyl group of FAME. To do this, $NaBH_4$ interacts with methanol generating alkoxyborohydride species $[BH_{4-n}(CH_3O)_n]^-$ (n = 1, 2, 3) that are more effective reducing agents than the borohydride anion $[BH_4]^-$, as concluded from results obtained previously [Vallejo Orrego et al., 2020]. This reducing effect increases each time a methoxy group is attached to $[BH_4]^-$ species. After reducing species formation, MO is activated via the interaction between C=O group and the dimethoxyborohydride anion. The hydride addition of the reducing species originates a tetrahedral intermediate anion, which immediately interacts with the B atom of an incipient species of $BH(OCH_3)_2$ through a polar B-O bond. By subsequent removal of a methoxide specie, which is incorporated into the dimethoxyborohydride anion, an aldehyde intermediate is formed, which rapidly is reduced by interaction with the trimethoxyborohydride anion. Indeed, the H^- of the reducing species attacks the carbon of the C=O group of the aldehyde leading to the formation of a tetrahedral intermediate anion and the tetramethoxyborate species. In the last part of mechanism, another methanol molecule protonates this tetrahedral intermediate to form oleyl alcohol. In order to address the study of the mechanism from a theoretical approach, slight modifications were made to the successive steps described above, which will be described later.

Taking into account that postulated mechanism, metal cations have been incorporated to Al_2O_3 before the incorporation of the co-reactant $NaBH_4$, and thus, *x*MAl catalysts were synthesized. The goal was to increase the acidity and thus favor the polarization of the C=O group of the ester and the $[BH_4]^-$ anion bond facilitating the formation of reducing species and their attack on the C=O of the ester. The requirements of these metal cations to favor polarization are: 1) to have a low ionic radius; 2) to possess high charge. With this in mind, the 7.0CeAl, 7.7FeAl and 8.9MoAl catalysts were tested in the reduction of MO to OA. Figure 6 shows the evolution of MO conversion with reaction time on these solids, while Table 2 summarizes the final yields to OA (Y_{OA}) and the initial conversion rates of FAME (r^0_{MO}) obtained. In all cases the selectivity to FOL were 100%. The 8.9MoAl solid exhibits the highest final OA yield value. In fact, this catalyst reached a Y_{OA} of 81.6% after 6 h reaction (Table 2), which is higher than the obtained on Al_2O_3 (Y_{OA} = 53.0%).

On the other hand, the reduction of MO on 7.0CeAl and 7.7FeAl catalysts allow to obtain lower OA final yield (48.8% and 58.7%, respectively). This result confirms that, in order to favor the bond polarization of the functional groups involved in the reaction, small metallic cations with high charge are required, that is, high *q/r* values. On the other hand, structural features, characterizes by XRD analysis (Figure 1 and Table 1), would influence in catalytic results since *x*MoAl is the only catalyst where metal species are well spread out on the surface of the support.

The effect of the surface acid-base properties and cation polarizing power (*q/r* parameter) of *x*MAl solids on the catalytic activity was also investigated. In this way, the initial MO conversion rate was related with n_b, n_a, and *q/r*. Results obtained are shown in Figure 7A and 7B and Table 2. Results from Table 2 show that 8.9MoAl is the most active catalysts during MO reduction. This was evidenced through its high value of r^0_{MO} (0.20

417 mol/hg), which favored a rapid formation of reducing species that concludes with
418 obtaining the non-reducing anion $[B(OCH_3)_4]^-$ and therefore the Y_{OA} increases more
419 slowly up to reach a final value of 81.6%. A similar behavior is exhibited by the 7.7FeAl
420 catalyst, which showed high activity (Table 2) and therefore, the final Y_{OA} is rapidly
421 reached after 2 h of reaction (Figure 6).

422 The catalytic activity of *x*MAl solids (r^0_{MO}) seems not to correlate clearly with n_b
423 values, although apparently a maximum appears for 8.9MoAl catalyst (Figure 7A). In
424 general, this result suggests that surface basic sites would not be directly involved in the
425 conversion of MO to OA. On the other hand, Figure 7B clearly shows that r^0_{MO} values
426 increase as n_a and q/r increase, suggesting that the M^{n+} cations whose nature have higher
427 polarizing power (q/r values) and that are found in greater quantity on the surface of the
428 catalyst (n_a values) are those that promote the polarization of the ester C=O and anion
429 $[BH_4]^-$ bonds.

430

431 ***3.4. Molecular modeling by DFT of reaction steps involved in fatty alcohol synthesis***

432 The reaction mechanism proposed for FAME reduction was studied from a theoretical
433 approach. The molecular modeling was carried out optimizing reactants, products,
434 transition states and intermediate states. During the search for the transition states (TS),
435 the frequencies of the optimized structures were calculated in order to verify that one of
436 them was negative. The result of this frequency was contrasted with the movement of the
437 atoms involved in the reaction in order to confirm that this structure belonged to a
438 transition state.

439 As previously mentioned, the calculations were made using methyl acetate as model
440 molecule to represent FAME, whose reduction using $NaBH_4$ would lead toward ethanol
441 (model molecule for FOL). The purpose of this choice is to decrease the size of the

calculations involved reducing both the time needed as well as the computational resources. During calculations it was possible to establish a general balance of atoms between reactants and products from the generation of the reducing species toward the formation of the alcohol through interaction of FAME (methyl acetate) and alkoxyborohydride species, and thus, was possible to normalize the free Gibbs energies as a function of the energy of the initial reactants [Foresman et al., 2015] (ΔG, Kcal/mol).

In the first instance, the mechanism for reducing species (alcoxyborohydrides) generation was evaluated, taking into account that in each step, methanol is part of the reactants and there is hydrogen generation. In effect, the investigated methanolysis reaction involves, two moles of borohydride anion $[BH_4]^-$ and eight moles of methanol (CH_3OH) as starting reactants and two moles of tetramethoxyborate anion $[B(OCH_3)_4]^-$ and eight moles of hydrogen (H_2) as reaction products. The initial step of the global mechanism for FAME reduction (also for methyl acetate) comprises a series of sub-steps in which the anion $[BH_4]^-$ reacts with methanol through successive reactions to produce initially the monosubstituted anion $[BH_3(OCH_3)]^-$ and hydrogen (Scheme 3), until the fully substituted anion $[B(OCH_3)_4]^-$ is reached. The successive steps involved in methanolysis reaction and used to perform the calculations are represented by Equations 6 to 9,

$$2\,[BH_4]^- + 2\,CH_3OH \rightarrow 2\,[BH_3(OCH_3)]^- + 2\,H_2 \qquad \text{(Eq. 6)}$$

$$2\,[BH_3(OCH_3)]^- + 2\,CH_3OH \rightarrow 2\,[BH_2(OCH_3)_2]^- + 2\,H_2 \qquad \text{(Eq. 7)}$$

$$2\,[BH_2(OCH_3)_2]^- + 2\,CH_3OH \rightarrow 2\,[BH(OCH_3)_3]^- + 2\,H_2 \qquad \text{(Eq. 8)}$$

$$2\,[BH(OCH_3)_3]^- + 2\,CH_3OH \rightarrow 2\,[B(OCH_3)_4]^- + 2\,H_2 \qquad \text{(Eq. 9)}$$

while Equation 10 represents the global methanolysis reaction of $[BH_4]^-$ of sodium borohydride that has been widely discussed in the literature [Demirci et al., 2010; Fernandes et al., 2009; Lo et al., 2007]:

$$2\,[BH_4]^- + 8\,CH_3OH \rightarrow 2\,[B(OCH_3)_4]^- + 8\,H_2 \qquad \text{(Eq. 10)}$$

Since there is no information available about the coordinates of a structure that represents a transition state that allows to simplify the calculations, a special strategy was used to start the calculations. This strategy involves the use of synchronous quadratic transit method (TSQ) [Foresman et al., 2015; Devia, 2018; Barroso, 2021] which consists of finding a possible transition state from the coordinates of reactants, products and optionally a third molecule corresponding to a supposed transition state. The coordinates of the two reactants ($[BH_4]^-$ and methanol) and the two products ($[BH_3(OCH_4)]^-$ and hydrogen) involved were first used, however, it failed to reach a satisfactory transition state at negative energy and frequencies. Consequently, it was decided to build a pseudo-transition state that resembled the reactants and products structures. Then, verifying the presence of a single imaginary frequency and confirming that the energy of the structure results higher than the energy of the reactants and products, this first structure was taken as the basis for calculating the other transition states involved in methanolysis.

Figure 8A shows the initial optimized geometries of anionic borohydride species $[BH_4]^-$, alkoxyborohydrides $[BH_{4-n}(OCH_3)_n]^-$ (n = 1, 2 and 3), tetramethoxyborate $[B(OCH_3)_4]^-$ and the compounds methanol, methyl acetate, acetaldehyde and ethanol. In addition, optimized structures obtained during the sub-steps of reaction pathway presented in Scheme 3, including the corresponding transition state TS1, TS2, TS3 and TS4, in which the bonds that are formed and broken are represented with dotted lines, are presented in Figure 8B.

On the other hand, Figure 9 shows the progress of all steps involved in methyl acetate reduction mechanism through the various intermediates and its different energy levels on the potential energy diagram (PED), where the energy of the structures is represented as a function of the reaction coordinate. Total Gibbs free energy of eight methanol

492 molecules, two $[BH_4]^-$ species, one hydrogen atom and one methyl acetate molecule has
493 been considered as the reference of the reaction in the energy profile (ΔG = 0 Kcal/mol).
494 As can be seen, the formation of each alkoxyborohydride and tetramethoxyborate
495 species proceed spontaneously, i.e., they are reaction steps that are energetically favored
496 and therefore do not require an energy supply to be carried out. These results are
497 consistent with the experimental results presented in the literature on $[BH_4]^-$ methanolysis
498 [Ocon et al., 2013; Kaya et al., 2019]. The transition states found during the theoretical
499 study of the generation of reducing species have an imaginary frequency, the movement
500 of their atoms are consistent with formation of products and they have an energy higher
501 than the sum of the energies of the reactants or products. This allows us to conclude that
502 these structures correspond to the transition states (TS) of the reaction. In general, in the
503 transition states, the H^- from the borohydride or methoxyborohydride anion and the H^+
504 from methanol react to form gaseous hydrogen and the following substituted
505 alkoxyborohydride species. In conclusion, the results obtained in the generation of the
506 reducing species from theoretical calculations are in total agreement with the mechanism
507 proposed from experimental evidence in Scheme 1.
508 After studying, from a theorical point of view, the formation of the reducing species,
509 we evaluated the second part of the mechanism proposed in Scheme 1, which consists of
510 obtaining the fatty alcohol from the reduction of the ester. Considering that methyl acetate
511 is used as a model ester to represent FAME, the aldehyde that would be formed in the
512 first stage of the mechanism would be acetaldehyde and the alcohol that would be
513 generated as the final product would be ethanol. In order to simplify the analysis of the
514 interaction of reducing species with FAME (Scheme 1), to facilitate understanding of the
515 theoretical approach in the reaction pathway of Scheme 3 and taking into consideration
516 the time required to perform and analyze the results of the calculations, the theoretical

analysis that was carried out involves the species $[BH_2(OCH_3)_2]^-$ as unique reducing agent of methyl acetate and acetaldehyde. Taking the above into account, Equations 11, 12 and 13 detail the sub-steps involved in the formation of ethanol.

$$CH_3COOCH_3 + [BH_2(OCH_3)_2]^- \rightarrow CH_3CHO + [BH(OCH_3)_2] + (OCH_3)^- \quad \text{(Eq. 11)}$$

$$CH_3CHO + [BH_2(OCH_3)_2]^- \rightarrow [BH(OCH_3)_2] + (OCH_2CH_3)^- \quad \text{(Eq. 12)}$$

$$(OCH_2CH_3)^- + [H]^+ \rightarrow CH_3CH_2OH \quad \text{(Eq. 13)}$$

Equation 11 represents the general expression to obtain the first intermediate of the reaction, which corresponds to acetaldehyde for the model proposed in this study. As shown in the Scheme 3, acetaldehyde in turn is rapidly reduced by $[BH_2(OCH_3)_2]^-$ species or by another alkoxyborohydride species to form an ethoxide intermediate $(OCH_2CH_3)^-$ (Scheme 3), which is then converted to ethanol by H^+ from methanol. This last part of the process is represented in Equations 12 and 13. General equation representing the whole process is depicted in Equation 14:

$$CH_3COOCH_3 + 2\,[BH_2(OCH_3)_2]^- + [H]^+ \rightarrow CH_3CH_2OH + 2\,[BH(OCH_3)_2]^- + (OCH_3)^- \quad \text{(Eq. 14)}$$

In order to evaluate their energetic behavior and compare theoretical results of calculations with the proposed experimental mechanism, frequencies of all the molecules involved in each sub-step of the mechanism were calculated. For the TS5, TS6, TS7 and TS8, the existence of an imaginary frequency (negative value) in the structures proposed as a TS was verified.

Analysis of the results obtained in the theoretical calculation carried out on the synthesis of ethanol was divided for a better understanding into two steps: formation of the acetaldehyde intermediate and formation of the final product, ethanol.

To form acetaldehyde from methyl acetate, the presence of a nucleophilic compound containing H^- ions is necessary to transfer electrons to the carbonyl group of the ester. Results obtained are shown in Figures 8 and 9. The transition state TS5 is initially formed

542 from the attack of the anion $[BH_2(OCH_3)_2]^-$ to the C=O bond of methyl acetate (Figure
543 8B); then an intermediate (EI1 in Figure 8C) is formed in which the H^- forms a single
544 bond to the C=O group at the same time that the other single bond C-O between carbon
545 and the leaving group $(OCH_3)^-$ of methyl acetate begins to break, leaving the oxygen of
546 the C=O with negative charge. In the second transition state (TS6) formation, the C=O
547 bond is reformed and the $(OCH_3)^-$ group is lost (Scheme 3) leading to acetaldehyde
548 $[BH(OCH_3)_2]$ and $(OCH_3)^-$ species.

549 Figure 9 shows that the acetaldehyde formation results an exergonic reaction and is
550 energetically favored, since the products have a lower energy state (ΔG = -100.1
551 Kcal/mol) than the reactants (ΔG = -53.9 Kcal/mol).

552 The last part of ethanol formation mechanism requires the initial formation of an
553 ethoxide intermediate through reduction of acetaldehyde and then, the last step, involves
554 its conversion into ethanol (Scheme 3). The ethoxide formation (Equation 12) is
555 represented in Figure 8B while Figure 9 shows the energy profile as a function of the
556 reaction coordinate. As can be seen in Figure 8B, for the conversion of acetaldehyde (P5)
557 to ethoxide intermediate (EI2), a transition state (TS7) is formed in which a H^- of the
558 species $[BH_2(OCH_3)_2]^-$ attacks the carbon of acetaldehyde C=O group.

559 This approximation favors the breaking of alcoxyborohydride B-H bond and the
560 formation of the C-H bond that gives rise to ethoxide species. Ethoxide is considered an
561 intermediate between acetaldehyde and ethanol, in which the carbon atom of the C=O
562 group forms three bonds: two simple C-H bonds and other bond that corresponds to the
563 partial formation of a double bond between carbon and oxygen, in which the oxygen atom
564 meets delocalized electrons that would favor the formation of ethanol. Results presented
565 in Figure 9 show that the energy change involved in going from P5 to EI2 is not
566 energetically favored to form the ethoxide, indicating that this step requires extra energy

to be carried out. The fact that this structure is not energetically favored confirms that it is a reaction intermediate state. The final sub-step of the reaction involves the formation of ethanol (Equation 13). Calculation results obtained on this step are shown in Figures 8B and 9. To carry out the theoretical calculations in this sub-step, the H atom of methanol was used as a proton source, which, as was verified in the theoretical studies of methanolysis steps comes from the alcohol O-H group. On the other hand, in the mechanism showed in Scheme 3, the H^+ of methanol participates in both the generation of hydrogen and the alcohol formation. Thus, structures of Figure 8B show that in the transition state (TS8), the H atom approaches the ethoxide to favor the formation of the O-H bond leading to ethanol. Furthermore, in Figure 9 allow concluding that alcohol formation occurs exergonically and thus, this sub-step is energetically favored.

In conclusion, the mechanism involved in the generation of reducing species was theoretically elucidated. In this part of global mechanism, it was possible to confirm the formation of alcoxyborohydride species is energetically favored. Furthermore, the results obtained during the theoretical calculations for ethanol formation through methyl acetate reduction, allowed us to understand the events at the microscopic level involved in the mechanism of the reaction under study. In addition, the exhaustive study of the sub-steps involved in the mechanism confirmed the formation of several structures (alkoxyborohydride, acetaldehyde and ethoxide species) which act as intermediate compounds in obtaining alcohol. Finally, reducing the size of the system in the theoretical study allows to reach a first approach to the intermolecular interactions that exist between the different species involved in the reduction of shorter ester than FAME; during extrapolation of this theoretical study involving the synthesis of ethanol toward the synthesis of fatty alcohols (FOL) derived from FAME, it was possible to confirm the

591 analysis carried out at macroscopic level (experimental results) by proposing in Scheme
592 1 the reaction mechanism for FOL synthesis.
593
594 **4. Conclusions**
595 Oleyl alcohol (OA) synthesis could be improved through non-catalytic and catalytic
596 experiments with selectivities of 100% from methyl oleate and methanol using both
597 unsupported $NaBH_4$ and catalyst-supported $NaBH_4$. In order to optimize the synthesis,
598 different reaction conditions (temperature, methyl oleate/$NaBH_4$ molar ratio and catalyst
599 nature) were employed without the supply of H_2 gaseous. Thus, in non-catalytic
600 experiments a final yield of the valuable unsaturated fatty alcohol OA of 93.9% was
601 achieved using a methyl oleate/$NaBH_4$ molar ratio of 0.11 and a reaction temperature of
602 333 K.
603 The effect of the incorporation of different metal cations M (M = Fe, Ce, Mo) to the
604 alumina support on the activity and OA yield was studied and it was found that
605 $8.9Mo/Al_2O_3$ solid, the catalyst with the highest acid site number and the highest
606 polarizing power, allow obtaining the best activity value. In fact, this catalytic solid favors
607 the C=O bond polarization of the ester and the anion $[BH_4]^-$ to form the actual reducing
608 species that then interact with the methyl oleate.
609 Reaction mechanism previously postulated for fatty acid methyl esters reduction
610 towards fatty alcohols using methanol and $NaBH_4$ was studied in this work from a
611 theoretical approach using density functional theory (DFT) method at B3LYP/6-
612 31++G(d,p) computational level. Calculations were made using methyl acetate as model
613 molecule to represent fatty acid methyl esters, whose reduction would lead toward ethanol
614 (model molecule for fatty alcohols). This choice allowed to decrease the size of the
615 calculations involved, reducing both the time needed as well as the computational

resources. It was possible to confirm that the formation of reducing alcoxyborohydride species is energetically favored. On the other hand, results obtained during the theoretical calculations for ethanol formation from methyl acetate, allowed to understand the events at the microscopic level involved in the reaction mechanism studied. Finally, it was possible demonstrate, that the reduction of the system size during the theoretical study allows to reach a first approach to the intermolecular interactions that exist between the different species involved in the acetate reduction. During extrapolation of the DFT study performed for ethanol synthesis toward the fatty alcohol synthesis from fatty acid methyl esters, we confirmed the analysis carried out at macroscopic level based on experimental results.

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Authorship

V.K.D. Conceived and designed the study; conceptualized, supervised and analyzed the data; and wrote the first draft of the manuscript. **C.A.F.** Conceptualized and supervised theoretical research (DFT) and analyzed the data. **A.V.O.** Carried out the experimental and theoretical research and analyzed the data. All authors contributed to and approved the final draft of the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Captions to Figures and Schemes

Scheme 1. Reaction mechanism for fatty acid methyl ester reduction using methanol as proton donor and sodium borohydride as hydride donor.

Scheme 2. Stoichiometry of oleyl alcohol (OA) synthesis reaction from methyl oleate, methanol and sodium borohydride.

Scheme 3. Possible mechanisms involved in the methyl acetate reduction reaction used for DFT calculations.

Figure 1. Diffractograms obtained on *x*MAl samples.

Figure 2. CO_2 TPD (A) and NH_3 TPD (B) profiles for *x*MAl solids.

Figure 3. Relation between n_a and q/r for *x*MAl catalysts.

Figure 4. Effect of reaction temperature during methyl oleate conversion to oleyl alcohol (T = 308 K, 320 K, 333 K; FAME/$NaBH_4$ molar ratio = 0.28; methanol/$NaBH_4$ molar ratio = 6.0; $NaBH_4$ as reducing solid).

Figure 5. Effect of varying FAME/$NaBH_4$ molar ratio during methyl oleate conversion to oleyl alcohol (T = 333 K; methanol/$NaBH_4$ molar ratio = 6.0; $NaBH_4$ as reducing solid).

Figure 6. Figure 6. MO conversion as a function of reaction time on xMAl catalysts (T = 333 K; MO/$NaBH_4$ molar ratio = 0.11; methanol/$NaBH_4$ molar ratio = 6.0; $NaBH_4$/MAl as reducing solid).

Figure 7. Relation between r^0_{MO} and n_b (A) and, r^0_{MO} and q/r and n_a (B) for *x*MAl catalysts (T = 333 K; MO/$NaBH_4$ molar ratio = 0.11; methanol/$NaBH_4$ molar ratio = 6.0).

Figure 8. Different optimized initial geometries (A), transitions states (A) and intermediates (C) found for methyl acetate reduction reaction obtained from DFT calculations.

Figure 9. Reaction energy profile for methyl acetate reduction toward ethanol formation obtained from DFT calculations.

Table 1. Chemical, textural, structural and acid-base characterization of *x*MAl catalysts.

Catalyst	Metal content, x^a (wt. %)	Textural properties			Acid-base properties			Structural phases detected by XRD
		SA^b (m^2/g)	Pore volume, Vg (cm^3/g)	Pore size, dp (⊕)	$n_b{}^c$ (μmol/g)	$n_a{}^d$ (μmol/g)	Ionic potential, q/r	
CeAl	7.0	173	0.41	95.2	16	111	3.96	CeO_2, γ-Al_2O_3
FeAl	7.7	53	0.10	76.7	9	128	4.62	Fe_2O_3, $AlFeO_3$, γ-Al_2O_3
MoAl	8.9	128	0.27	84.1	12	977[e]	9.68	γ-Al_2O_3
γ-Al_2O_3	-	230	-	-	19	24	-	γ-Al_2O_3

[a] by ICP; [b] BET surface areas; [c] by TPD of CO_2; [d] by TPD of NH_3; [e] from reference [19]

Table 2. Non-catalytic and catalytic results obtained during methyl oleate reduction using $NaBH_4$.

Catalyst	Reaction conditions			Results obtained during MO reduction		
	Reaction temperature (K)	MO/$NaBH_4$ molar ratio	Methanol/$NaBH_4$ molar ratio	S_{OA} [a] (%)	X_{MO} or Y_{OA} [b] (%)	r^0_{MO} [c] (mol/hg)
-	308	0.28	6.0	100.0	31.9	-
-	320	0.28	6.0	100.0	40.2	-
-	333	0.28	6.0	100.0	58.6	-
-	333	0.11	6.0	100.0	93.9	-
-	333	0.72	6.0	100.0	21.4	-
γ-Al_2O_3	333	0.11	6.0	100.0	53.0	0.16
CeAl	333	0.11	6.0	100.0	48.8	0.16
FeAl	333	0.11	6.0	100.0	58.7	0.18
MoAl	333	0.11	6.0	100.0	81.6	0.20

[a] during the whole 6-hour experiment; [b] at t = 6 h; [c] Initial MO conversion rate (at t = 0).