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ORIGINAL ARTICLE

Acylation of sugar amides over Algerian bentonite and mcm-41 materials

S. Bellahouel [a,*], E. Belhadj [a], H. Sekkiou [b], R. Hamacha [b], N. Kambouche [a], A. Derdour [a], A. Bengueddach [b]

[a] *Laboratoire de Synthèse Organique Appliquée, Université d'Oran, BP 1524 El M'naouer, Algeria*
[b] *Laboratoire de Chimie des Matériaux, Université d'Oran, BP 1524 El M'naouer, Algeria*

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Abstract The condensation of sugar with fatty acids in an organic media is possible by chemical amidification without fastidious steps by hydroxyl group protection/deprotection. The acylation of sugar (*N*-methyl glucamine) with fatty acids (lauric acid, palmitic acid and stearic acid) is catalyzed in the presence of two inorganic and acid solid catalysts: Algerian clay called bentonite of Maghnia and mesoporous material of type (Al–MCM-41). The results obtained with this last solid (i.e. MCM-41) are very encouraging.

1. Introduction

Glycamide surfactants are non- ionic surfactants in which the hydrophilic moiety (an amino-sugar derivative) and the hydrophobic moiety (a fatty acid) are linked via amide bonds (Hildreth, 1982). This results in a chemical linkage, which is highly stable under alkaline conditions of key interest for many surfactant applications (Hildreth, 1983).

The sugar amides have recently received increasing interest because of their improved surface and performance properties as well as their reduced environmental impact (Bellahouel et al., 1997; Maugard et al., 1997), due to their nontoxic, non- irritating and biodegradable character. These surfactants molecules are largely used in various fields particularly in: food industry (Gong et al., 1994), and cosmetic and pharmaceutical industry (Battiglia et al., 2000). Interesting biological activities were observed (Albasheer et al., 1996; Al-Naoe et al., 1999).

In order to carry out sugar amides syntheses and in particular the selective acylation of sugars, the use of a simple, effective and inoffensive chemical process for health as well as for the environment (Neimer and Blomberg, 2004) is to be considered. This is the purpose of our work, ie: the coupling of the *N*-methyl glucamine with fatty-acids using the bentonite of Maghnia or a mesoporous material (MCM-41) as a catalyst.

The bentonite of Maghnia is a clay largely abundant in west Algeria. It was successfully tested in several catalytic reactions (Saoudi et al., 2003) and environment applications such as water de-pollution (Bouras, 2003).

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* Corresponding author. Tel.: +213 667335513.
E-mail address: salimabellahouel@yahoo.fr (S. Bellahouel).

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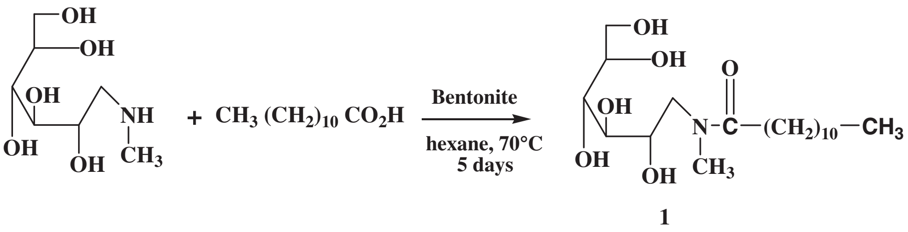
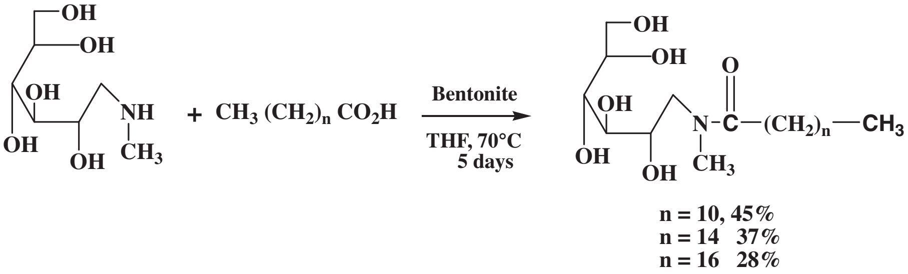


Scheme 1



Scheme 2

Mesoporous materials of the family of M41S were discovered in 1992, and were widely used as supports or catalysts (Beck et al., 1992; Taguchi and Schuth, 2005; Corma et al., 2009). They have an extremely high surface (1000 m^2/g), sizes of the pores going from 20 to 30 Å and a great thermal stability (Galarneau et al., 2001). Our choice was turned toward the aluminic form of the MCM-41 which we protonated in order to exalt the acid properties (Occelli and Biz, 2000).

MCM-41 mesoporous materials have been successfully used for typical acid catalyzed reactions like isomerization (Suguru et al., 2009; Kumar et al., 2004), alkylation (Yamamoto et al., 1998), debenzylation (Itoh et al., 1998) and esterification (Rabindran Jermy and Pandurangan, 2005a,b). Due to their interesting textural properties and their important specific surface, their application (use) in glycochimy is imperative. Several studies showed their effectiveness in the processes of selective alkylation of non- protected mono and disaccharides (Jermy and Pandurangan, 2006; Van der Heijdin et al., 2002).

2. Results

2.1. In the presence of bentonite

No product is obtained, when coupling *N*-methyl-glucamine with a fatty-acid or a fatty acid chloride at room temperature, in the presence of bentonite and solvent (THF, DMF, 2-methylbutan-2-ol).

When working at a temperature of 70 °C, in hexane, an *N*-acylated product 1 is obtained after 24 h with a yield of 6%. Below this temperature, no *N*-acylated product is obtained.

In order to increase the yield, the reaction is carried out again for longer durations. Thus, compound 1 (Lauroyl *N*-methyl-glucamide) is obtained with a yield of 26% after 5 days of reaction (Scheme 1).

The use of the THF under the same conditions gave the same compound with a better yield (45%). Under these same conditions, the couplings of *N*-methyl-glucamine/palmitic acid, or *N*-methyl-glucamine/stearic acid led to their *N*-acylated homologs with a yield of 37% and 28%, respectively (Scheme 2). We note that the yield decreases when the alkyl chain increases.

Such selectivity modifications could be due to changes in the hydrophobicity of the hydrocarbon chain length of the acid. Indeed, the hydrophilicity of the acid decreases as the chain length increases, so that a decrease in the yield with the chain length of the acid should be expected. The same variation was observed by Barrault et al. (2004) in the case of glycerol trans-esterification in the presence of Mg–MCM-41 catalyst.

Since the temperature and the solvent seem to play an important role in the reaction, we have studied their influence on the course of the reaction of coupling the *N*-methyl-glucamine with the lauric acid in the presence of bentonite (Table 1).

According to Table 1, the increase in the temperature gives better yields and we also note that the solvent has a notable influence on the course of the reaction. Indeed, with the DMF, we could reduce reaction time and increase the yield (53%).

Table 1 Influence of solvent and temperature on the coupling of *N*-methyl-glucamine with lauric acid in the presence of bentonite.

Solvent	Temperature (°C)	Time (days)	Yield (%)
Hexane	40	6	No product
Hexane	70	5	26
THF	50	5	No product
THF	70	5	45
THF	80	5	45
DMF	90	1	53

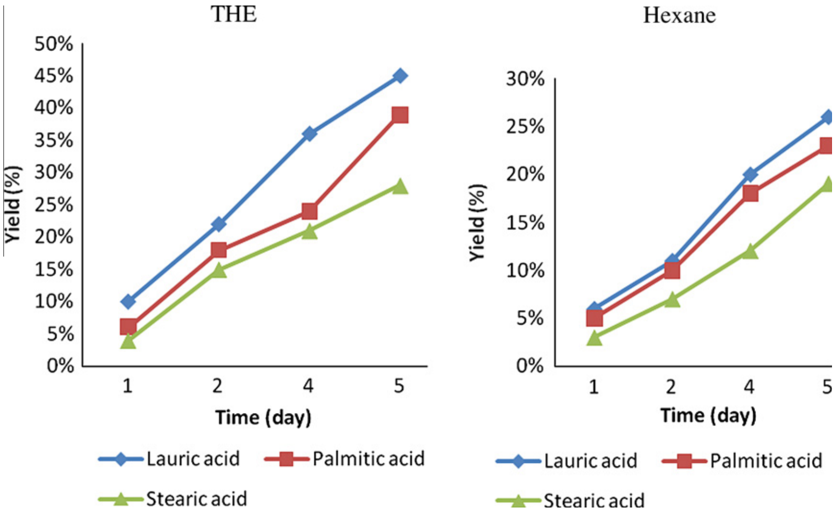


Figure 1 Effect of solvent and fatty chain length on acylation over Algerian bentonite.

Table 2 Influence of time and solvent on the reaction of acylation in the presence of bentonite.

Time (days)	Solvent	Lauric acid (%)	Palmitic acid (%)	Stearic acid (%)
1	Hexane	6	5	3
2	Hexane	11	10	7
4	Hexane	20	18	12
5	Hexane	26	23	19
1	THF	10	6	4
2	THF	22	18	15
4	THF	36	24	21
5	THF	45	39	28

We have studied the influence of time on the course of the coupling reaction of *N*-methyl-glucamine with lauric acid, at 70 °C, in two solvents hexane and THF. The results are represented in Fig. 1.

We noticed that with the hexane (non-polar solvent), products are obtained with poor yields and longer reaction time (Fig. 1). We also note that the reactivity decreases with the increase of the length of fatty chains. Such reactivity modifications could be due to changes in the hydrophobicity of the hydrocarbon chain length of the acid. Indeed, the hydrophilicity decreases as the chain length increases. In the THF, the results are slightly improved.

By using a more polar solvent the 2-methyl butan-2-ol, the *N*-acylated compound is obtained in only 24 h with a better yield (44% in the case of lauric acid).

According to Table 2, the acylation in the 2-methyl butan-2-ol is carried out with shorter durations (2 days instead of 5) with better yields. There is always a reduction of yield with the increase of the fatty chain length.

2.2. In the presence of Al–MCM-41

In search of better yields, we reproduced the process described previously by using the Al–MCM-41 as acid catalyst. The results are represented in Fig. 2.

According to Fig. 2, we notice an important increase of the yield in the presence of Al–MCM-41 compared to bentonite. The same reactivity frequency is found (reduction in the yield with the increase of the fatty chain).

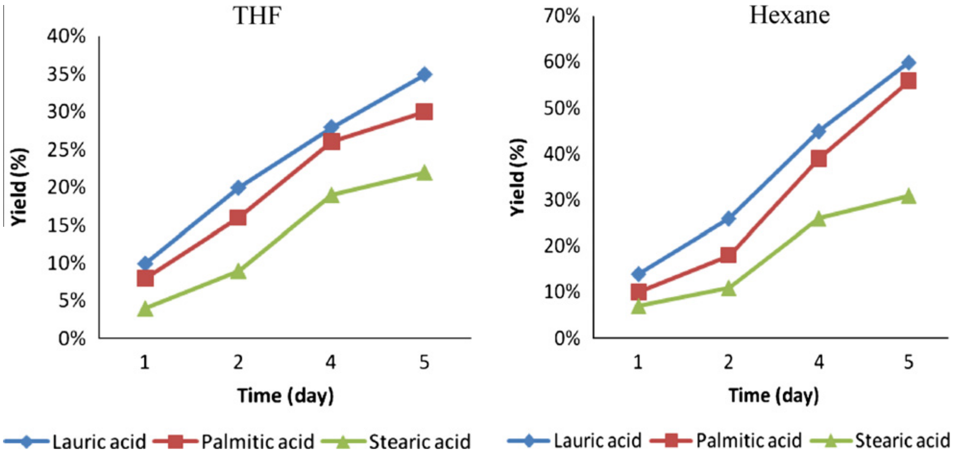


Figure 2 Effect of solvent and fatty chain length on the yield.

Table 3 Amidification in 2-Methyl-butan-2-ol over Al–MCM 41 at 70 °C.

Temperature (h)	Lauric acid (%)	Palmitic acid (%)	Stearic acid (%)
24	49	34	18
48	66	62	55

We have also tested the effect of solvent (2-methyl butan-2-ol) on the course of the reaction. Yields obtained in only 48 h are very conclusive (Table 3).

3. Conclusion

The chemical acylation of amino sugar with fatty-acid, in the presence of the two catalysts bentonite and Al-MCM-41, is regio-selective and led in both cases to a mono-amide without affecting the hydroxyl in C6 position.

The Al–MCM-41 appeared more powerful than bentonite since it allowed better yields.

The use of the 2-methyl butan-2-ol as solvent permits to decrease reaction time and to have better yields than those obtained in the THF and hexane. Thus, it was possible to synthesize di-modular compounds.

The best activity of Al–MCM-41 can be explained by the larger specific area developed by this catalyst compared to bentonite. The circulation of bulky chemical species is thus facilitated. The superiority of Al–MCM-41 over bentonite is probably due to the more efficient interaction between the organic substrate and solid surface caused by the concentration effect inside the ordered hydrophobic mesopores with high-surface area.

In addition, the protonic form of Al–MCM-41 has also acid sites of Lewis as those of Brönsted: because of this fact, the activity in the reaction is clearly improved.

4. Experimental part

NMR spectra were recorded in a Brucker AC 250 MHz (1H, 13C) apparatus. The chemical shifts are given in ppm and the coupling constants in hertz, TMS being taken as internal reference. The signal multiplicities are indicated in miniscule letter: s (singlet), d (doublet), t (triplet), q (quadruplet), m (multiplet).

The IR spectra were recorded on a spectrometer with Fourier transform Ft/IM-4200.

The mass spectra were recorded on spectroscopy JEOL JMSDX 300 according to the Electro Spray (ES). The melting points were taken using a banc Kofler. The analytical chromatographies (CCM) were carried out on an analytical silica plate.

4.1. Preparation and caracterization of solid catalysis

(i) Bentonite: The natural bentonite used in this work, comes from the town of Maghnia (western Algeria) and was used after purification and activation with sulfuric acid. The chemical composition is given in Table 4. The majority components are Silicon and Aluminium with small quantities of other elements such as: Fe, Ca, Na (Table 4). Textural and structural properties of the bentonite are summarized in Table 5.

*(ii) Synthesis of the Al–MCM-41:*The aluminic form of MCM 41 was prepared by hydrothermal synthesis. Three solutions S_1, S_2 and S_3 containing, respectively an aqueous solution of an aluminium source ($Na_2Al_2O_3$) mixed with TEAOH (tetraethylammonium hydroxyde) (S_1), an aqueous solution of silicium (S_2) and an aqueous solution of CTABr (S_3) were mixed. The molar ratio of Si/Al is 50 and the gel chemical composition SiO_2:0.25 CTBr, 0.2 TEAOH, xAl_2O_3, 40 H_2O. The reactional mixture obtained after 2 h of homogenization is heated at 100 °C during 2 days. The products are calcined at 550 °C during 6 h.

For the synthesis of the protonic form of Al–MCM-41:

The product of calcination is mixed with a solution of NH_4Cl (1 M) and refluxed at 60 °C during 2 h. The resulting products are calcined under air atmosphere at 400 °C during 4 h to finally obtain the protonic form of the material H–Al–MCM-41.

Textural and structural properties of this material are summarized in Table 6.

Nitrogen adsorption was performed at −196 °C in a TriStar 3000 V6.04 A volumetric instrument. The samples were outgassed at 80 °C prior to the adsorption measurement until a 3.10^{-3} Torr static vacuum was reached. The surface area was calculated by the Brunauer–Emmett–Teller (BET) method, distribution of pores was evaluated by BJH method (Rabindran Jermy and Pandurangan, 2005b). Powder X-ray diffraction (XRD) patterns of samples dried at 80 °C were collected at room temperature on a Bruker AXS D-8 diffractometer with Cu Kα radiation.

Table 4 Chemical composition of natural bentonite.

	SiO_2	Al_2O_3	FeO_3	MgO	CaO	Na_2O	K_2O	TiO_2
Natural bentonite	65.01	13.65	2.21	0.21	0.50	0.37	0.05	0.19

Table 5 Textural and structural properties of natural bentonite.

	d_{100} (Å)	Surface (m^2g^{-1})	Micro porous volume (cm^3/g)
Natural bentonite	15.01	58	0.0096

Table 6 Textural and structural properties of prepared material a_0 (Å) = 2 $d_{100}/(3)^{0,5}$, a_0: cell parameter.

Catalyst	a_0 (Å)	Surface (m^2g^{-1})	Porous volume (cm^3/g)	Porous diameter BJH (Å)
Al–MCM-41	46.2	1053	0.84	38.65

(iii) Coupling of amino-sugar/fatty acid:

(iv) Coupling with lauric acid: A solution of 0.5 g (1eq, 2.56 mmol) of *N*-methyl-glucamine and 0.51 g (1 eq, 2.56 mmol) of lauric acid in 15 ml of THF are added to 0.1 g of bentonite (or 0.1 g of Al–MCM-41) then refluxed at 70 °C during 5 days. The reaction mixture is then filtered and the bentonite washed several times with methanol. After evaporation of solvent, the *N*-acylate product (**1**) is obtained by precipitation in dichloromethane with a yield of 45%, (Al–H–MCM-41: 60%), R_f = 0.26 (CHCl$_3$/MeOH: 5/5) ninhydrine, T_f = 78 °C. Mass [M + 1] = 378.1 **(ES$^+$). IR** (KBr, solid):

$\nu_{(OH)} = 3285\ \text{cm}^{-1}$, $\nu_{(CH)} = 2800\text{–}2900\ \text{cm}^{-1}$, $\nu_{(CO\text{–}N)} = 1620\text{–}1646\ \text{cm}^{-1}$.

^{1}H NMR/D$_2$O (δ in ppm): 0.8 (t, 3H, CH$_3$), 1.3 (s, 16H, (CH$_2$)$_8$), 1.5 (m, 2H, CH$_2$–CH$_3$), 2.3 (t, 2H, CH$_2$CO), 3.2 (s, 3H, NCH$_3$), 2.5–4 (m, 8H, 2H$_1$, H$_2$, H$_3$, H$_4$, H$_5$, 2H$_6$). **^{13}C NMR**/D$_2$O (δ in ppm): 175 (CO–N), 25.2–36.5 (10 CH$_2$), 14 (CH$_3$), 72.2–74.5 (4 CH–OH), 62.4 (CH$_2$OH), 52.3(CH$_2$N), 37.6 (CH$_3$N).

(v) Coupling with palmitic acid: Same procedure.

Yield = 39% (bentonite), 56% (Al–MCM-41). R$_f$ = 0.29 (CHCl$_3$/MeOH : 5/5) ninhydrine. T$_f$ = 84 °C. Mass [M + 1] = 434.2 **(ES$^+$)**, **IR** (KBr, solid): $\nu_{(OH)} = 3287\text{cm}^{-1}$, $\nu_{(CH)} = 2800\text{–}2900\ \text{cm}^{-1}$, $\nu_{(CO\text{–}N)} = 1620\text{–}1646\ \text{cm}^{-1}$. **^{1}H NMR**/D$_2$O (δ in ppm): 0.8 (t, 3H, CH$_3$), 1.3 (s, 24H, (CH$_2$)$_{12}$), 1.33 (m, 2H, CH$_2$–CH$_3$), 2.18 (t, 2H, CH$_2$CO), 3.2 (s, 2H, NCH$_3$), 2.5–4 (m, 8H, 2H$_1$, H$_2$, H$_3$, H$_4$, H$_5$, 2H$_6$). **^{13}C NMR**/D$_2$O (δ in ppm): 175 (CO–N), 22.7–35.8 (14 CH$_2$), 14 (CH$_3$), 70–73 (4 CH–OH), 63.7 (CH$_2$OH), 51 (CH$_2$N), 37.5 (CH$_3$N).

(vi) Coupling with stearic acid: The procedure is the same as with lauric acid.

Yield = 28% (bentonite), 31.1% (Al–MCM-41), R_f = 0.31 (CHCl$_3$/MeOH: 5/5) ninhydrine.

T_f = 86 °C. Mass [M + 1] = 462.1 **(ES$^+$)**. **IR** (KBr, solid): $\nu_{(OH)} = 3287\text{cm}^{-1}$, $\nu_{(CH)} = 2800\text{–}2900\ \text{cm}^{-1}$, $\nu_{(CO\text{–}N)} = 1620\text{–}1646\ \text{cm}^{-1}$. **^{1}H NMR**/D$_2$O (δ in ppm): 0.8 (t, 3H, CH$_3$), 1.3 (s, 28H, (CH$_2$)$_{14}$), 1.33 (m, 2H, CH$_2$–CH$_3$), 2.18 (t, 2H, CH$_2$CO), 3.2 (s, 3H, NCH$_3$), 2.5–4 (m, 8H, 2H$_1$, H$_2$, H$_3$, H$_4$, H$_5$, 2H$_6$). **^{13}C NMR**/D$_2$O (δ in ppm): 175 (CO–N), 22.7–35.8 (16 CH$_2$), 14 (CH$_3$), 70–73 (4 CH–OH), 63.7 (CH$_2$OH), 51 (CH$_2$N), 37.5 (CH$_3$N).

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