

Acylation of different amino derivatives with fatty acids on UL-MFI-type catalysts*

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Abstract: Acylation of different amino derivatives (ethanol amine, diethanol amine, *N*-aminoethylpiperazine) was carried out under green conditions with oleic acid or tail oil fatty acids. The experiments were carried out using as heterogeneous catalysts mesoporous Al-Meso and UL-ZSM-5 with Si/Al ratios between 100 and 20, in the range of the temperatures 80–180 °C without any solvent or in octane or water. The efficiency of the catalysts for the acylation of the investigated substrates appeared to be directly dependent on the Si/Al ratio and the size of the pores. The selectivity toward esters or amides was firstly controlled by temperature, and then by the Si/Al ratios. Additionally, both the conversion and selectivity were controlled by the solvent in which the reaction was carried out. The use of water led mostly to a mixture of esters and amides.

Keywords: acylation; amino derivatives; oleic acid; mesoporous catalysts; fatty acids.

INTRODUCTION

Selective acylation of fatty acids has multiple applications and leads to valuable products. Acylation of fatty acids with amino alcohols leads to valuable surfactants. In spite of this practical importance, the literature is scarce, and the very few contributions to this subject refer to synthesis of pharmaceutical applications [1]. In biology, *N*-terminal fatty-acylation of sonic hedgehog enhances the induction of rodent ventral forebrain neurons [2]. Some *N*-acyl imidates and heterocyclic amines act as anticancer and antioxidant agents [3].

Esters of fatty acids are integral subunits of various important natural products [4,5]. Often, the formation of these products through acylation poses a problem for which no general solution has been formulated since acylation is impeded by a combination of increased electron density and steric hindrance (*ortho*-substitution) at the acyl carbon center [5]. A solution to this problem might be circumvention through reactivity umpolung with Mitsunobu-type chemistry, but is limited to relatively unhindered alcohol substrates [6].

Conducting polymers with terminal COOH and NH₂ group units have been explored for several applications, including the preparation of new electro-catalytic materials and the construction of biosensors [7]. Acylation with fatty acids is a versatile technique for preparing such materials.

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One of the major problems encountered in these syntheses is the regioselectivity. For the regioselective acylation of the primary hydroxyl group of unprotected sugars with fatty acids, the literature made frequent reference to the use of lipases and proteases [8]. The enzymatic acylation of sugars with fatty acids can be accomplished in organic solvents [9], in a minimum of organic solvent (adjuvant technique) [10], or solvent-free [11]. Recently, supercritical CO₂ has also been used [12]. Insulin is also stimulating fatty acid acylation of various proteins [13].

O- or N-acylation is evidently leading to compounds with different properties [14]. To control O-acylation, Kihara et al. [15] suggested the use of trifluoromethanesulfonic acid as catalyst in the presence of crown ether. Another serious problem concerns the conditions in which these reactions are carried out. Most of the reported acylations occur under very non-green conditions, using fatty acid chlorides and homogeneous Lewis acid catalysts.

This aim of this study was to investigate a green route for the acylation of different amino derivatives with oleic or tail oil fatty acids. Following this route, it was intended to prepare surfactants as additives for road working, exhibiting free OH or NH₂ groups. To fulfil these objectives, instead of enzymes, this study proposes the use of heterogeneous catalysts, which are easier to handle and more robust vs. operation conditions and recycling. Since the molecules subjected in this reaction are very large, this study proposes the use of a new family of mesoporous catalysts, i.e., of Al-Meso and UL-MFI-type ones. These are mesoporous materials with amorphous walls (Al-Meso) or with semi-crystalline zeolitic mesopore walls exhibiting a ZSM-5 structure (UL-MFI). Details about their synthesis have been presented elsewhere [16]. The regioselectivity was expected to be controlled by combining the shape-selectivity concept conferred by the mesopores and the acidity conferred by the zeolite structure. For the same reasons, the acylation was carried out without any solvent or in water or octane.

EXPERIMENTAL

UL-MFI materials were prepared according to the synthesis method described previously [16]. Mesostructured precursors having Si/Al ratio from 100 to 20, designated as Al-Meso-*x* (where *x* is the atomic Si/Al ratio), were synthesized using SiCl₄ and AlCl₃ as silicon and aluminum sources, respectively, and Pluronic P123 in ethanol as surfactant. UL-ZSM-5 materials were obtained from surfactant containing the above precursors, which were impregnated with 10 % aqueous solution of tetrapropylammonium hydroxide followed by drying for several days. The solid-state crystallization was performed at 120 °C for different lengths of time in a Teflon-lined autoclave after the addition of a small quantity of water not contacting the sample. Gel and catalyst composition are given in Table 1. The final partially crystalline products were dried in air at 80 °C and calcined at 550 °C for 6 h to remove organics. The effect of crystallization conditions on the mesopore structure as well as the crystalline phase has been obtained from nitrogen adsorption experiments, and from X-ray diffraction (XRD) patterns.

Table 1 Chemical composition and textural characteristics of the investigated catalysts.

Catalyst	Si/Al ratio		S _{BET} (m ² g ⁻¹)	Mesopore volume (cm ³ g ⁻¹)	Mesopore diameter (nm)	Crystallinity (%)
	in gel	in product				
Al-Meso-100	100	100.2	800	1.626	6.9	–
Al-Meso-50	50	50.8	745	1.586	6.2	–
Al-Meso-20	20	20.3	680	1.424	5.4	–
UL-ZSM-5-100	100	100.5	440	1.235	30.0	58
UL-ZSM-5-50	50	51.3	470	1.275	32.5	60
UL-ZSM-5-20	20	21.2	395	1.205	27.0	40

The adsorption/desorption isotherms were collected on an Omnisorp-100 sorptometer at liquid nitrogen temperature (77 K). All the calcined samples were degassed at 200 °C and 10^{-5} mmHg for at least 4 h before adsorption measurements. The specific surface areas (SBET) of the samples were calculated from adsorption isotherm data using the Brunauer–Emmett–Teller (BET) method. The micropore volume was also calculated from the nitrogen adsorption branch using an as-plot method, while the pore diameter and mesopore volume were obtained from the nitrogen desorption branch using the standard Barrett–Joyner–Halenda (BJH) method. Textural characteristics of these catalysts are given in Table 1.

Powder XRD patterns were recorded on a Philips X-ray diffractometer using nickel-filtered $\text{CuK}\alpha$ radiation. The acidity was studied using the pyridine adsorption/desorption experiments. Prior to pyridine adsorption, the sample wafers were evacuated overnight at 400 °C under high vacuum followed by pyridine adsorption at room temperature. Subsequently, the wafers were evacuated at various temperatures. The Fourier transform infrared (FTIR) spectra were recorded using a Biorad FTS-60 spectrometer on sample wafers.

Batch catalytic tests were performed by reacting oleic acid or tail oil fatty acid (1 mmol) with ethanolamine, diethanol amine, or *N*-aminoethylpiperazine (1 mmol) in the presence of 30 mg catalyst in a range of temperatures (room temperature to 180 °C) with octane, water, and without solvents. The experiments were carried out in a 50-mL Teflon-lined autoclave, under a vigorous stirring. To make a correct quantification of each component, all the products were analyzed by high-performance liquid chromatography (HPLC) and FTIR techniques. Blank experiments, namely, acylation of the investigated substrates with the fatty acids without any catalysts has been carried out as well.

HPLC analyses were performed using a Varian Prostar liquid chromatograph consisting of a quaternary pump, a solvent degasser, manual injection, a column oven, and a wavelength UV detector. The reaction products were analyzed in the following elution conditions: Chromspher C18 column, 5 μm , 150×4.6 , mobile phase: 10 % aqueous component (with 0.3 % H_3PO_4); 90 % methanol with 0.3 % H_3PO_4 , detection: 215 nm.

RESULTS AND DISCUSSIONS

Figure 1 presents the XRD patterns for the investigated UL-MFI catalysts as well as Al-Meso-50 and ZSM-5-50 as references. These patterns display distinct broad diffraction peaks in the 8–10 and 20–25° 2θ ranges, which is consistent with the ZSM-5-50, while Al-Meso-50 did not show any crystalline features. The crystallinity of these samples was established considering ZSM-5-50 as being 100 % crystalline. The respective values are reported in Table 1.

All four UL-MFI samples have crystallinity higher than 40 %. The crystallinity increased in the order UL-ZSM-5-20 < UL-silicalite < UL-ZSM-5-100 < UL-ZSM-5-50.

Figure 2 shows the FTIR spectra after pyridine desorption at 200 °C of UL-ZSM-5-50, Al-Meso-50, and ZSM-5-50 for comparison. These results clearly indicate that the density of Brønsted acid sites in UL-ZSM-5-50 is higher than in Al-Meso-50. However, all samples have lower densities of Brønsted acid sites than purely crystalline ZSM-5-50. In these studies, the overall content of Brønsted acid sites in UL-ZSM-5 (medium-strong) materials was found to be intermediate between those of Al-Meso (medium) and ZSM-5 (strong). On the other hand, the intensity of the bands corresponding to Lewis acid sites ($1446\text{--}1455\text{ cm}^{-1}$) decreases in the following order: Al-Meso-50 > UL-ZSM-5-50 > ZSM-5-50. The decrease in Lewis acidity was assigned to the elimination of the hexa-coordinated extra-framework aluminum, which may exist in the semicrystalline walls of UL-MFI materials after treatment with diluted aqueous solution of NaCl or NH_4Cl .

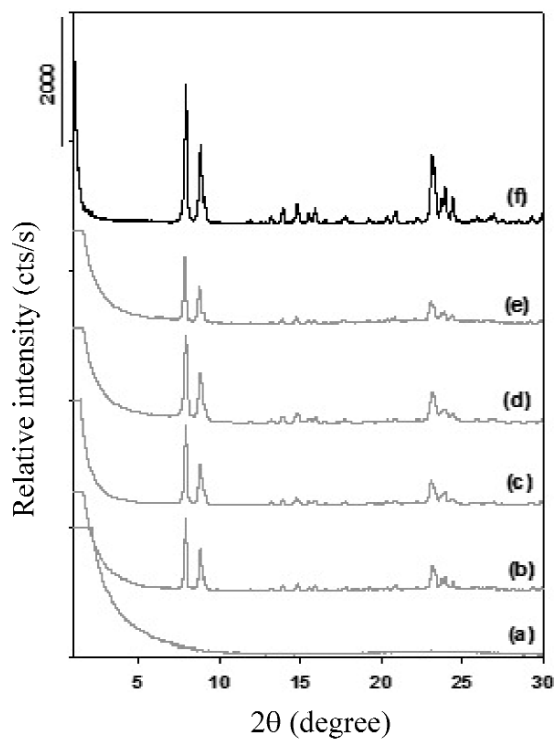


Fig. 1 XRD patterns (a) Al-Meso-50, (b) UL-silicalite, (c) UL-ZSM-5-100, (d) UL-ZSM-5-50, (e) UL-ZSM-5-20 (f) ZSM-5-50, shifted by 0, 1000, 2400, 3600, 5100, and 6800 cts/s, respectively.

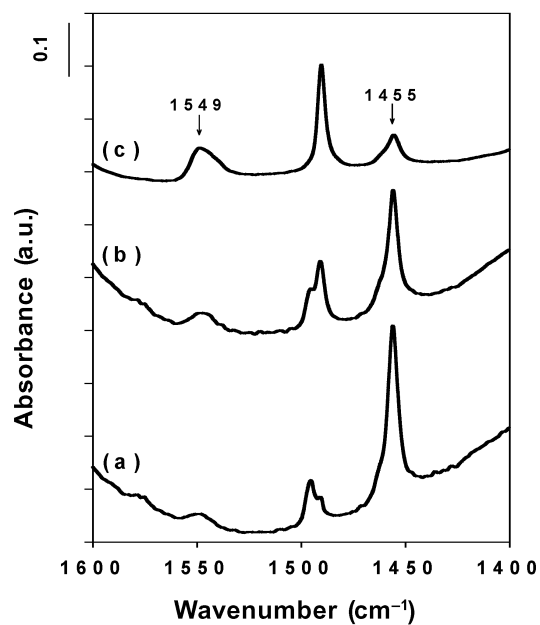


Fig. 2 FTIR spectra of adsorbed pyridine in the 1400–1600 cm^{-1} range for (a) Al-Meso-50, (b) UL-ZSM-5-50, and (c) ZSM-5-50 following thermal treatment at 200 °C.

Acylation of ethanolamine with oleic acid

Acylation in the absence of any solvent

Figure 3 describes the acylation of ethanolamine with oleic acid at different temperatures on catalysts with Si/Al ratio of 20 in absence of any solvent. The Si/Al ratio of 20 corresponded to the most active and selective catalysts in the respective series. The main reaction products are the ester and amide indicated in Scheme 1. Blank experiments indicate that this reaction also takes place in the absence of the catalysts, but the yields in ester at lower temperatures and in amide at high temperatures are rather low, leaving un-reacted oleic acid. Besides this aspect, up to 80 °C, there was no reaction of oleic acid. The presence of the catalyst enhanced the yields and controls the selectivity.

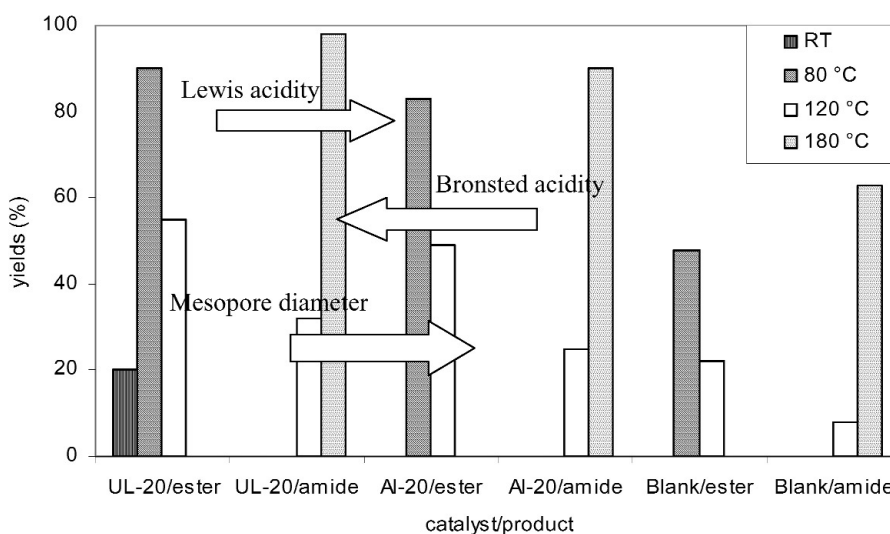
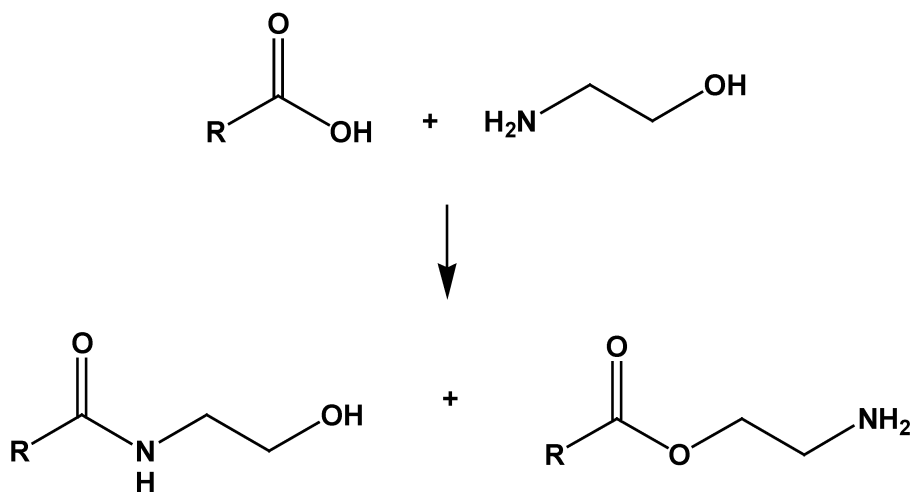


Fig. 3 Acylation of ethanol amine with oleic acid without solvent (30 mg catalyst, 4 mmol oleic acid, 4 mmol ethanolamine, 4 h).



Scheme 1 Acylation of ethanolamine with oleic acid (R: C₁₇H₃₃-).

Up to 120 °C, the predominant reaction is the esterification of the OH. For temperatures higher than 120 °C, the acylation of the NH₂ group starts to predominate, and the NH-acylated compound becomes the most important product. Data presented in Fig. 3 might suggest that the increase of the Lewis acidity exhibits a positive effect on this reaction. Actually, this increase should be also correlated to the increase of the pore size. In accordance, the conversion was higher on UL-ZSM-5 catalysts, than on Al-Meso. On the other side, the selectivity to desired products, i.e., esters up to 120 °C, and amides around 180 °C, was found to be correlated with the acidity of these catalysts. For both series, the catalysts with Si/Al 20 led to the higher yields in the desired products.

Summarizing, it results that as a function of the temperature, using UL-ZSM-5 catalysts it is possible to produce selectively the ester or the amide.

Acylation in octane and water

For the reactions carried out in the absence of any solvent, once the reaction advanced, the viscosity also increased. Therefore, the presence of a solvent can make the mixing of the reactants with the catalysts easier. The selection of the solvents has been made following the green chemistry principles. Accordingly, we selected octane and water.

Like for the experiments made without solvents, the blank experiments carried out in octane corresponded to small yields, while using catalysts, the best results were obtained with those with the Si/Al ratio of 20 (Fig. 4). Again, among the different catalysts, UL-ZSM-5-20 led to the higher yields, which is a confirmation of a good correlation between the textural characteristics and the acid properties of this catalyst.

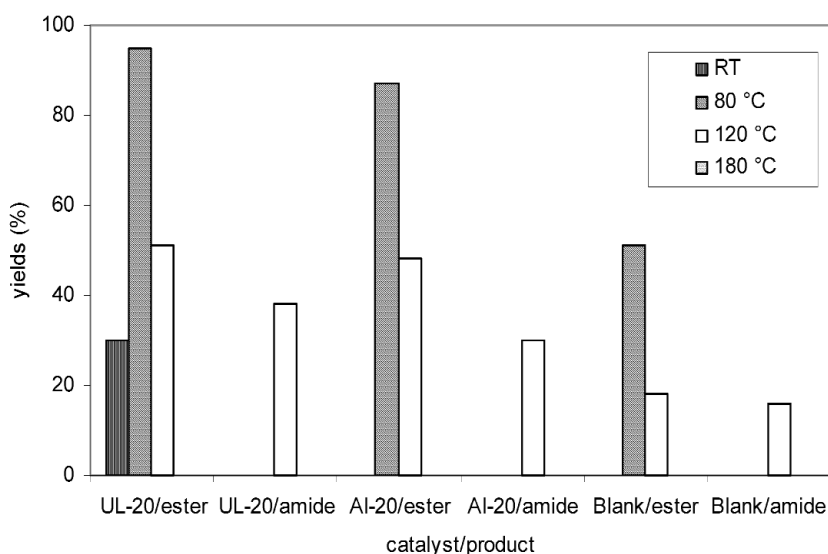


Fig. 4 Acylation of ethanol amine with oleic acid in octane (4 h, 30 mg catalyst, 1 mmol oleic acid, 1 mmol ethanolamine, 10 mL octane).

As a specific behavior, for the experiments carried out in octane, for each catalyst the yields in esters resulted at 80 °C were superior to those determined in the tests carried out without any solvent, while at higher temperatures, the yields in amides were smaller.

Figure 5 shows the behavior of the two series of catalysts in acylation of ethanol amine with oleic acid in water at 120 and 180 °C, respectively. Working in water corresponded to a change in the yields as compared with the experiments carried out without any solvent or in octane. As expected, the yields were smaller, in agreement with the thermodynamics of this reaction, since water is a reaction product.

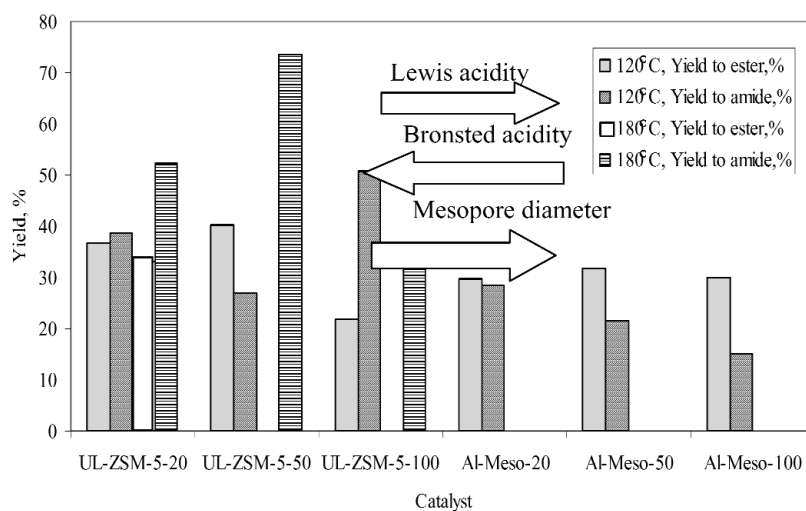


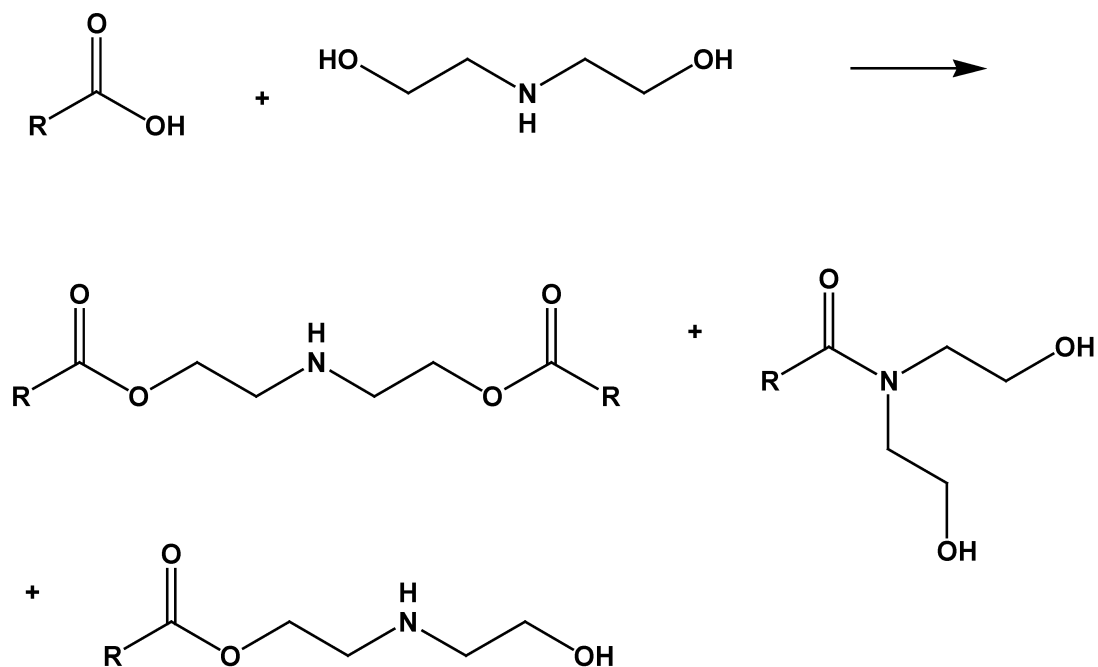
Fig. 5 Acylation of ethanol amine with oleic acid in water at 120 and 180 °C, octane (4 h, 30 mg catalyst, 1 mmol oleic acid, 1 mmol ethanolamine, 10 mL).

Except for UL-ZSM-5-100, at 120 °C, instead of a pronounced selectivity to ester, a mixture of ester and amide resulted for all the catalysts. Such a behavior may account for an interaction of water with the surface of the catalysts keeping a high concentration of Brønsted acid sites. As expected, FTIR spectra collected for the samples treated outside the cell with a 1000 ppm H₂O/He flow indicated indeed an important increase of the intensity of the band assigned to OH groups (spectra not shown). The increase of the temperature at 180 °C led to increased yields of amide. However, on UL-ZSM-5-20, which was still the most active catalyst in the investigated series, the selectivity in amide was the smallest in the UL-ZSM-5 series, indicating that the effect of water is still persisting at this temperature.

Summarizing, working in different solvent conditions led not only to a different catalytic behavior, but also to a different selectivity to the different products. It is worth noting that for the application it was intended to prepare these surfactants, i.e., as additives for road working, there are cases in which a mixture of esters and amides is necessary. In conclusion, the selectivity of this reaction can be tuned, changing the solvent, or the solvent composition.

Acylation of diethanolamine with oleic acid

Scheme 2 indicates the main reaction products in acylation of diethanolamine with oleic acid. From this reaction, it may result in either an amide exhibiting two free OH groups, or two esters, one still exhibiting a free OH group, or a diester. Therefore, for this reaction, the control of the selectivity becomes even more important. Working without any solvent, on the best catalyst (UL-ZSM-5-20) at 80 °C predominated the monoester (70 % selectivity), at 120 °C the dominant product was the diester (60 % selectivity), and at 180 °C the amide (85 % selectivity). Using water as solvent led to an additional drop in the selectivity in the range of all the investigated temperatures. Figure 6 shows the behavior of these catalysts in acylation of diethanolamine with oleic acid at 180 °C using water as solvent. Except for UL-ZSM-5-50 and Al-Meso-100, the amide was still the dominant product. The decrease of the Si/Al ratio paralleled the decrease in the selectivity to amide, and for Al-Meso-100 the monoester was the main reaction product even at 180 °C.



Scheme 2 Acylation of diethanolamine with oleic acid (R: C₁₇H₃₃-).

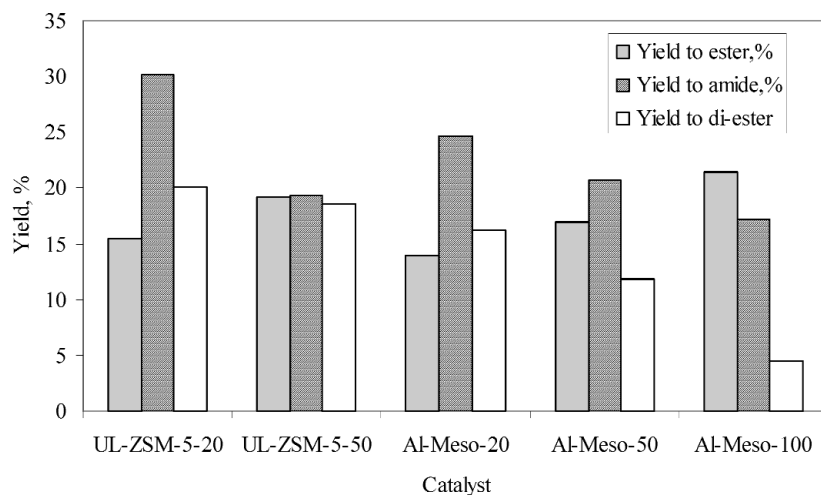
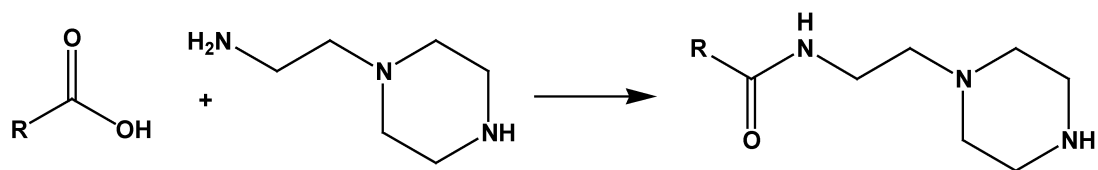


Fig. 6 Acylation of diethanol amine with oleic acid in water, 180 °C (4 h, 30 mg catalyst, 1 mmol oleic acid, 1 mmol ethanolamine, 10 mL).

The effect of the pore size was more evident in this case, in good agreement with the molecular size of these products. Thus, the conversion of oleic acid was smaller than in the case of acylation of ethanolamine with oleic acid irrespective of the catalyst. Under the investigated conditions, on UL-ZSM-5-20, which was still the most active catalyst, the conversion was smaller than 70 %.

Acylation of N-aminoethylpiperazine with fatty acids

Acylation of *N*-aminoethylpiperazine with fatty acids led to one single product, i.e., the amide indicated in Scheme 3. The reaction occurred also in the absence of the catalyst, but as in the previous cases, the conversions were smaller than 30 % in the investigated time.



Scheme 3 Acylation of *N*-aminoethylpiperazine with fatty acids (R: C₁₇H₃₃-; tail oil).

The results collected for the experiments carried out in water by comparison with experiments carried out in the absence of any solvent indicated only a partial decrease of the yields. This was due to the decrease of the conversion since the selectivity to amide was total in all the experiments. This behavior is in agreement with the results we obtained in water using the other substrates and should be associated with the increase of the population of the Brønsted acid sites. As expected, the increase of the temperature led to higher conversions of the fatty acids. While at 120 °C the maximum in conversion on UL-ZSM-5-20 was smaller than 70 %, at 180 °C a total conversion of oleic acid was determined (Fig. 7). Replacing oleic acid with tail oil fatty acid corresponded to an increased conversion. This occurred as well in experiments carried out without any solvent and for the experiments carried out in water (Fig. 7).

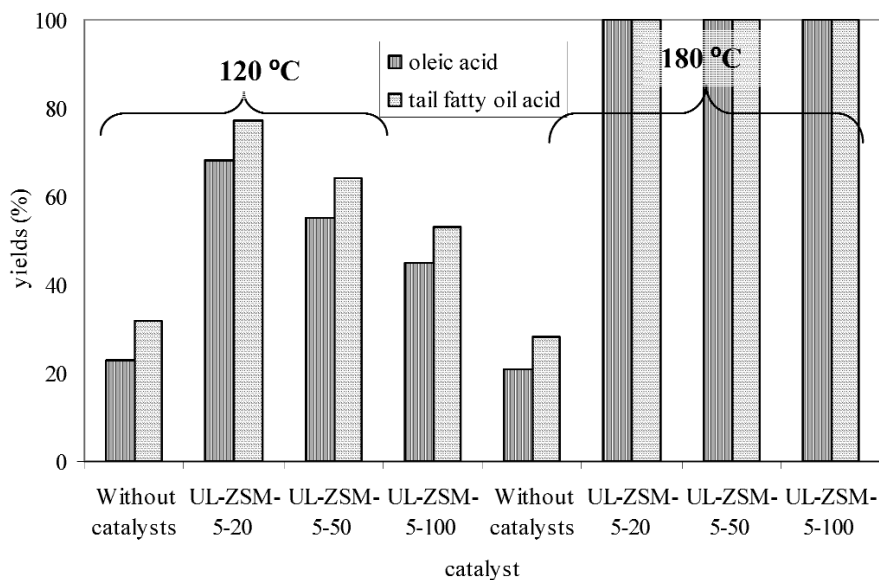


Fig. 7 Acylation of *N*-aminoethylpiperazine with fatty acids on UL-ZSM-5 catalysts at 120 and 180 °C (4 h, 30 mg catalyst, 1 mmol oleic acid, 1 mmol ethanolamine, 10 mL water).

CONCLUSIONS

Acylation of various amino derivatives with fatty acids was achieved with good conversion and selectivities using large porous acid materials under green conditions. The conversion of the investigated substrates was directly dependent on the Si/Al ratio and the size of the pores. This study demonstrated that this acylation can be carried out under green conditions: directly with fatty acids, in the absence of any solvent or in water or octane. The nature of the solvent influenced the selectivity to ester and amide. The use of water led mostly to a mixture of esters and amides.

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