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Catalysis Today 75 (2002) 177–181

CATALYSIS TODAY

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Catalysis and fine chemistry

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Abstract

Triglycerides from vegetable oils are very important raw and renewable materials for the preparation of products useful for foods, pharmaceutics, cosmetics, From the methanolysis or hydrolysis of that glycerides, methyl esters or fatty acids and glycerol are obtained. Furthermore it is demonstrated in this paper that solid and basic materials may replace the usual homogeneous catalysts with the same activity and selectivity but without formation of by-products and wastes. Moreover, in the presence of mesoporous solids with an accurate pore size the glycerol is selectively transformed to linear di and triglycerol; and a yield of more than 80% is obtained. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Diglycerol; Triglycerol; Glycerol esterification

1. Introduction

The following analysis is found in a recent document about the development of catalysis [1]: catalysis is a privileged way to a clean and powerful chemistry. Without being consumed, a catalyst is a mean to: (i) obtain new structures, (ii) increase the productivity, (iii) decrease the raw material and energy consumption, (iv) minimize the wastes production and get a better environment. Therefore, 80% of the industrial reactions use catalysts. The British agency Frost and Sullivan, which published a study in 1998 [1] evaluates the catalysts European market to $ 3.7 billions turnover in 1998. With about 4% growth per year, it should tend to $ 5 billions in 2005. Catalysis in chemistry—from intermediate products to fine chemistry—represents about a quarter of the market. The other sectors are car industry, polymer industry, refining, and environment.

In the field of fine chemistry (including reactions starting from the renewable products (agroressources)), about 80% of the reactions are done without catalyst, so that one may expect for the next future:

- A particular interest for the reactions using less raw materials and energy, and leading to 100% selective processes without formation of wastes.
- An important development of catalysis and biocatalysis (for example, immobilized enzymes).
- The significant use of chiral catalysis in the industrial processes in order to obtain enantiomeres (Frost and Sullivan suggested that in the pharmaceutical market of about $ 270 billions, chiral molecules represent about $ 90 billion [1]. The “natural chiral pool” should be more often used to obtain the desired products or synthesis intermediates.

Moreover, these orientations are included in the Chemical Sciences Department of CNRS report “La Chimie à l’aube du 3$^{\text{ème}}$ millénaire”, published in the second trimester of 1999 [2] and in the European and North American Programs [3–5].

The goal of Fine Chemistry is, therefore, the selective and now the clean synthesis of molecules—often polyfunctional—currently using multistep processes. In order to reach this goal and to simplify the known

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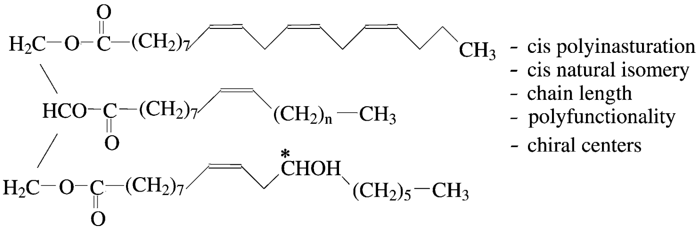
PII: S0920-5861(02)00062-7



Scheme 2. Example of tryglyceride structure.

processes, we have to implement new catalytic steps called *chemio-*, *regio-* or *enantioselective* steps.

Until recently, the catalysts coming from the petrochemistry could not be used for such reactions because of their poor selectivity.

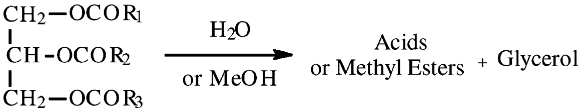
The development of fine chemistry, the renewing of organic synthesis, the association of coordination chemistry, modelization, supramolecular chemistry, and recently of combinatorial chemistry allow to imagine the synthesis of better catalysts and then a higher selectivity in much more multistep reactions.

2. Agroresources, catalysis and fine chemistry

The unavoidable disappearing of the fossil carbon compounds reserves and the numerous environmental problems lead to a growing interest for the use of renewable raw materials, more especially because they already have very important and complex patterns, which are expensive to fully synthesize.

From easily growing plants (soya, colza, sunflower, palm, olive, etc.), vegetable oils and some minor products can be easily extracted, from which the interest of developing catalysis processes (especially with heterogeneous catalysts) will clearly appear in the following paragraphs.

Vegetable oils are triglycerides, and their hydrolysis or methanolysis leads to acids or methyl esters and glycerol as a side-product (Scheme 1).



Scheme 1. Hydrolysis or methanolysis of triglycerides.

The catalysts used are often homogenous acids or bases even if some of them are solids at the beginning of the reaction.

The hydrocarbon chain of the acids or methyl esters can be extremely different and represents a starting point for many reactions (Scheme 2).

Apart of the triglycerides and of the glycerol, other compounds, called minor constituents have also a great importance: phosphatides, cerides, sterols, chlorophylls, as well as some degradation products [6].

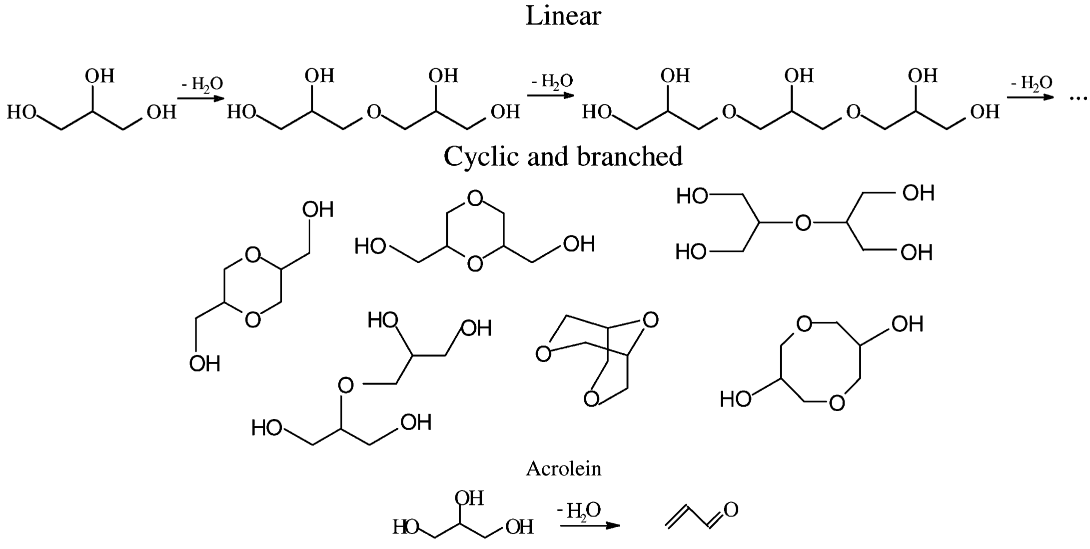
Using these compounds as reagents for the selective synthesis of valuable products (amines, amides, alcohols, ethers, esters, etc.) implies the making of polyfunctional catalysts. Moreover, mastering the porosity—mostly the mesoporosity—of these materials is very important for polar or heavy products. At last, these catalysts must be stable in polar media and in the presence of unusual products in heterogeneous catalysis.

3. Some reactions: selective transformations of glycerol

Glycerol, the side-product of the triglycerides hydrolysis or methanolysis (Scheme 1), can be the starting reagent for monoglycerides, polyglycerols and polyglycerols esters preparation; these compounds having numerous applications in foods, cosmetics and detergent industries.

3.1. Polyglycerol synthesis

Previous works showed that the selectivity of the glycerol etherification was similar to a pseudo-polymerization and that a mixture of linear and cyclic polyglycerols was obtained especially in the presence of



Scheme 3. Reactions from glycerol.

homogeneous catalysts such as sodium, potassium hydroxide or carbonate [7–10] (Scheme 3).

The synthesis of a desired polyglycerol by a chemical route is rather difficult and expensive as shown in recent works [11,12]. On the other hand, the use of a selective and solid catalyst should be of a great interest [13]. In order to get such selectivity, especially to di and triglycerols, we have prepared nanostructured and basic materials from a modification of a method proposed by Kloestra et al. [14].

The results reported in Table 1 clearly showed that the homogeneous catalysts were very active but not selective.

On the other hand, mesoporous and basic materials were not so active but a 100% selectivity to di and triglycerol was obtained at a 80% glycerol conversion which was a quite new result never obtained before in such conditions.

The characterizations of the mesoporous structures before and after deposition of cesium showed these important facts [15]:

- A significant decrease of the BET surface area and of the XRD peaks intensity could indicate a partial collapsing of the structure in the basic media required for the cesium addition.
- The transmission electron microscopy (TEM coupled with elemental analysis EDX) showed that even if there were structure changes, it still appeared some well-defined mesoporous domains (ϕ3.7 nm) after the cesium addition and the catalytic reaction.

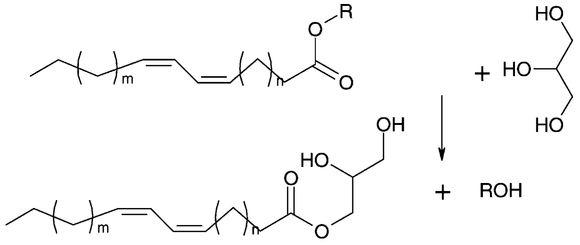
Table 1
Activity and selectivity of some catalysts in the glycerol etherification[a]

Catalyst	Glycerol conversion (%) after 8 h (24 h)	Selectivity (%) after 8 h (24 h)			
		Diglycerols	Triglycerols	Tetraglycerols	Others
Na_2CO_3	94	27	31	21	21
$K5/Al_2O_3$	42 (62)	83 (65)	17 (31)	0 (3)	0 (1)
Meso Al(20)[b]	9 (21)	74 (91)	26 (9)	0 (0)	0 (0)
Meso Cs_{25}Al (20)[c]	25 (80)	100 (80)	0 (20)	0 (0)	0 (0)

[a] Experimental: $T = 260\,^{\circ}C$, batch reactor, 50 g of glycerol without solvent, catalyst = 2 wt.%.

[b] (20) represents the atomic Si/Al.

[c] Cs_{25} means that 25×10^{-4} mol of Cs was deposited over the Meso Al(20) support.



Scheme 4. Glycerol esterification (R = H) and transesterification (R = CH_3) examples.

- These characteristics could explain the very high selectivity to di and triglycerol even in the presence of amorphous domains which are in fact inactive.

3.2. Glycerol esterification

Glycerol monoesters (monoglycerides) can be obtained from glycerol esterification with fatty acids or from glycerol transesterification with fatty methyl esters (Scheme 4) in the presence of homogeneous catalysts similar to that reported above. Such reactions give naturally a mixture of mono, di and triesters (40, 50, 10%) and a great amount of salts and by-products [6].

A molecular distillation as well as various purification and decoloration steps are necessary to get high purity products especially monoglycerides. The transesterification step in the presence of solid and basic materials was first studied in order to replace such homogeneous catalysts.

A general survey of basic solids is reported in Table 2 [16].

The results indicated that basic and solid catalysts such as MgO and CeO_2 can easily replace homogeneous catalysts while having the same selectivity. Over lanthanum oxide which was also very active there was a formation of acrolein coming from the glycerol dehydration. In fact, the turnover number increased with the increase of the global basicity and the secondary reaction observed with La_2O_3 seemed to be due to the presence of some strong acid sites identified from NH_3 thermodesorption experiments.

The comparison of the formation of esters obtained in the presence of these solids showed that the nature of the oxide had a low effect on the selectivity. The esters repartition was rather similar to that obtained with homogeneous basic catalysts. This could be explained by the fact that these catalysts cannot induce a “shape selectivity” coming from the use of a material with a controlled pore size.

In a second step of this work, the changes of catalytic properties coming from the modification of the basicity of magnesium oxide were discussed.

In order to increase the basicity of magnesium oxide, alkali-doped magnesium oxides were synthesized. The properties of some of these oxides are presented in Table 3.

Adding an alkali element in the MgO structure led to a decrease of the BET surface area. Moreover, the addition of lithium gave a more basic solid, whereas adding sodium decreased the basicity of the resulting

Table 2
Activity and selectivity of some basic oxides in the transesterification of methylstearate with glycerol[a]

Catalyst	Basicity[b], μmol g^{-1} (μmol m^{-2})	S_{BET} ($m^2\,g^{-1}$)	Activity (mmol $h^{-1}\,g^{-1}$)	Conversion[c] (%)	Selectivity (%)		
					Mono	Di	Tri
Without	–	–	–	2.5	100	0	0
ZnO[d]	21 (0.6)	33	4.5	18	80	20	0
MgO[e]	345 (2.3)	151	20.2	80	38	50	12
CeO_2[f]	345 (2.6)	135	20.7	82	42	52	6
La_2O_3[g]	80.6 (18)	5	24.5	97	28	61	11

[a] Experimental: methylstearate/glycerol (m/m) = 1, $T = 220\,^{\circ}C$, catalyst = 2.7 wt.%.
[b] From CO_2 adsorption.
[c] Methylstearate conversion.
[d] From zinc carbonate.
[e] Hydrolysis and calcination of a sample prolabo.
[f] From cerium citrate.
[g] Sample from prolabo.

Table 3
Physicochemical and catalytic properties of alkali-doped magnesium oxides

Catalyst	Alkaline (wt.%)	S_{BET} ($m^2\,g^{-1}$)	Basicity, $\mu mol\,g^{-1}$ ($\mu mol\,m^{-2}$)	Activity ($mmol\,g^{-1}\,h^{-1}$)	Selectivity[a]	
					Mono	Di
MgO		151	345 (2.3)	20.2	38	58
Li/MgO	0.9	20.8	303 (14.6)	44.2	37	54
Na/MgO	0.73	50.6	168 (3.3)	17.9	36	55

[a] Conversion = 80%.

oxide, which could be due to the respective size of the cations. Indeed, Na^+ is bigger than Li^+ and Mg^{2+}, which have a similar size. So, lithium ions were inserted more easily in the framework of MgO and then led to the creation of oxygen gaps, which are responsible for the strong basicity.

The catalytic properties also reported in Table 3 showed that the activity increased with the addition of lithium without change of the selectivity. In fact, we have shown from the substitution of different alkaline element that there was also a direct relationship between the activity and the basicity of the catalyst as in the previous case.

Of course, the next step was the preparation and use of mesoporous basic catalysts for the formation of monoglycerides, but up to now, we got a mixture of polyglycerols and glycerol esters. It follows that the reaction conditions so that new catalysts preparation are under investigation in order to get the desired reaction.

4. Conclusion

The use of solid catalysts in the transformation of renewable products such as glycerol is of great interest for the synthesis of high-valuable products cheaper and more efficient that with the classical methods. Several reactions can be carried out, giving good quality (often better quality) products while creating few wastes. In the present paper, we demonstrated that the selective synthesis of di and triglycerol could be done over new mesoporous and basic materials without leaching of the basic element. At a glycerol conversion of 80–90%, a yield higher than 80% was obtained.

Concerning the glycerol esters preparation, it was shown that the homogeneous catalysts could be replaced by solid and basic catalysts while keeping the same selectivity. Moreover, the clear relationship was established between the rate of transesterification and the global basicity of the catalysts and we are now looking for the preparation of new mesoporous, basic and solid catalysts for the selective synthesis of monoglycerides.

Acknowledgements

The authors gratefully acknowledge support from the European Community “FAIR Program” and from ADEME-AGRICE (France).

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