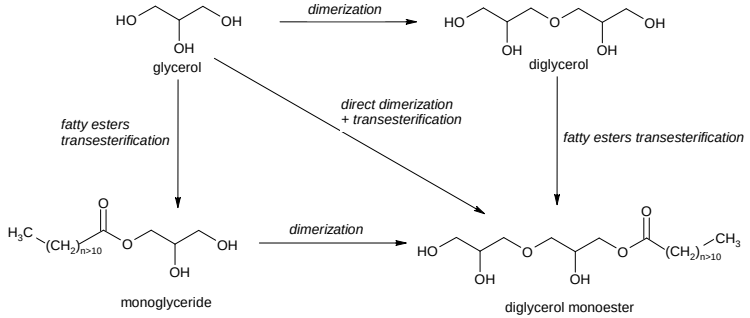
Designed of modified mesoporous silica for selective preparation of diglycerol esters in one-step process.

Yannick POUILLOUX, Alfonso E. RAMIREZ, Gwenaelle CHARLES, Joël BARRAULT
Laboratoire de Catalyse en Chimie Organique, UMR6503 CNRS-Université de Poitiers, ESIP, 40 avenue du recteur Pineau, 86002 Poitiers Cedex, France.
E-mail: yannick.pouilloux@univ-poitiers.fr; Fax: 33 5 49 45 39 99; Phone: 33 5 49 45 35 40; website: http://labo.univ-poitiers.fr/umr6503.

Introduction

As an alternative to the exhaustion of the earth petroleum reserves, intensive efforts over the last decade were directed towards the chemical potentialities of agroressources which represent a huge renewable natural carbon sources. However, molecules extracted from biomass are often polyfunctionalized and the catalytic control of the regio-, chemio- or enantioselectivity is a tremendous challenge to avoid many protection and deprotection steps.
One of our main research interests consists in designing new solid catalysts able to selectively react with one of the chemical functions of these molecules (1-4). The direct glycerol transformation into polyglycerol esters is a remarkable illustration since only the resulting low substituted polyglycerol have significant applications as biodegradable emulsifiers (5).

In this paper, the catalytic control of the glycerol oligomerization and its selective esterification over well ordered mesoporous silica is presented. The comparison between homogeneous and heterogeneous catalysts will be also discussed.



***Scheme 1**: catalytic pathway for the selective monoglycerides and diglycerol esters synthesis*

Materials and Methods

The catalytic glycerol polymerization was carried out without solvent at 260°C and catalyzed either with homogeneous (Na_2CO_3) or heterogeneous catalysts. The heterogeneous catalyst is a MCM-41 mesoporous silica modified by impregnation of basic promoters. The esterification reaction was performed with glycerol or diglycérol and fatty methyl esters in a molar ratio of 1 at 240°C

Impregnated Mesoporous Materials are prepared as following : a certain amount of alkali or alkaline earth salt is added to 5 g of pure silica or aluminosilica mesoporous material, prepared (with cethyltrimethylammonium bromide) as described above (5) and 50 g of methanol. The reaction was performed at 240-260°C for 8 hours with 50g of glycerol under nitrogen, the weight percentage of catalysts was around 2-4%.

Results and Discussion

1. Catalytic control of the glycerol 'polymerization'

The catalytic glycerol polymerization was carried out without solvent at 260°C and catalyzed either with homogeneous (Na_2CO_3) or heterogeneous catalysts such as a MCM-41 mesoporous silica modified by incorporation, impregnation or exchange of basic promoters.
The glycerol etherification was faster over sodium carbonate (x 3) but led to a statistic distribution of glycerol oligomers (till decaglycerol) containing both cyclic and linear polyglycerols. Reversely a fraction containing **di-** , **tri-** and tetraglycerol with more than 95% yield was obtained with a Cs/MCM catalyst. It was suggested that the difference of selectivity could be due to the regular mesoporosity (3-4 nm) of the Cs/MCM-41 material where the reaction took place.

2. Direct and catalytic synthesis of polyglycerol esters.

In the course of our work the direct and selective synthesis of polyglycerol esters starting from unprotected glycerol and fatty methyl esters was investigated. In this second part, glycerol was reacted with fatty methyl esters in a molar ratio of 1 at 240°C over magnesium oxide or Mg modified MCM-41.
Over bulk magnesium oxide (after 4 hours of reaction) glycerol diesters and triesters were mainly formed whereas polyglycerol esters were selectively obtained over mesoporous catalysts. Indeed due to a preferential adsorption of glycerol on silica materials the first step was the fast formation of diglycerols inside the pores where a consecutive transesterification took place leading to the formation of diglycerol esters. The esters distribution was highly dependent of the hydrocarbon chain length of the methyl ester which was a strong indication of a shape selective catalysis. In all cases a diglycerol esters yield of about 80 % was claimed.

Finally basic well ordered mesoporous silica are efficient catalysts to control the glycerol oligomerization and its regioesterification. Moreover, according to the preparation process, the basic element can be strongly anchored over the support so that no leaching was observed during the reaction.

References

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