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 cetyltrimethylammonium 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\(_2\)CO\(_3\)) or heterogeneous catalysts such as a MCM-41 mesoporous silica modified by incorporation, impregnation or exchange of basic promoters. The glycerol esterification 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 basic element can be strongly anchored over the support so that no leaching was observed during the reaction.

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