Glycerol as a platform molecule: scaling and shaping of basic catalysts for selective etherification and esterification

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Using glycerol as starting raw material for the synthesis of high-valued chemicals is currently a focus of global industrial research. A large portfolio of reaction pathways for the catalytic conversion of glycerol is available, among which the selective oligomerization to polyglycerols (PGs). Taking into account European Union regulations, the mixture of PGs should be composed of short-chain oligomers for most of the applications. In this respect, the aim of the present work deals with the heterogeneous catalyzed etherification of glycerol to low molecular-weight oligomers, with particular emphasis on the preparation of catalysts (scaling and shaping) and the scaling up of the reaction.

In this context, a series of extrudates was elaborated through direct extrusion of various bulk Mg or Ca precursors with specific binders. A specific attention was devoted to the study of the synthesis parameters (nature and content of the bulk precursor, of the binder, presence or not of a blowing agent, size and shape of the extrudates), as well as to the type and temperature of the post-treatment applied. Such catalysts proved not only mechanically and chemically stable in hot glycerol, but were highly efficient in selectively obtaining a restricted cut-off of PGs. Di- to hepta oligomers were selectively obtained with a major contribution of di- to tetra glycerols (80%). Regarding the activity, high reaction rates were obtained as a result of limited diffusional effects (Fig.1), in contrast to those observed with unshaped powdered mesoporous catalysts.

Additionally, the selective synthesis of polyglycerol esters starting directly from glycerol and methyl esters could also be efficiently performed with these shaped catalysts. Similar activity and selectivity values were remarkably obtained when starting from crude glycerol (80% purity) instead of pure glycerol without any change of the catalyst stability, which is a crucial property in catalysis.

A thorough characterization using *in situ* IR spectroscopy to investigate the acid-base properties of the catalysts was performed through the adsorption of adapted probe molecules, such as CO, pyridine, methanol, acetonitrile and propyne. A ranking of the materials in terms of site strengths and concentrations was established. Among the different samples, magnesium and calcium carbonates mixed with clay which appeared as particularly promising for the catalytic requirements. The structures formed during the initial phase of preparation exhibit a reduced Lewis acidity, which increases the catalytic performances. Additionally, the basicity shows an intermediate strength, which is the key property to obtain a high conversion of glycerol into polyglycerol.

Our study demonstrated that PGs and PG esters can be prepared reproducibly either in a batch or in a continuous process in the presence of stable shaped heterogeneous catalysts, thereby fully fulfilling the specifications required for an industrial viewpoint.

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