

Abstract

Abstract

In this Doctoral Thesis, the research has been focused on the development of different heterogeneous catalytic processes using hybrid porous organic-inorganic materials (MOFs and functionalized silicas) and organic aromatic materials (PAFs), which have been studied in various organic reactions. After the preparation of the MOFs under study, their structural properties have been characterised and their active centres in the metal clusters (zirconium, hafnium or cerium) have been determined. The reactivity of these MOFs and the hybrid silica-mine materials has been studied considering their catalytic centres; these reactions have been optimised by carrying out a study of the reaction mechanisms. Finally, homochiral PAF-type solids have been prepared with the binafil system, whose reactivity has also been tested.

More specifically, the esterification of amides has been studied in Chapter 3. This reaction allows to convert the amides into esters, which are more versatile functional groups. This transformation has been approached from the heterogeneous catalysis *via* MOFs based on zirconium, hafnium and cerium of the MOF-808, UiO-66 and MOF-801 series. The most efficient catalyst for amide esterification has been MOF-808-Zr. Using TGA analysis and the adsorption of a basic probe molecule (CO) studied using FT-IR spectroscopy, the acid centres of Lewis and Brønsted present in them have been determined. Among the MOFs prepared in this work, MOF 808-Zr has a lower metal cluster connectivity and a larger pore size than UiO-66 and MOF-801; it also has the appropriate balance of acid and basic Brønsted and Lewis centres to activate the reaction substrates. The scope of n-butanol alcoholysis has been extended to a large number of substrates (primary, secondary and tertiary amides; aromatic and aliphatic). The reaction has also been studied in non-solvolytic conditions with more complex alcohols. The catalyst is stable during the reaction and can be easily reused. The reaction mechanism in the esterification of benzamide with n-butanol catalysed by MOF-808-Zr has been investigated through kinetic analysis using the LHHW model and the *in situ* study of molecular interactions by FT-IR.

In Chapter 4, the deuteration by isotopic deuterium/hydrogen exchange catalysed by commercial silica-supported amines using D₂O as a source of deuterium has been investigated. This procedure is applicable to a wide range of substrates, such as carbonylic compounds, organophosphonium salts, nitro compounds and, even, steroid hormones. The stability of the catalyst, SiO₂-(CH₂)₃-NH₂, is maintained for up to 10 reaction uses without significant loss of activity.

Finally, in Chapter 5, the synthesis and application of homochiral PAFs, in which the structure of BINOL (1,1'-binaftil-2,2'-diol) and BIN-BAM (1,1' binaftil-2,2'-disulfonimide) has been integrated, is discussed. Three new PAFs active in asymmetric catalysis has been generated: PAF-3,3'-(*S*)-BINOL, PAF-6,6'-(*R*)-BINOL and PAF 3,3'-(*S*)-BINBAM. In particular, PAF-6,6'-(*R*)-BINOL has demonstrated its catalytic activity in the alkylation reaction of aromatic aldehydes with diethyl zinc and the catalyst PAF-3,3'-(*S*)-BINBAM is active in the Mukaiyama aldolic reaction and the reduction of the double bond of carbonylic α,β -unsaturated compounds.