

TIN BETA ZEOLITE FOR REGIOSELECTIVE BAEYER-VILLIGER OXIDATION OF LIGNIN MODEL COMPOUNDS

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Lignin is the second most abundant terrestrial biopolymer, and the largest source of natural aromatic functionality. Currently, most of the lignin produced by the pulp and paper industries is used as a low-grade fuel. However, the products of lignin depolymerization have potential as both renewable fuel (e.g., BTX) and fine chemicals (e.g., vanillin). Due to lignin's characteristic irregularity and insoluble nature, models of lignin's various linkage motifs are commonly used to investigate lignin depolymerization. The most abundant linkage is the β -O-4 unit, which comprises as much as 60% of linkages in lignin. The β -O-4 linkage is characterized by a benzylic alcohol moiety along with a bridging ether linking two aromatic monolignols. Many studies have been performed on lignin and lignin model compounds focusing on cleavage of the bridging ether groups using thermal and reductive techniques, which generally require high temperatures and pressures. Recently, a milder benzylic oxidation has attracted attention as a route to lignin depolymerization. After carbonyl functionality is introduced, we have observed that this moiety can be converted directly into a hydrolysable ester *via* heterogeneous Baeyer-Villiger Oxidation (BVO). Though BVO is a well-known reaction, there are few reports of heterogeneously catalyzed BVO of aromatic molecules. In this work a tin beta BVO catalyst was synthesized using a post-synthetic grafting technique that is previously unreported for zeolite beta. The hydrophobic pores of tin beta zeolite enable the use of polar protic oxidants such as hydrogen peroxide. Notably, the tin beta/hydrogen peroxide oxidizing system results in almost quantitative conversion of acetophenone derivatives and lignin model dimers. Using a biphasic dichloroethane/water solvent system, 4'-methoxyacetophenone can be converted to 4'-methoxyphenylacetate in 90% yield at 45 °C. In addition, studies on the β -1 linkage show that it can also be oxidized in moderate yields.