

Catalytic synthesis of amides from carboxylic acids and amines: evidence of surface carboxylates as activated species

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Research activities related to amide bond synthesis are among the most significant modern chemical topics [1]. A general problem of common amidation methods is the consumption of large amounts of reagents, usually including activators of carboxylic groups, with the consequent increase of synthesis cost and waste production. Searching for more effective methods, in 2007 the American Chemical Society Green Chemistry voted the "amide bond formation avoiding poor atom economy reagents" as the most preferable approach [2].

In this respect, significant efforts have been put to disclose catalytic routes both of the homogeneous [3] and heterogeneous type [4]. Nevertheless, the mechanism of direct amidation of unactivated carboxylic acid has not been elucidated yet.

Here we report evidences, provided by in-situ IR spectroscopy, of the possible activation of carboxylate groups at the surface of TiO_2 nanoparticles towards the nucleophilic attack by the nitrogen atom of amine molecules. The origin of such activation is proposed to be the withdrawing of electron density from carboxylate moieties by surface Ti^{4+} ions acting as strong Lewis acid centers.

Furthermore, the catalytic activity of TiO_2 towards amidation has been tested in the oligomerization of amino acid (mainly Glycine).

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