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Solid Base Catalysts: Generation, Characterization, and Catalytic Behavior of Basic Sites

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Studies of solid base catalysis performed in our group are summarized. Strongly basic sites for most solid base catalysts are generated by removal of water and carbon dioxide by pretreatment at high temperatures from the surfaces. The nature of the surface basic sites varies with the severity of the pretreatment conditions. Rearrangement of surface and bulk atoms occurs, in addition to the removal of water and carbon dioxide, during the pretreatment. The optimum pretreatment temperature varies with the type of reaction. Characterization of basic sites by the indicator method, TPD of CO_2, O exchange between adsorbed CO_2 and MgO surface, NMR of ^{133}Cs and ^{19}F are described. The catalytic behaviors of solid base catalysts are described for the following reactions; (1) double bond migration, (2) hydrogenation, (3) amination, (4) aldol addition, (5) nitroaldol reaction, (6) Michael addition, (7) conjugate addition of alcohol, (8) cyanoethylation, (9) transesterification of ethyl acetate and alcoholysis of propylene oxide, and (10) the Tishchenko reaction. The strength of basic sites relevant to different reactions is discussed based on the activity order among alkaline earth oxides, and the optimum pretreatment temperatures of MgO for different reactions. Reactions with hydrocarbons need strongly basic sites, whereas reactions with compounds containing functional groups proceed even on weakly basic sites. Finally, important issues to be investigated for the development of solid base catalysis are pointed out.

Keywords: Catalysis, Solid base, Reaction mechanism, Organic synthesis

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