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Acid-Base Bifunctional Catalysis of Silica-Alumina-Supported Organic Amines for Carbon–Carbon Bond-Forming Reactions

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Silica-Alumina-Supported Amine Catalysts for C–C Bond Formations

Significance: Acid-base bifunctional silica-alumina-supported amine catalysts (SA-NEt₂ and SA-NH₂) were prepared and applied to the carbon–carbon bond-forming reactions. Thus, SA-NEt₂ was prepared from an amorphous silica-alumina (SA) N633HN (SiO₂: 66.5%; Al₂O₃: 25.1%; 380 m²g^{−1}) and 3-(diethylamino)propyl trimethoxysilane in toluene under reflux conditions. The cyanoethoxycarbonylation of **1** with **2** was catalyzed by SA-NEt₂ to give the corresponding carbonates **3** in 88–99% yield (12 examples). The Michael reaction of **4** and **5** was performed with SA-NEt₂ to give the corresponding adducts **6** in 94–99% yield (3 examples). SA-NH₂-promoted the nitroaldol reaction of **7** and **8** to afford the nitroalkenes **9** in 88–99% yield (4 examples).

Comment: SA-NEt₂ and SA-NH₂ were reused four times without loss of catalytic activity in Michael and nitroaldol reactions. ¹H NMR spectroscopic analysis of the filtrate of the reaction mixture showed no leaching of amine compounds. SA-NEt₂ and SA-NH₂ were characterized by solid-state ¹³C and ²⁹Si NMR spectroscopy, FT-IR spectroscopy, and elemental analysis. The authors emphasized that the co-existence of acidic and basic sites at the same solid surface without neutralization realized the catalyses with high efficiency.

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