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Catalytic applications of an organosuperbase dendron grafted on mesoporous SBA-15 and a related palladium complex in Henry and Suzuki–Miyaura coupling reactions

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ABSTRACT

An efficient synthetic method for the synthesis of a basic amine dendron grafted on SBA-15 and a related Pd(II) complex as two novel catalysts has been developed. The prepared catalysts were evaluated in Henry and Suzuki–Miyaura coupling reactions and were found to exhibit excellent heterogeneous catalytic activity in green media, and could be easily separated and reused several times.

Mesoporous materials have attracted considerable interest as catalysts, catalyst supports, adsorbents, sensors, etc.[1–6] Ordered mesoporous silicas (OMSs), particularly SBA-15 between other silica materials, have relatively good hydrothermal stabilities, and possess hexagonal arrays of uniform pores with high specific surface areas, and large pore volumes. The presence of palladium species on mesoporous silicas as heterogeneous catalysts is frequently used in various coupling, hydrogenation and oxidative transformations.[7–12] Mesoporous silica supports have high surface areas, good thermal and mechanical stability and are insoluble in organic and aqueous solvents.[13,14] These properties can lead to the presence and uniform distribution of active metals such as palladium, rhodium, ruthenium and copper on their surfaces, which can be accomplished either by doping metal salts into the pores or by grafting organic functional groups, with spacers, which have associated metal ions on OMSs.[15–21] Production of high density hybrid materials containing organic functional groups on OMSs is difficult because distribution of catalytically active sites is often non-homogeneous. To achieve higher densities of homogeneous organic functional groups, the use of surface patterning and molecular imprinting techniques can circumvent this issue.[22–25] In addition, surfaces functionalized with dendrimers are another choice to obtain high organic group densities.[26–28]

Recently, Alizadeh et al. reported immobilization of organosuperbase groups on the surfaces of SBA-15 materials.[29] The current investigation represents a new method for the synthesis of an organosuperbase-functionalized SBA-15 (SBA-15/CCMet), its related palladium complex SBA-15/CCMet/Pd(II),[30] and describes the catalytic testing of these materials in Henry (nitroaldol) and Suzuki–Miyaura coupling reactions.

In this Letter, the amine-functionalized SBA-15-anchored palladium(II) complex SBA-15/CCMet/Pd(II) was synthesized conveniently from cheap and commercially available materials via immobilization on SBA-15 according to our previous report.[30] The routes employed for the fabrication of the catalysts are shown in Scheme 1.

The content of linked metformin on triazine was measured through back titration which revealed a loading of ~1.1 mmol of metformin per gram of SBA-15. In addition, the Pd content of the catalyst, as estimated by the atomic absorption spectroscopy, was 0.920 ± 0.001 mmol g^{-1}. This indicated that approximately all of the anchored organic ligand moieties have efficiently coordinated with Pd^{2+} ions providing catalytically active sites.

In order to evaluate the basic activity of SBA-15/CCMet and metal containing SBA-15/CCMet/Pd(II) as heterogeneous catalysts, the nitroaldol (Henry reaction) and Suzuki–Miyaura coupling

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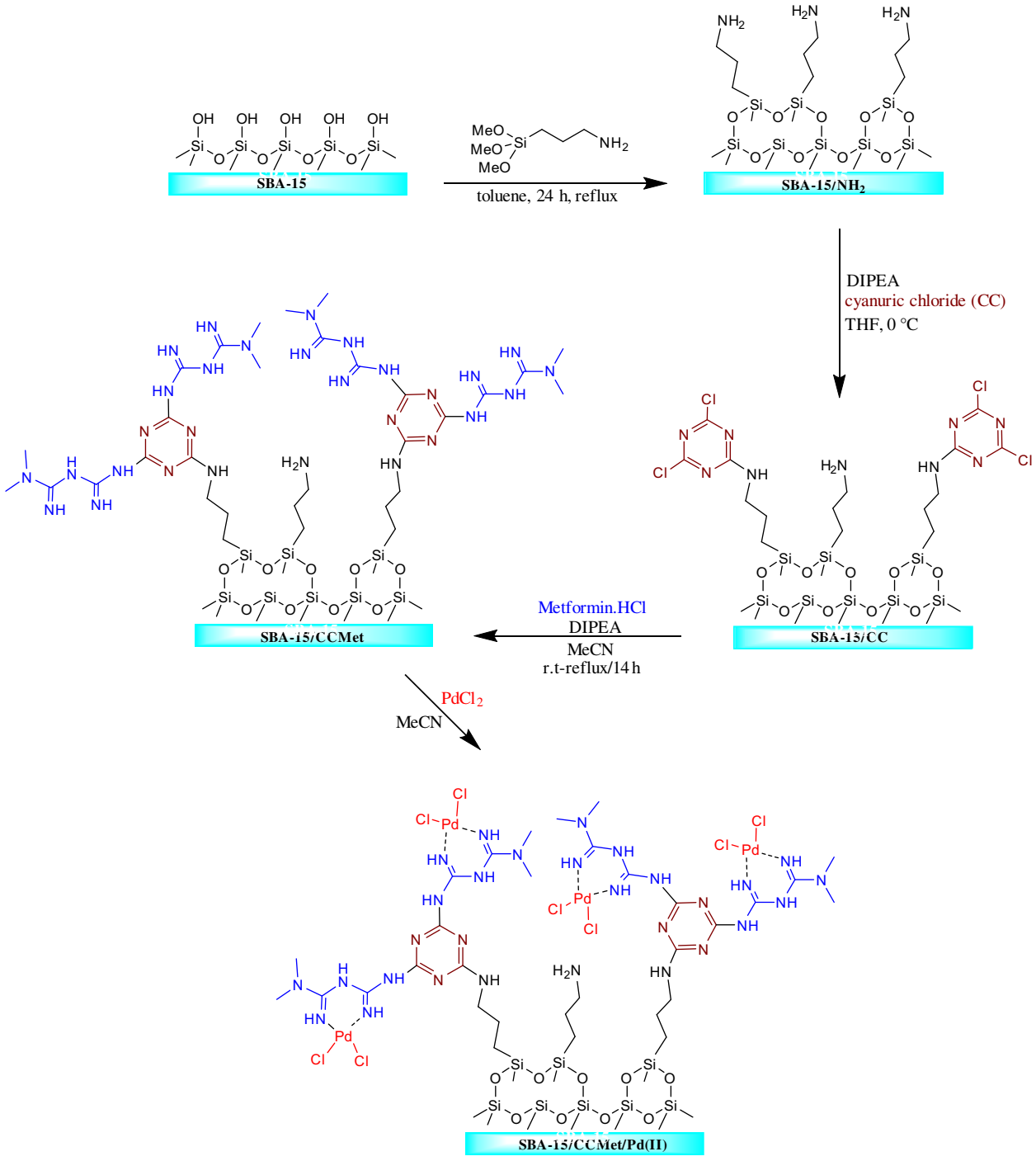

Scheme 1. Preparation of the catalysts SBA-15/CCMet and SBA-15/CCMet/Pd(II).

reactions were chosen, respectively. The addition of nitromethane to various benzaldehydes using SBA-15/CCMet was performed under air. To optimize the reaction conditions, 4-chlorobenzaldehyde (1 mmol) and nitromethane were used as model substrates. Conditions such as the catalyst amount, solvent and time were investigated. The best result was obtained by carrying out the reaction with a 1:2 molar ratio of 4-chlorobenzaldehyde and nitromethane at room temperature in 1 mL of EtOH for two hours. The results are shown in Table 1.

In the presence of the heterogeneous catalyst and optimized conditions, β-nitroalcohols were obtained in excellent yields. It is important to note that dehydration did not occur and related unsaturated products were not obtained.

With a reliable set of conditions in hand, we also probed the scope and generality of the developed protocol with a variety of substituted aryl and hetaryl benzaldehydes and nitromethane (Table 2). The corresponding adducts were obtained in good to excellent yields. It was found that aromatic aldehydes with both electron-withdrawing and electron-donating groups reacted with nitromethane to give the desired products with excellent conversions.

The catalytic activity of SBA-15/CCMet/Pd(II) was evaluated in the Suzuki–Miyaura reaction. Initially, we optimized the conditions for the coupling reaction between 4-bromoacetophenone and phenylboronic acid as a model reaction.

The influence of reaction parameters such as the base (Et_3N, NaOAc or K_2CO_3), solvent (nonpolar, protic or aprotic) and catalyst