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Sulfur promoted Pt/SiO_2 catalyzed cross-coupling of anilines and amines

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ABSTRACT

Pt/SiO_2 (Pt = 5 wt%) catalysts with average Pt particle size of 3.3 and 6.8 nm and sulfur-loaded Pt/SiO_2 (S/Pt ratio = 0.1 and 0.13; Pt size = 5.2 and 5.5 nm), prepared by adding ammonium sulfate on Pt/SiO_2 followed by H_2-reduction at 500 °C, are tested for mono-*N*-alkylation of aniline with di-*iso*-propylamine. The turnover frequency (TOF), defined as the reaction rate per number of surface Pt species, increases with sulfur loading. The catalyst with S/Pt ratio of 0.13 shows more than 5 times higher TOF than unmodified catalysts, and it acts as effective and recyclable catalyst for cross-coupling of various anilines and amines. Combined with kinetic results and characterizations, XAFS (X-ray absorption fine structure), TEM, and CO adsorption IR, a possible reason for the promotion effect of sulfur species (probably sulfidic species) is discussed.

1. Introduction

Pt catalyst has been the most industrially relevant and widely investigated catalysts [1–13]. Recent reports demonstrated some Pt-catalyzed green organic reactions such as selective oxidation [1–3], hydrogenation [4,5] and hydrogenolysis [6]. However, their application to multi-step one-pot organic synthesis is limited. Sulfur is widely recognized as a poison of metallic Pt catalysts for many reactions. Under reducing conditions the presence of sulfur in general decreases the catalytic activity. There are a few reports of promotional effects of sulfur species on Pt catalysts [7–13]. These examples are based on the promotion effects of sulfate species on the activity of Pt catalysts for hydroisomerization of alkanes and combustion of hydrocarbons. For the former system, Hattori and co-workers have established that sulfate species play an important role in the formation of the molecular hydrogen-originated protonic acid site. For the latter system, the formation of acidic site at the Pt/support/sulfate interface is suggested to be important [10]. However, to the best of our knowledge, positive effects of sulfur species on Pt metal catalyzed multistep organic synthesis were not reported.

Amines are intermediates and products of enormous importance for chemical and life science applications. In addition to the well established Pd-catalyzed aminations of aryl halides [14] and the metal-catalyzed amination of alcohols [15,16], the transition-metal-catalyzed alkylation of amines by amines is an attractive alternative method of alkylamine synthesis [15–29]. The reaction proceeds thorough a hydrogen-borrowing (hydrogen auto-transfer) mechanism [15–21]. The process begins with the dehydrogenation of an alkylamine to the corresponding imine. The imine undergoes addition of another nucleophilic amine and elimination of ammonia to form an *N*-alkyl imine, which is hydrogenated by in situ formed hydride species to the secondary amine product. Ru [18,19] and Ir [20] complexes are successful catalytic systems for selective amine cross-coupling of different amines, leaving ammonia as the only by-product. From the environmental and economic viewpoints, it is preferable to accomplish the selective cross-coupling reaction using reusable heterogeneous catalysts. There are many reports of heterogeneous catalysis for cross-coupling [16,17,21–24] or self-coupling [25–28] of amines. However, previous examples of cross-coupling reactions suffer from reusability [17], low turnover number (TON), and need of stoichiometric amount of additives [21] or special reaction methods (microwave heating [21,22], electrocatalysis [23], photocatalysis [24]). Recently, we reported that Pt nanocluster-loaded γ-Al_2O_3 (Pt/Al_2O_3) was effective for mono-*N*-alkylation of amines with different amines [29]. In this paper, we found that S-loaded Pt/SiO_2 showed higher TOF (per number of surface Pt) than Pt/SiO_2 and Pt/Al_2O_3. Kinetic and structural studies are carried out to discuss a possible reason of the promotion effect of sulfur.

2. Experimental

Commercially available organic compounds (from Tokyo Chemical Industry or Kishida Chemical) were used without further purification. The GC (Shimadzu GC-14B) and GC–MS (Shimadzu

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