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C—Cl bond activation with Pd(II)-NiO nanoparticles supported on zeolite-Y: The role of charge transfer transition

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ABSTRACT

Well dispersed Pd-NiO nanoparticles (Pd-NiO NP's) formed over zeolite-NaY was found to be highly efficient catalyst for the Suzuki-Miyaura cross-coupling reaction of aryl chlorides and phenylboronic acid derivatives. Exceptional C—C coupling products up to 92% were obtained within short period of time with chlorobenzene and their derivatives under microwave irradiation. Cyclic voltammetry (CV) study predicted that the leached Pd-NiO species were the "*true catalyst*" in the C—Cl bond activation process. *Insitu* generation of active Pd(0) via a charge transfer transition from NiO → Pd(II) was confirmed from CV study and was believed to be the crucial step in C—Cl bond activation. Filtration and CV analysis suggested for quick re-deposition of Pd-NiO NP's on zeolite-NaY surface and confirmed for the non-consumption of $Ni(OH)_2$ species.

Introduction

Suzuki-Miyaura cross-coupling reactions of aryl bromides and aryl iodides with phenylboronic acids are well known in literature [1–14]. Different homogeneous [15–21] and heterogeneous palladium based catalyst [22–29] are reported to catalyze the C—C coupling reaction. Apart from palladium (Pd), other transitions metal like Au, [30] Cu/Ni, [31] and Fe-Ni [32] are found to give biaryl products. Still Pd metal is considered to be the best choice due to its high selectivity and product yield [4,33,34]. With aryl bromides and iodides, cross coupling products are obtained in excellent yield with Pd-catalyst [33,34]. But aryl chlorides are considered to be odd candidate for such coupling process. Most of the reported results are therefore mainly based on coupling of aryl bromides or iodides, but reports on activation of aryl chlorides are sparse [35,36]. C—Br and C—I bond activation using Pd-based catalysts are not cost effective. Therefore, development of suitable catalyst for C—Cl bond activation due to the low cost of chloro-derivatives is highly desirable. Homogeneous Pd-complexes with *N*-heterocyclic carbenes (NHC) and electron rich phosphanes are reported to be effective catalyst for C—Cl bond activation [37–39], but those homogeneous catalysts have some disadvantages with recyclability and formation of some contaminated products. Hence, focused has been made on supported Pd-catalyst because of their advantage over the homogeneous counterparts [35,40–45]. And in recent progress there has been a number of reports addressing the C—Cl bond activation with heterogeneous or supported Pd- based catalyst [4,35,40].

Although the effective C—Cl bond activation has been achieved with various Pd-based heterogeneous catalysts and problems associated with homogeneous catalyst has been counterpoised to some extent. But one of the most important and much debated aspect in Suzuki-Miyaura cross-coupling reaction using supported catalyst is on the nature of *true catalyst* [19]. Many literature report supports for the leached Pd-species as the active species in Suzuki-Miyaura cross-coupling reaction [18,24,25]. However, it leads to question mark on the actual heterogeneous nature of the catalyst. Filtration, Sheldon or mercury test or three phase test [19,46,47] are often employed to confirm about the heterogeneous nature of the catalyst. However, till now no any solid evidence has been provided in understanding actual nature of the active species. Therefore, in continuation to this endeavor, herein we report for Pd-NiO supported zeolite-NaY as a highly effective catalyst for C—C coupling reaction

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