Palladium Nanoparticles Supported on Metal Oxide as an Efficient and Reusable Heterogeneous Catalyst for Suzuki-Miyaura Cross Coupling Reaction

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Abstract: Highly active Palladium nanoparticles immobilised on a fluorine-doped tin oxide (FTO) was developed. Nanoparticles of fluorine-doped tin oxide (FTO) was used as a support for Pd nanoparticles. Highly dispersed Pd nanoparticles were impregnated on FTO using simple impregnation method, followed by the chemical reduction with hydrazine hydrate. The catalyst was characterized by SEM, EDX, XRD and BET. The effect of catalyst and the influences of solvents on catalytic activity of Pd/FTO were examined by using the Suzuki coupling of aryl halide and phenylboronic acid. The prepared organocatalyst showed an excellent catalytic activity for Suzuki reactions of various aryl halides used in low amount (0.1 mmol%) using DMF and H_2O as solvent with a yield over 75-96%. Furthermore, Pd/FTO showed good recyclability of up to five cycles without significant decrease in its catalytic activity and relatively high stability in H_2O than in DMF as solvent in Suzuki reaction.

Keywords**:** Palladium, FTO, Suzuki-Miyaura, Heterogeneous

INTRODUCTION

Suzuki-Miyaura coupling reaction catalyzed by Pd catalyst is performed in the presence of homogeneous or heterogeneous catalyst [1]. The use of heterogeneous Pd catalyst is increased dramatically in both chemistry academic field as well as industrial field [2-3]. The major concern of isolation, recyclability and reusability of catalyst can be overcome by using heterogeneous catalysts which have attracted much attention in chemistry [4]. SnO_2 has unique sensing properties which are able to improve its electronic conductivity, IR reflectivity, selectivity and sensitivity through doping of impurities such as copper (Cu) and indium (In) [5-7]. Noteworthy, the doping of high electronegative fluorine (F) content onto SnO_2 displayed remarkable improvement in terms of electronic conductivity and selectivity [6, 8]. The amphoteric FTO has a great potential to be a sustainable matrix as a Pd heterogeneous catalyst due to its porous properties, good thermal and chemical stability [9]. Herein, a new and versatile Pd-supported catalyst is synthesized via immobilization of Pd NPs on FTO and further evaluated in Suzuki-Miyaura cross coupling reaction.

MATERIALS AND METHODS

All chemicals were used as received and without any further purification. Pd/FTO was synthesized according to the following procedure as reported by Liew et. Al [10]. The Pd/FTO catalysts synthesized consist of 0.10 mmol/g of Pd by the confirmation of ICP analysis.

RESULTS AND DISCUSSION

The catalytic performance of Pd/FTO catalyst was evaluated in Suzuki-Miyaura cross-coupling reaction by using different Pd content. The Pd/FTO used in Suzuki-Miyaura cross-coupling reaction of phenylboronic acid with 1-bromo-4-nitrobenzene reactant was varied from 0.05, 0.1, 0.2, 0.3, 0.5, 1.0, and 1.5 mmol%. The obtained result showed that Pd/FTO catalyst exhibited optimal reaction condition for Pd/FTO catalyst in Suzuki-Miyaura cross-coupling reaction is 0.1 mmol% and thus it

has been chosen to be proceed for recyclabiity. The final product obtained was characterized by FTIR, ^{13}C NMR and ^{1}H NMR.

As shown in Fig. 1, the catalytic activity of Pd/FTO in Suzuki-Miyaura cross coupling reaction of aryl halide to biphenyl preserved its activity up to fifth reaction runs. These findings indicated that Pd/FTO catalyst is performed better in H2O solvent than in DMF solvent for Suzuki reaction. Nonetheless, the Pd/FTO catalyst can be used as an effective heterogeneous catalyst in cross-coupling reaction with good reusability and excellent catalytic activity.

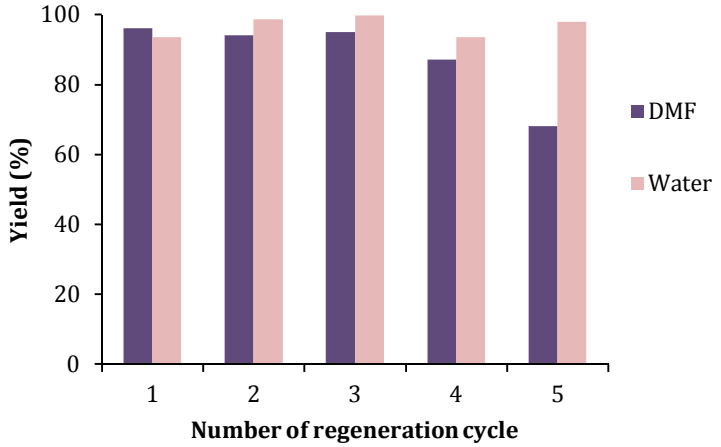

Fig. 1. Yield of Suzuki reaction for each cycle of Pd/FTO in DMF and H_2O

CONCLUSIONS

The present study has proved the nano-sized FTO is a promising catalyst support in catalysis. The efficiency of the Pd/FTO was examined in the Suzuki-Miyaura cross-coupling reaction. Pd/FTO was performed excellently and showed high recyclability in the cross-coupling reaction at moderate temperature of 80 °C in both DMF and H_2O solvent. Moreover, this promising recoverable catalyst exhibited high catalytic performance in Suzuki reaction of phenylboronic acid using 1-bromo-4-nitrobenzene over very low molarity, which is 0.1 mmol%.

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