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A Novel Pd Catalyst Attached on a SiO_2 Surface via Immobilized Ionic Liquid

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Introduction

Recently, ionic liquids have been paid attention as green and designable solvents which are categorized as fused salts at room temperature and their applications to organic synthesis as new reaction media are extensively studied [1]. Pd catalyst prepared from ionic liquid (1-n-butyl-3-methylimidazolium chloride, BMICl) was reported, which is designated as $(BMI)_2PdCl_4$ and is active for hydrodimerization of 1,3-butadiene [2]. This is an example that ionic liquid can offer a new effective catalyst. In order to utilize the characteristics of ionic liquid in heterogeneous catalysis, we synthesized a derivative of ionic liquid molecule (1-methyl-3-trimethoxysilyl-propyl imidazolium chloride **1**) which can be immobilized on a silica surface to prepare a novel attached metal catalyst. In this study a novel Pd catalyst which is active for Suzuki cross coupling reaction was prepared and its structure was analyzed by EXAFS.

Experimental

Sample preparation: The compound **1** was synthesized by the reaction between 1-methyl-imidazol and 3-trimethoxysilyl-propyl chloride and its structure in solution was determined by ^{1}H-NMR and ^{13}C-NMR after purification. The compound **1** was immobilized on silica (Aerosil 300) which was calcined and evacuated at 573 K by the reaction between silanol group and surface OH group. Attached Pd catalyst **2** was prepared by heating a mixture of silica with immobilized compound **1** and $PdCl_2$ in acetonitrile at reflux temperature and removing excess $PdCl_2$. For comparison, silica supported $PdCl_2$ catalyst and $(BMI)_2PdCl_4$ catalyst were prepared.

EXAFS measurement and analysis: Pd K-edge EXAFS spectra for the Pd catalysts were measured at 15 K at BL-10B in a transmission mode. After background subtraction, k^3-weighted EXAFS functions were Fourier transformed into a R space and curve-fitting analyses were carried out in the R space using the FEFFIT program [3]. The k and R ranges for the Fourier transformation and curve fitting were 30-130 nm^{-1} and 0.11-0.27 nm, respectively. Backscattering amplitudes and phase shifts were calculated by the FEFF8 code [4].

Results and Discussion

Suzuki cross coupling reaction between derivatives of bromobenzene and phenylboronic acid in m-xylene in the presence of K_2CO_3 to yield corresponding derivatives of biphenyl was examined for prepared Pd catalysts. It was found that in the case of the reaction of bromobenzene the homogeneous catalyst $(BMI)PdCl_4$ gave very high yield (>99 %) which is better than conventional catalysts, e.g., $Pd(OAc)_2$ and the supported $PdCl_2$ catalyst gave yields of 86 % and 81 %, respectively. The attached Pd catalyst **2** exhibited the yield of 89 - 94 % with different bases and it was found that this catalyst was reusable up to three times with almost unchanged yield.

In order to determine the local structure of the attached catalyst, EXAFS spectra were measured. Figure 1 shows Fourier-transformed EXAFS spectra for the supported $PdCl_2$ catalyst and immobilized Pd catalyst, whose structural parameters are given in Table 1. Both catalysts exhibit almost the same Pd-Cl distance, but the former has the lower coordination number and FT spectra shows a broadened feature, while the latter one exhibit the coordination number of 3.5 which is close to 4 and all the features were in agreement with those for $(BMI)_2PdCl_4$ diluted with BN, whose X-ray diffraction analysis is given [2]. These results show that the immobilized Pd catalyst which is active and reuseable was prepared quite uniformly on silica surface as depicted in Fig. 2. It is expected that the present method is a new and effective way for preparation of novel metal catalysts.

Table 1: Structural parameters derived from EXAFS curve-fitting analyses for the Pd catalysts

Shell		CN	R /Å	σ^2 / Å^2
Supported	Pd-Cl	2.7±0.2	2.32±0.02	(5±2)x10^{-3}
Attached	Pd-Cl	3.5±0.1	2.31±0.01	(2.1±0.3)x10^{-3}

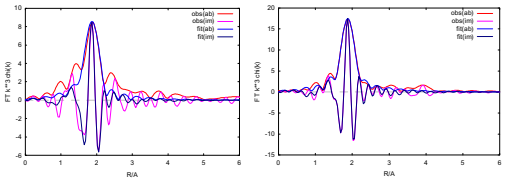

Fig. 1 Fourier-transformed EXAFS spectra for the supported (left) and attached (right) Pd catalysts.

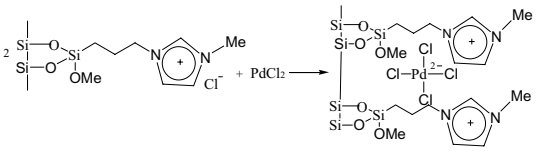

Fig. 2 Scheme of the attached Pd catalyst **2** on SiO_2.

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