Effect of Mesopore Internal Surface on Structure of Immobilized Pd-Bisphosphine Complex Analyzed by Variable-Temperature XAFS

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Abstract: Mesoporous and nonporous silica-supported Pd complex were synthesized and characterized. Variable-temperature XAFS measurement and curve-fitting analysis shows slightly larger contribution of σ_{static} in the case of nonporous support than mesoporous support. On the other hand, the catalytic performance of attached Pd complex for Suzuki-Miyaura coupling reaction was not affected by such small differences of static disorder of the Pd complex.

Keywords: Variable-temperature XAFS, Heterogeneous catalyst, Suzuki-Miyaura coupling reaction.

1. Introduction

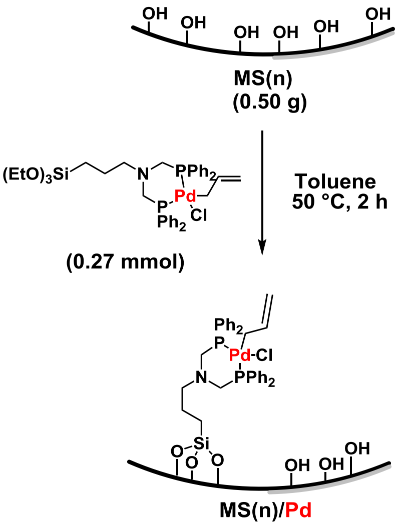
Mesoporous silica (MS) is an ideal support material for preparation of highly active catalysts because of its high surface area, inert nature of SiO_2, and functionalization ability. Among various functionalization methodologies of mesoporous silica, silane-coupling reaction, the reaction between surface silanol and functional molecules containing trialkoxy group, is one of the most usable procedure for preparation of supported catalyst. Despite the frequently use of silane-coupling reaction for functionalization of mesoporous silica materials, detailed analysis of the effect of mesoporous silica internal surface curvature on the structure of immobilized functionality is still a challenging object.

Recently, our group reported mesoporous silica-supported Pd-bisphosphine complex as a highly active catalyst for allylation of nucleophiles.[1] Herein, we examined the variable-temperature XAFS analysis of both mesoporous and nonporous silica-supported Pd-bisphosphine complex to clarify not only local structure of Pd complex but also small differences of the Pd complex structure due to their morphologies of silica support.

2. Experimental

MS supports with different pore diameters in the range of 16-31 Å were prepared by using primary amine as a structure-directing agent[2]. Mesoporous silica with n Å pore diameter was denoted as MS(n). Nonporous silica (Aerosil300, denoted as SiO_2) was also used as a reference support material. MS-supported PP-Pd was prepared by silane coupling reaction using Pd-bisphosphine complex with triethoxylsilyl group (PP-Pd) (Scheme 1)[1]. Prepared samples were characterized by ^{13}C, ^{29}P, ^{31}Si MAS NMR, SEM, XPS, XAFS, and elemental analysis.

Variable-temperature Pd K-edge XAFS measurement was carried out at 18, 100, 200, and 300 K. Curve-fitting analysis of obtained EXAFS spectra were performed by standard sample method.



Scheme 1. Preparation of MS(n)/PP-Pd

3. Results and discussion

Maintenance of PP-Pd structure after immobilization on MS surface (MS/PP-Pd) was confirmed by spectroscopic techniques.

Figure 1 represents Pd K-edge FT-EXAFS spectra of MS(16)/PP-Pd measured at 18, 100, 200, and 300 K. No significant change of local structure was observed by any measurement temperature. PP-Pd attached on other MS and nonporous silica (SiO_2) also showed similar phenomena.

Figure 2 shows plots of DW factor values obtained by curve-fitting analysis of Pd K-edge EXAFS spectra against measurement temperature. We found that lowering the temperature the DW factor of SiO_2 supported catalyst becomes larger compared to that of MS supported catalysts. The DW factor has contributions from both static disorder and dynamic disorder, i.e. $\sigma^2 = \sigma_{static}^2 + \sigma_{dynamic}^2$. The slightly larger DW value of SiO_2/PP-Pd at 100-18 K indicates that Pd complex on nonporous silica support has a larger structural distortion than MS support.

In order to investigate the influence of such structural distortion by support morphology on catalytic activity, Suzuki-Miyaura coupling reaction using supported Pd complex was investigated (Table 1). Table 1 exhibited that catalytic activity was not strongly affected by the type of silica.

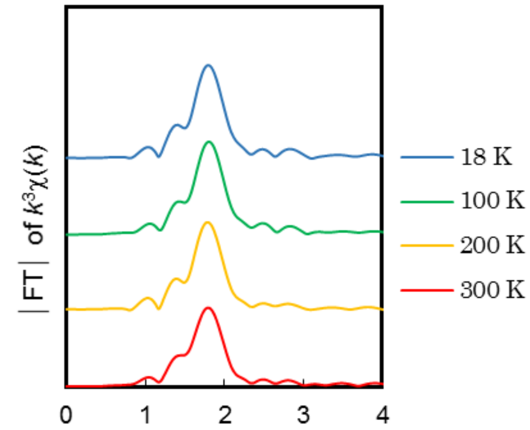


Figure 1. FT of k^3-weighted Pd K-edge EXAFTS spectrum of MS(16)/PP-Pd.

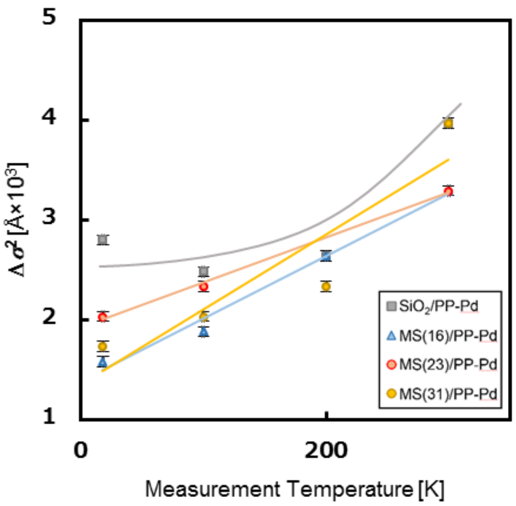
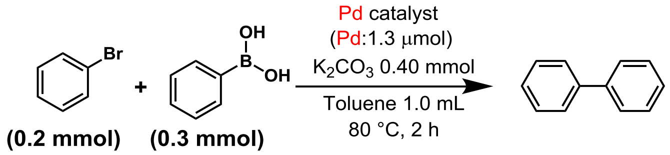


Figure 2. DW factor values plotted against measurement temperature.

Table 1. Suzuki-Miyaura coupling reaction using supported Pd complex



Catalyst	Conversion [%]	Yield [%]	TON $[Pd^{-1}]$
MS(16)/PP-Pd	91	82	126
MS(23)/PP-Pd	86	86	132
MS(31)/PP-Pd	93	90	138
SiO_2/PP-Pd	87	83	128

4. Conclusions

Effect of support morphology on attached Pd complex was evaluated by variable-temperature XAFS analysis. In the case of nonporous SiO_2 support, relatively larger contribution of σ_{static} is observed compared with MS. This result suggests the slightly distorted structure of Pd complex; however, this small difference of Pd complex structure does not affect their catalytic activity of Suzuki-Miyaura reaction.

References

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