

Enhancement of Catalytic 1,4-Arylation Activity by N-Heterocyclic Carbene Ligand Decoration on Cr and Rh-incorporated Ceria Catalysts

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Decoration of organic ligands onto heterogeneous catalysts is one of the effective strategies to functionalize heterogeneous catalysis; for examples, catalytic activity enhancement¹ and chemoselectivity tuning² by the decoration of N-heterocyclic carbene (NHC) ligands on the supported metal nanoparticle. We have succeeded in functionalizing a Cr- and Rh-incorporated ceria catalyst³ with a NHC ligand (1,3-dicyclohexylimidazol-2-ylidene (ICy)) (denoted as ICy-Cr_{0.19}Rh_{0.06}CeO₂) and found that catalytic 1,4-arylation activity of cyclohexenone and phenylboronic acid was newly emerged on ICy-Cr_{0.19}Rh_{0.06}CeO₂ (Figure 1(A)).⁴ The active sites and the catalytic activity enhancement by the NHC decoration were investigated.

Rh *K*-edge EXAFS of ICy-Cr_{0.19}Rh_{0.06}CeO₂ (ICy: 0.8 wt%) showed similar Rh-Rh bonds (coordination number = 2.8 ± 0.4) to H₂-reduced Cr_{0.19}Rh_{0.06}CeO₂, indicating that small Rh nanoclusters remained after the NHC decoration. N 1s XPS of ICy-Cr_{0.19}Rh_{0.06}CeO₂ at 400.6 eV (Figure 1(B)) and the photoluminescence spectral analyses strongly suggested that the decorated ICy “carbene” was interacted with the active Rh nanoclusters on the catalyst surface.

DFT calculation suggested the influence of NHC coordination onto the active Rh cluster.

Phenyl group (from phenylboronic acid) was adsorbed at a bridge site of a modelled tetrahedral Rh₄ cluster on CeO₂ (Rh₄/CeO₂) (Figure 1(C-a)). On the other hand, phenyl group was adsorbed on a top site of ICy-decorated Rh₄/CeO₂, which was closer to cyclohexenone (Figure 1(C-b)). DFT results suggested that ICy controlled the adsorption site of a phenyl group closer to cyclohexenone on the Rh clusters, resulting in facilitation of C-C bond formation.

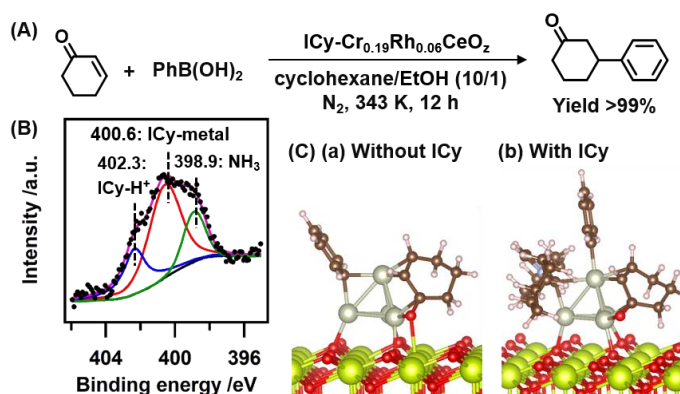


Figure 1. (A) 1,4-Arylation of cyclohexenone with phenylboronic acid. (B) N 1s XPS of ICy-Cr_{0.19}Rh_{0.06}CeO₂. (C) DFT optimized structure of Rh₄/CeO₂ (a) without ICy and (b) with ICy coordinated with phenyl group and cyclohexenone.

1) Ernst, J. B. *et al. J. Am. Chem. Soc.* **2017**, *139*, 9144. 2) Ernst, J. B. *et al. J. Am. Chem. Soc.* **2016**, *138*, 10718. 3) Ikemoto, S. *et al. Phys. Chem. Chem. Phys.* **2019**, *21*, 20868. 4) Ikemoto, S. The 101st CSJ Annual Meeting, **2021**, A07-2am-10.