Abstract

In the past few decades, C-C cross coupling reactions have been extensively utilised in the advancement of synthesis protocols for agricultural and pharmaceuticals. Of all the reported C-C cross coupling reactions, Suzuki-Miyaura reaction is one of the most preferred reactions because of its mild reaction conditions, commercial availability of associated reagents and the ease of removal of boron containing by-products. Recently, Corma and co-workers [Leyva-Perez et al., *Angewandte Chemie*, 2013, 125, 11768] reported water-stabilized Pd_3 and Pd_4 clusters as highly active catalytic species for C-C cross coupling reactions. Due to inadequate information on the detailed mechanistic insights of Pd_n cluster catalysed Suzuki-Miyaura reaction, we carried out computational investigations under the density functional theory (DFT) framework to explore the mechanistic insights into Suzuki-Miyaura reaction with Pd_3 and Pd_4 clusters. In this study, we analysed the role of the base, which was found to lower the transmetalation barriers over both Pd_n clusters. Free energy landscapes for Suzuki-Miyaura coupling of bromobenzene and phenylboronic acid over Pd_3 and Pd_4 clusters were developed. Oxidative addition is found to be rate limiting step, in the presence of base, with free energy barriers of 1.50 and 1.32 eV over Pd_3 and Pd_4, respectively. The active nature of small-atom Pd clusters was demonstarted by our detailed energetics in catalyzing Suzuki-Miyaura reaction.

In search for heterogeneous catalysts, graphene nanosheets have been widely used as a support for immobilising catalytically active Pd nanoparticles or clusters. By using DFT, we performed a systematic investigation of binding energetics, electronic charge analysis, and migratory surface barriers of free and solvated Pd_n clusters over pristine and defect-ridden graphene. Intrinsic as well as extrinsic defects were considered. In intrinsic defects, Stone-Wales defect, single vacancy

defect and double vacancy defect were considered while in extrinsic defects, boron, nitrogen and oxygen doped systems were considered. Our investigation suggested that double vacancy defected graphene and B-doped graphene as excellent materials providing strong traps for Pd_3 and Pd_4 clusters which not only immobilised Pd clusters on them but also hindered their surface migration.

In the series of desiging heterogeneous catalysts for C-C cross coupling reactions, we came across CeO_2 as a support, which is known to stabilise transition metal (TM) nanoparticles or clusters on its surface preventing the loss of their catalytic activities. To understand the reasons behind the stability of Pd_n clusters over CeO_2 (111) and (110) surfaces, we carried out DFT calculations. Our analysis revealed the effect of the vacancy defects to be marginal on the binding of the clusters over the studied surfaces. However, surface diffusion barriers were significantly altered by the presence of vacancies. Our investigation highlighted pristine CeO_2(110) and sub-surface vacancy defected CeO_2(111) surfaces as excellent materials providing good binding and high surface diffusion barriers for the localised binding of Pd_3 and Pd_4 clusters.

In continuation to the above stability of Pd_n clustes over graphene and CeO_2 supports, we investigated the activities of small Pd_n (n=3,4) clusters immobilised over both graphenes and CeO_2 surfaces for the oxidative addition of bromobenzene in the presence of water solvation, which is rate limiting. We calculated the adsorption energetics and activation barriers of oxidative addition for a series of graphene and CeO_2 supports and compared with homogeneous free Pd_n catalysts. Our theoretical investigations reveal that the graphene and CeO_2 supports acts as charge donors, reducing the activation barriers of oxidative addition drastically when compared to free Pd_n clusters. Double vacancy defected graphene, B-doped graphene and pristine CeO_2(110) surfaces were concluded as the potential supports providing stronger anchoring sites for small Pd_n (n=3,4) clusters and reducing the oxidative addition barriers, making them suitable heterogeneous catalysts for C-C cross-coupling reactions.