Abstract

Synthesis of novel and efficient catalysts for acetylene hydrogenation exhibiting high selectivity towards ethylene and for C-C cross coupling reactions of pharmaceutical importance, *viz.*, Heck and Suzuki-Miyaura cross coupling, is important due to the presence of selective acetylene hydrogenation reaction in petrochemical processing and to get the poison-free product in pharmaceutical industries, respectively. Since adsorption of C₂-gases and halobenzenes constitutes the primary step in catalytic hydrogenation and C-C cross coupling reactions, respectively, and governs the selectivity of the catalysts, we have explored the C₂-gas and halobenzene adsorption potentials of modified C₆₀ and reducible CeO₂-based systems.

Density functional theory (DFT) investigations of palladium and nickel substituted fullerenes ($C_{59}M$; M = Pd/Ni) were carried out probing the changes in their surface adsorption potential. Structure and bonding in the proposed heterofullerenes were established with insights into metal-carbon bond character, stability and adsorption potential. C₂-gases (C₂H₂, C₂H₄ and C₂H₆) and halobenzenes (C₆H₅X; X = F/Cl/Br/I) were used as probes for adsorption tests. Adsorption of C₂H₂, C₂H₄ and C₂H₆ was studied with different adsorption sites over pure and heterofullerenes. Adsorption of C₂H₂ was found to be stronger than the adsorption of C₂H₄ and C₂H₆ over C₆₀. Surface modification of C_{60} with a foreign metal improved gas-substrate (C_2 -heterofullerene) interactions. Adsorption of halobenzenes was observed to be mildly exergonic over both the heterofullerenes with an activation of all halobenzenes over both the heterofullerenes. Oxidative addition of C_6H_5I was found to be the least energy intensive process with a free energy requirement that was three times smaller than that for C_6H_5F over $C_{59}Pd$.

Enhanced surface interactions and differential adsorption behaviors of different heterofullerenes made them potential catalysts for acetylene hydrogenation and C-C cross coupling reactions. Free energy landscapes for hydrogenation of C_2H_2 and C_2H_4 over C_{60} and heterofullerenes were developed. The energy barriers for various elementary steps during hydrogenation were significantly smaller over the heterofullerenes when compared to those over C_{60} . Whereas the substitution of either metal resulted in a reduction of activation barriers, the activation barriers for post-ethylene formation reactions were smaller over $C_{59}Ni$ making $C_{59}Pd$ a good selective acetylene hydrogenation catalyst. Oxidative addition, a step common to both Heck and Suzuki-Miyaura cross coupling reactions, was observed to proceed with smaller activation barriers over C_{59} Pd. Heck coupling of C_6H_5I with styrene was observed to proceed via oxidative addition, migratory insertion and reductive elimination steps. The free energy barriers for oxidative addition, migratory insertion and reductive elimination steps were 14.8, 11.6 and 4.8 kcal/mol, respectively, over C₅₉Pd, and 17.4, 79.3 and 17.4 kcal/mol, respectively, over $C_{59}Ni$, indicating oxidative addition and migratory insertion to be the rate-determining steps over C_{59} Pd and C_{59} Ni, respectively. Similarly for Suzuki-Miyaura coupling reaction, activation barriers for oxidative addition, transmetalation and reductive elimination steps were 14.8, 52.4 and 7.9 kcal/mol, respectively, over C_{59} Pd, and 17.4, 64.7 and 60.2 kcal/mol, respectively, over C_{59} Ni, indicating transmetalation step to be the rate-determining

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step over both the heterofullerenes.

DFT calculations were carried out on a periodic slab of $\text{CeO}_2(1\ 1\ 1)$ with cationic and anionic surface defects. The role of surface defects of both types on adsorption of C₂-gases and halobenzenes was studied. The synergistic effect of the presence of cationic substitution and anionic vacancies was observed to contribute to an increase in Lewis acid-base interactions resulting in improved adsorption characteristics. The effect of Pd^{2+} substitution on adsorption was studied. The addition of Pd^{2+} -ions was found to enhance the adsorption of the C₂-gases and halobenzenes. Pd-substituted reduced CeO_2 showed good activity for the adsorption of all C₂-gases and halobenzenes.

DFT calculations, carried out in this study, provided insights into the preferred adsorption sites, modes of adsorption, adsorption energetics and reactantcatalyst interactions. On the basis of these theoretical observations, Pdsubstituted C_{60} and CeO_2 -based system was found to be a potential catalysts for selective acetylene hydrogenation and C-C cross coupling reactions.

Keywords: Density functional theory; heterofullerenes; doped ceria; hydrogenation; C-C cross coupling; rate-determining step