Catalysis at the interfaces: a DFT study

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Abstract: In this contribution, we carry out density functional theory (DFT) calculations to show how the interfacial OH could boost the oxidation of CO as well as the hydrogenation of ester. Additionally, we would explore the influence of organic modification, and proposed that such an enhancement in selectivity can be understood in terms of steric effect and/or electronic effect.

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Keywords: Coordination Chemistry, Metal/Organic Interface, Metal/Oxide Interface, Selective Hydrogenation

1. Introduction (11-point boldface)

To provide high surface area while prevent aggregation, nano metal catalysts should be distributed over supports (usually metal (hydr)oxides) or encapsulated by organic ligands. Interestingly, some catalytic processes prefer to take place at the interface of metal/oxide or metal/organic ligand, in which two compositions are able to work in synergy to improve the reactivity and/or selectivity. Though DFT calculations, the molecular mechanisms behind interfacial catalysis are disclosed.

2. Results and discussion

Supports often play critical roles in stabilizing and promoting the catalysis of supported metal nanoparticles. The concept of "support effects" has been brought for long, but the chemistry behind them remains obscure. A desirable model nanocatalyst for investigating the chemistry at the interface between metal and support components should have uniform catalytically active sites and ideally minimize either metal or support components only at the interface at the atomic scale. When sub-monolayer Fe-OH was deposited onto Pt, obtained was a model catalyst highly active for CO oxidation at room-temperature. Both DFT calculations and isotope-labeling experiments strongly confirmed that the interfacial Fe^{3+}-OH-Pt sites were the active sites for room-temperature CO oxidation initiated by the oxidative coupling of coordinated CO on Pt and interfacial –OH. Such a mechanism nicely explains why FeO_x is a promoter for Pt catalysts in CO oxidation [1]. Atomically dispersed catalysts are another ideal system that allows the identification of local coordination environment of metal active sites. we have recently developed a photochemical strategy to prepare a highly stable atomically dispersed Pd catalyst (Pd_1/TiO_2) with Pd loading over 1.5wt% on ultrathin TiO_2 nanosheets. According to DFT calculations, H_2 adsorbed on Pd atom was readily dissociated in a heterolytic way. One of the H atoms moved to nearby oxygen on EG to yield O-$H^{\delta+}$, leaving the other H atom on Pd as $H^{\delta-}$. In the hydrogenation of styrene over Pd_1/TiO_2, both $H^{\delta-}$ and $H^{\delta+}$ were involved, which was confirmed by both IR and NMR measurements performed with deuterium-labeled reagents [2].

Recently, ligand modification strategy has been introduced to enhance the catalytic performance in selective hydrogenation reaction. Experimentally, amine-capped Pt_3Co alloyed nanoparticles can be used as efficient catalysts for the selective hydrogenation of α, β-unsaturated aldehydes. DFT calculations showed that long carbon chains that are capped onto the Pt_3Co nanocatalysts imparted steric hindrance so that CAL molecules did not lie flat on the nanoparticle surface. Hence, CAL molecules can only enter into the array of OAm molecules edge on with their aldehyde groups while the C=C bonds directed away from the catalytically active surface. This finding indicated that the presence of long-chain amines on the surface to create an metal/organic ligand interface was essential to the high hydrogenation selectivity towards α, β-unsaturated alcohols [3]. In addition, the metal/organic ligand interface would control the selectivity through electronic effects. The hydrogenation of nitroaromatics is a typical consecutive reaction that yields many products including nitrosoaromatics, N-hydroxyanilines, and anilines. Experimentally, the high (>95%) selectivity to N-hydroxyaniline was first achieved by ethylenediamine (EDA) coated ultrathin Pt nanowire. DFT calculations demonstrated that the strong binding of en significantly altered the adsorption behaviors of the Pt catalysts, making the coordinated unsaturated Pt atoms only accessible by the electron deficient species, such as nitrobenzene and the nitroso intermediate. In contrast, the binding of N-hydroxyaniline with en-coated Pt nanowire becomes relative weak, which would be displaced by other stronger adsorbates (such as EDA, nitrobenzene or nitrosobenzene) easily once it was formed, thus switching off the deeper hydrogenation [4].

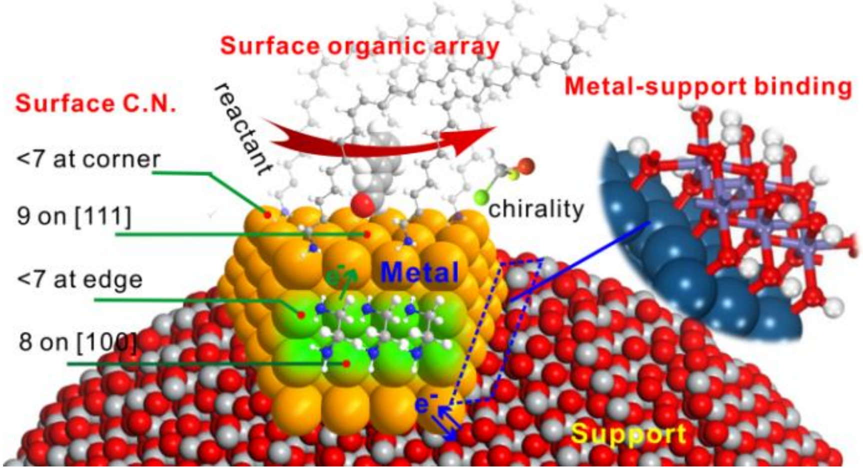

Figure 1. Coordination chemistry on the surface and interface of metal nanomaterials in different aspects.

4. Conclusions

To summarize, the surface coordination chemistry that is linked to the catalytic performaces of metal nanocatalysts. Although many unique physical and chemical properties of nanocatalyts appear at the size scale of nanometers, the chemistry at the molecular level plays important roles in understanding the essential factors that influence the activity and selectivity via steric and electronic effects.

References

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