Engineering Surface Ligands of Noble Metal Nanocatalysts in Tuning the Product Selectivity

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Abstract: Nanosized noble metal catalysts supported on high-surface-area support are of great importance for numerous industrial chemical processes to mediate reaction pathways in heterogeneous catalysis. Control of surface area and surface energy of nanocatalysts is a key to achieving high activity and selectivity for desired products. In the past decade, new synthetic methodologies for noble metal nanocatalysts with well-defined nanostructures have been developed. Wet-chemical preparation of noble metal nanocatalysts usually involves the utilization of specific surfactants that can bind the surface of nanocatalysts as ligands to control the nanostructures and prevent the coalescence of nanocatalysts. Surface ligands that form a densely packed self-assembled monolayer offer a facile solution to tune the surface energy of nanocatalysts, and, therefore, the selectivity of products. In this minireview, we highlight the recent advances in understanding the role of surface ligands in control over the product selectivity in a multi-product reaction using noble metal nanocatalysts. The review is outlined according to the three possible roles of surface ligands, including steric effect, orientation effect and surface charge state, in varying the adsorption/binding of reactants/transition states.

1. Introduction

Nanosized noble metal (e.g., Pt, Pd, Au and Ag) particles supported on high-surface-area support are of great importance for numerous industrial chemical processes in order to mediate reaction pathways known as heterogeneous catalysis [1–3]. In heterogeneous catalysis, control of surface area (i.e., more exposed reactive surface sites) and surface energy (i.e., preferentially exposed crystal facets or surface atoms) of catalysts is a key to achieving a high catalytic activity and selectivity to desired products. When decreasing the size to a nanometer scale, nanocatalysts with intrinsic "nano effects" can boost turnover frequency (TOF) that cannot be achieved using their bulk compartments. One of these "nano effects" is their high percentage of surface atoms, particularly edge and corner atoms, which increases with a smaller particle size [4]. These surface atoms having a lower coordination number compared to the lattice are considered to be catalytically more active.

In the past decade, new synthetic methodologies for noble metal nanocatalysts with well-defined nanostructures have been developed. Current synthetic advances offer a rational design of sizes (~1 to 100 nm), shapes and morphologies (spheres, rods, wires, tubes, cubes and polyhedron) of these noble metal nanocatalysts [5–9]. The effect of particle sizes, topologies and surface crystal facets on catalytic activity of noble metal nanocatalysts has been well documented and reviewed [1,4,8,10–13]. However, wet-chemical preparation of noble metal nanocatalysts involves the utilization of specific surfactants that can bind the surface of nanocatalysts as ligands to control the nanostructures and prevent the

coalescence of nanocatalysts by lowering the free energy of the surface. For example, oleylamine is often used as a surface ligand to grow noble metal nanoparticles (NPs) in oil-phase synthesis, e.g., Pd, Ag, and Au [14,15]; however, citrate is often used to grow noble metal NPs in aqueous-phase synthesis, e.g., Ag and Au [16,17]. The conformation of surface ligands on a confined NP surface is largely determined by the chain length/charge/density of ligands and the curvature of NP cores [18,19]. In the presence of excess surface ligands (essentially necessary during the wet-chemical synthesis), ligands can form a densely packed self-assembled monolayer (SAM) in the thickness of 0.5–3 nm by maximizing van der Waals interactions of alkyl chains [18]. The surface ligands are demonstrated to be detrimental to the catalytic activity in many examples [20–27]. The formation of SAMs is often considered to block the surface accessibility, leading to a decrease in the accessibility of catalytic sites [20,23], although there are many reported examples showing that surface ligands do not depress catalytic activity of metal NPs [28–31]. This will not be our focus but will be briefly discussed in the outlook.

The scope of this minireview is on the recent understanding of the role of surface ligands in control over the selectivity of products. Compared to homogeneous catalysts of the same species, heterogeneous noble metal catalysts have advantages in recovering and recycling of precious metals and high turnover number (TON), but drawbacks in product selectivity in a multi-product reaction [4,32]. The selectivity is highly important in the fine chemicals industries to yield a high portion of the desired products that simplifies the separation of products. A fundamental question always interesting to the community is how to control the selectivity of heterogeneous noble metal catalysts. We take the inspiration from metalloenzymatic catalysis where ligands, i.e., protein frameworks, modulate the steric and electronic nature of catalytic sites. The presence of a large protein framework on metal ion(s) does not slow down or prevent the binding of reactants, but restrains the binding of specific reactants and even transition states [33]. Protein frameworks acting as a secondary coordination environment for metal ion(s) are responsible to the high selectivity in metalloenzymatic catalysis. Surface ligands on noble metal nanocatalysts provide the coordination environment for surface atoms to likely tune the binding of reactants in a similar role.

Three possible mechanisms are involved in deliberating the roles of surface ligands in tuning the selectivity of noble metal catalysts, including steric effect, orientation effect and surface charge state (Scheme 1). First, the steric effect can confine the adsorption/binding dominantly on edge and corner sites (Scheme 1a). Although surface ligands form dense SAMs on the surface of metal NP cores, the edge and corner atoms have less organized ligands [18]. Binding and activating of reactants preferentially occur at surface edge and corners, which can restrain the types of adsorption sites. The regulation of adsorption will change the product selectivity in these structure-sensitive reactions. The steric effect can also be interpreted as to impose steric hindrance to reactants with complex molecular geometry [22] (Scheme 1b). The crowdedness of surface ligands can alter the binding types and/or specific functional groups of reactants to catalytic sites. Second, the orientation effect is to enable the binding of reactant in restrictive orientation (Scheme 1c), analogous to that of metalloenzymes [33,34]. The orientation effect is generally based on the non-covalent interaction of surface ligands and reactants. The exerted interaction will orient reactants to vary the distance of active sites to a specific group/bond of reactants that contributes to a high selectivity to desired products. Finally, surface ligands can alter the charge state of surface atoms. The charge density is a key to governing the binding affinity of reactants and/or transition states to active sites. The fine-tuning of surface charge density, therefore, can change the reaction pathways and may favor the formation of a specific intermediate involved in a complex reaction [35]. In this minireview, we highlight a few recent reports on how to use surface ligands on heterogeneous noble metal nanocatalysts (mainly on Au, Pd and Pt) to modulate their catalytic selectivity. The review is outlined according to the three mechanisms as discussed.
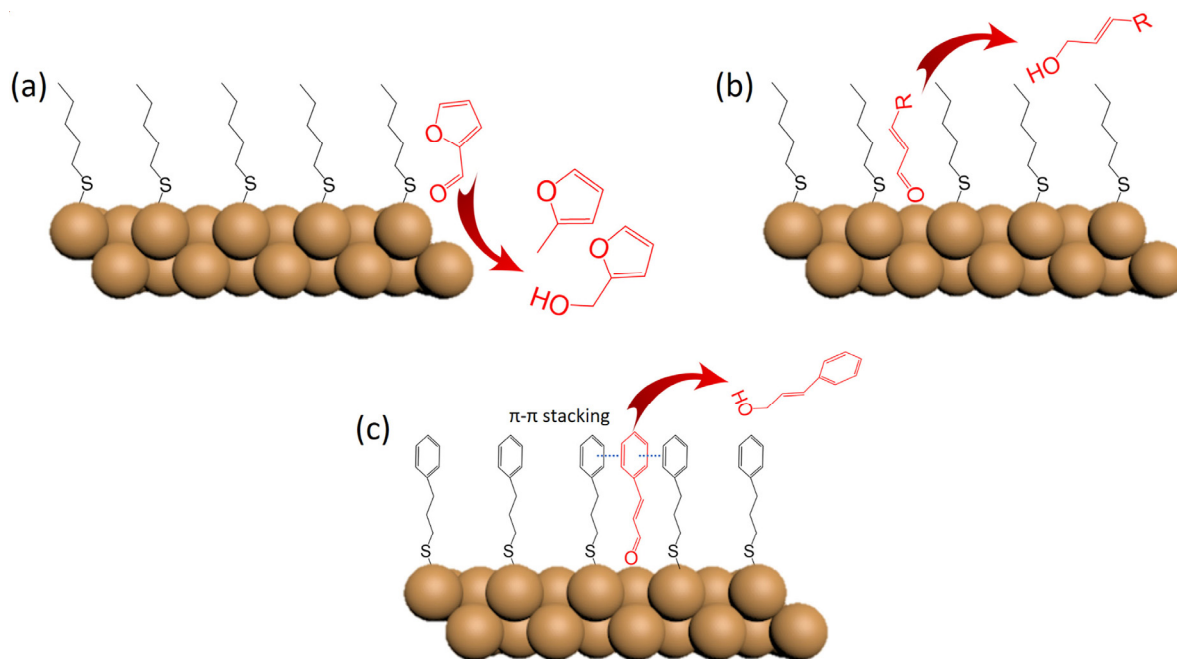
Scheme 1. Three possible mechanisms to show the roles of surface ligands in tuning the selectivity of noble metal catalysts: (**a**) steric effect to control the adsorption/binding of reactants mainly on edge and corner sites; (**b**) orientation effect through steric hindrance and (**c**) non-covalent interaction of reactants and surface ligands.

2. Steric Effect of Surface Ligands

Surface ligands on noble metal nanocatalysts inevitably result in surface crowdedness that blocks the accessibility of active sites and the adsorption of reactants, as well the elimination of the products. The crowdedness is determined by the density and the bulkiness of surface ligands as demonstrated by Medlin's group [22,36,37]. When modifying Pd/Al_2O_3 with two thiol-functionalized ligands of long-chain alkanethiol of 1-octadecanethiol (C18) and bulky caged hydrocarbon thiol of 1-adamantanethiol (AT) (Figure 1a–c) [36], the crowdedness of C18 SAMs was higher than that of AT SAMs where the average ligand-to-ligand distance is 4.7 Å for C18 and 6.9 Å for AT, respectively. The adsorption sites on Pd/Al_2O_3 were largely dependent on the crowdedness of ligands, even though the two ligands did not alter the adsorption strength of CO significantly. The results of CO diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) suggested that C18-modified Pd/Al_2O_3 showed less adsorption of CO compared to that of AT-modified catalysts. The adsorption sites for C18-modified Pd/Al_2O_3 were primarily three-fold hollow sites and a single-type of atop sites; while, for AT-modified Pd/Al_2O_3, additional surface bridging sites (two-fold) and a second-type linear sites are available. For hydrogenation reaction of ethylene, AT-modified Pd/Al_2O_3 catalysts showed a 17 times faster TOF, compared to that of C18-modified catalysts.

When partially blocking catalytic sites and increasing the surface crowdedness, the steric hindrance can confine the binding of complex reactant molecules to undergo different competing reaction pathways, leading to a higher selectivity of specific products [37]. The same group investigated furfural hydrogenation reaction using C18 and AT modified Pd/Al_2O_3 catalysts (Figure 1d) [37]. Furfural from dehydration of sugars is an important biomass product and its hydrogenation usually produces furan and tetrahydrofuran through a decarbonylation and full hydrogenation on noble metal catalysts. The selectivity of furfural hydrogenation was found to be dominated by the type of surface ligands. A high selectivity for furfural alcohol and methylfuran (>70%) was obtained using C18-modified Pd/Al_2O_3, while a high selectivity for tetrahydrofuran and furan (>90%) was obtained using AT-modified Pd/Al_2O_3 and uncoated Pd/Al_2O_3. The hydrogenation pathway was readily

controlled by the surface crowdedness. C18-modified Pd/Al$_2$O$_3$ catalysts had a dense SAM which largely limits bridging and three-fold adsorption sites on the surface. A standing-up orientation of furfural was mostly directed on the terraces on Pd atop sites. The restrictively oriented reactants resulted in the increase of the physical distance of the furan rings to surface atoms. Therefore, a high selectivity for furfural alcohol and methylfuran was observed. By contrast, a flat-lying structure of furfural stabilized on the edges and steps as well as top surfaces was hypothesized for AT-modified Pd/Al$_2$O$_3$ catalysts, due to less crowded ligands. This favored the hydrogenation of furan rings to form furan and tetrahydrofuran. C18 ligands blocked all edges and steps as well as top surfaces on Pd, therefore inhibiting the formation of tetrahydrofuran and furan.
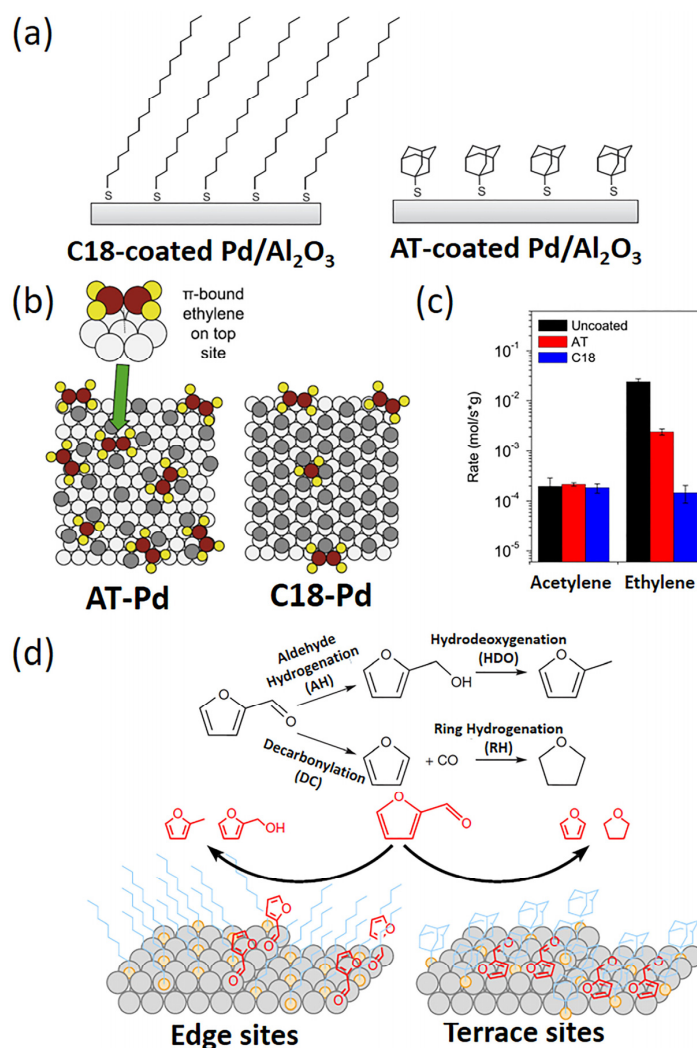
Figure 1. Steric effects of surface ligands on Pd nanocatalysts. (**a**) Chemical structures of 1-octadecanethiol (C18) and 1-adamantanethiol (AT), both of which are coated on the surface of 5 wt % Pd/Al$_2$O$_3$ catalysts; (**b**) proposed adsorption mechanism of ethylene on C18-Pd/Al$_2$O$_3$ and AT-Pd/Al$_2$O$_3$ catalysts. On C18-Pd/Al$_2$O$_3$, only the edges and steps on the top sites are accessible for ethylene in a π-bound configuration. On AT-Pd/Al$_2$O$_3$ catalysts, atop sites on terraces are also accessible; (**c**) the acetylene (left) and ethylene (right) hydrogenation activities on Pd/Al$_2$O$_3$ catalysts with different surface ligands. (**a**–**c**) are reprinted with permission from [36]. Copyright Elsevier, 2013; (**d**) proposed adsorption mechanism of furfural on C18-Pd/Al$_2$O$_3$ and AT-Pd/Al$_2$O$_3$ catalysts. On C18-Pd/Al$_2$O$_3$, furfural binds upright on step edges and defects, whereas, on AT-Pd/Al$_2$O$_3$, furfural can lie flat on a terrace; (**d**) is reprinted by permission from [37]. Copyright Nature publishing group, 2013.

The non-specific binding of reactant molecules on a ligand-coated surface can be regulated by the length of ligands. When the length of surface ligands becomes shorter, no dense monolayer can form since the van der Waals interactions between short alkyl chains cannot overcome the entropy loss of ligands. Therefore, the shorter surface ligands can only form a loose surface coverage. Wu et al. [38] showed a systematic study on the effect of the amine ligand length on the hydrogenation selectivity using Pt_3Co nanocrystals (Figure 2). The model reaction of cinnamaldehyde hydrogenation was used to examine the hydrogenation competition over C=C and C=O bonds. Pt_3Co nanocrystals coated with amine ligands having a long alkyl chain (C12-C18) showed a high selectivity of >90% to unsaturated cinnamyl alcohol even at 100% conversion. The selectivity decreased when decreasing the alkyl chain of ligands. Pt_3Co nanocrystals coated with n-butyl amine did not show obvious selectivity of C=C and C=O bonds during hydrogenation. These results suggested that surface ligands with long alkyl chains blocked the binding of C=C bonds to surface atoms in which ligands were hypothesized to face cinnamaldehyde linearly; that is, C=O bonds were closer to surface atoms. This surface crowdedness lacked shorter ligands and the diffusion/adsorption of cinnamaldehyde occured in a more randomized way.

The steric effect can regulate the product selectivity by varying the interaction of products and ligands. In the case of reactants having a large volume, e.g., linoleic acid, the hydrogenation selectivity of two C=C bonds is controllable through the repulsion of ligands to products [22]. Using uncoated Pd/Al_2O_3 catalysts, the hydrogenation of linoleic acid favored the formation of stearic acid with the two C=C bonds reduced. When modified by thiol ligands with various chain lengths, the selectivity of hydrogenation to monounsaturated fatty acids (e.g., oleic acid and octadecenoic acid) could be improved to >80% even at conversion of 70%. The most likely reason is because monounsaturated fatty acid, in the presence of surface ligands, was sterically hindered to further adsorb and react at a highly crowded surface of Pd.
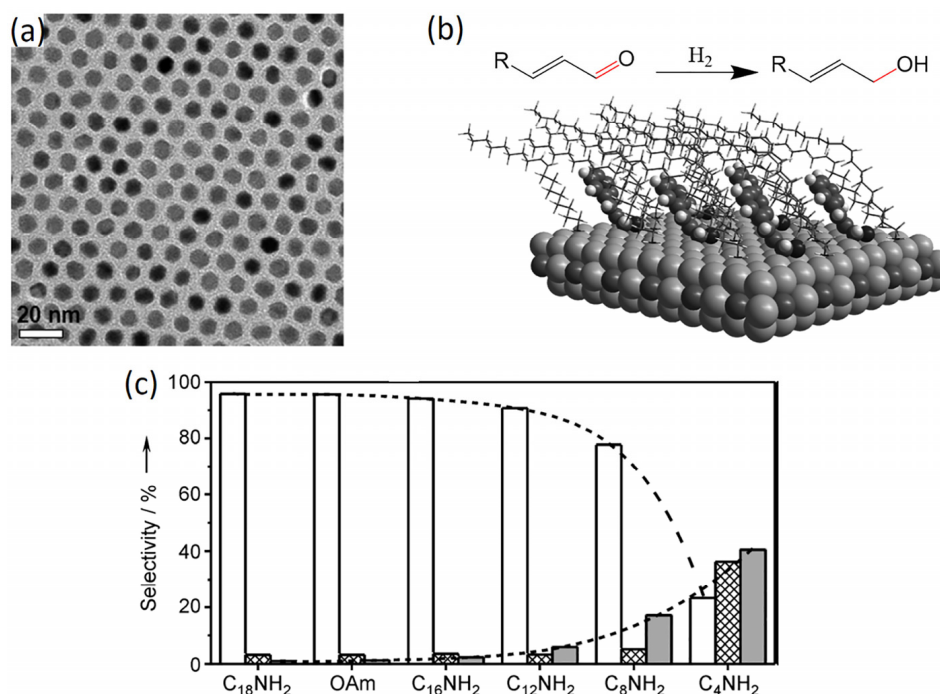

Figure 2. Steric effect of amines modified Pt_3Co NPs toward the hydrogenation of α,β-unsaturated aldehyde. (**a**) TEM images of Pt_3Co NPs; (**b**) the proposed reaction mechanism; (**c**) selectivity for cinnamylalcohol (white), hydro-cinnamaldehyde (crosshatch) and hydrocinnamyl alcohol (gray); Reprinted by permission from [38]. Copyright Wiley Materials, 2012.

The surface crowdedness is profoundly influenced by the density of ligands. Only with a high density of the surface coverage by ligands should the surface crowdedness be critical to determine the selectivity. Using hydrogenation of 4-octyne as a model reaction, Kwon et al. [39] demonstrated that the product selectivity to 4-octene was controlled by the concentration of amine ligands on Pt nanocatalysts. The selectivity to 4-octene only showed at a critical concentration of octylamine ligands of 1–2 mM, which was high enough to result in surface crowdedness on a Pt surface. A higher selectivity was observed at a higher concentration of octylamine until reaching the saturation at 100 mM. Density functional theory (DFT) simulation results suggested that the change of adsorption energy of alkenes was likely responsible for the selective exclusion of alkenes as partial hydrogenation products, thus preventing further hydrogenation of alkenes.

Au NPs show high activity for a number of selective oxidation reactions [40–43]. The catalytic activity of Au NPs is primarily due to metal–support interaction. The reports on ligand-modulated selective oxidation using Au NPs are few. Yoskamtorn et al. [24] reported that the surface ligands of supported Au_{25} nanoclusters had a profound influence on the product selectivity of aerobic benzyl alcohol oxidation reaction (Figure 3). By reducing surface ligands through high-temperature calcination at 400–500 °C, as-resulted Au nanocatalysts exhibited a continuous decrease in selectivity to benzaldehyde from 100% to 15%, along with the increase of TOF. In the presence of dodecanethiol ligands, partially covered surface reduced the catalytic ability of Au_{25} nanocatalysts by restricting the adsorption of reactants and intermediate states (including benzaldehyde). Thus, only partially oxidized benzaldehyde was obtained for dodecanethiol-coated Au_{25}. In the absence of surface ligands, a high selectivity for a fully oxidized product of benzoic acid and ester was observed. The selective hydrogenation reaction of 4-nitrobenzyl aldehyde was investigated using Au_{99} [44]. A high selectivity to the hydrogenation of aldehyde groups (close to 100%) was attributed to the formation of -S(R)-Au-S(R)-Au-S(R) staple-like motifs, which resulted in the strong interaction of 4-nitrobenzaldehyde with C=O bonds.
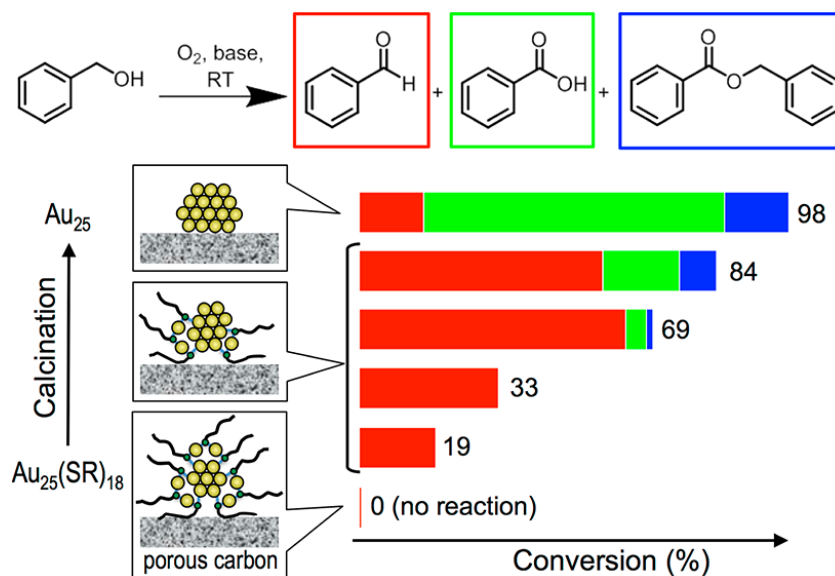

Figure 3. Au_{25} nanocatalysts coated with dodecanethiol for selective aerobic alcohol oxidation. Reprinted with permission from [24]. Copyright American Chemical Society, 2014.

3. Orientation Effect of Surface Ligands

As aforementioned, high efficiency and selectivity in metalloenzymatic catalysis arise from a specific coordination environment, namely, the second coordination sphere. The protein frameworks that are not involved in a catalytic process play an important role in terms of proximity and orientation. The reactant molecules can be oriented in closer proximity in a restricted conformation

that facilitates the occurrence of binding/activating/reacting. The mechanism to enhance the proximity and orientation is the non-covalent interaction, e.g., hydrogen bonding and π-π interaction, between the protein frameworks and reactants/transition states. As such, surface ligands on noble metal nanocatalysts may provide a similar orientation effect to improve the product selectivity through molecule recognition and/or specific regulation on adsorption. One straightforward way is to utilize the structural and chemical similarity of reactants and ligands that potentially can orient reactants through an enthalpy-driven path [45–47].

The selective hydrogenation reaction of cinnamaldehyde has been demonstrated by modification of surface ligands on Pt nanocatalysts as shown in Figure 4a [37,48–50]. By coating a variety of surface ligands on supported Pt nanocatalysts, the non-covalent interaction between cinnamaldehyde and surface ligands could be varied by simply tuning the chemical structures of ligands. It is interesting to note that Pt nanocatalysts coated by 3-phenylpropanethiol, in which both the phenyl moiety and carbon chain are chemically and structurally identical to that of cinnamaldehyde, could give a high selectivity of >90% to cinnamyl alcohol [48]. Unmodified Pt nanocatalysts or Pt nanocatalysts coated by ligands with linear alkyl chains showed a poor selectivity to cinnamyl alcohol. The aromatic stacking interaction (or π-π interaction) between phenylpropanethiol and cinnamaldehyde was found to be critical to orient cinnamaldehyde at an optimal distance and conformation toward selective hydrogenation of the aldehyde moieties. The missing of such interaction would cause a non-orientated adsorption of reactants, resulting in poor selectivity over the hydrogenation of C=C and C=O bonds.
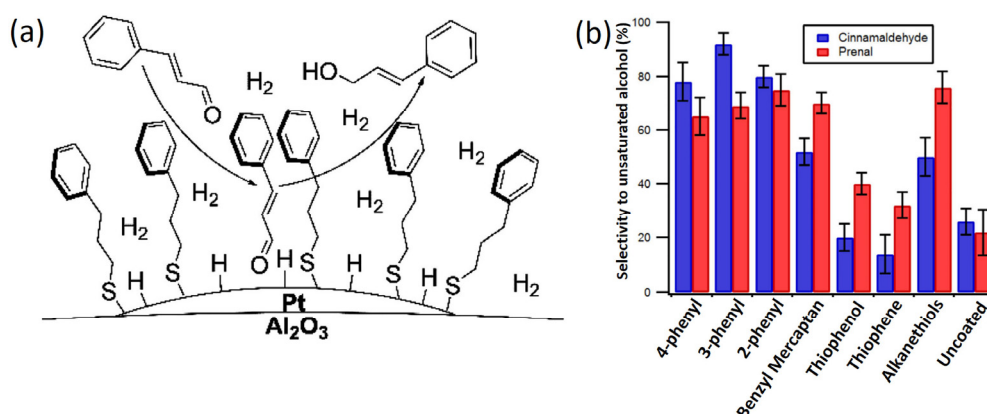
Figure 4. Orientation effect on Pt nanocatalysts toward selective hydrogenation. (**a**) Proposed mechanism of selective hydrogenation of cinnamaldehyde on 3-phenylpropanethiol modified Pt nanocatalysts; (**b**) the selectivity of cinnamaldehyde and prenal hydrogenation to unsaturated alcohol. Reprinted with permission from [48]. Copyright American Chemical Society, 2013.

The interaction between surface ligands and the reactants can vary stereoselectivity of noble metal nanocatalysts. When chiral ligands are coated on metal nanocatalysts to yield a chiral environment, as-obtained catalysts can potentially be the most promising platform to selectively catalyze enantiopure products [51–59]. The interaction between reactant and ligand is essential for asymmetric catalytic reactions. There are a few examples to chirally modify Pd and Pt NPs using cinchona alkaloids to produce a chiral environment toward enantioselective catalysis [52,60–63]. LeBlond showed that heterogeneous Pt nanocatalysts coated with 10,11-dihydrocinchonidine catalyzed asymmetric hydrogenation of α-keto esters with 94% ee [62]. The enantioselectivity also exhibited a strong dependence on the ligand density. Low surface coverage of Pt nanocatalysts only resulted a poor enantioselectivity. The mechanism was thought to be "stereoinduction" of chemisorbed chiral surface ligands, which yielded a stoichiometric interaction between prochiral reactants and anchored chiral ligands (Figure 5) [58,63]. The formation of a N-H-O hydrogen bond interaction between surface ligands of cinchona and ketone was essential to produce enantioselectivity [64]. Enantioselective allylic

alkylation reaction was also reported using chiral diphosphate modified Pd NPs [65]. The chiral monolayer of peptides as surface ligands for Au nanocatalysts supported on mesoporous SiO$_2$ showed asymmetric olefin cyclopropanation with a >50% enantioselectivity [66]. The formation of hydrogen-bonding network of chiral surface ligands resulted in a chiral environment to reactants. In addition, there are a few systems using polymer-coated Pt [61] and Au [67] nanocatalysts, which also showed enantioselective reactions [68]. However, it remains challenging to have a full picture of how the chiral ligand environment controls the enantioselectivity and whether the viable chiral heterogeneous nanocatalysts can be achieved using inexpensive, largely available surface ligands [62].
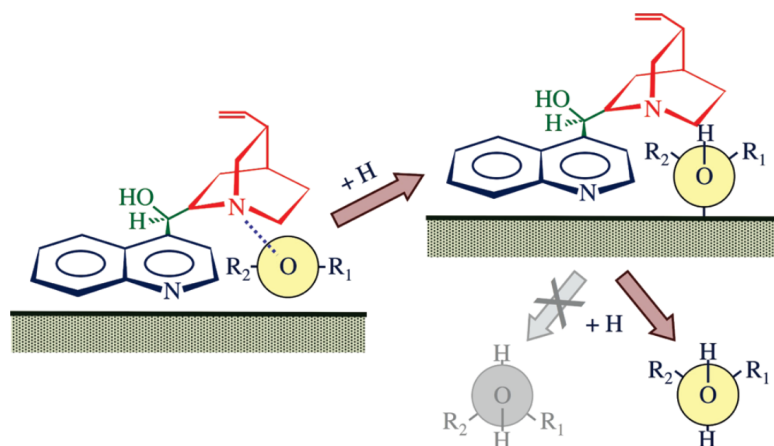
Figure 5. Schematic illustrations of chiral surface ligands on noble metal nanocatalysts with the reactants toward enantioselective reactions. Possible interaction model between the chiral surface ligand (cinchonidine) and the reactant (*cis* pro-(*R*) methylpyruvate) on Pt nanocatalysts toward asymmetric hydrogenation of α-ketoesters. Reprinted with permission from [58]. Copyright American Chemical Society, 2009.
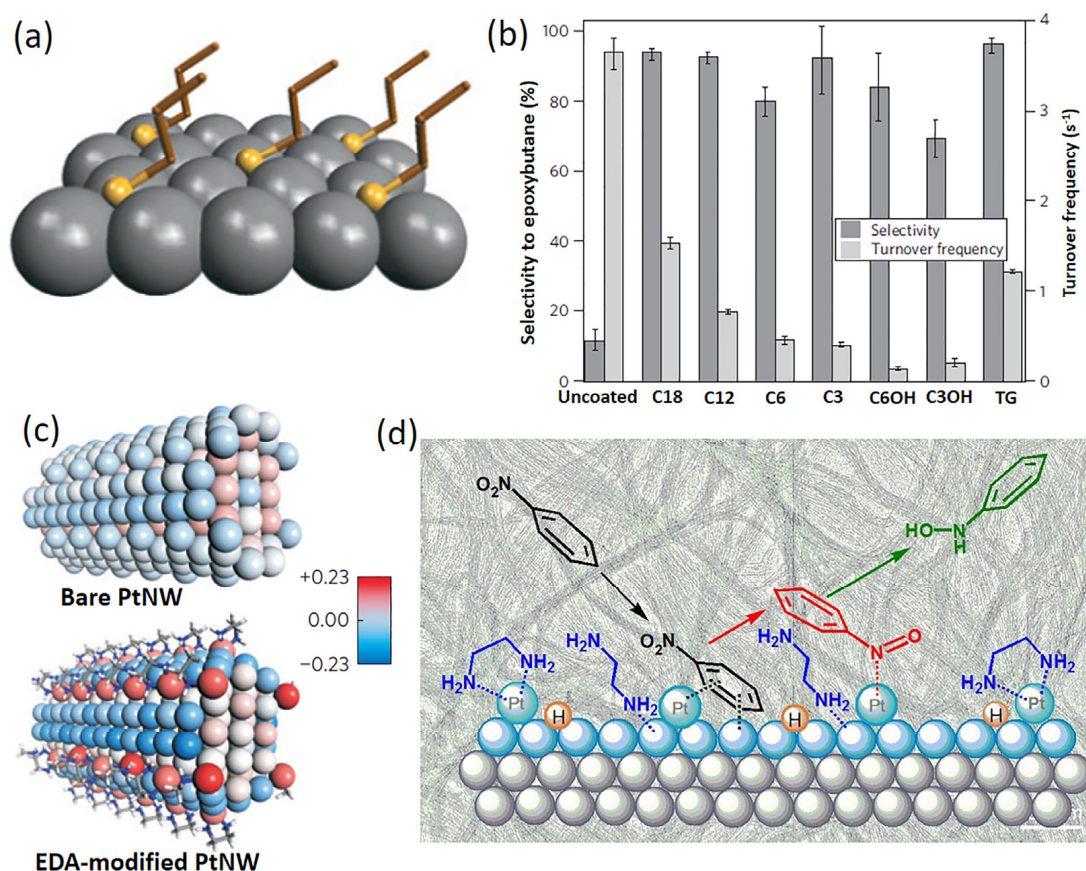
4. Electronic Effect by Surface Ligands

Electronic nature of surface metal atoms is one of the key parameters that dominates their binding. The anchor of surface ligands through the coordination with N, S and O atoms has been confirmed to change the intrinsic electronic states of metal by metal–ligand charge interaction. The change in electronic states of surface atoms can vary the key transition states that in turn control the product selectivity [35,69–72], particularly for parallel reactions and consecutive reactions. For example, when Pt/Al$_2$O$_3$ catalysts were modified by thiol-ended ligands with various lengths, all catalysts showed every similar selectivity for the hydrogenation of epoxybutene [73]. A high selectivity of >70% to epoxybutane was observed for thiol-coated Pt/Al$_2$O$_3$ catalysts in regardless of the chain lengths of ligands, compared to that of ~10% using uncoated Pt/Al$_2$O$_3$ catalysts. The sulphur head of thiol ligands can vary the geometric and electronic structures of Pd surface. The electronic perturbation of surface Pd atoms that caused by the transfer towards the adsorbed sulfur resulted in electron deficiency of Pd atoms. This favored the binding and hydrogenation of C=C bonds.

Very recently, Chen et al. [35] reported the use of ligand-modulated electronic effect on Pt nanowires to control the hydrogenation selectivity of nitroaromatics (Figure 6c,d). The hydrogenation of nitrobenzene to aniline went through an intermediate of hydroxylaniline, known as a high-value, industrially important compound. Pt nanowires coated by ethylenediamine showed a high selectivity of ~100% to hydroxylaniline, while commercial Pt/C showed a high selectivity (>90%) to aniline. The selectivity was attributed to the strong ligand-to-metal charge transfer that enhanced the charge density of surface Pt atoms. Such an interfacial electronic effect intrinsically favored the adsorption of nitrobenzene, and gave rise to a high selectivity for thermodynamically unfavorable *N*-hydroxylanilines. More importantly, this principle in tuning the electronic effect can be applied to

commercial Pt/C catalysts in which the surface treatment with ethylenediamine could give similar selectivity as Pt nanowires.

Figure 6. Electron transfer effect of surface ligands to control the catalytic selectivity. (**a**) Proposed structure of propanethiol ligands on Pd(111); (**b**) epoxybutane selectivity and reaction rate for Pd nanocatalysts with different thiol ligands. (**a**,**b**) are reprinted by permission from [73]. Copyright Nature publishing group, 2010; (**c**) constructed models of bare Pt nanowire and ethylenediamine (EDA)-modified Pt nanowire and corresponded Bader charge analysis; (**d**) TEM image and selective catalytic hydrogenation of nitrobenzene to *N*-hydroxylaniline. (**c**,**d**) are reprinted by permission from [35]. Copyright Nature publishing group, 2016.

Surface ligands are usually unwanted in electrocatalysis, since the charge transfer of catalysts can be significantly slowed down or completely shut down with a ligand length of >2 nm. Electrocatalytic activity of noble metal catalysts can be suppressed by ligands in various reactions [26,27]. However, when surface ligands are short and they can strongly interact with surface atoms, electrocatalytic selectivity can be modulated similar to other chemical reactions. Cao et al. [74] lately reported *N*-heterocyclic carbene coated Au NPs with an improved Faradaic efficiency (83%) for the electrochemical reduction of CO_2 to CO, compared to that of parent Au NP, about 53% in aqueous solution. Carbene-coated Au NPs enhanced the electrochemical reduction of CO_2 over water by a factor of 4. The carbine coordination likely varied electronic states of surface Au atoms via strong σ-donation. This ligand-to-metal charge transfer made gold NPs highly electron-rich which favored the binding of electrophilic C in CO_2.

5. Outlook

Engineering surface ligands on catalytically active noble metal nanocatalysts to control their catalytic activity and selectivity is a new era in heterogeneous catalysis. However, we cannot simply

pass over the influence of surface ligands to the activity, which is not discussed in the main text. The capping effect of surface ligands is particularly obvious in gas-phase reactions where the dynamics of ligands is largely inhibited [36,73]. The capping effect can exist at both interfaces of metal-reactants and metal-support. Using CO oxidation as a model reaction, Wu et al. studied the catalytic activity of $Au_{25}(SR)_{18}$ supported on CeO_2 [75]. A strong site-blocking effect was found on fully covered Au nanoclusters where the CO adsorption was completely suppressed. CO oxidation reaction could take place, only when removing the surface ligands partially to activate the interfacial binding between Au and CeO_2. The same $Au_{25}(SR)_{18}$ catalysts were examined to be active in many solution reactions. These results suggest that surface ligands lose the flexibility in gas phase reactions, leading to lowering the catalytic activity of noble metal nanocatalysts, while surface ligands with flexible movement and confirmation to partially expose accessibly active sites in liquid-phase reaction are less detrimental to the catalytic activity. In view of the metalloenzymatic catalysis, the protein frameworks do not slow down the binding of reactant or give non-specific interaction to dissimilar reactant to catalytic sites. It is convincing that these surface capping effects are likely the origin of the catalytic selectivity of noble metal catalysts because they blocked the access for uncontrollable reactions occurring rapidly on the planar sites.

Current experimental results are insufficient to draw a conclusion on the effect of surface ligands on the reaction selectivity. Our knowledge is still limited to a few model reactions, and much effort is needed before the ligand engineering becomes practically useful in common organic reactions. One of the main challenges in studying the ligand effects in catalysis is how to ensure that surface ligands are unchanged before and after reactions. For example, under harsh reaction conditions at high temperatures, the "coke" formation on the surface of catalysts can potentially bias the observed results that are indistinguishable from the effect of surface ligands or "coke" [36]. In the meantime, the design of surface ligands at the current stage, in terms of fine-tuning the chemical or physical interaction between reactants and ligands, is still lacking. If the specific interaction in the secondary coordination environment can be incorporated, the selectivity in heterogeneous catalysis can be further promoted.

Conflicts of Interest: The authors declare no conflict of interest.

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