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ARTICLE TYPE

Tunability of catalytic properties of Pd-based catalysts by rational control of strong metal and support interaction (SMSI) for selective hydrogenolytic C-C and C-O bond cleavage of ethylene glycol units in biomass molecules

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It is shown that catalytic properties of Pd can be fine-tuned by rational varying of metal-support interaction through the formation of bimetallic nanoparticles with support after hydrogen reduction; in hydrogenolysis of -CHOHCHOH- vicinal diol unit, the ability of breaking C-C bond over C-O bond is found to increase significantly with decrease in d-band filling while the ability of breaking C-O bond is enhanced by the upshift of d-band center of modified Pd.

It is well accepted that the present non-renewable energy resources cannot dominate the energy and commodity chemicals market for a long time due to their finite reserve and rapid consumption¹⁻⁴. As one of the primary renewable energy resources in nature, biomass especially the non-food based resources becomes a promising alternative and has been receiving increasing attention⁵. Poly alcohols (poly-ols) with repeating units of ethylene glycol, -CH(OH)CH(OH)- are commonly found in most biomass materials, either in the form of carbohydrates, or as the by-products in the hydrolysis of fats and oils, etc. Due to the limitations of the direct use of macroscopic biomass, controlled degradation to value-added chemicals is therefore essential. The skill of ethanol production from sugars through the actions of enzymes (yeast) has been known since prehistoric time. But the process is not only food dependent, also painstakingly slow. There is a recent work studying the production of alcohol from carbohydrate using non-fermentative approach by bacteria *Escherichia coli* on glucose⁶. However, the non-enzymatic breaking down of large biomass molecules to fuels or commodity chemicals over inorganic based catalyst materials at elevated temperature with significant enhanced kinetics and productivity is more attractive to industry. For fuel applications, the present research is focused on catalytic transformation of biomass to liquid alkanes in hydrogen through selective C-O cleavage but the similar homolytic cleavage energy (ΔH_{C-C} 348 kJ/mol and ΔH_{C-O} 360 kJ/mol) in both C-C and C-O activation always produces undesirable light alkanes (CH₄, C₂H₆, C₃H₈)^{7,8}. On the other hand, the control synthesis of small alcohol molecules (methanol, ethanol) through selective hydrogenolytic cleavages of C-C and C-O bonds in biomass is economically very appealing^{9,10,11}, as these volatile and high energy density liquids can be used as transportation fuels, also as key platform chemicals in synthesis³. Nevertheless, the random combinations of C-C cleavages and C-O cleavages without selectivity cause a wide distribution of the catalytic products and raise considerable separation problems. This complicated situation posts an important scientific and technological challenge to achieving ultra-selectivity of a specific product in the hydrogenolysis

reaction. Thus, an active catalyst with tunable ability in selectively cleaving C-C bond or C-O bond of the ethylene glycol unit in hydrogen with a controlled kinetics is highly desired.

It has been demonstrated that many catalytic reactions including the hydrogenolysis of biomass molecules require a specific and strong metal and support interaction (SMSI) to give a high catalytic performance¹², which is generally attributed to the high dispersion of the noble metal by the support. With the development of advanced and sensitive instruments, it is becoming clear that the decoration of supported metal particles with the reactive metallic elements derived from the support as bimetallic species is another important factor^{13,14,15}. The enhancement of catalytic properties of bimetallic nanoparticles (NPs) is assigned to the modified chemical and physical properties of the primary metal^{16,17}. However, the successful synthesis of bimetallic NPs with variable composition at high dispersity through the rational tuning of support composition is still a sharp challenge. Palladium is reported to be active in the hydrogenolysis of biomass molecules^{8,18,19}; but the selectivity to a specific product is low. Thus, we are interested in investigating how the electronic properties of the Pd can be modified through the formation of variable bimetallic NPs by rational control of the SMSI, also in establishing a fundamental relationship between the electronic structure and the catalytic activation of C-C or C-O bond of basic -CH(OH)CH(OH)- unit in biomass molecules.

Here, we note extremely small size (ca. 1-2 nm) supported bimetallic PdM (M = Fe, Co, Ni, Zn) nanoparticles was obtained through a controlled reduction of co-precipitated powder with a narrow size distribution (see SI). The composition of the surface bimetallic nanoparticles can be tailored by varying the composition of the supports. Aqueous hydrogenolysis of ethylene glycol in hydrogen over these new supported bimetallic catalysts of controlled dimensions is used as a model reaction, the molecule of which represents the simplest biomass derived molecule containing the -CH(OH)CH(OH)- units without encountering much phase (solubility and mass transfer) issues and instability problem against rearrangement. Besides, ethylene glycol can also be produced selectively from catalytic degradation of cellulose in hydrogen over carbide catalysts²⁰. It is reported that the supported Pd bimetallic nanoparticles with adjustable electronic properties by variable supports exhibit highly tunable ability in selective cleavage of C-C or C-O of ethylene glycol in hydrogen to form energy valuable methanol or ethanol (with a decent conversion). It is believed the findings could lead to the rational design of new nanocatalysts for biomass molecules activation. We have previously reported Pd/FeOx catalyst is highly selective for breakage of both C-C and C-O

bonds to give methanol/ethanol mixture of over 80% selectivity (with methanol selectivity > 50% at 4.3% conversion) from ethylene glycol with good recyclability¹¹.

Different amount of cobalt nitrate was firstly blended into the Fe₂O₃ support to tune the SMSI, which is expected to influence the catalytic properties of Pd. The synthesis and characterization details are summarized in the SI. It is confirmed that the formation of Pd atoms upon hydrogen reduction can selectively assist reduction of Co(II) to Co(0) from the supports and produce supported PdCo bimetallic NPs with maintaining high dispersion as the reduction potential of Co(II) to Co(0) is less negative than that of Fe(II) to Fe(0) ($E^0[\text{Co(II)/Co(0)}] = -0.28$ eV, $E^0[\text{Fe(II)/Fe(0)}] = -0.44$ eV).

The extended X-ray absorption fine structure (EXAFS) results of the Pd samples with variable content of cobalt in the support are displayed in Fig. 1 and Table S3. It is interesting to see the low but slightly increasing total coordination number (CN) (from 6.8 to 7.9) with an increasing Co content. We have estimated the average size of Pd containing NPs to be 1.5-2.0 nm from the analysis of the total CN within acceptable R- and D-W factors, based on the calibration curve of a recent EXAFS study alongside with other multiple techniques including gas adsorption, TEM and XRD²¹. (Noted that our commercial Pd/C with 2 nm Pd particles giving a CN of ca. 8.0 at Pd-Pd distance of 2.73 Å was fitted well in the calibration curve.) Indeed our TEM images in SI (Fig. S6) shows typical small Pd containing NPs around 1.5-2 nm in size, which also reflects the excellent dispersing ability of the supports. Another striking feature that we noted in EXAFS is the direct observation of a Pd-Co distance (2.0 to 4.7) at 2.57 Å, and a distorted Pd-Pd distance at 2.70 Å after reduction (kept in inert atmosphere); this confirms the formation of surface 'PdCo' bimetallic NPs of variable composition but with virtually the same particle size. As shown in Fig. 1(a), the number of first shell Co around Pd atom changes as sample 4 > sample 5 > sample 3 > sample 2, which reflects the controllable composition of the PdCo bimetallic NPs by varying the composition of supports. These results also agree with the TPR result (Fig. S2, Table S2).

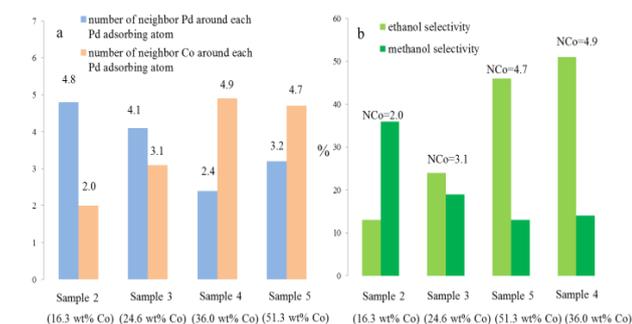


Fig. 1 (a) The numbers of first shell neighbour Pd and Co around each Pd adsorbing atom in samples 2-5 (the labelled Co concentration indicates the original amount of cobalt in the supports before reduction); (b) the variation of selectivity of methanol and ethanol in the hydrogenolysis of EG with Co content in PdCo catalyst.

The catalytic properties of the supported PdCo bimetallic nanoparticles were probed by the hydrogenolysis of ethylene glycol. The testing results are summarized in Fig. 1(b) and Table S5. As shown in Table S5, only 4 major primary products (CH₄, CO₂, CH₃OH and C₂H₅OH) are detected. The catalytic cleavage of C-O in hydrogen produces C₂H₅OH whilst the C-C cleavage produces CH₃OH. CH₄ and CO₂ are produced by the breakage of all the bonds in ethylene glycol followed by extensive hydrogenation reaction or steam reforming, respectively⁹. Thus, only the CH₃OH and C₂H₅OH selectivity are analyzed as a simple

but straight reflection of the activity of selective C-O and C-C bond rupture of the substrate molecule respectively. From Fig. 1(b), the ethanol selectivity increases with respect to the number of neighbor Co around Pd in PdCo bimetallic NPs at the expense of methanol and methane selectivity (as shown in Table S5a), the production of which involves C-C bond cleavage. Clearly, the observed variation of catalytic performance alludes to the change of the catalytic ability of Pd in the bimetallic NPs with different Co content for selectively breaking C-C bond or C-O bond. The calculated mole ratios of "selective cleavage of C-O: selective cleavage of C-C" in term of ethanol selectivity/methanol selectivity ratios are displayed in Fig. 2(a); as shown, the value increases linearly with the number of neighbor Co around each adsorbing Pd. This clearly suggests the enhanced ability of the PdCo catalyst in breaking C-O bond over C-C bond of the substrate is correlated with increasing Co content, which is controlled by the SMSI. At sample 4 which has the highest Co concentration, ethanol becomes the dominant liquid product. Through further optimization of reaction conditions (by varying reaction temperature, reaction time and ratio of noble metal: substrate), the ethanol selectivity can reach 91.7% (the total alcohols selectivity is 92.9% at 4.0% conversion- SI) with extremely high value of "selective cleavage of C-O: selective cleavage of C-C", which confirms that PdCo catalyst with high Co content is highly selective in breaking C-O bond over C-C bond (as shown in Table S5b,c).

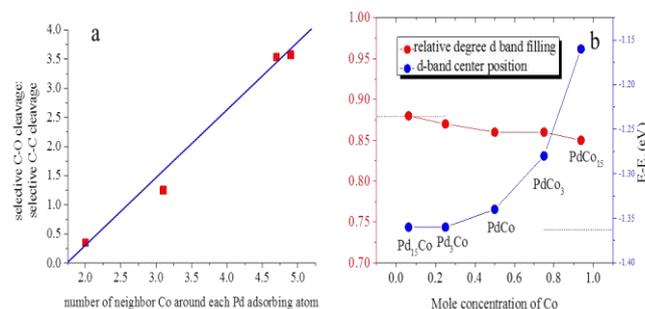


Fig. 2 (a) Plot of "selective C-O cleavage: selective C-C cleavage" (ethanol selectivity/methanol selectivity collected under typical conditions-see Table S 5(a) in SI) versus number of neighbor Co around Pd from EXAFS data; (b) Calculated d-band filling and d-band center position of PdCo with different Co content (the corresponding values of Pd are labelled in the figure as dash lines).

We have calculated the effect of progressive substitution of the top surface Pd atoms with Co atoms on the surface d-band structure of Pd based on a 4x4x4 atomistic model by density functional theory (DFT) (SI, Fig. S7). The compiled surface d-band center position and the d-band filling of Pd in a series of PdCo bimetallic nanoparticles are displayed in Fig. 2(b); the shift of surface d-band center becomes more significant than the marginal decrease of d-band filling at higher degree of Co substitution. This is consistent with the prediction from the d-band center theory that the center gravity will shift to higher energy level for the 'hybrid' (HOMO) d-band of PdCo at higher Co content because the dominant effect of mixing higher energy orbital of Co 3d with that of Pd 4d (ligand effect) overrides the initial downshift in d-band center due to lattice compression²². But the total degree of electron filling for the new hybrid d-band of PdCo only shows a minor decrease, presumably due to the similar number of valence electrons for Pd (10 valence electrons) and Co (9 valence electrons). Consequently, it is evident from our study that the progressive energy uplift of the d-band center at higher Co content by the enhanced SMSI can increase the C-O cleavage/C-C cleavage ratio in the catalytic hydrogenolysis of

ethylene glycol accordingly. Note that the recent density functional theory (DFT) calculations in literature²³ suggest that the kinetic adsorption of C-O bonds of ethylene glycol is much more favorable than both C-H and C-C adsorptions over the extended (111) metal surfaces. It is thought that the bidentate nature of the adsorbed EG forces the C-O bonds into an angle more closely perpendicular to the plane of the surface than one C-O bond in the case of monoalcohols on a flat metal surface. This facilitates the activation of C-O bonds but destabilizes the approach of α C in C-C at the other end of the molecule at the terrace metal sites. However, we argue that the contribution of this geometric reasoning may not be significant in our case as the relaxation of the steric constraints on the ‘nano-size’ bimetallic particles should also facilitate C-C activation, leading to the scission of the molecule then followed by the C-H formation which produces methanol. Nevertheless, from our results, we show the electronic effect is undoubtedly the key parameter in determining the extent of C-C and C-O cleavage.

It is known that the d-band energy of the first row transition metals is similar, but their electron filling is progressively increasing at a more significant degree across the period. As a result, the d-band filling of Pd containing NPs is possible to be well tuned by the decoration of variable transition metallic atoms through varying the corresponding support and carefully controlling the reduction process. Thus, supported PdM (M = Fe, Co, Ni, Zn) nanoparticles were synthesized using different supports as described in SI. Their metallic states and surface coverages are confirmed by their X-ray photoelectron spectroscopy (XPS) (Fig. S3, Fig. S9). The coordination environments of Pd in the bimetallic NPs, derived from EXAFS at the Pd K edge, are summarized in Fig. 3(a) and Table S4. The secondary atom M (M = Fe, Co, Ni, Zn) is indeed observed in the first scattering shell of the absorbing Pd, which indicates the neighbourhood between Pd and M (M = Fe, Co, Ni, Zn) atoms and confirms the formation of PdM bimetallic NPs, which reflects the existence of SMSI in all the samples. Also, the total coordination numbers of each absorbing Pd atom is within the range of 6-7 indicative of a similar particle size as discussed (confirmed by TEM, Fig. S10). In addition, their number of neighbour M (M = Fe, Co, Zn) around each Pd atom is selected around 2 which indicates the uniform composition in the bimetallic particles. (As shown in Fig. 3a, the number ratio of neighbour Pd to M around Pd is around 2, which corresponds to a 3:1 ratio of Pd:M in the composition of the alloy based on the face center cubic (fcc) structure as shown in Fig. S11a in SI.)

The catalysis of PdM (M = Fe, Co, Zn) NPs in the hydrogenolysis of ethylene glycol was thus studied under the same reaction conditions to investigate the effect of d-band filling parameter despite the fact that optimization conditions for maximum performance of individual catalysts were not the same. The results are shown in Fig. 3(b) and Table S6; the corresponding methanol selectivity decreases significantly from 50.1% of PdFe to 18.6% of PdZn. Meanwhile, the ethanol selectivity increases accordingly from 3.0% to 23.6%. The mole ratios of “selective cleavage of C-O: selective cleavage of C-C” (represented by “R”) calculated from the mole product ratios of ethanol to methanol are labelled in Fig. 3(b). For PdFe, the value is 0.06 which reveals the extremely high selectivity for C-C cleavage over C-O cleavage and thereby, methanol is produced as the dominant liquid product. PdM bimetallic NPs were successfully produced by the well-controlled SMSI in reduction process and the catalytic ability of selective C-O cleavage over C-C cleavage is enhanced in the following order: PdFe < PdCo < PdZn.

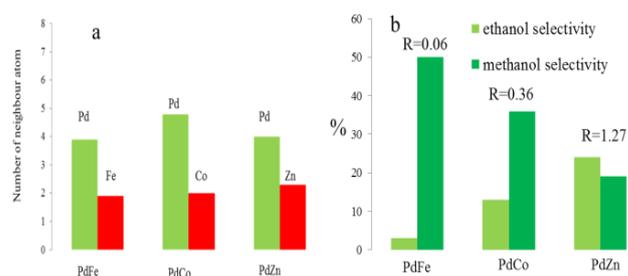


Fig. 3 (a) The number of neighbor Pd (NPd) and secondary atom M (NM, M = Fe, Co, Zn) around each Pd absorbing atom in the PdFe, PdCo and PdZn bimetallic NPs. (For PdNi, NNi=6.3 NPd=0, which indicates the much higher concentration of Ni than that of Fe, Co, Zn in PdM NPs); (b) the variation of selectivity of methanol and ethanol in the hydrogenolysis of EG among PdFe, PdCo and PdZn under same reaction conditions.

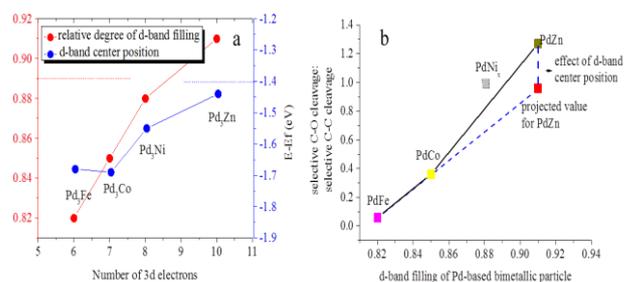


Fig. 4 (a) Calculated d-band filling and d-band center position of Pd₃M (M = Fe, Co, Ni, Zn) (the corresponding values of Pd are labelled in the figure as dash lines); (b) The effect of d-band filling and d-band center position of Pd₃M bimetallic nanoparticles (M = Fe, Co, Ni, Zn) on selective C-O/C-C cleavage.

The calculated d-band structure of the PdM bimetallic NPs are shown in Fig. 4(a); the d-band filling of homogenous 3:1 alloys indeed shows an increasing trend across the periodic elements with an increasing number of d-orbital electron. On the other hand, the resulting surface d-band center positions of Pd₃M for the four transition metals are being uplifted accordingly, presumably by the dominant effect of an increasing electron filling, despite the fact that the 3d energy levels for the transition metals should be slight but gradually decreasing due to increasing effective nuclear charge (Z_{eff}) across the period (d-band contraction). Note that Pd₃Fe and Pd₃Co have similar d-band center positions due to the two contradictory factors (the uplift by increase in electron filling is cancelled out by downshift due to d-band contraction). As a result, both the significant changes in electron filling and d-band center position could affect the catalytic hydrogenolysis reaction of ethylene glycol. Fig. 4(b) shows a plot of “selective cleavage of C-O: selective cleavage of C-C” versus the calculated d-band filling of the four transition metals (M) blended Pd₃M alloys. The catalytic result of PdNi was also placed in Fig. 4(b), despite the much higher concentration of Ni (NNi=6.3, as shown in Table S4) than that of Fe, Co, Zn in the PdM NPs (NM=2.0, as shown in Fig. 3(a)), as the calculated d-band filling value of PdNi alloys remains constant at 0.88 for a wide range of Ni content (SI, Table S8). From Fig. 4b, the increasing ability of the catalysts for C-O bond cleavage over C-C bond cleavage due to increasing d-band filling value is very apparent. However, the selective bond cleavage may also be affected by the uplifted d-band center positions of the alloys. According to Fig. 4(a), the d-band positions of Pd₃Fe and Pd₃Co are close to each other, while Pd₃Zn and Pd₃Ni show higher values. Coincidentally, the values of “selective cleavage of C-O: selective cleavage of C-C” for Pd₃Zn and Pd₃Ni show a more positively deviation from the linear projected line of d-band

filling effect over PdFe and PdCo alloys, which reflects the enhancement effect of d-band center position on C-O cleavage. Although the quantitative assessments of the d-band filling and the d-band position to this particular bond cleavage tendency have not yet been achieved due to the interplay between the two important factors and also the challenge for fine control in synthesis, it is believed that this analysis could guide the refinement of the synthesis for catalytic materials needed for selective C-C or C-O bond cleavage in biomass activation.

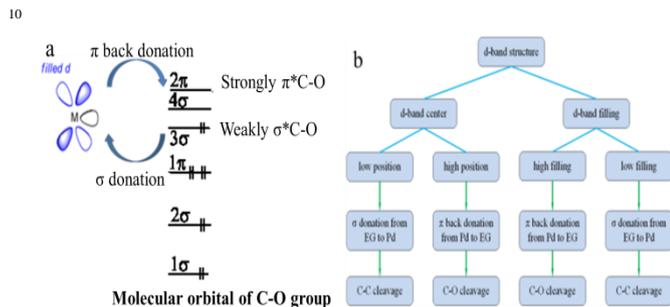
the decrease in d-band filling by interacts with early transition metal would favour C-C cleavage. The relationship between the d-band structure of Pd and the catalytic properties are summarized in Scheme 1(b). Thus, the tunability of the Pd based catalysts by SMSI for hydrogenolysis of ethylene glycol is clearly demonstrated.

Conclusion

As stated, there is an increasing interest in both academic and industrial communities to transform biomass molecules to fuel and commodity chemicals in green synthesis particularly using the heterogeneous catalytic hydrogenolysis reaction route. However, there is very limited literature to guide the selection of catalysts for any target product. There have been considerable experimental efforts in synthesizing a wide variety of catalysts, but it is very difficult, if not impossible, to exhaust all of the possibilities by a trial-and-error approach. This study has employed ethylene glycol as a representation for the basic repeating units in macroscopic biomass molecule as a substrate model. By rationally tuning the SMSI (which promotes the formation of PdM bimetallic NPs) it illustrates, for the first time, the possible fine-tuning of electronic factors in product specificity for this important natural resource.

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Scheme 1(a) Electronic interaction of Pd and the C-O function group of ethylene glycol; (b) The relationship between the d-band structure of Pd and the catalytic properties.

Apparently, the propensity for hydrogenolytic C-O or C-C bond cleavage of ethylene glycol of the PdM alloy catalysts synthesized by careful co-precipitation followed by hydrogen reduction is directly governed by their electronic structure, as demonstrated in Scheme 1(a). Through the hybridization of HOMO d-bands, the neighbor secondary atoms M (M = Fe, Co, Zn) are expected to modify the d-band structure of Pd significantly. The d-band filling increases from PdFe to PdCo, PdNi and PdZn due to increasing number of valence electrons in the transition metals ($\text{Fe } 3d^6 < \text{Co } 3d^7 < \text{Ni } 3d^8 < \text{Zn } 3d^{10}$). It is anticipated that the increasing d-band filling enables electronic π back donation to the π^* orbital of the adsorbed -C-O- moiety, which facilitates the -C-O- bond activation. Meanwhile, the σ interaction with the electrons donated from adsorbate through Pd-C bond to the metal would be disfavoured due to the increasing d-band filling, which would also reduce the tendency for the -C-C- bond cleavage. This could account for the observation that the value of “selective cleavage of C-O: selective cleavage of C-C” increases with the d-band filling of Pd by well tuning the SMSI which promotes the formation of PdM as $\text{Fe} < \text{Co} < \text{Ni} < \text{Zn}$. Besides d-band filling, the d-band center position is also found significantly affecting the bond cleavage tendency. The upshifted d-band center position of Pd is expected to match better with the π^* orbital of C-O, then the π back donation from Pd to the π^* of C-O group is thus much enhanced, leading to the breakage of the C-O bond in ethylene glycol. Therefore, the value of “selective cleavage of C-O: selective cleavage of C-C” increases with the up-shift of d-band center by increasing Co content in PdCo bimetallic NPs through the modification of support; the value is maximized at sample 4.

With the combined results of the rational synthesis of catalysts, the DFT calculations and the detailed catalytic evaluations, it is concluded that the ability of selectively breaking of C-O bond over C-C bond of ethylene glycol in hydrogen can be tailored with a good degree of accuracy, by rationally tuning the interaction between Pd NPs and the supports which is mainly attributed to the formation of PdM bimetallic NPs. The progressive increase in the transition metal content with respect to the corresponding upshift of d-band center position as well as the increase in d-band filling through the incorporation with a late 5th row transition metal element would favor C-O cleavage, whilst