DOI: 10.1002/anie.201407236

Selective Hydrogenation

Atomic Layer Deposition Overcoating: Tuning Catalyst Selectivity for Biomass Conversion**

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Abstract: *The terraces, edges, and facets of nanoparticles are all active sites for heterogeneous catalysis. These different active sites may cause the formation of various products during the catalytic reaction. Here we report that the step sites of Pd nanoparticles (NPs) can be covered precisely by the atomic layer deposition (ALD) method, whereas the terrace sites remain as active component for the hydrogenation of furfural. Increasing the thickness of the ALD-generated overcoats restricts the adsorption of furfural onto the step sites of Pd NPs and increases the selectivity to furan. Furan selectivities and furfural conversions are linearly correlated for samples with or without an overcoating, though the slopes differ. The ALD technique can tune the selectivity of furfural hydrogenation over Pd NPs and has improved our understanding of the reaction mechanism. The above conclusions are further supported by density functional theory (DFT) calculations.*

For decades, numerous surface science studies have reported differences in catalytic activity or selectivity when reactions occur on different single-crystal surfaces. Davis and coworkers[1] reported that the aromatization of hexane to benzene or heptane to toluene occurred on a Pt(111) surface much more readily than on a Pt(100) surface. Concurrently, in the hydrogenolysis of methylcyclopentane, the ring is broken much more frequently on a Pt(100) surface than on a Pt (111) surface.[2] Recently, as synthetic techniques for nanomaterials have been developed,[3–5] various types of shaped nanocrystals with well-defined surfaces have been fabricated. Surfaces can thus be tuned to achieve the desired reaction performance based on the catalyst nanostructure. For example, Xie and coworkers[6] found that tricobalt tetraoxide nanorods not only catalyze CO oxidation at temperatures as low as −77 °C, but also remain stable in a moist stream of feed gas. In the fuel cell and photocatalysis areas, it has been shown that the activity, selectivity, and stability of the working catalysts can be modified on the basis of the different indexes of the facets exposed.[7–10] Others have reported that the corners, edges, and defects of the catalyst nanoparticles (NPs) are the active sites for the catalytic reactions.[11,12] This situation presents a problem with regard to the catalytic performance being influenced by facet exposure, especially in real systems. If the active sites of the NPs are located only at defects, corners, or edges, the effect of the surface crystal structures can be overestimated.

Lu et al.[13] found that a thin layer of alumina over Pd NPs made by the atomic layer deposition (ALD) method can increase the resistance toward coke formation in the oxidative dehydrogenation of ethane. They proposed that the ALD-generated layers preferentially coat the defect sites of Pd NPs, which are believed to be active for coke formation. O'Neill et al.[14] also found that the overcoating of Cu with Al_2O_3 by ALD can suppress the deactivation of Cu caused by sintering and leaching of the metal under trickle bed conditions. However, both research groups primarily focused on increasing the stability of the catalysts using the ALD method and did not question whether an overcoat could modify the catalytic selectivity. Infrared spectroscopy measurements by Feng et al.[15] indicated that overcoatings by ALD may initiate

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[**] This material is based upon work supported as part of the Institute for Atom-Efficient Chemical Transformations (IACT), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science and Office of Basic Energy Sciences. Use of the Advanced Photon Source is supported by the U.S. Department of Energy, Office of Science, and Office of Basic Energy Sciences, under Contract DE-AC02-06CH11357. MRCAT operations are supported by the Department of Energy and the MRCAT member institutions. We thank Dr. HengShou for helpful discussions. We thank Dr. Neil M. Schweitzer for the FTIR experiment.

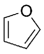
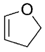
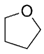
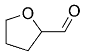
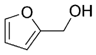
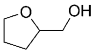
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201407236.

at the edges and then extend to the facet sites. If this is true, the method can be used to fabricate samples with edges, corners, or defects covered by a coating, which leaves only the terrace sites of the NPs exposed. Analysis of such samples should indicate the difference between step and terrace sites on reaction performance.

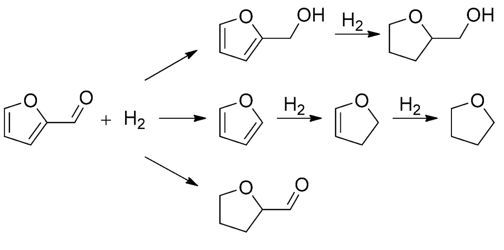
Here, we applied an alumina overcoating by ALD to cover the step sites of Pd NPs, whereas the terrace sites remain free to act as the active component for furfural hydrogenation reaction. This technique should lead to different selectivities for the hydrogenation of furfural on uncoated and coated catalysts.

The gas-phase hydrogenation of furfural was carried out with uncoated samples of 2 wt% Pd catalyst on Al_2O_3 substrate and an alumina-overcoated Pd catalyst on Al_2O_3 substrate (see Table 1). Two reaction temperatures were studied (190 °C and 210 °C) for the ALD-derived catalysts. The furfural conversions of the Pd-2 wt%/Al_2O_3 was tuned from 19.7% to 4.1% by changing the weight hourly space velocity (WHSV). The selectivity changes along with the conversions for the furfural hydrogenation. As shown in Scheme 1, the three primary reaction products are furan, furfuryl alcohol (FA), and tetrahydrofurfural (THFur); and the three minor products are dihydrofuran (DHF), tetrahydrofuran (THF), and tetrahydrofurfuryl alcohol (THFA). This finding is in good agreement with previous work by the groups of Sitthisa and Resasco.[16] Both DHF and THF yields diminished at lower conversion, which was achieved by increasing the WHSV. In our tests, FA is always the main product when Pd-2 wt%/Al_2O_3 is used. Other groups[16,17] have reported furan as the main product for furfural hydrogenation over Pd NP catalysts. This difference is a consequence of different reaction conditions, such as space velocity, reaction temperatures, furfural and hydrogen partial pressure, and, of course, catalyst preparation methods including the precursors used. The selectivity to furan constantly increases with decreasing reaction conversion. The formation of tetrahydro products implies that the adsorption mode of furfural on the surface of the working catalysts should be parallel to the Pd surface, as proposed earlier based on DFT calculations.[17] Since the amount of THFur is small, we focused on the selective hydrogenation of the C=O group and the decarbonylation reaction, which are known to be competing reactions along with furfural hydrogenation. Both furan and FA are believed to be the primary products of the furfural hydrogenation and to occur by parallel reactions.[16,18] High temperature and low space velocity favor the formation of furan.[16] The secondary products DHF and THF were derived from furan, whereas THFA and a small amount of dimer should be formed by FA hydrogenation and dimerization, respectively. Since the amount of dimer was small (less than 0.5% yield), it is not shown in Table 1 even though it was identified by GC-MS analysis.

Table 1: Furfural hydrogenation with uncoated and alumina-overcoated Pd catalysts.

Catalyst[a]	Conv. [%]	Selectivity [%] 					
Pd-2 wt%/Al_2O_3[b]	19.7	13.4	2.9	1.6	10.9	65.0	6.3
Pd-2 wt%/Al_2O_3[c]	9.6	17.3	0	0	12.6	63.9	6.2
Pd-2 wt%/Al_2O_3[d]	8.3	17.5	0	0	10.4	65.9	6.2
Pd-2 wt%/Al_2O_3[e]	4.1	18.4	0	0	20.6	54.4	6.7
ALD-Pd/Al_2O_3-10c	4.6	23.7	0	0	24.1	47.4	4.7
ALD-Pd/Al_2O_3-20c	3.6	26.0	0	0	9.7	64.3	0
ALD-Pd/Al_2O_3-30c	2.5	28.4	0	0	11.8	57.5	2.3
ALD-Pd/Al_2O_3-10c[f]	5.5	36.8	0	2.3	13.6	43.7	3.6
ALD-Pd/Al_2O_3-20c[f]	4.2	39.5	0	0	9.1	44.0	7.4
ALD-Pd/Al_2O_3-30c[f]	3.0	41.7	0	0	6.1	48.8	3.5

[a] Hydrogenations were carried out continuously at 190 °C at a 25:1 molar ratio of H_2 to furfural, unless otherwise noted. The designations 10c, 20c, and 30c indicate number of ALD cycles, WHSV: 6.9 h^{-1}. [b] Catalyst mass of 75 mg, WHSV: 6.9 h^{-1}. [c] Catalyst mass of 25 mg, WHSV: 20.6 h^{-1}. [d] Catalyst mass of 20 mg, WHSV: 25.7 h^{-1}. [e] Catalyst mass of 5 mg, WHSV: 102.9 h^{-1}. [f] The reaction was carried out at 210 °C.



Scheme 1. Reaction pathways of furfural hydrogenation.

Overcoated Pd catalysts were synthesized by ALD to modify the selectivity for furfural hydrogenation. (The morphology and particle size distributions were determined by TEM and can be found in Figure S1.) As stated earlier, the alumina overcoating can also cover active sites of the Pd NPs. As a result, the total activity of all coated catalysts is lower than that of 75 mg Pd-2 wt%/Al_2O_3[b] at constant WHSV (6.9 h^{-1}). At a constant space velocity, the activity of ALD-Pd/Al_2O_3-10c (4.6%) is about 75% lower than that of 75 mg Pd-2 wt%/Al_2O_3[b] (19.7%). The selectivities for the secondary products DHF, THF, and THFA decrease along with the total conversion of furfural. Since the selectivity can be influenced by the conversion of furfural, we chose the 5 mg Pd-2 wt%/Al_2O_3[e] as the uncoated catalyst standard, which shows a similar furfural conversion as the ALD-derived catalysts. The selectivity of ALD-Pd/Al_2O_3-10c to furan (23%) is 5% higher than that of Pd-2 wt%/Al_2O_3[e](18%), though the conversions are almost the same. The selectivity to furan increases to 26.0–28.4% when additional ALD coating cycles with Al_2O_3 are applied. If the reaction temperature is increased from 190 °C to 210 °C, while the conversion of furfural is kept constant, the selectivity to furan increases by 14%. Previous work reported that higher reaction temperatures favor the formation of furan.[16] We found that the activation energy for furan formation is 20 kJ mol^{-1} greater than that for FA formation, which is in good agreement with our kinetics data (Table S1). Unfortunately, the Arrhenius method did not yield an accurate enough activation energy characterization. We could not tell the difference between different catalysts until it exceeded 10–15 kJ mol^{-1}. A more accurate method is needed to elucidate the difference in activation energies between coated and uncoated catalysts. The selectivity to FA decreases when the selectivity to furan increases, but not so systematically correlated to the changes of conversion, as furan does. That might be due to secondary product formation from FA.

Plotting the selectivity for furan versus the furfural conversion with the catalysts in Table 1 reveals a linear correlation (Figure 1). The linearity covers the range from 2 % to 24 % furfural conversion at 190 °C. The linearity does not extend to 40 % conversion (data point not shown). The slope of the linear correlation is different between uncoated and alumina-coated catalysts. Different loadings of Pd (2 and 5 wt %) show different slopes. This is due to the intrinsic properties of the catalyst, e.g., the turnover frequency, and is related to the relative activity of each site and not to the number of active sites. Figure 1 also shows that this linearity is not temperature-dependent for the coated catalysts (i.e., the slopes are the same when the reaction temperature is increased to 210 °C). The slopes for the coated catalysts are greater than those obtained with Pd-5 wt %/Al$_2$O$_3$, followed by Pd-2 wt %/Al$_2$O$_3$. Higher loadings of Pd should result in larger NPs and a greater percentage of terrace sites versus step sites. In addition, the alumina-coated catalysts should have an even higher percentage of terrace sites, because the overcoatings are also expected to cover the step sites of the Pd NPs first.[15] Feng and co-workers[15] found that the defect sites in Pd NPs can be fully covered by eighth ALD cycles with alumina. Therefore, most of the remaining active sites after ten ALD cycles of alumina overcoating should be terrace sites; thus, ALD-Pd/Al$_2$O$_3$-10c should have a higher ratio of terrace to step sites than Pd-5wt %/Al$_2$O$_3$. CO adsorption studies further confirmed that most of the defect sites of the Pd NPs were covered by alumina overcoatings (Figure S2). Thus, two methods were applied to increase the ratio of terrace versus step sites of Pd NPs. The results showed that the selectivity to furan was also increased by increasing the ratio of terrace to edge sites. The activity of furfural hydrogenation decreased with the number of ALD cycles. Furthermore, the linear correlation between furan selectivity and furfural conversion for the three ALD-derived catalysts suggests that the active sites for these catalysts should be very similar. Since terrace sites are most likely the only available active sites of these three coated catalysts, they behave in a similar fashion. Pang et al.[19] found a similar phenomenon using alkanethiolate self-assembled monolayers with varying surface densities that cover either step or terrace sites. They found that the desired products (furan or furfuryl alcohol) were formed on special active sites (terrace or step sites) of palladium catalysts covered by alkanethiolate during the furfural hydrogenation on supported palladium catalysts. Pd step sites favored the formation of furfuryl alcohol, whereas terrace sites favored the formation of furan. However, the alumina overcoating by ALD should be more stable and easier to both synthesize and apply than the coating obtained by the alkanethiolate self-assembly method. Our work on using ALD for overcoating catalysts indicates that single-crystal surface effects can be studied without influence from the step sites. The ALD process shows potential for the industrial area even though it is still expensive right now. A comparison with previously reported Pd catalysts in terms of activity (TOF), selectivity, and stability is shown in Table S2.

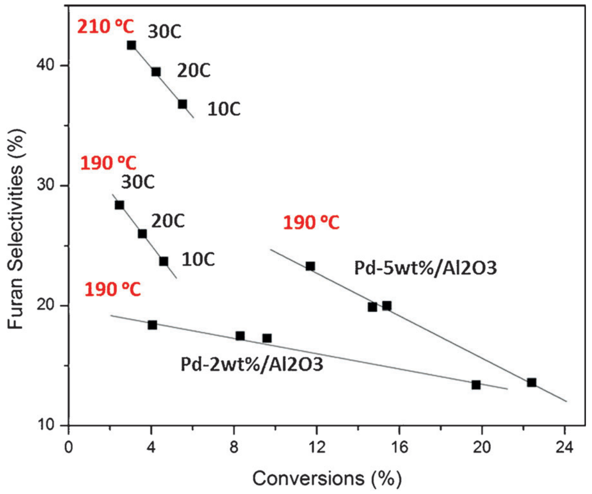


Figure 1. Gas-phase hydrogenation of furfural. Furan selectivity for each catalyst is plotted versus furfural hydrogenation conversion.

The chemical state of the working catalysts may also influence the performance of furfural hydrogenation. However, Pd NPs are easily reduced. “Pd^0” should be the active species for all the catalysts based on in situ H$_2$ temperature-programed reaction (TPR) studies (Figures S3 and S4) and in situ furfural hydrogenation studies (Figure S5). All Pd catalysts, whether covered or not, can be fully reduced below 0 °C, whereas the reduction temperature was thought to be 100 °C in previous studies.[16] All catalysts remained in the Pd^0 chemical state even when purged with furfural/H$_2$ during the reaction. The biggest difference between the uncoated and alumina-coated Pd catalysts is the higher reduction and oxidation temperatures for the latter. For example, based on extended X-ray absorption fine structure (EXAFS) analysis after calcination at 530 °C for 15 min, the coordination numbers of Pd^0/Pd–Pd for the ALD catalysts were still high, whereas the Pd–O coordination numbers were lower compared with uncoated Pd-2 wt %/Al$_2$O$_3$ (Figure S6 and Table S3). A similar result is shown in Figure S7 for calcination at 700 °C. The difference becomes more apparent with an increasing number of ALD cycles. The oxidation temperature of Pd NPs is increased by an overcoating with alumina, a finding that is in good agreement with a previous study on the reduction properties of copper chromite coated by ALD.[20]

To elucidate the underlying mechanism for the different selectivities of furfural hydrogenation on terrace and step sites, periodic DFT calculations are performed on Pd(111) and Pd(211) surfaces, which are chosen as models for terrace and step sites, respectively. The optimized most stable geometries and calculated binding energies of the key intermediates involved in furfural hydrogenation are shown in Figure S8; a general trend to stronger binding on the steps is evident. Because both furfural adsorption and H_2 dissociative adsorption are essentially barrierless processes on Pd surfaces, and because a comparison of the relative selectivities of surface reactions is the primary goal of this study, reaction barriers and energies are reported with respect to adsorbed reactants (Figure 2). For the hydrogenation of adsorbed furfural to FA, the formation of $C_4H_3(CHOH)O$ is kinetically and thermodynamically more favorable than the formation of $C_4H_3(CH_2O)O$ on both surfaces (Table S4); $C_4H_3(CHOH)O$ is then hydrogenated to FA. In this favorable hydrogenation pathway, the calculated barriers on Pd(111) and Pd(211) are comparable (Figure 2a) although the FA formation on step sites is more thermodynamically favored, due to the stronger binding energies of intermediates on these step sites. The latter result may suggest that FA formation is slightly more facile on step surfaces than on terraces; however, because of the existence of secondary products derived from FA such as THFA as well as some dimers, this conclusion is not clearly evident from the reaction kinetics data in Table 1.

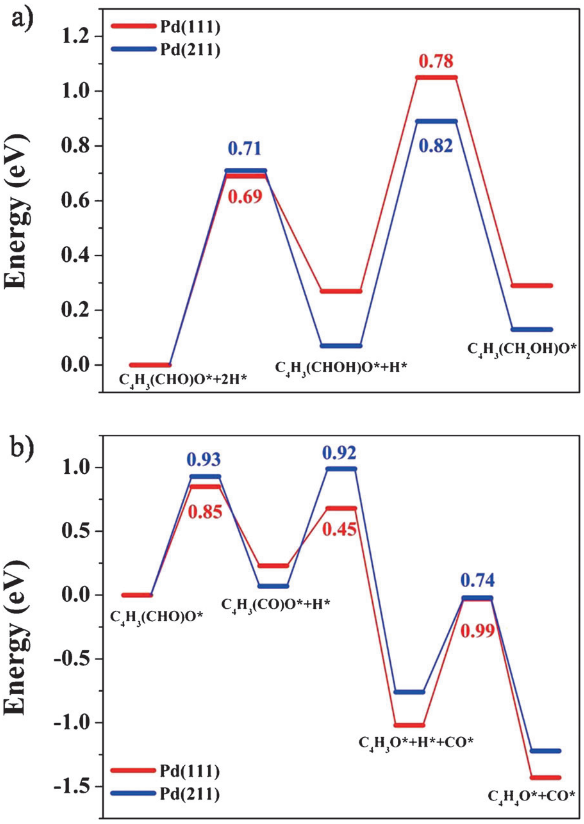


Figure 2. The favorable reaction pathways for furfural hydrogenation on Pd(111) and Pd(211). a) Hydrogenation to furfuryl alcohol; b) hydrogenation to furan.

For the formation of furan, C–C bond breaking is crucial. We found that the direct C–C bond breaking of furfural to form C_4H_3O and CHOH is difficult on both considered surfaces. The calculated barriers are 1.47 and 1.57 eV on Pd(111) and Pd(211), respectively (Table S4). Alternatively, furfural can dehydrogenate first through the carbonyl group with modest barriers (Figure 2b). Then, C–C bond breaking becomes facile to form C_4H_3O and CO, which is in agreement with previous work by the groups of Sitthisa and Resasco.[16] In this case, the calculated barriers for C–C bond breaking are 0.45 and 0.92 eV on Pd(111) and Pd(211), respectively. Moreover, this process is highly exothermic by −1.25 eV on Pd(111) and −0.83 eV on Pd(211). Interestingly, the C–C bond breaking on terrace sites is significantly more favorable both kinetically and thermodynamically than that on step sites, implying that the furan formation on terrace sites of Pd NPs is more facile than that on step sites. Finally, the C_4H_3O hydrogenates to furan with the barrier of 0.99 and 0.74 eV on Pd(111) and Pd(211), respectively.

From the above results, it can be concluded that the furfural hydrogenation to FA on step sites is more thermodynamically favorable than on terrace sites, whereas the furfural hydrogenation to furan on step sites is less favorable than on terrace sites. Therefore, on supported Pd NPs, the FA selectivity is high, due to the presence of defect and edge sites. On the other hand, the furan selectivity would be increased on the overcoated Pd NPs, because the defect sites were covered by alumina. These conclusions are largely consistent with the experimental results. Finally, we note that, although the selectivity trends in Figure 2 are determined assuming that hydrogen is present on the Pd surface and these trends do show good agreement with our experimental results, it is possible that atomic H on Pd at relatively high coverages could be present in the subsurface and may influence the hydrogenation catalysis,[21] because the diffusion of hydrogen from the subsurface to the surface is facile with essentially no barrier. Indeed, it is conceivable that such a process might permit hydrogenation to continue even in situations, in which the surface is poisoned by CO product from furan formation, thereby keeping FA selectivity high on all surfaces (Table 1).

In summary, the furfural hydrogenation selectivity over Pd nanoparticle catalysts is improved by applying alumina overcoatings by ALD. Thicker layers of alumina favor furan formation, because the step sites of Pd nanoparticles are preferentially covered by the overcoating, increasing the ratio of terrace to edge sites in the Pd nanoparticles. Also, the furan formation is more favored on terrace sites based on both DFT calculations and reaction kinetics studies. The ALD overcoating method proved to be able to modify the shape and active sites of supported metal nanoparticles to control the selectivity in hydrogenation reactions.

Experimental Section

Materials. $Pd(NH_3)_4(NO_3)_2$, Pd-5 wt%/Al_2O_3, and 2-furfuraldehyde (Reagent, >99%) were purchased from Sigma–Aldrich. Hydrogen and nitrogen gases were all ultra-high purity (UHP), obtained from Airgas. The Pd-2 wt%/Al_2O_3 catalyst was synthesized by the impregnation method using $Pd(NH_3)_4(NO_3)_2$ as the precursor and alumina Nanodur (purchased from Alfa Aesar) as the support. The loading of Pd was 2 wt%.

ALD overcoating. ALD was performed in a viscous flow reactor described in detail elsewhere.[22] 0.5 g Pd-2 wt%/Al_2O_3 powder was spread uniformly onto a stainless steel sample plate with a mesh top to contain the powder while still allowing gaseous access of the precursor vapors. The samples were loaded into the reactor and kept for at least 30 min at 200°C in a 160 sccm flow of UHP N_2 at 1 torr pressure to allow temperature stabilization. Next, Pd/Al_2O_3 was coated with Al_2O_3 in 10, 20, or 30 ALD cycles ("ALD Pd/Al_2O_3-10c" indicates 10 ALD cycles to obtain alumina-coated Pd-2 wt%/Al_2O_3). The Al_2O_3 ALD method used alternating exposures to trimethylaluminum (TMA, Sigma–Aldrich, 97%) and deionized water at 200°C. Typical timing sequences for a single Al_2O_3 ALD cycle are: TMA dose (60 s), purge (120 s), H_2O dose (60 s), and purge (120 s). Post-treatment in flowing N_2 at 700°C was performed to obtain activated ALD-Pd/Al_2O_3 catalysts.

Catalytic reactions. Vapor phase conversion of 2-furfuraldehyde (furfural) over ALD-Pd/Al_2O_3 was conducted at atmospheric pressure in a $^1/_2$ in. stainless steel tubular reactor placed in a clam-shell furnace equipped with temperature controllers. For each reaction test, 5–75 mg of ALD-Pd/Al_2O_3 or Pd-2 wt%/Al_2O_3 catalyst were diluted with SiC (70 mesh, mass ratio of sample to diluent is 1:12) to mitigate hot spot formation in the catalyst bed. Prior to reaction, the catalyst was reduced in situ in 10% H_2/He for 1 h at 200°C. Furfural was introduced to the reactor by sweeping a carrier gas of 50% H_2/He through a bubbler containing pure furfural. The temperature of the bubbler was controlled by a circulating bath. Reactor effluents were analyzed by an online gas chromatography equipped with flame ionization detector and a packed column (EC-Wax, 30 m × 0.32 mm × 1 μm, ECONO-CAP, Grace Davison). All the chemical transfer lines and valves were heat-traced to prevent condensation of either the reactant or the products. A typical reaction condition was 2% furfural and 50% of H_2 for a ratio of H_2/furfural of 25:1. The total gas flow rate was between 50 and 100 cc/min. The selective hydrogenation of furfural was studied over Pd-2 wt%/Al_2O_3, Pd-5 wt%/Al_2O_3, ALD-Pd/Al_2O_3-10c, ALD-Pd/Al_2O_3-20c, and ALD-Pd/Al_2O_3-30c. Fresh catalyst was used each time to make sure reactions were conducted under identical conditions.

Computational methods. All DFT calculations were performed by VASP.[23] Additional computational details can be found in the Supporting Information.

Received: July 15, 2014
Revised: August 20, 2014

Keywords: atomic layer deposition · biomass · catalyst selectivity · hydrogenation · palladium

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