Title: Ultrathin coating of confined Pt nanocatalysts by atomic layer deposition for enhanced catalytic performance in hydrogenation reactions

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To be cited as: Chem. Eur. J. 10.1002/chem.201601039

Link to VoR: http://dx.doi.org/10.1002/chem.201601039
Ultrathin coating of confined Pt nanocatalysts by atomic layer deposition for enhanced catalytic performance in hydrogenation reactions**


Abstract: Metal-support interfaces play a prominent role in heterogeneous catalysis. However, tailoring the metal-support interfaces to realize full utilization remains a large challenge. In this work, we propose a graceful strategy to maximize the metal-oxide interfaces by coating confined nanoparticles with an ultrathin oxide layer. This is achieved via sequential deposition of ultrathin Al₂O₃ coats, Pt, and a thick Al₂O₃ layer on carbon nanocoils templates by atomic layer deposition (ALD), followed by removal of the templates. Compared with the Pt catalysts confined in Al₂O₃ nanotubes without the ultrathin coats, the ultrathin coated samples have larger Pt-Al₂O₃ interfaces. The maximized interfaces significantly improve the activity and the protecting Al₂O₃ nanotubes retain the stability for hydrogenation reactions of 4-nitrophenol. We believe that applying ALD ultrathin coats on confined catalysts is a promising way to achieve enhanced performance for other catalysts.

Heterogeneous catalyst systems comprising metals and oxide supports are widely used. The metal oxides not only work as supports to help the dispersion of supported metal nanoparticles, but also affect catalytic performance through interaction with the supported metal nanoparticles. The recognition that important catalysis is localized at the metal-oxide interfaces suggests that the rational design and engineering of metal-oxide interfaces are critical in developing highly efficient catalytic systems.[1] However, in conventional supported metal catalysts, the density of the metal-oxide interfaces is limited because of the small contact areas between the metal and the oxide (Fig. 1a).

To further increase the interfacial sites, highly dispersed oxide can be coated on the surfaces of the metal nanoparticles, forming inverse catalysts in which rich boundaries can be produced between the oxide surfaces and the metals (Fig. 1b).[2] Many groups have constructed oxide-on-metal structures with prominent catalytic performance.[3] Atomic layer deposition (ALD) has been demonstrated to be a promising method to apply oxide coatings onto supported metal catalysts with atomically precise thickness control, which allows for the optimization of the metal oxide interfaces.[4] For instance, Lu and co-workers reported that porous Al₂O₃ overcoats on supported Pd catalysts can inhibit coke formation and improve thermal stability.[5] Previously, our group observed improved activity of Ni nanoparticles supported on the outer surface of Al₂O₃ nanotubes with a few cycles of Al₂O₃ overcoats by ALD.[6] Overall, previous reports primarily focused on coating unconfined catalysts, but there are still some disadvantages: ultrathin coatings suffer from poor stability, whereas a thick oxide coating results in the loss of catalytic activity.

Confining metal nanoparticles in nanotubes has proven to be an alternative strategy for improving the metal oxide interaction and has triggered wide research interest.[7] The rigid nanotubes exert a spatial restriction on the metal particles, hampering their aggregation, and develop interactions between the encapsulated molecules and the nanotube surfaces (Fig. 1c).[8] Bao reported that confining metal nanoparticles inside CNTs results in improved catalytic activity with respect to the same metals deposited on the CNTs exterior surface.[9] Our group demonstrated that Ni nanoparticles confined in Al₂O₃ nanotubes and also embedded in the cavities of the inner walls of Al₂O₃ nanotubes have striking catalytic performance in hydrogenation reactions.[10]

Previous endeavours devoted to increasing the metal-support interfaces inspired us to coat the confined catalysts with an ultrathin coating to maximize the metal-support interfaces while retaining good stability. In this work, we report on the precisely controlled ultrathin coating of ALD alumina on confined Pt catalysts to maximize the metal-support interfaces (Fig. 1d). The increased interfacial sites significantly improve the activity and the protecting Al₂O₃ nanotubes (ANTs) retain the stability of confined Pt catalysts for hydrogenation reactions of 4-nitrophenol (4-NP).

![Figure 1](image_url)

Figure 1. Schematic diagram showing the strategy for tailoring the metal nanoparticles/support interfaces. (a) Conventional supported nanoparticles, (b) Inverse catalysts, (c) Confined nanocatalysts, (d) Ultrathin coating of confined nanoparticles.

Pt nanoparticles confined in Al₂O₃ nanotubes (Pt-in-ANTs) and Al₂O₃ ultrathin coated samples (xAl-Pt-in-ANTs) were obtained by ALD using carbon nanocoils (CNCs) as the sacrificial templates. Compared with carbon nanotubes (CNTs), the CNCs have lower annealing temperature for convenient
The catalytic performance of Pt-in-ANTs and xAl-Pt-in-ANTs was evaluated by the catalytic reduction of 4-NP. The reduction process of 4-NP was monitored by UV-Vis spectroscopy at different time intervals. The intensities of the UV absorption peak at 400 nm were used to quantify the concentration of 4-NP. The absorption peak at 400 nm significantly decreased as the reaction proceeded, due to the reduction of 4-NP. Simultaneously, a new peak appeared at 300 nm, which was ascribed to the formation of 4-aminobenzenol (4-AP). With respect to the conversion of 4-NP (Figure 3), the ultrathin coated samples with Al₂O₃ coatings in the range of 1 to 2 cycles showed higher activity than that of the Pt-in-ANTs sample. The sample coated with 2 cycles of Al₂O₃ (2Al-Pt-in-ANTs) exhibited the highest activity. With increasing Al₂O₃ cycles (3-5), the catalysts exhibited even lower activity than the Pt-in-ANTs sample because most of the surfaces of the metal particles were covered by Al₂O₃ and it was difficult for the reactants to access the active surface, even if the system had larger metal-support interfaces. In a word, the catalytic activity was significantly improved for 2Al-Pt-in-ANTs compared to Pt-in-ANTs. Fig. 4A shows that for 2Al-Pt-in-ANTs, the complete reduction of 4-NP (the peak at 400 nm disappeared) occurred within 10 min. The three marked isosbestic points (at 244, 281 and 313 nm) indicate a complete conversion of 4-NP to 4-AP without generating by-products. In contrast, the reaction time for Pt-in-ANTs is 40 min (Fig. 4B). The turnover frequency (TOF) was calculated on the basis of the surface Pt atoms, which was determined according to the CO chemisorption analysis. The TOF values (Table 1) are 147.2 and 18.3 s⁻¹ for 2Al-Pt-in-ANTs and Pt-in-ANTs, respectively.

Fig. 4C shows the logarithm plot of the concentration (⁻\ln(C/C₀)) with reaction time, which allows us to further examine the catalytic activity of these catalysts. The apparent kinetic rate constant (k_app) is proportional to the total reactive sites of the catalyst, which can be estimated based on the regression of the slope from the logarithm plot (⁻\ln(C/C₀)). As listed in Table 1, the k_app value is 7.2×10⁻³ s⁻¹ for 2Al-Pt-in-ANTs, approximately 4-fold higher than that of Pt-in-ANTs (1.7×10⁻³ s⁻¹). To precisely compare the activity of these catalysts, the normalized rate constant (k_nor) defined as the ratio of k (the rate constant) to the loading amount of catalyst was introduced. Based on the inductively coupled plasma-atomic emission spectrometry (ICP-AES) data, the loading amounts of Pt were 2.56%, 2.39%, 2.27%, 2.24%, 2.21% and 2.18% for Pt-in-ANTs, 1Al-Pt-in-ANTs, 2Al-Pt-in-ANTs, 3Al-Pt-in-ANTs, 4Al-Pt-in-ANTs and 5Al-Pt-in-ANTs, respectively. As shown in Table 1, the k_nor value of 2Al-Pt-in-ANTs (63.4 s⁻¹g⁻¹) was much higher than that of Pt-in-ANTs (13.3 s⁻¹g⁻¹). These results further indicate the enhanced catalytic activity of the ultrathin coated samples (2Al-Pt-in-ANTs).

The catalysts were reused to test their stabilities, as displayed in Fig. 4D. The reaction time is 4min for each run. A slight decrease in the conversion appeared after the two catalysts were reused four times, indicating both catalysts were relatively stable. The good stability of both catalysts is due to the Al₂O₃ tubular channel structure of these confined catalysts, which can inhibit the leaching and detachment of Pt nanoparticles under reaction conditions.
The above results reveal that 2Al-Pt-in-ANTs does possess greatly improved catalytic activity compared to Pt-in-ANTs and retains good stability, which is consistent with our expectation. To further verify the effect of the ultrathin coating, we performed the following characterizations for these catalysts.

The TEM images of 2Al-Pt-in-ANTs and Pt-in-ANTs (Figure 5) show their hollow structures. There was no significant difference between the morphology of these two catalysts due to the limited cycle numbers of the ultrathin Al2O3 for the 2Al-Pt-in-ANTs. Pt nanoparticles were uniformly encapsulated in the Al2O3 nanotubes, and the shell thickness of Al2O3 nanotubes was approximately 10 nm for both catalysts. This perfect encapsulation can hardly be obtained by traditional preparation methods. The average diameters of Pt nanoparticles measured by the TEM images were 2.1 and 2.2 nm, corresponding to 2Al-Pt-in-ANTs and Pt-in-ANTs, respectively. The morphology of Pt nanoparticles in 2Al-Pt-in-ANTs and Pt-in-ANTs after reaction does not have significant changes (Figure S1).

Figure 5. TEM images of 2Al-Pt-in-ANTs (A,C) and Pt-in-ANTs(B,D).

CO chemisorption experiments were used to measure the accessibility of the Pt nanoparticles (Table 2). The CO uptake was assumed to be equal to the number of surface Pt atoms. The amount of CO adsorbed by 2Al-Pt-in-ANTs (1.74 mmol/g-Pt) was approximately 42% smaller than that of Pt-in-ANTs (2.96 mmol/g-Pt), which indicates that 2Al-Pt-in-ANTs had a lower Pt accessibility than that of Pt-in-ANTs.

The hydrogen temperature programmed desorption (H2-TPD) tests of 2Al-Pt-in-ANTs and Pt-in-ANTs were conducted (Figure 6A). Both curves displayed three desorption peaks, indicating the existence of different forms of surface hydrogen species. The low temperature desorption peaks (centred at 60 °C) are ascribed to the hydrogen adsorbed on the surface of Pt, and the high temperature desorption peaks nearly 400 °C are assigned to spillover hydrogen.14 The intensity of the low temperature peak of 2Al-Pt-in-ANTs is less than that of Pt-in-ANTs. The H2 uptake (Table 2) related to the low temperature of 2Al-Pt-in-ANTs (1.81 mmol/g-Pt) is approximately 47% smaller than that of Pt-in-ANTs (3.44 mmol/g-Pt), indicating that 2Al-Pt-in-ANTs has a lower exposed fraction of Pt atom than that of Pt-in-ANTs. This result coincides with the CO chemisorption result. However, the intensity of the high temperature peak of 2Al-Pt-in-ANTs is greater than that of Pt-in-ANTs. The peak area of 2Al-Pt-in-ANTs related to hydrogen spillover is 50% larger than that of Pt-in-ANTs. This result indicates that the hydrogen spillover effect for 2Al-Pt-in-ANTs has been greatly enhanced compared with Pt-in-ANTs.

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) CO chemisorption measurements were used to characterize the samples (Figure 6B). The adsorbed CO on the Pt-in-ANTs shows a sharp peak at 2076 cm⁻¹, which corresponds to CO molecules linearly bonded onto surface Pt atoms. For 2Al-Pt-in-ANTs, the Al2O3 coating results in a redshift of the CO weak band to 2093 cm⁻¹, which can be assigned to the weakly adsorbed CO on the Pt sites.15 This result is similar to the observation of noble metals supported on Fe2O3 in which strong metal-support interaction results in a shift of the CO stretching frequency to high values.16 It is also observed that the intensity of the linearly CO adsorbed peak of 2Al-Pt-in-ANTs decreases, which is caused by the partial coverage of Pt surface by ultrathin coated Al2O3 species. This result is consistent with the CO chemisorption and H2-TPD measurements.

The XRD patterns of Pt-in-ANTs and 2Al-Pt-in-ANTs were also obtained (Figure S2). The feeble diffraction peaks are attributed to the small size particles. For these two samples, the three peaks at 39°, 45°, and 66° are indexed to the (111), (200), and (220) planes of Pt, whereas there is another feeble peak located at 34° in 2Al-Pt-in-ANTs, which is assigned to the (101) planes of PtO.

In addition, to conveniently observe the surface chemical states of Pt by X-ray Photoelectron Spectroscopy (XPS), 20 cycles of ALD Al2O3 were deposited to obtain a thin Al2O3 nanotubes shell. For both samples, the three peaks in the spectra could be resolved into three components (Fig. 6C). The peak with a binding energy of 74.3 eV can be ascribed to Al 2p. The peaks located at 71.0 eV and 73.0 eV are related to Pt6 and Pt2+ species, respectively.17 Pt species are dominated by metallic Pt0 in Pt-in-ANTs, whereas Pt species in 2Al-Pt-in-ANTs carry more positive charges (Pt2+). This result is consistent with the XRD and DRIFTS results. However, after reaction Pt species in 2Al-Pt-in-ANTs are existed mainly as metallic Pt0 (Fig. 6D). This result indicates that the oxidized platinum in 2Al-Pt-in-ANTs has been reduced during hydrogenation reactions.18

Discussion
For the first few cycles of ALD, Al₂O₃ deposits preferentially onto specific sites, rather than uniformly blanketin the particles entirely. Therefore, the ultrathin Al₂O₃ coating should be discontinuous on the metal nanoparticles, through which more effective Pt-Al₂O₃ interfacial sites can be obtained. From the ICP-AES and TEM results, it can be concluded that 2Al-Pt-in-ANTs and Pt-in-ANTs almost possess the same Pt content, Pt nanoparticle size, and thickness of Al₂O₃ shell. However, the CO chemisorption, H₂-TPD and DRIFTS results demonstrate that 2Al-Pt-in-ANTs has a much lower Pt accessibility than Pt-in-ANTs, indicating increased Pt-Al₂O₃ interfacial sites of 2Al-Pt-in-ANTs. This result is in agreement with our expectation. In addition, the DRIFTS, XRD and XPS results demonstrate that 2Al-Pt-in-ANTs contain more oxidized Pt species compared to Pt-in-ANTs. The difference can be ascribed to the stronger interaction between the Pt and Al₂O₃ of 2Al-Pt-in-ANTs samples. This result further demonstrates that 2Al-Pt-in-ANTs have larger interfaces, resulting in stronger Pt-Al₂O₃ interactions than that of Pt-in-ANTs. However, during hydrogenation reactions the oxidized Pt in 2Al-Pt-in-ANTs has been reduced. The influence of the oxidized platinum to the improved activity can be eliminated. The spillover of the dissociated hydrogen is highly dependent on the metal-support interfaces. Previous works revealed that increased metal-support interfaces can lead to the enhanced hydrogen spillover effects. Because of the larger Pt-Al₂O₃ interfaces, the hydrogen spillover effect for 2Al-Pt-in-ANTs is greatly enhanced, as confirmed by H₂-TPD analysis. Hydrogen spillover can exert a strong influence on the catalytic activity in hydrogenation reactions. Therefore, 2Al-Pt-in-ANTs exhibit enhanced catalytic activity compared with Pt-in-ANTs, even though the exposed Pt surface area has been substantially decreased. In a word, compared with Pt-in-ANTs, 2Al-Pt-in-ANTs have larger Pt-Al₂O₃ interfaces and the resultant enhanced hydrogen spillover effect, which lead to the significantly improved hydrogenation activity.

Conclusion
We have demonstrated a novel way to precisely apply ultrathin Al₂O₃ coats on the confined Pt catalyst using ALD. Compared with Pt-in-ANTs, the catalytic activity of the synthesized 2Al-Pt-in-ANTs for 4-NP hydrogenation was significantly improved by maximizing the Pt-Al₂O₃ interfaces. This method of maximizing metal-oxide interfaces through ultrathin coating by ALD can be extended for other heterogeneous catalysts.

### Table 1. Comparison of the catalytic performance of Pt-in-ANTs and 2Al-Pt-in-ANTs for the reduction of 4-NP under identical conditions.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>kcat (10⁻³ s⁻¹)</th>
<th>ksp (s⁻¹·g⁻¹)</th>
<th>Pt loadingₜ</th>
<th>TOF (s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Al-Pt-in-ANTs</td>
<td>7.2</td>
<td>63.4</td>
<td>2.27</td>
<td>147.2</td>
</tr>
<tr>
<td>Pt-in-ANTs</td>
<td>1.7</td>
<td>13.3</td>
<td>2.56</td>
<td>18.3</td>
</tr>
</tbody>
</table>

[a] kcat=ksp/(mₜ·Pt). [b] Measured by ICP-AES. [c] The number of 4-NP molecules converted per atom of exposed Pt on the surface per unit time at initial reaction times of 2 minutes and 10 minutes for 2Al-Pt-in-ANTs and Pt-in-ANTs.

### Table 2. Physicochemical characteristics of Pt-in-ANTs and 2Al-Pt-in-ANTs.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>COuptakeₚₜ (μmol/g-cat)</th>
<th>CO uptake (μmol/g-Pt)</th>
<th>H₂uptakeₚₜ (μmol/g-cat)</th>
<th>H₂ uptake (μmol/g-Pt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2Al-Pt-in-ANTs</td>
<td>39.63</td>
<td>1.74</td>
<td>41.00</td>
<td>1.81</td>
</tr>
<tr>
<td>Pt-in-ANTs</td>
<td>75.84</td>
<td>2.96</td>
<td>88.00</td>
<td>3.44</td>
</tr>
</tbody>
</table>

[a] Measured by CO chemisorption experiments. [b] Measured by the H₂ uptake of H₂ TPD related to the low temperature.

**Keywords:** atomic layer deposition • interfaces • ultrathin coating • confined catalyst • hydrogenation reaction
COMMUNICATION


Entry for the Table of Contents (Please choose one layout)

Layout 1:

COMMUNICATION

Ultrathin coating of confined Pt catalysts: atomic layer deposition was applied to deposit ultrathin Al₂O₃ coats on Pt nanoparticles which are confined in Al₂O₃ nanotubes. Compared with the confined catalysts without the ultrathin coats, the ultrathin coated samples possess more Pt-Al₂O₃ interfacial sites. The maximized interfaces significantly improve the activities and the protecting nanotubes retain the stabilities for hydrogenation reactions of 4-nitrophenol.

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