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Precisely Controlled Porous Alumina Overcoating on Pd Catalyst by Atomic Layer Deposition: Enhanced Selectivity and Durability in Hydrogenation of 1,3-Butadiene

Hong Yi,[†] Hongyi Du,[†] Yingli Hu,[‡] Huan Yan,[†] Hai-Long Jiang,[‡] and Junling Lu^{*,†}

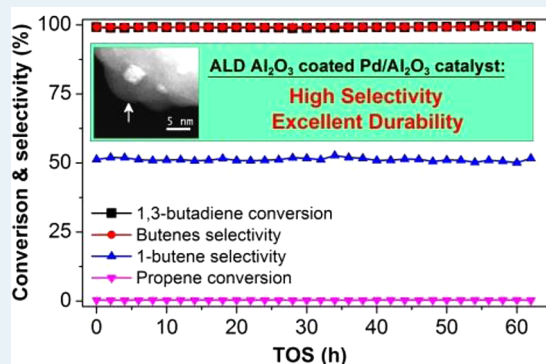
[†]Department of Chemical Physics, Hefei National Laboratory for Physical Sciences at the Microscale, iChEM, CAS Key Laboratory of Materials for Energy Conversion, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

[‡]Department of Chemistry, Hefei National Laboratory for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, P. R. China

Supporting Information

ABSTRACT: Metal catalyst in selective hydrogenation reactions often suffers from low selectivity and especially poor durability due to heavy coke formation. Here we report that precisely controlled porous alumina overcoating on a Pd catalyst using atomic layer deposition (ALD) not only remarkably enhances the selectivity to butenes, especially to 1-butene, but also achieves the best ever durability against deactivation in selective hydrogenation of 1,3-butadiene in the absence (or presence) of propene. Therein no visible activity declines or selectivity changes were observed during a total 124 h of reaction time on stream.

KEYWORDS: atomic layer deposition, Al_2O_3 overcoating, Pd catalyst, hydrogenation of 1,3-butadiene, durability, selectivity



Light alkenes are of great importance as the raw materials in the industrial organic synthesis. Light alkene streams produced by catalytic cracking of petroleum often contain a few percent of alkynes or dienes as impurities.¹ For subsequent polymerization processing, the level of impurities must be reduced to less than 10 ppm to avoid polymerization catalyst poisoning.² One most promising way to achieve this goal is to convert these molecules to alkenes while avoiding hydrogenation of the alkene streams.^{1,2}

In selective hydrogenation of 1,3-butadiene, extensive efforts have been devoted to improving the alkenes selectivity and extending the catalyst lifetime by modifying the electronic properties of Pd nanoparticles with a second metal, such as Au, Cu, Co, Sn, Pb, and so forth.^{3–9} In some cases, significant improvement of alkene selectivity was achieved.^{4,8} However, the durability of Pd-based bimetallic catalysts is still very poor.^{3,7,10–14} The Au catalyst containing small gold nanoparticles (between 2 and 5 nm in average) has been proved to be another potential candidate, which shows butenes selectivity as high as 100% at the complete conversion of 1,3-butadiene.^{15–17} But it is much less active than Pd-based catalyst, and often reaches 100% conversion at $\sim 170^\circ\text{C}$.^{4,15} Moreover, significant deactivation overtime was also observed on the Au catalyst through the formation of carbonaceous deposits.^{17–20} Recently, Gates et al. reported partially carbonylated MgO-supported rhodium clusters are even more selective than the Au catalyst for selective hydrogenation of 1,3-

butadiene to *n*-butenes while operating at a much lower temperature of 40°C .²¹ However, the catalyst again underwent a gradual decarbonylation process during reaction and could only maintain the high selectivity for about 10 h. Therefore, the urgent need in this field is to develop a specific catalyst with high selectivity of alkenes at high conversions of alkynes or dienes and long durability against coking in the presence of an excess of alkenes.^{7,15}

ALD has been demonstrated to be a promising method to apply oxide overcoating layers onto supported metal catalyst with atomically precise thickness control, which allows optimizing both stability and activity.^{22–28} Recently, we found that the thin ALD alumina film on the Pd surface is porous, and the porosity can be further tuned through high-temperature treatment.^{23,25,26,29} More interestingly, the ALD alumina overcoat preferentially decorates the low-coordination Pd sites while leaving the (111) facet sites accessible for catalytic function, which remarkably enhanced the selectivity and durability of Pd catalyst in methanol decomposition and oxidative dehydrogenation of ethane reactions.^{23,26} More recently, Marshall and co-workers further demonstrated that the ALD alumina overcoat can also tune the Pd catalyst

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selectivity to a certain extent in furfural hydrogenation reaction.³⁰ However, no work has shown that ALD alumina overcoating could enhance the durability of metal catalyst against deactivation via coking in hydrogenation reactions. In this work, we first report that precisely controlled porous ALD alumina overcoating on the Pd catalyst not only remarkably enhances the selectivity to butenes, especially to 1-butene, but also achieves the best ever durability against deactivation in selective hydrogenation of 1,3-butadiene in the absence (or presence) of propene.

A Pd/Al₂O₃ sample was first synthesized by Pd ALD on a spherical alumina support for one cycle at 150 °C.³¹ Next, different cycles of alumina ALD were executed on the Pd/Al₂O₃ sample to deposit the porous alumina overcoating layer with different thicknesses demonstrated in the schematic illustration in Figure 1a (α Al/Pd/Al₂O₃, number of ALD

ALD process here. On the 30Al/Pd/Al₂O₃ sample, the Pd particle size was about 2.3 nm in average (Figure 1d), and there was no visible change after applying ALD alumina overcoat.^{23,26,29}

The accessibility of Pd nanoparticles embedded under the porous ALD alumina overcoat was verified by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) CO chemisorption measurements (Figure S1). Similar to our previous results,^{23,26,32} the preferential decoration of the low-coordination sites of Pd nanoparticles by the ALD alumina overcoat was again observed on the ALD alumina coated Pd samples, which is indicated by the dominated bridge-bonded CO peak at between 1907 and 1944 cm⁻¹ on these samples. Increasing the number of alumina ALD cycles, the CO peak intensity decreased quickly, and it was below the IR detection limit on the 30Al/Pd/Al₂O₃ sample.²³

According to their catalytic performance, we first examined the Pd/Al₂O₃ catalysts with and without porous alumina overcoats in hydrogenation of 1,3-butadiene. After the initial deactivation under the reaction conditions for 2 h at room temperature (Figure S2), we increased the reaction temperature to improve the conversion of 1,3-butadiene. As shown in Figure S3, 100% conversion of 1,3-butadiene was reached at about 65–70 °C on Pd/Al₂O₃, 10Al/Pd/Al₂O₃, and 20Al/Pd/Al₂O₃, and at about 100 °C on 25Al/Pd/Al₂O₃ and 30Al/Pd/Al₂O₃, respectively. Apparently, the activities were relatively lower on the samples with larger alumina overcoat thickness, in line with the DRIFTS CO chemisorption results in Figure S1. Nevertheless, the activation energies of all these catalysts were quite similar, which were in the range of 67–73 kJ/mol (Figure S4). These values are consistent well with the ones reported in the literatures for Pd catalyst (i.e., between 48 and 66^{11,33–35} and 75³⁶ kJ/mol).

To compare the butenes selectivity at the same conversion, we plotted the butenes selectivity as a function of 1,3-butadiene conversion. As shown in Figure 2a, we clearly observed that at high conversions, the selectivity to all butenes increased remarkably with an increase in the overcoat thickness. On 30Al/Pd/Al₂O₃, the selectivity to all butenes was 99% at a conversion of 95%, comparable to the Au catalyst;^{4,37} however, it was only 46% at the same conversion on the uncoated Pd/Al₂O₃ catalyst. Such remarkable enhancement of butenes selectivity through the porous alumina overcoat by ALD is obviously superior to either TiO₂ or FeO_x modification of Pd catalysts via wet-chemistry in previous studies.^{3,38} We speculate that the remarkable increase of butenes selectivity could partly attribute to the confinement effect within the microspores of the overcoat observed by N₂ physisorption measurements (Figure S5). Figure 2b illustrates the detailed selectivity to different butenes at a conversion of 95%. It is obvious that the improvement of 1-butene selectivity with an increase in the overcoat thickness was the most pronounced one, compared to *trans*-2-butene and *cis*-2-butene. Apparently, the isomerization reaction of 1-butene to *trans*-2-butene and *cis*-2-butene was retarded to a large extent by the confinement effect.³⁸ It is worthwhile to note that high-temperature pretreatment of ALD alumina-coated Pd samples would cause a large decrease in butenes selectivity (Figures S6 and S7), which is very likely due to the larger pores formation (greater than 2 nm in diameter) indicated by N₂ physisorption measurements (Figures S5 and S8),^{26,39} weakening of the confinement effect. Therefore, the micropores with a dominated size approximately below 1 nm likely play an important role in enhancing the butenes

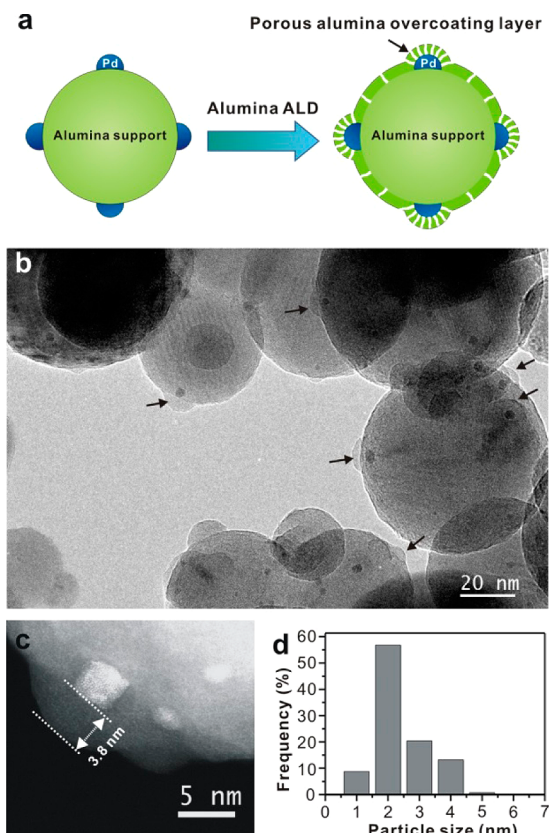


Figure 1. (a) Schematic illustration of porous ALD alumina overcoat on Pd/Al₂O₃ catalyst. Representative high-resolution TEM (b) and aberration-corrected HAADF STEM (c) images of as-prepared 30Al/Pd/Al₂O₃. (d) Pd particle size distribution histogram of the as-prepared 30Al/Pd/Al₂O₃ sample.

cycles, $\alpha = 10, 20, 25, 30$).²⁹ After 30 cycles of alumina ALD, high-resolution transmission electron microscopy (TEM) and aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF STEM) images both showed that the thickness of porous alumina overcoat was about 3.8 nm (Figure 1b,c) on the as-prepared 30Al/Pd/Al₂O₃ sample, indicating a growth rate of about 1.3 Å/cycle. This value is consistent very well with the growth rate of ALD alumina on flat surfaces and slightly smaller than the one we previously reported,²⁹ which implies that chemical vapor deposition (CVD) occurred to a lesser extent during the

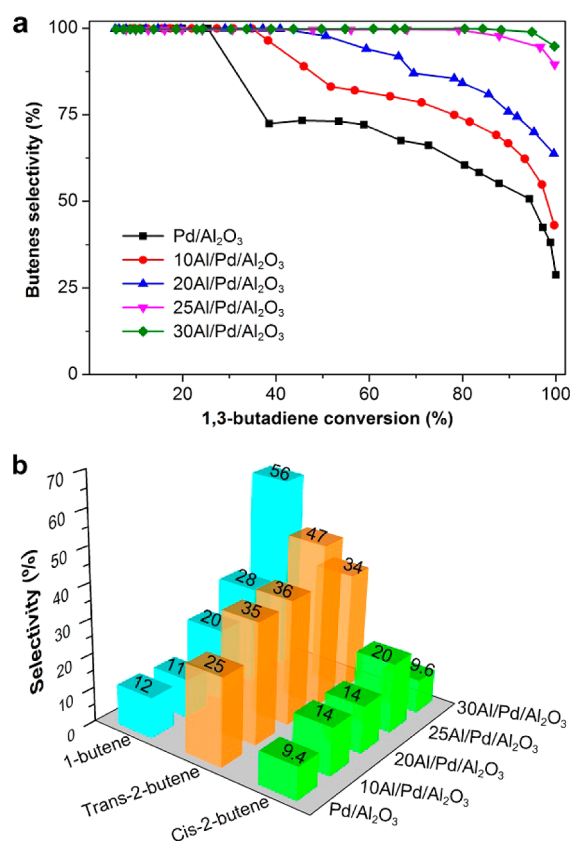


Figure 2. Catalytic performance of the Pd/Al₂O₃ samples with and without ALD alumina overcoats in the absence of propene. (a) Selectivity to all butenes as a function of 1,3-butadiene conversion. (b) The detailed selectivities to 1-butene, *trans*-2-butene and *cis*-2-butene at a conversion of 95%. The feed gas was 1.9% 1,3-butadiene and 4.7% H₂ with Ar as the balance gas at a total flow rate of 25 mL/min.

selectivity. Therein, the exposed Pd atoms via the micropores have much smaller ensembles, on which the adsorption mode of 1,3-butadiene might be modified to favor selective catalyst performance due to the steric effect.³⁸

Meanwhile, we noticed that when 1,3-butadiene conversion on Pd/Al₂O₃ was higher than 95%, 2-butenes selectivity started decreasing and the formation of butane accelerated, which indicates hydrogenation of 2-butenes occurred as a secondary reaction (Figure S9a). In contrast, on 30Al/Pd/Al₂O₃, the selectivity to 2-butenes started increasing at the expense of decrease in 1-butene selectivity, meanwhile the formation of butane was still very limited, which implies that isomerization of

1-butene to 2-butenes was the dominated secondary reaction over hydrogenation of butenes (Figure S9b). Therefore, we postulate that the porous alumina overcoat might reduce the concentration of dissociated hydrogen atoms on the surface of exposed small Pd ensembles to a level that is still sufficient for 1,3-butadiene hydrogenation and 1-butene isomerization but too low for the hydrogenation of butenes, similar to the role of CO additive on the Pd surface.⁴⁰

The Pt catalyst is well-known as less selective compared to the Pd catalyst in selective hydrogenation of 1,3-butadiene.^{3,41–43} The difference between the reaction on Pd and Pt surfaces was previously ascribed to the different adsorption strength, wherein the adsorption strength of 1,3-butadiene is considerably stronger than that of butene on the Pd surface, whereas the heat of adsorption for 1,3-butadiene and butenes was similar on the Pt surface.^{43,44} As a control experiment, we examined a Pt/Al₂O₃ catalyst (Figure S10) with and without ALD alumina overcoating in hydrogenation of 1,3-butadiene under the same conditions. Indeed, we found that the selectivity to all butenes significantly decreased after applying 20 cycles of ALD alumina overcoat (Figure S11). Therefore, stronger adsorption of 1,3-butadiene than butenes on Pd could play another important role in the selectivity enhancement of butenes by alumina overcoat.

In order to simulate the process required for purification of industrial alkene streams, we further investigated the catalytic performance of the uncoated and ALD alumina coated Pd/Al₂O₃ samples in the presence of 70% propene. As shown in Table 1, on Pd/Al₂O₃, a considerable propene conversion of 3.9% was observed, meanwhile the selectivity to all butenes increased due to the large hydrogen consumption by propene hydrogenation. The catalytic performance of the 10Al/Pd/Al₂O₃ sample was rather similar to the uncoated one. Further increasing the thickness of porous alumina overcoat led to a significant decrease of propene conversion along with a remarkable increase of 1-butene selectivity. On 30Al/Pd/Al₂O₃, the propene conversion was expressively suppressed to only 0.3% even at a 1,3-butadiene conversion of 99%; meanwhile, the 1-butene selectivity was preserved at as high as 51%. Meanwhile the negative effect was again observed on the 30Al/Pd/Al₂O₃-600C sample calcined at high temperature: the propene conversion considerably increased to 2.2% at a 1,3-butadiene conversion of 99%, and the 1-butene selectivity dropped to 43% (also seen on another Pd sample synthesized by the wet impregnation method in Table S1). Therefore, the micropores with a dominated size approximately below 1 nm can effectively suppress hydrogenation of alkenes even in an alkene-rich environment.

Table 1. Catalytic Performance of the Pd/Al₂O₃ Samples with and without ALD Alumina Overcoats in the Presence of an Excess of Propene^a

samples	reaction temperature (°C)	propene conversion (%)	1,3-butadiene conversion (%)	selectivity (%)		
				1-butene	<i>trans</i> -2-butene	<i>cis</i> -2-butene
Pd/Al ₂ O ₃	44	3.9	93	30	46	22
10Al/Pd/Al ₂ O ₃	82	3.7	95	32	42	22
20Al/Pd/Al ₂ O ₃	82	1.4	95	40	38	20
25Al/Pd/Al ₂ O ₃	88	0.9	95	50	33	15
30Al/Pd/Al ₂ O ₃	100	0.3	99	51	37	12
30Al/Pd/Al ₂ O ₃ -600C ^b	102	2.2	99	43	39	14

^aThe feed gas was 1.9% 1,3-butadiene, 4.7% H₂, and 70% propene with Ar as the balance gas at a total flow rate of 25 mL/min. ^bThe 30Al/Pd/Al₂O₃ sample was calcined at 600 °C in 10% O₂ in Ar for 2 h, then reduced at 250 °C in 10% H₂ in Ar for another 1 h.

Lastly, the durability of the ALD alumina-coated Pd/Al₂O₃ sample was examined first in the absence of propene for 62 h at a 1,3-butadiene conversion of 95% and then in the presence of 70% propene for another 62 h at a 1,3-butadiene conversion near 100%. As shown in Figure 3, the 30Al/Pd/Al₂O₃ sample

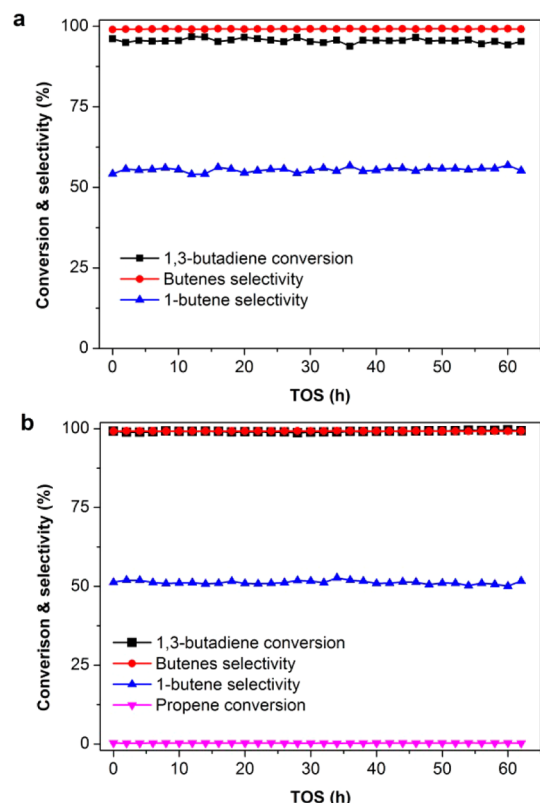


Figure 3. Durability test on the 30Al/Pd/Al₂O₃ sample at 100 °C first in the absence of propene for 62 h (a) and then in the presence of 70% propene for another 62 h (b) at high 1,3-butadiene conversions. TOS = time on stream.

showed excellent durability against deactivation during a total 124 h of reaction time on stream (TOS) without any visible activity declines or selectivity changes. X-ray diffraction (XRD) and HAADF-STEM on the used samples also showed that the sintering of Pd nanoparticles did not occur (not shown here). It is worthy to note that the highly sufficient suppression of propene conversion to only 0.3% at a 1,3-butadiene conversion near 100% was preserved during the long period of reaction test (Figure 3b). To the best of our knowledge, this is the best ever durability of metal catalyst in hydrogenation of 1,3-butadiene in the presence (or absence) of alkenes, among the metal catalysts reported in the literatures so far, including Pd catalysts,^{3,10–14} Pd-based bimetallic catalysts,^{3,7,10} Au catalysts,^{15,17,18,20} and others.²¹ This is very different from the previous work, wherein the Pd/ α -alumina,^{11,45} Pd/SiC,¹¹ and AuCu/TiO₂¹⁸ catalysts showed a progressive deactivation and selectivity changes with time due to the continuous accumulation of carbonaceous deposits on the catalyst surface. Therefore, it appears that the porous ALD alumina overcoat can prevent such continuous carbon accumulation under current conditions after the initial deactivation. Actually, reaching a steady state at low conversions after the initial deactivation has been observed in some cases.^{11,13} However, it is very surprising that there has been no study of the “steady-state” catalyst associated with

complete conversion at elevated temperatures. The uncoated Pd/Al₂O₃ catalyst in our work also exhibited good durability at high conversions, but the selectivity to butenes and the ability to suppress propene conversion were very poor (Figure S12, Tables 1 and S1). As a consequence, microporous ALD alumina overcoating, for the first time, provides a promising method of achieving both high selectivity and excellent durability at near complete conversions in selective hydrogenation of 1,3-butadiene in the absence (or presence) of propene.

In conclusion, we have successfully demonstrated that precisely applying a microporous Al₂O₃ overcoat onto a Pd/Al₂O₃ catalyst using ALD can remarkably enhance the selectivity to butenes, especially to 1-butene in selective hydrogenation of 1,3-butadiene. In the presence of an excess of propene, the alumina overcoat significantly suppressed the propene conversion to only 0.3% while preserving 100% butenes selectivity at a 1,3-butadiene conversion near 100%. Such significant improvement in butenes selectivity is attributed to the confinement effect within the micropores of the overcoat and stronger adsorption of 1,3-butadiene than alkenes on Pd. More importantly, the best ever durability against progressive deactivation was simultaneously achieved on the Al₂O₃ coated Pd catalysts during a total 124 h of reaction time on stream without any visible activity decline or selectivity changes. Finally, we propose that applying such porous oxide overcoating on a metal catalyst might be a new promising way to achieve high selectivity and stability in other hydrogenation reactions such as alkynes.

■ ASSOCIATED CONTENT

§ Supporting Information

The following file is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.5b00129.

Experimental section and catalytic performances of additional Pt and Pd catalysts (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: junling@ustc.edu.cn.

Notes

The authors declare no competing financial interest.

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