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Pd-on-Si catalysts prepared via galvanic displacement for selective hydrogenation of para-chloronitrobenzene†

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Qian Wei, Yu-Sheng Shi, Ke-Qiang Sun*, Bo-Qing Xu*

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Direct redox reaction (galvanic displacement) between Pd²⁺ and substrate Si was used to deposit Pd on Si, and the Pd-Si catalysts enabled a chemoselective hydrogenation of para-chloronitrobenzene with a selectivity to para-chloroaniline higher than 99.9 % at complete conversion of para-chloronitrobenzene.

Selective reduction of halogenated nitroarenes constitutes a kind of important reaction for the synthesis of halogenated anilines, which are important intermediates in the chemistry of pesticides, herbicides, drugs, pigments and dyes.^{1,2} The most efficient and environmental-benign method for large-scale halogenated aniline production is catalytic hydrogenation of halogenated nitroarenes by using heterogeneous catalysts. However, undesired hydrodehalogenation (carbon-halogen bond scission) is generally observed, particularly at high conversions. Although the selectivity to haloanilines could be enhanced by adding dehalogenation inhibitors (e.g., potassium thiocyanate, amidine derivatives)³ in the reaction liquid and by using unconventional solvent (e.g., supercritical CO₂⁴ and ionic liquids⁵), the choice of catalyst, i.e., supported precious metal catalyst, is the key in determining the product distribution of the reactions.^{1,2}

Palladium is valued among other precious metal catalysts for its high activity for hydrogenation of halogenated nitroarenes as well as its relatively cheaper price (ca., 580 vs. 1020 \$/oz as compared with Pt⁶). However, Pd is also notorious for its high activity in catalyzing dehalogenation reaction.^{1,2} Extensive interests have been directed to design chemoselective palladium catalysts that could minimize or even eliminate dehalogenation reaction at high conversions of halogenated nitroarenes. Some promising results have been reported. A selectivity of 99.2 % for para-chloroaniline (*p*-CAN) at a complete conversion of para-chloronitrobenzene (*p*-CNB) was achieved on partially reduced Pd/γ-Fe₂O₃ nanocomposite catalyst.⁷ *Para*-chloroaniline as the sole product (no numerical selectivity data were given) was reported over a Pd/ZnO catalyst

when varying *p*-CNB conversion in the range of 0-84%.⁸ Recently, a selectivity of 100 % to *p*-CAN was observed on CNT and graphene supported Pd nanoparticles.⁹ Factors identified that are critical to reaction selectivity include the size of Pd nanoparticles¹⁰, electronic interaction between Pd and support^{7,11} and alloy formation^{8,12}. However, to develop selective and active Pd catalyst is still highly desirable for the hydrogenation of halogenated nitroarenes.

Galvanic displacement has widely adopted in preparing solid catalysts (particularly those for electrocatalysis).^{13,14} These studies generally involved reactions between noble metal ions and base metals, while less attention was paid to redox reaction between noble metal ions and metalloid or semimetal elements such as Si. Herein we report a new method for preparing Pd catalyst by deposition of Pd on Si via galvanic displacement reaction between Pd ions and Si powders in aqueous solution. Without introducing any promoters and dehalogenation inhibitors, the Pd-Si catalysts show excellent performance for the hydrogenation of *p*-CNB: a selectivity to *p*-CAN higher than 99.9 % was obtained at complete conversion of *p*-CNB.

When adding Si powders to the aqueous solution of PdCl₂, galvanic displacement reaction occurs spontaneously, because the reduction potential of Pd²⁺ (Pd²⁺/Pd, E[⊖] = 0.931 V vs. normal hydrogen electrode (NHE)) is much larger than that of Si²⁺ (Si²⁺/Si, E[⊖] = -1.241 V) (supplementary information). By varying the concentration of PdCl₂ in the precursor solution, a series of Pd-Si catalysts with different Pd loadings were obtained and denoted as xPd-Si, where “x” represents the weight percentage (wt %) of Pd analysed by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The specific surface area (Table 1), measured by Kr physisorption, increased gradually from 0.63 m²/g for the Si powder to 0.64, 0.64, 1.00, 1.02, 1.36, 1.42 and 1.58 m²/g with the increment of Pd loading to 0.06, 0.12, 0.38, 0.62, 1.05, 2.80 and 3.28 wt%, respectively. Scanning electron microscopy (SEM) images (Figure S1) show that pores were created on Si particles on depositing Pd on Si and the depth and number of the pores increased with Pd loading. These observations are in line with the deposition mechanism of Pd according to the galvanic replacement.¹⁵⁻¹⁷

^a Innovative Catalysis Program, Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China. E-mail: kqsun@mail.tsinghua.edu.cn; bqxu@mail.tsinghua.edu.cn

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Table 1 BET surface area, Pd crystalline size and quantified XPS results for xPd-Si catalysts.

Catalyst	S_{BET} (m^2g^{-1})	Pd crystalline size ^a (nm)	Pd/Si _(ICP) atomic ratio ^b ($\times 10^{-4}$)	Pd/Si _(XPS) atomic ratio ^c ($\times 10^{-2}$)	PdSi _x /Pd ⁰	$\frac{\text{Pd/Si}_{(\text{XPS})}}{\text{Pd/Si}_{(\text{ICP})}}$
Si powder	0.63					
0.06Pd-Si	0.64	-	1.58	1.7	0.73	110.3
0.12Pd-Si	0.64	-	3.16	1.0	0.81	30.8
0.38Pd-Si	1.00	8.6	9.74	2.1	0.98	21.1
0.62Pd-Si	1.02	9.0	16.31	2.6	1.63	16.2
1.05Pd-Si	1.36	9.2	27.63	3.2	2.45	11.7
2.80Pd-Si	1.42	9.7	73.67	4.4	2.57	6.0
3.28Pd-Si	1.58	11.1	83.67	4.8	2.56	5.7

^a Estimated by the Scherrer equation based on the diffraction of (111) plane at $2\theta = 40.1^\circ$. ^b Obtained by ICP-AES analysis. ^c Obtained by XPS analysis.

The nature of Pd entities on Si was then probed using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). All of the catalysts showed peaks characteristic of Si phase ($2\theta = 28.5^\circ$, 47.3° , 56.1° , 69.1° , 76.4° , JCPDS 065-1060). No diffractions corresponding to Pd metal or any Pd-containing compounds could be detected for 0.06Pd-Si and 0.12Pd-Si samples (Fig. 1A). For samples with Pd loading no less than 0.38 wt%, diffraction at $2\theta = 40.1^\circ$ due to metallic Pd (JCPDS 065-6174) was detectable, and its intensity increased gradually with increasing Pd loading (insert of Fig. 1A). The average crystalline size of Pd (Table 1), estimated by the Scherrer equation based on the diffraction at $2\theta = 40.1^\circ$ (Pd (111) plane), increased steadily from 8.6 nm for 0.38Pd-Si to 11.1 nm for 3.28Pd-Si (Table 1).

The XPS spectra of all the xPd-Si catalysts could be deconvoluted into two pairs of doublets (Fig. 1 B). Peak at 335.0 eV is due to metallic Pd $3d_{5/2}$ (the corresponding Pd $3d_{3/2}$ was at around 340.3 eV), and peak at 336.5 eV is due to PdO and/or PdSi_x $3d_{5/2}$ (the corresponding $3d_{3/2}$ level was at 341.8 eV)¹⁸⁻²². It should be noted that both 0.06Pd-Si & 0.12Pd-Si samples showed $3d_{5/2}$ peaks at 335.2 eV, whereas for samples with higher Pd loadings this peak shifted to 335.0 eV. This slight but clear shift would suggest the presence of partial-positively charged Pd entities when Pd loading was no higher than 0.12 wt%. The Pd $3d_{5/2}$ peak for PdO and/or PdSi_x remained at 336.5 eV with Pd loadings. Note that PdO species also show O 1s peak at 530.2 eV,²¹ the absence of peaks at 530.2 eV for these xPd-Si samples (Figure S2) suggest the formation of Pd silicide (PdSi_x), which is in line with the attribution of a Pd $3d_{5/2}$ peak at 336.5 eV to PdSi_x formation during thermal evaporating Pd on a Si surface.²²⁻²⁶

The XPS results were then quantified and the data were organized in Table 1. The PdSi_x/Pd⁰ ratio in these samples increased sharply from 0.79 to 2.45 when increasing Pd loading from 0.06 to 1.05 wt %, and then levelled off at higher Pd loadings. This increased formation of PdSi_x with increasing Pd loading could be due to an enhanced counter-diffusion of Pd and Si when galvanic replacement reaction proceeds more extensively at higher PdCl₂ concentrations, which is similar to the observation of Au-Ag alloy formation when depositing Au on Ag nanoparticles via galvanic replacement.²⁷

On the other hand, the Pd/Si_(XPS) to Pd/Si_(ICP) ratio (Table 1) could be used to indicate the surface/bulk ratio of Pd entities, thus to reflect Pd dispersion in these xPd-Si samples. The ratio decreased

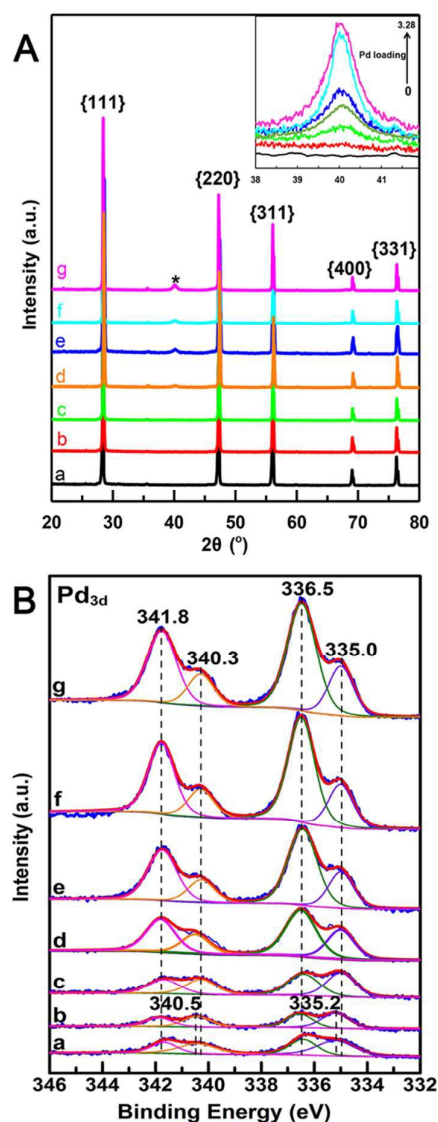


Fig.1 XRD patterns (A) and XPS spectra of the Pd 3d regions (B) of xPd-Si samples: (a) 0.06Pd-Si; (b) 0.12Pd-Si; (c) 0.38Pd-Si; (d) 0.62Pd-Si; (e) 1.05Pd-Si; (f) 2.80Pd-Si; (g) 3.28Pd-Si.

Table 2 Catalytic performance of selective hydrogenation of *p*-CNB over xPd-Si catalysts and reference catalysts.^a

Catalyst	Catalyst amount (mg)	Rxn time (h)	Conv. (%)	Selectivity (%) ^b			MSA ^c (mol h ⁻¹ g _{Pd} ⁻¹)
				<i>p</i> -CAN	AN	NB	
Si powder	100	2.0	0.07				
0.06Pd-Si	100	3.0	17.95	> 99.9	< 0.02	< 0.01	2.00
0.12Pd-Si	50	2.0	17.86	> 99.9	< 0.04	< 0.02	2.98
0.38Pd-Si	25	1.5	14.56	99.3	0.3	0.4	2.10
0.62Pd-Si	25	1.5	17.23	99.0	0.4	0.6	1.48
1.05Pd-Si	25	1.0	16.80	98.8	0.7	0.5	1.28
2.80Pd-Si	25	1.0	18.62	98.2	1.1	0.7	0.53
3.28Pd-Si	25	0.8	14.03	98.0	1.1	0.9	0.41
Pd black ^d	5	0.4	16.23	88.8	9.4	0.2	0.16
10Pd/C ^e	5	0.3	17.78	84.4	15.3	0	2.37
0.12Pd-Si	25	36.0	> 99.9	> 99.9	< 0.1	0	-
Pd black ^f	15	1.5	> 99.9	34.9	62.0	0	-
10Pd-C ^g	5	2.5	> 99.9	66.8	32.5	0	-

^a Reaction temp = 100 °C ; P_{H₂} = 1.0 MPa; *p*-CNB = 2 mmol; toluene = 5 mL; stirring speed = 900 rpm. ^b No formation of azo or azoxy products could be detected for reactions on xPd-Si catalysts. The carbon balance of the reaction on xPd-Si catalyst was always within 100 ± 5 %. ^c Mass-specific activity of Pd. ^d The selectivity to azo compounds is 1.6 %, the carbon balance of the reaction is 82 %. ^e The selectivity to azo compounds is 0.3 %, the carbon balance of the reaction is 95 %. ^f The selectivity to azo compounds is 3.1 %, the carbon balance of the reaction is 72 %. ^g The selectivity to azo compounds is 0.7 %, the carbon balance of the reaction is 90 %.

exponentially with the increment of Pd loading, suggesting that Pd dispersion decreases sharply with increasing of Pd loading from 0.06 to 0.38 wt%. We speculate that the direct redox reaction between Pd²⁺ and Si, according to the mechanism of galvanic displace reaction,²⁸ would lead to the formation of raft-like Pd entities in strong interaction with the underlying Si at the initial stage of Pd deposition. This strong Pd-Si interaction would also electronically affect the nature of Pd, which should be responsible for the formation of electron deficient Pd entities. The speculation is also in line with the XRD results that no diffraction relating to Pd species could be detected when Pd loading is no higher than 0.12 wt %. On further depositing Pd, the raft-like Pd entities would grow in height and finally transformed into Pd particles detectable with XRD.

The performance of xPd-Si catalysts for *p*-CNB hydrogenation was then studied. To compare rigorously the catalytic activity and selectivity, the conversion level of *p*-CNB over these Pd-Si catalysts was limited in the range of 11 ~ 20 % by adjusting the reaction duration and catalyst amount. Mass specific activity of Pd (MSA_{Pd}) was calculated by normalizing the *p*-CNB consumption rate to the amount of Pd (Table 2).

The MSA_{Pd} for xPd-Si samples first increased from 2.00 to 2.98 mol h⁻¹ g_{Pd}⁻¹ when Pd loading in xPd-Si catalysts increased from 0.06 to 0.12 wt %, and then decreased gradually to 2.10, 1.48, 1.28, 0.53 and 0.41 mol h⁻¹ g_{Pd}⁻¹ on further increasing the Pd loading to 0.38, 0.62, 1.05, 2.80 and 3.28 wt %, respectively. On the other hand, both the 0.06Pd-Si and 0.12Pd-Si catalysts showed a *p*-CAN selectivity higher than 99.9 % by careful checking with GC-MS analysis. On further increasing Pd loading to 0.38, 0.62, 1.05, 2.80 and 3.28 wt %, the selectivity to *p*-CNB then decreased monotonously to 99.3 %, 99.0 %, 98.8 %, 98.2 % and 98.0 %, respectively. It should be noted that special attention has been paid to distinguish products of the reaction, and no other condensation

products such as 4,4-dichloroazoxybenzene and 4,4-dichloroazobenzene and their dechlorination derivatives could be detected for xPd-Si catalysts, and the selectivities of *p*-CAN on these xPd-Si catalysts remained above 98%. In contrast, Pd black (Alfa Aesar) as a reference catalyst showed a *p*-CAN selectivity of 89.7 % and MSA_{Pd} of 0.16 mol h⁻¹ g_{Pd}⁻¹. The commercial 10Pd/C (Alfa Aesar) catalyst showed a MSA value of 2.37 mol h⁻¹ g_{Pd}⁻¹, but a *p*-CAN selectivity as low as 84.6 %.

Because dehalogenation is more favoured at higher *p*-CNB conversion, the *p*-CAN selectivities at complete conversion of *p*-CNB over 0.12Pd-Si and the reference 10Pd/C and Pd black were further compared (Table 2). Interestingly, 0.12Pd-Si catalyst could still maintain a *p*-CAN selectivity higher than 99.9 %, whereas Pd black and Pd/C catalyst showed a *p*-CAN selectivity of only 36.0 % and 67.3 %, respectively.

The above results demonstrate clearly that the Pd-on-Si catalyst prepared via galvanic displacement method could not only achieve a selective (> 99.9 %) hydrogenation of *p*-CNB to *p*-CAN at complete *p*-CNB conversion, but also offer activity even superior to the conventional Pd/C catalyst in term of MSA_{Pd}.

In order to better understand this unique chemoselective catalysis of xPd-Si catalyst, the effects of *p*-CNB concentration on the performance of 0.12Pd-Si and the reference Pd/C catalysts were further compared by limiting *p*-CNB conversion in the range of 10 ~ 20 %. With the increase of *p*-CNB concentration from 0.2 ~ 1.0 mol L⁻¹, the *p*-CAN selectivities over the two catalysts remained unchanged. However, the reaction rates over 0.12Pd-Si decreased gradually from 4.4 mol h⁻¹ g_{Pd}⁻¹ at a *p*-CNB concentration of 0.2 mol L⁻¹ to 2.8 mol h⁻¹ g_{Pd}⁻¹ at a *p*-CNB concentration of 1.0 mol L⁻¹, while the rates on 10Pd/C remained essentially unchanged. By logarithmically plotting reaction rate against *p*-CNB concentration (Figure 2), the line slopes would give the reaction order with respect to *p*-CNB, which was -0.35 over 0.12Pd-Si and 0.01 over 10Pd/C catalyst.

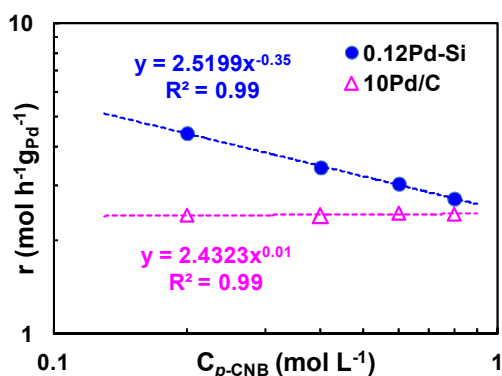


Fig. 2. Effect of p -CNB concentration on the overall rate of p -CNB hydrogenation over 0.12Pd-Si and 10Pd/C.

The negative reaction order of p -CNB over 0.12Pd-Si catalyst is in line with the Langmuir-Hinshelwood mechanism which is generally used to describe the hydrogenation of nitrobenzene on precious metal catalysts.²⁹ The fact that the reaction order of p -CNB on 0.12Pd-Si catalyst was smaller than that on 10Pd/C would indicate a stronger adsorption of p -CNB on 0.12Pd-Si than on 10Pd/C catalyst. It is known that the nitro groups are more electronegative than chlorine group, and the electron density of the nitro groups would be further enhanced due to the para-substituted Cl through inductive and conjugation effects.^{1,2} The adsorption and activation of nitro groups would be more favourable on electron-deficient Pd species, and consequently, results in a stronger adsorption of p -CNB on 0.12Pd-Si with electron deficient Pd entities and PdSi_x species.

The relative adsorption strength of p -CNB and its hydrogenation product p -CAN strongly affects the product selectivity of p -CNB hydrogenation.^{29,30} The stronger adsorption of p -CNB would favour the desorption of p -CAN which is deemed most prone to undergo dehalogenation due to the activation of the C-Cl bond by electron donating amino group, thus lowers the possibility of dehalogenation of p -CAN. Therefore, the stronger adsorption of p -CNB on 0.12Pd-Si than on 10Pd/C would be one important reason for the excellent selectivity observed on 0.12Pd-Si catalyst. On the other hand, the presence of electron-deficient Pd entities as well as PdSi_x species on xPd-Si would also decrease the electron back-donation from Pd to the adsorbed p -CAN, and weaken to a less extent the p - π conjugation between the chlorine and the benzene ring atom,^{1,2} and consequently suppress the hydrodehalogenation.

In summary, the direct reduction and oxidation reaction between Pd²⁺ ions and the substrate Si was used to prepare Si supported Pd catalyst. The Pd-Si catalyst suppressed undesirable hydrodehalogenation reaction at complete p -CNB conversion, while the high catalytic activity of Pd was essentially maintained in term of MSA_{Pd} when compared to the commercial 10Pd/C catalyst. The excellent performance of Pd-Si catalysts was attributed to the formation of electron-deficient Pd entities due to the strong Pd-Si interaction. The present results identified a highly chemoselective Pd catalyst for the hydrogenation of halogenated nitroarenes. This method of catalyst preparation would also be applicable to develop other high-performing metal catalysts.

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