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Wettability-Driven Palladium Catalysis for Enhanced Dehydrogenative Coupling of Organosilanes

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ABSTRACT: Direct coupling of Si–H bond has emerged as a promising strategy for designing chemically and biologically useful organosilicon compounds. Heterogeneous catalytic systems sufficiently active, selective, and durable for dehydrosilylation reaction under mild conditions have been lacking to date. Herein, we report that the hydrophobic characteristics of the underlying supports can be advantageously utilized to enhance the efficiency of palladium nanoparticles (Pd NPs) for dehydrogenative coupling of organosilanes. As a result of this prominent surface wettability control, the modulated catalyst showed a significantly higher level of efficiency and durability characteristics toward the dehydrogenative condensation of organosilanes with water, alcohols, or amines as compared to existing catalysts. In a broader context, this work illustrates a powerful approach to maximize the performance of supported metals through surface wettability modulation under catalytically relevant conditions.

KEYWORDS: *Dehydrocoupling, Organosilanes, Pd Nanoparticles, Heterogeneous Catalysis, Hydrophobicity*

1. INTRODUCTION

The search for new robust solid catalysts for selective chemical processes has spurred the onset of meticulous design strategies along with ingenious synthesis of active phases (i.e., active sites).¹ Alternatively, a facile and more straightforward approach for catalyst tailoring lies in modulating surface wettability such that the substrate–catalyst interaction can be favorably manipulated in a targeted and controlled manner.² In this sense, one of the most elegant examples is the enhanced activity and selectivity of hydrophobic titanosilicate (TS-1) for the catalytic oxidation of organic compounds using aqueous H₂O₂ as a terminal oxidant.³ Recent progress in the understanding of zeolite and zeotype solid acid materials with controlled wettability has led to the successful development of a plethora of benign acid-catalyzed processes for the production of renewable chemicals within the biorefinery context.⁴ Surprisingly, the potential offered by wettability control in regulating the characteristics of supported metal catalysts has remained largely unexplored,^{2c} despite the paramount importance of these materials in enabling various imperative catalytic processes.

Dehydrogenative cross-coupling (DCC) reactions have emerged as a promising tool to precisely construct new C–X and X–X (X = heteroatom) bonds via direct C–H or X–H activation.⁵ In this sense, organosilanes constitute

attractive DCC reagents to access various functionalized organosilicon compounds serving both as highly useful building blocks or key intermediates for polymeric and other advanced organic materials.⁶ To date, several efficient DCC strategies for silanes using hydrogen acceptors (i.e., oxidants) such as hydrogen peroxide and molecular oxygen have been developed.⁷ From the viewpoint of atom efficiency and safety perspectives, an acceptor-free approach would be ideal. Advantageously, this may also provide a convenient route for simultaneous H₂ generation and storage.^{6d} However, with the aim to maximize the efficiency of organosilanes as DCC reagents, the inherently sluggish kinetics for Si–H cleavage must be circumvented.⁸ While several efficient homogeneous catalysts have been developed,⁹ the corresponding heterogeneous catalysts have generally displayed significantly lower efficiencies despite the large number of attempts.¹⁰ With the aim to overcome these issues, highly robust solid catalysts able to significantly improve the reaction kinetics under moderate conditions are thus urgently required.

Metallic palladium (Pd) is commonly used as an active component in hydrolytic oxidation of organosilanes or dehydrogenative silylation of alcohols at low temperature and additive-free conditions.^{10a–c,14a} However, heterogeneous Pd-based catalysts are typically limited by the low affinity interaction between organosilanes and water or alcohols, which hinders the efficiency of the desired

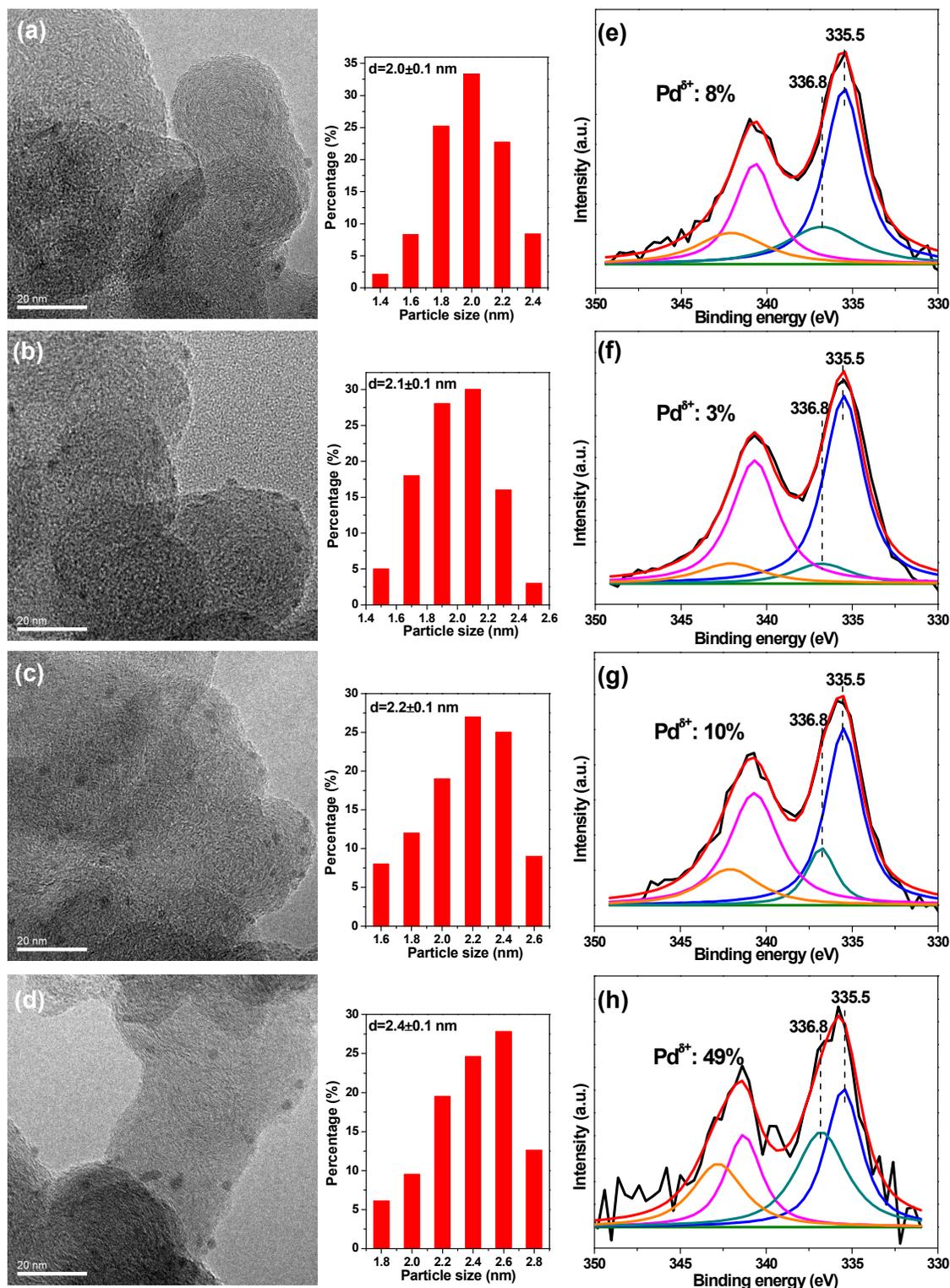


Figure 1. Transmission electron microscopy (TEM) images, particle distribution, and Pd 3d XPS spectra of: (a, e) Pd/XC-72; (b, f) Pd/XC-72-700-Ar; (c, g) Pd/XC-72-HNO₃; and (d, h) Pd/XC-72-700-Ar stored for two years.

transformation process.^{10a,b} Engineering metal-support interfaces displaying strong enough interactions with the reactants while weakly interacting with the products would offer an opportunity for enhanced catalytic efficiencies.^{2c,11} Although many studies have focused on regulating the electronic structure of the supported Pd or deliberately increasing the hydrophilic properties of the underlying supports,^{10a-d,f,h,j-1,n} a catalyst outperforming the

state-of-the-art homogeneous systems still remains elusive. We report, for the first time, that the use of highly hydrophobic carbon black (CB) as a support material can significantly enhance the efficiency of Pd nanoparticles (NPs) for dehydrogenative coupling of organosilanes. As a result of a noticeable surface wettability modulation, the engineered catalyst showed exceedingly enhanced activity and durability toward dehydrogenative condensation of

organosilanes with water, alcohols, or amines as compared to existing catalysts.

2. RESULTS AND DISCUSSION

To begin our studies on direct coupling of Si-H bond via hydrolytic oxidation, we selected a series of commercial CB as a supporting material for Pd NPs, anticipating that the inherent hydrophobic nature of these materials would have a positive impact on the outcome of the reaction.¹² In an effort to explore and evaluate the possible wettability effects via surface engineering, we opted for a systematic approach to progressively impart surface hydrophobicity on the modified CB materials.^{12b} This was achieved by subjecting the as-received commercial CB materials to an inert gas annealing treatment at elevated temperatures (for details, see the Supporting Information). Analysis by water and organosilane adsorption revealed an increased hydrophobicity in the sample exposed to temperatures above 300 °C, in contrast to the material treated with 32% HNO₃, which was shown to be particularly effective for generating a highly hydrophilic surface (ca. five-fold increase in water adsorption along with an eight-fold decrease in organosilane adsorption, Table S3). Essentially, the increased hydrophobicity was associated with a lower number of surface oxygenated species, as revealed by infrared and X-ray photoelectron spectroscopy (XPS) analysis (Figures S2, S3). Subsequent wet-chemical reductive processing¹³ of these wettability modulated CB materials led to the decoration with narrowly size-distributed Pd NPs (average size ca. 2 nm) having basically similar chemical states and metal-support interface structure (Figures 1, S1) on the surface of the carbon supports.

Initial experiments dealing with the hydrolysis of triethylsilane (**1a**) in THF at 25 °C were promising and suggested that CB-supported Pd NPs could certainly perform very well (Table 1, entries 1–4). The assessment of a number of CB structures revealed that surface-engineered Vulcan XC-72 carbons were particularly effective support classes, with the highly hydrophobic XC-72-700-Ar (obtained via annealing at 700 °C under Ar atmosphere) providing an outstanding dehydrogenative silylation efficiency with the exclusive production of triethylsilanol (**1b**) as a result of the reaction (Table 1, entries 5–7). As an illustration of the efficiency of XC-72-700-Ar as a support, Pd/XC-72-700-Ar with a palladium content of 1.0 wt % achieved complete hydrolysis of **1a** within 1 min at a substrate-to-catalyst (S/C, mol_{sub}/mol_{pd}) ratio of 10000, with a turnover frequency (TOF) of 1.6 × 10⁶ h⁻¹ for quantitative **1a** hydrolysis based on surface Pd atoms (Table 1, entry 6). This catalytic system showed fast kinetics while maintaining its activity for an extended period of time, as inferred by monitoring the H₂ release upon sequential injection of **1a** at intervals into a THF-H₂O solution containing Pd/XC-72-700-Ar.^{9d} This result was remarkable, and became more relevant as the H₂ gas produced using Pd/XC-72-700-Ar was easily controlled by slowly and continuously injecting **1a** into the catalytic system (Figure S4). Furthermore, this system also worked well under scale-up conditions (see Supporting Information). For example, 50 mmol of **1a** were successfully transformed into **1b** in nearly quantitative yield (> 99%). In this case,

the recovered Pd/XC-72-700-Ar material was reused at least ten times while maintaining its initial activity (i.e., total turnover number (TON) approached 8.0 × 10⁵, Figure S5). To the best of our knowledge, this result is far superior to any reported example on hydrolytic oxidation of organosilanes (Table S8).^{9,10}

Table 1. Study of CB-supported Pd catalysts for the dehydrocoupling of **1a and H₂O.^a**

Et ₃ Si-H (1a) + H ₂ O → H ₂ + Et ₃ Si-OH (1b)				
Entry	Catalyst ^b	Time [s]	Yield [%]	TOF [h ⁻¹] ^c
1	Pd/XC-72	72	>99	510 800
2	Pd/BP2000	119	97	299 900
3	Pd/M800	90	97	396 800
4	Pd/660R	146	98	247 100
5	Pd/XC-72-300-Ar	63	>99	583 600
6	Pd/XC-72-700-Ar	57	>99	645 300 (1686000 ^d)
7	Pd/XC-72-900-Ar	59	>99	623 400
8	XC-72-700-Ar	720	n.d.	-
9 ^e	Pd/XC-72-700-Ar	720	n.d.	-
10 ^f	Pd/XC-72-700-Ar	62	99	588 700
11	Pd/XC-72-HNO ₃	980	95	35 260
12 ^g	Pd/XC-72-HNO ₃ -400-Ar	470	96	75 540

^a Reaction conditions: 5 mmol **1a**, 0.5 mL water, 10 mL THF, S/C = 10000, air atmosphere, 25 °C, n.d.= not detected. ^b The Pd loading was 1.0 wt %. ^c Based on total Pd atoms. ^d Based on surface Pd atoms, the dispersion was calculated from CO chemisorption measurements. ^e 5 mmol **1a**, 10 mL dried THF, S/C = 10000, 25 °C. ^f The catalyst was stored for two years at ambient conditions. ^g The catalysts was obtained after post-heat treatment of Pd/XC-72-HNO₃ under Ar atmosphere.

Notably, this hydrolytic oxidation proceeded very efficiently even under sub-ambient temperatures, albeit the reaction rate significantly increased with temperature (Table S1). The apparent activation energy (E_a) was estimated to be 38.9 kJ mol⁻¹ (Figure S6), which is lower as compared to most of the previously reported systems.^{9f-h} The control experiments showed no reaction at all in the absence of Pd species or in dried THF under identical conditions (Table 1, entries 8 and 9), thereby confirming that the Pd species serve as the active sites for this reaction and the H₂ gas is formed from **1a** and water (i.e., water provides one H atom). With the aim to gain a better understanding of the nature of the catalytic active sites, a Pd/XC-72-700-Ar sample stored under air for a two-year period was evaluated. Interestingly, the catalytic activity remained nearly unchanged (Table 1, entry 10 and Figure S7), although the relative fraction of surface PdO in the air-stored sample, as confirmed by XPS, was significantly larger as compared to its freshly prepared counterpart (Figure 1h). This result excludes the possibility of the particular surface chemical state of Pd NPs markedly

influencing the activity, in contrast to recent studies underlining the positive role of surface oxygenated Pd species on the efficiency of the anaerobic hydrolytic oxidation of organosilane.^{10b,c}

Apart from CB, various other carbon nanostructures were also evaluated as supporting materials for the hydrolysis of **1a**. As shown in Table S2, Pd deposited on carbon nanotubes (CNTs), activated carbon (AC), and reduced graphene oxide (GO) nanosheets showed very poor performance under identical reaction conditions, although the content, shape, and size of the Pd species in these samples were similar to those of Pd/XC-72-700-Ar (Figure S1). It should be mentioned that Pd loaded on the hydrophilic surface of modified XC-72-HNO₃ also showed very low activity toward hydrolysis of **1a** (Table 1, entry 11). All these observations indicate that the hydrophobicity of the underlying support plays a key role in achieving high dehydrocoupling capability in this process. With the aim to clarify the role of the support wettability, the rate dependence on the substrate concentration was studied. The reaction orders with respect to **1a** were 0.0 and +0.51 for Pd/XC-72-700-Ar and Pd/XC-72-HNO₃ (Figure S8), respectively, thereby indicating that the substrate was more strongly adsorbed on the surface of Pd/XC-72-700-Ar, and this tendency was also supported by comparing the amount of adsorbed **1a** for all the catalysts examined (Table S3).

The important role of support wettability in facilitating the above Pd-mediated catalysis is further highlighted by the fact that dramatic enhancement of catalytic activity can be achieved by subjecting the hydrophilic Pd/XC-72-HNO₃ sample to a post-heat treatment in an inert atmosphere (Table 1, entry 12). In line with the pristine CB material case, annealing the Pd/XC-72-HNO₃ sample at elevated temperatures also leads to an effective removal of oxygen-containing surface functional groups, as verified by the IR analysis as well as the organosilane and water adsorption data (Figure S2 and Table S3). Additional TEM measurements shown in Figure S1 revealed an essentially equivalent Pd size (ca. 2.5 nm) for the 400 °C-treated Pd/XC-72-HNO₃ samples. These facts, together with the evidently enhanced activity registered for the similarly post-heat treated Pd catalysts loaded on other carbon nanostructures (Table S2), strongly favor the suggestion that the hydrophobicity of the underlying support is one of the key factors in contributing the observed high activity.

Having demonstrated the superiority of the surface modulation approach, we sought to further elucidate the fundamental aspects underlying the wettability-driven phenomenon. Considering that water is also involved in **1b** formation, an additional set of experiments focused on examining the dependence of **1a** conversion on H₂O concentration was undertaken. As opposed to the trends observed with **1a** concentration, the reaction rate was found to be H₂O insensitive for both Pd/XC-72-700-Ar and Pd/XC-72-HNO₃ samples (Figure S9). Coupled with the inherently low kinetic isotope k_H/k_D value of only ca. 1.1-1.2 observed for the reaction of **1a** with H₂O and D₂O at 25 °C (Table S4), these results indicate that the activation of H₂O is extremely facile, whereas the Si-H cleavage could be relatively slow.^{10b} This is especially the case

when the surface of the catalyst is hydrophilic in nature. Therefore, it seems that the favorable interaction between the organosilane molecules and the underlying hydrophobic support can provide a unique driving force to significantly decrease the activation barriers associated with silane activation during the **1a** transformation.

On a Pd-decorated hydrophobic surface, an excess of surface metal coverage may disfavor the adsorption of silanes at the microenvironment surrounding the Pd NPs, thereby resulting in lower catalytic activities. In this sense, a Pd loading of 1.0 wt % on XC-72-700-Ar was beneficial to a cooperative metal-support interaction, as shown in Figure S12. It was also noticed that a polar solvent (i.e., THF) played an important role in ensuring good miscibility of the organosilanes with water (Figure S13). When compared with Pt, Ru, Rh, and Ir NPs supported on XC-72-700-Ar as reference catalysts, Pd on hydrophobic CB showed a unique activity for silane hydrolysis (Table S6), thereby stressing the indispensable role of metallic Pd in facilitating the crucial Si-H activation at conditions relevant to dehydrogenative silylation. Meanwhile, Pd catalysts supported on conventional solid oxides showed very poor performance under identical conditions (Table S6, entries 5-8), thereby showing that the coupling of XC-72-700-Ar with Pd is essential for achieving a high dehydrocoupling activity. Note that the use of hydrophobically-modified TiO₂ (P25) and Al₂O₃ as supports resulted in markedly enhanced dehydrocoupling activities (Table S6, entries 9 and 10), further confirming that surface hydrophobicity is imperative for this reaction system. Nevertheless, in view of the significantly lower performance levels associated with the hydrophobically modified mineral oxide supported systems, it is likely that the modification of the electronic properties of surface anchored Pd by the underlying support might also contribute to the enhanced silane activation observed in the Pd-decorated CB materials.

Pd/XC-72-700-Ar also showed high activity for hydrolytic oxidation of various organosilanes (Table 2). In this sense, trialkylsilanes and aromatic silanes were effectively

Table 2. Dehydrocoupling of various silanes and H₂O over 1.0 wt % Pd/XC-72-700-Ar.^a

$R_{(4-n)}Si-H_n + n H_2O \rightarrow R_{(4-n)}Si-(OH)_n + n H_2$				
Entry	Silane	Time [min]	Yield [%]	TOF [h ⁻¹] ^b
1	Et ₃ SiH	1	>99	645 300
2	Et ₂ SiH ₂	6	90	97 700
3 ^c	(i-Pr) ₃ SiH	21	98	7164
4	(n-Bu) ₃ SiH	2.4	98	263 500
5	PhMe ₂ SiH	3	99	213 200
6	Ph ₂ MeSiH	23	98	27 500
7 ^c	Ph ₃ SiH	60	99	2482
8 ^d	Et ₃ SiH	15	99	628 400

^a Reaction conditions: 5 mmol silane, 0.5 mL water, 10 mL THF, S/C = 10000, air atmosphere, 25 °C. ^b Based on total Pd atoms. ^c S/C = 2500. ^d 50 mmol **1a**, 5 mL water, 100 mL THF, S/C = 80000, air atmosphere, 25 °C.

oxidized to their corresponding silanols without the formation of any disiloxane products. It was noted that the reactions involving less sterically hindered trialkylsilanes proceeded significantly faster as compared to their bulky counterparts (Table 2, entries 1 and 4). The same reactivity trend was also observed upon increasing the number of phenyl substituents on the organosilanes (Table 2, entries 5–7). Remarkably, we attempted the oxidation of sterically hindered triisopropylsilane which is well known to be problematic (i.e., it requires either an extensive reaction time of 24 h^{10d} or low S/C ratio of 33^{10e}). In our case, a significantly shorter time of 20 min with a high S/C ratio of 2500 was sufficient for the reaction until completion. In addition, considerably higher organosilanol yields were also obtained (via conversion of triphenylsilane into triphenylsilanol) for Pd/XC-72-700-Ar (99%, 60 min) as compared to the previously reported supported-gold catalyst (28%, 24 h).^{10d}

Table 3. Production of various silyl ethers via dehydrocoupling of **1a and alcohol.^a**

$$n \text{ Et}_3\text{Si-H (1a)} + \text{R(OH)}_n \rightarrow (\text{Et}_3\text{Si-O})_n\text{R} + n \text{ H}_2$$

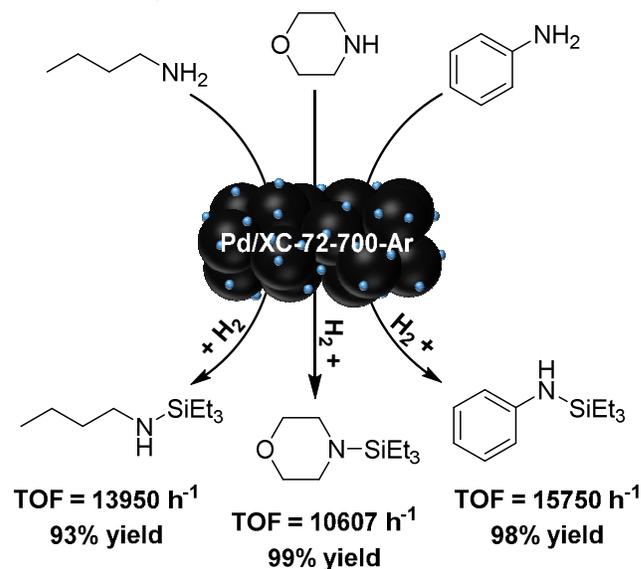
Entry	Alcohol	Time [min]	Yield [%]	TOF [h ⁻¹] ^b
1	MeOH	1	>99	619 300
2	EtOH	2.7	>99	230 400
3	<i>i</i> -PrOH	25	>99	24 930
4	<i>n</i> -BuOH	3	>99	208 100
5	benzyl alcohol	1.8	99	346 500
6 ^c	ethylene glycol	3	96	48 230
7 ^d	glycerol	35	94	4101
8 ^e	MeOH	53	99	11 570

^a Reaction conditions: 20 mmol **1a**, 30 mmol alcohol, 1.0 wt % Pd/XC-72-700-Ar, S/C = 10000, air atmosphere, 25 °C. ^b Based on total Pd atoms. ^c 10 mmol alcohol, S/C = 2500. Yield refers to the bis-silylation product. ^d 6.7 mmol alcohol, S/C = 2500, 60 °C. Yield refers to the tri-silylation product. ^e 1.0 wt % Pd/XC-72-HNO₃.

Given the superb reactivity observed for Pd/XC-72-700-Ar toward silane hydrolysis, we were curious to check whether this hydrophobic-driven Pd catalysis would be also allow for the dehydrogenative condensation of organosilanes with alcohols. As an alternative method for the synthesis of valuable silyl ethers, this transformation has recently attracted considerable attention^{9d,14} because of its critical advantage over the conventional etherification method, which suffers from several drawbacks associated with the use of chlorosilanes¹⁵ or disilazanes.¹⁶ The results presented in Table 3 indicate that it is possible to achieve direct dehydrogenative alcoholysis of the organosilanes in pure alcohols, with the efficiency of this process being essentially comparable to that of silane hydrolysis. For example, at a S/C ratio of 10000, the silyl ether produced from **1a** and MeOH was exclusively obtained over a period of 1 min at 25 °C (corresponding to a TOF of 6 × 10⁵ h⁻¹ for alcohol silylation, entry 1). Note that polyalcohols such as ethylene glycol and glycerol, which can be derived from

biomass,¹⁷ were also suitable substrates for this etherification (entries 6, 7), thereby further substantiating the utility of this approach for Si–O–C bond construction together with on-demand H₂ generation.

Dehydrogenative condensation of organosilanes and amines also represents one of the most attractive and atom-economic synthetic approach to access silylamines, an important class of silicon compounds that have been widely used as silylation agents, ligands for organometallic compounds, and precursors for Si and N polymeric materials.¹⁸ Both homogeneous and heterogeneous catalysts have been reported for this reaction,¹⁹ although the control of the selectivity for Si–N coupling has been proved to be challenging as the reaction can lead to several products with different Si/N ratios (e.g., polysilazanes) as a result of multiple dehydrocoupling steps. Remarkably, we found that Pd/XC-72-700-Ar can robustly and selectively furnish the desired silylamines (Scheme 1), with activities (TOF) being orders of magnitude higher as compared to previously employed catalysts for this transformation.^{19b,c,j} As in the case of hydrolytic and alcoholic oxidations of organosilanes (see Tables 1 and 3), the hydrophobic Pd/XC-72-700-Ar catalyst persistently showed a boosted efficiency as compared to its hydrophilic counterpart (Table S7). To the best of our knowledge, this hydrophobic-driven catalysis represents the most efficient, simple, and eco-friendly catalytic system to date achieving convenient and controlled organosilane aminolysis (Table S10).



Scheme 1. Production of various silylamines via dehydrocoupling of **1a** and amines over 1.0 wt % Pd/XC-72-700-Ar. Reaction conditions: 5 mmol **1a**, 5 mmol amine, 5 mL dried THF, S/C=2500, Ar atmosphere, 60 °C.

3. CONCLUSIONS

In summary, the hydrophobic characteristics of the underlying supports were favorably utilized for boosting the efficiency of Pd NPs-catalyzed dehydrogenative coupling of organosilanes. The catalytic activities obtained for these dehydrogenative silylation reactions were, to our knowledge, the highest reported to date. Our results revealed the key role of the surface wettability modu-

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lation in maximizing the performance of supported noble metals under catalytically relevant conditions. While the reported system holds promise for the development of a practical dehydrogenative silylation technology based on Si-H activation, we believe that careful tuning of the support wettability to meet reaction requirements will open a new avenue for heterogeneous catalysis processes mediated by supported metals.

4. EXPERIMENTAL SECTION

4.1. Hydrolysis of organosilanes in an open system.

All catalytic experiments were carried out under ambient atmosphere of air, unless otherwise stated, the reactions were performed in a double-walled thermostatically controlled reaction vessel with a reflux condenser, which is connected to an automatic gas burette, where the gases are collected. Silane and H₂O (or D₂O) were mixed with 10 mL THF in a reaction vessel under steady magnetic stirring (800 rpm) at given temperature (17–33 °C). The reaction was started by the addition of a certain amount of catalyst. In addition, evolved gas was qualitatively and quantitatively analyzed by Agilent 6820 GC equipped with a TDX-01 column connected to a TCD. Catalyst was centrifuged and the yield of corresponding organosilanol was analyzed by Agilent 7820A GC equipped with a HP-5 column connected to a FID using ethyl-benzene as an internal standard. Identification of the products was performed by using a GC-MS spectrometer. The initial TOF was calculated on the organosilanes conversion at 15%.

4.2. Generation of hydrogen on-demand using 1 wt % Pd/XC-72-700-Ar as catalyst. H₂O (2.5 mL) and Pd/XC-72-700-Ar (S/C = 2500) were mixed with 50 mL THF in a two-neck flask under steady magnetic stirring (800 rpm) at 25 °C, which is connected to an automatic gas burette. The flask was sealed with an injector connected to an injection pump. For the stepwise hydrolysis process, **1a** (25 mmol) was sequentially injected into the flask at intervals until the **1a** was fully consumed. For the continuously controllable hydrolysis process, **1a** (25 mmol) was continuously injected into within 27 min until the **1a** was fully consumed. In addition, the evolved gas was qualitatively and quantitatively analyzed by Agilent 6820 GC equipped with a TDX-01 column connected to a TCD.

4.3. Large-scale durability of 1 wt % Pd/XC-72-700-Ar catalyst for hydrolysis of 1a. **1a** (50 mmol) and water (5 mL) were mixed with 100 mL THF in a reaction vessel (250 mL) under steady magnetic stirring (800 rpm) at 25 °C, which is connected to an automatic gas burette. The reaction was started by the addition of Pd/XC-72-700-Ar (S/C = 80000). After the reaction completed, the centrifuged catalysts from parallel activity tests were collected and washed with distilled water, followed by drying in air at 100 °C for 12 h. All catalytic activity tests were repeatedly carried out by following the same procedure as described above.

4.4. Triethylsilane adsorption ability of various supports. Various supports (0.5 g) were placed in a Schlenk tube and pretreated at 150 °C under outgassing for 30 min, followed by the addition of **1a** (5 mmol), H₂O (0.5 mL) and THF (10 mL). Then the mixtures were stirred

at 25 °C for 30 min under ambient atmosphere of air. The adsorption amounts were determined by changes of **1a** concentrations monitored by GC using ethylbenzene as an internal standard according to the previous report.²⁰

4.5. Alcoholysis of organosilanes in an open system.

1a (20 mmol) and alcohol were mixed in a reaction vessel under steady magnetic stirring (800 rpm) at given temperature under air atmosphere, which is connected to an automatic gas burette. The reaction was started by the addition of a certain amount of catalyst. In addition, the evolved gas was qualitatively and quantitatively analyzed by Agilent 6820 GC equipped with a TDX-01 column connected to a TCD. Catalyst was centrifuged and the yield of corresponding silyl ether was analyzed by Agilent 7820A GC equipped with a HP-5 column connected to a FID using bibenzyl as an internal standard. Identification of the products was performed by NMR analyses. The initial TOF was calculated on the organosilanes conversion at 15%.

4.6. Aminolysis of organosilanes in an open system.

1a (5 mmol), amine (5 mmol), dried THF (5 mL) and a certain amount of catalyst were mixed in a reaction vessel under steady magnetic stirring (800 rpm) at 60 °C under Argon atmosphere with a reflux condenser, which is connected to a drying tube and an automatic gas burette. In addition, the evolved gas was qualitatively and quantitatively analyzed by Agilent 6820 GC equipped with a TDX-01 column connected to a TCD. Catalyst was centrifuged and the yield of corresponding silylamine was analyzed by Agilent 7820A GC equipped with a HP-5 column connected to a FID using naphthalene as an internal standard. The product was isolated by distillation and identified by NMR analyses. The initial TOF was calculated on the organosilanes conversion at 15%.

4.7. Characterization. The metal loading was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) using a Thermo Electron IRIS Intrepid II XSP spectrometer. The BET specific surface areas of the prepared catalysts were determined by adsorption-desorption of nitrogen at liquid nitrogen temperature, using a Micromeritics TriStar 3000 equipment. Sample degassing was carried out at 300 °C prior to acquiring the adsorption isotherm. The crystal structures were characterized with X-ray diffraction (XRD) on a Bruker D8 Advance X-ray diffractometer using the Ni-filtered Cu K α radiation source at 40 kV and 40 mA. XPS data were recorded with a Perkin Elmer PHI 5000C system equipped with a hemispherical electron energy analyzer. The spectrometer was operated at 15 kV and 20 mA, and a magnesium anode (Mg K α , $h\nu = 1253.6$ eV) was used. The C 1s line (284.6 eV) was used as the reference to calibrate the binding energies (BE). The Fourier transform infrared spectroscopy (FT-IR) spectra were recorded by a Nicolet iS10 FT-IR spectrometer equipped with a DTGS detector, in the range 400 – 4000 cm⁻¹, by applying an optical resolution of 0.4 cm⁻¹. The samples were investigated by using the KBr pellet technique. A JEOL 2011 microscope operating at 200 kV equipped with an EDX unit (Si(Li) detector) was used for the TEM investigations. The samples for electron microscopy were prepared by grinding and subsequent dispersing the powder in

ethanol and applying a drop of very dilute suspension on carbon-coated grids. The size distribution of the metal nanoparticles was determined by measuring about 200 random particles on the images. *n*-hexane or H₂O adsorption experiment was performed at 25 °C on a BEL SORP-max adsorption instrument. The adsorption amount of *n*-hexane or H₂O was recorded at the saturated vapor pressure of *n*-hexane (25 °C, 20.16 KPa) or H₂O (25 °C, 3.169 KPa). Pd surface area was measured by CO chemisorptions using AutoChem HP 2950 apparatus with quantitative loop from Micromeritics. The sample was first pretreated with 5 vol % H₂/Ar at 200 °C for 2 h, and then pure CO was pulsed over the sample at 25 °C for several times to saturated adsorption. The total amount of CO adsorbed was measured by assuming a chemisorption stoichiometry of CO/Pd=1 and a Pd surface atomic density of 1.27×10¹⁹ m⁻².²¹ The dispersion (D) was calculated according to the formula of D = (surface number of Pd atoms)/(total number of Pd atoms).

ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publication website at DOI: xx.xxxx/acscatalxxxxxx

Experimental details of the catalyst preparation, TEM data, FT-IR data, adsorption capacity study, XPS data, optimization of reaction conditions, kinetic experiments, spectral parameters, and NMR data of products (PDF)

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Notes

The authors declare no competing financial interest.

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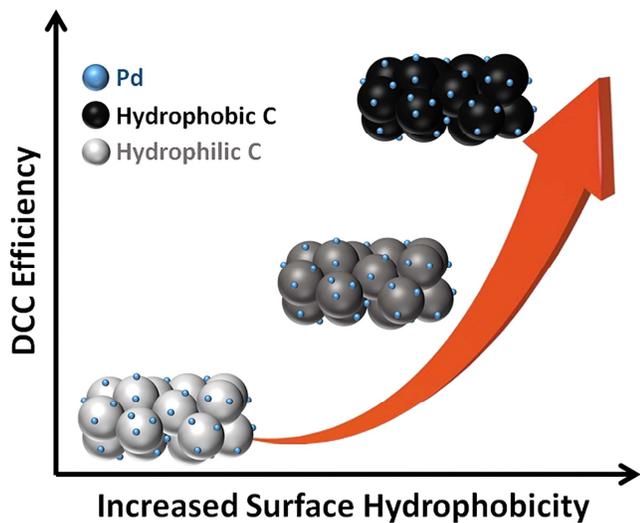
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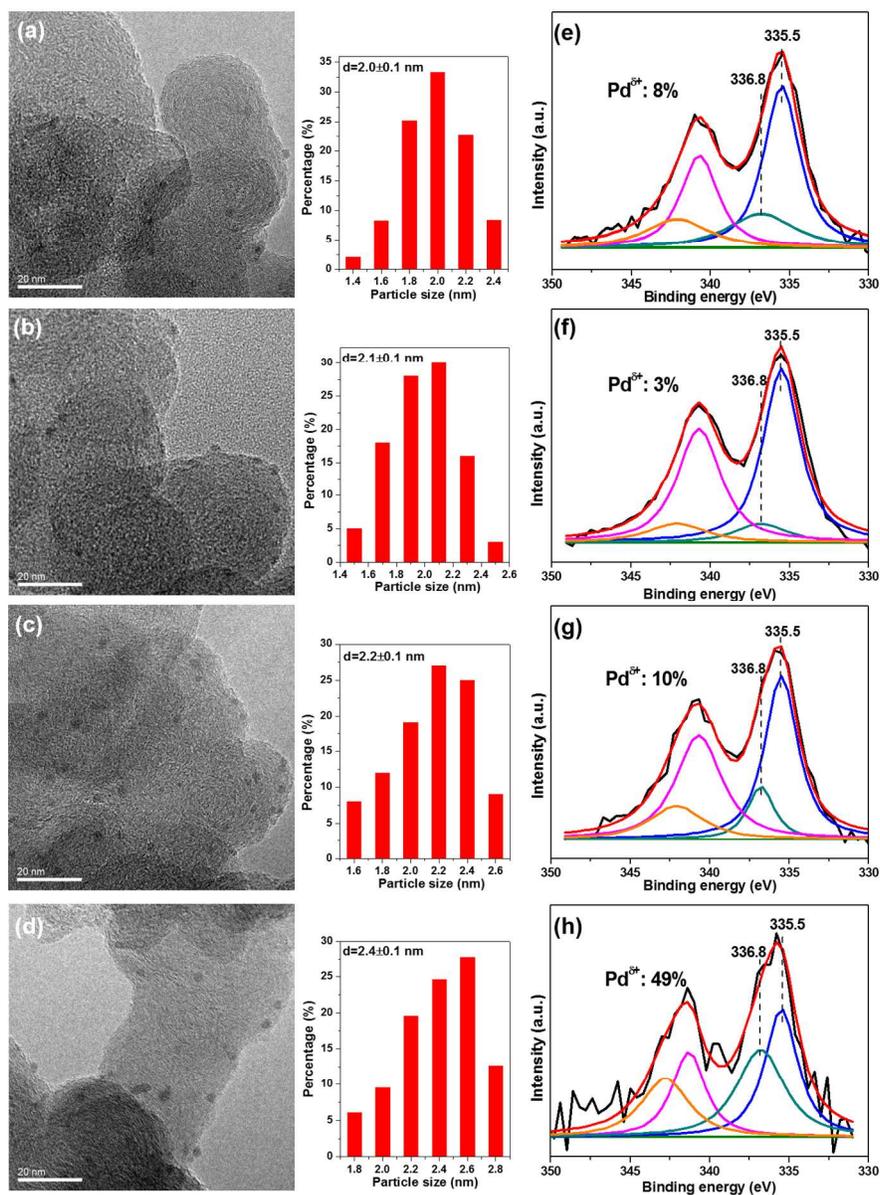
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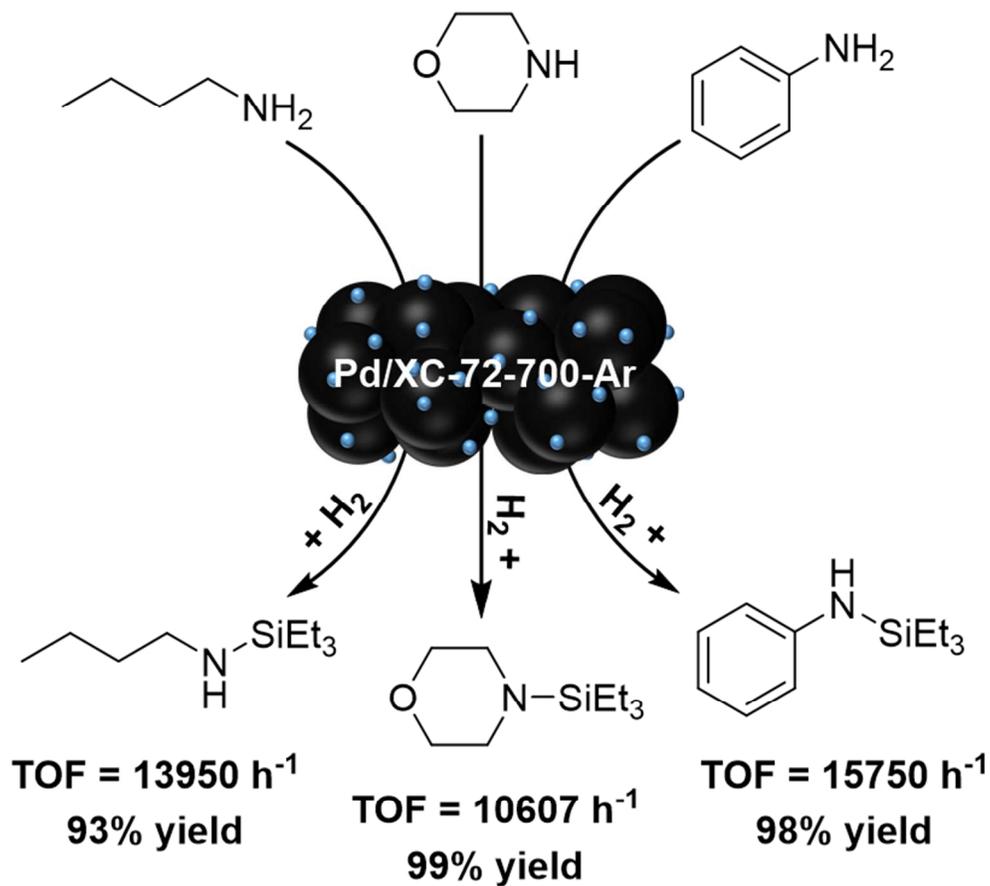
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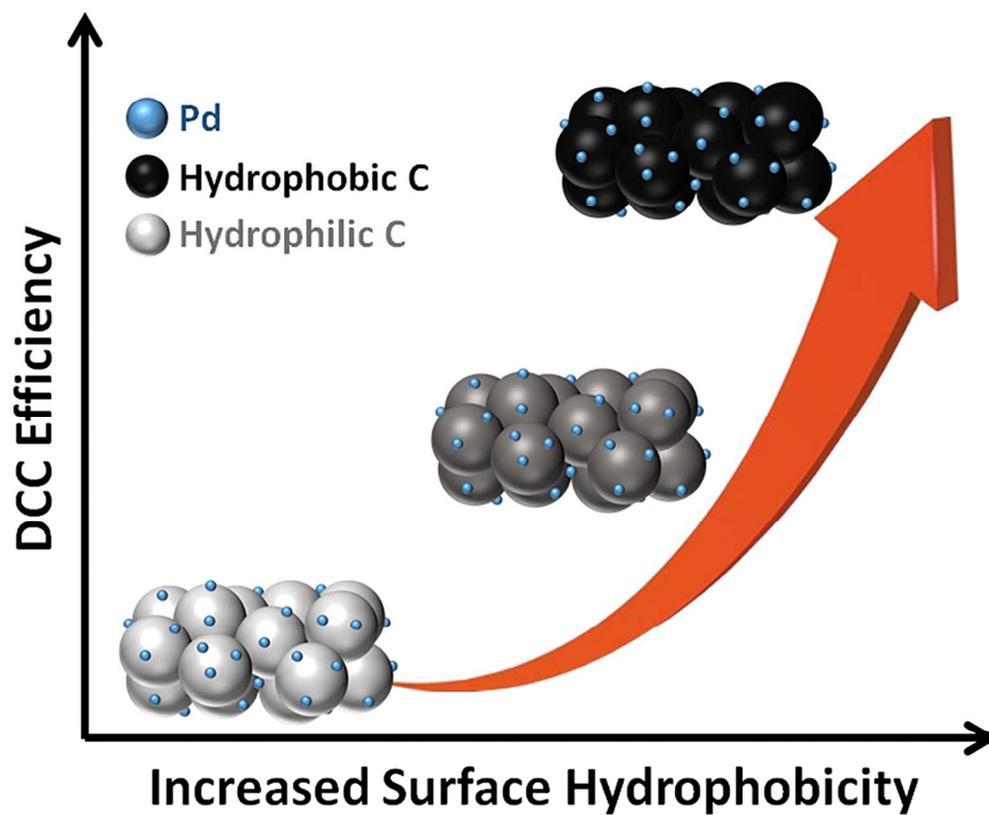
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