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### Formic Acid Dehydrogenation over Pd NPs Supported on Amine-Functionalized SBA-15 Catalysts: Structure-Activity Relationships

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Palladium nanoparticles (Pd NPs) supported on organoamine-functionalized SBA-15 mesoporous silica are known to have higher catalytic activity for formic acid dehydrogenation than Pd NPs supported on plain, unmodified SBA-15 mesoporous silica. The organoamine groups present around the Pd NPs play important roles in stabilizing the Pd NPs, providing strong metal-molecular support interaction (SMMSI) to the Pd NPs, and rendering enhanced catalytic activities to the materials toward formic acid dehydrogenation. However, detailed studies on the effects of different types of amine groups on the catalytic activities of mesoporous silica-supported Pd NPs toward formic acid dehydrogenation have not been reported. Herein, we describe the synthesis of SBA-15 mesoporous silica grafted with three types of organoamine groups (primary, secondary, and tertiary amine), which are further decorated with tetraamine palladium(II) complexes that are then reduced to Pd NPs *in situ* with 10 % of  $H_2/N_2$  at 250 °C. The effects of the different compositional and steric properties associated with the amine groups on *i*) the electronic properties of the Pd NPs, *ii*) the size of the Pd NPs, and *iii*) the structure-property relationships of the materials were closely examined. Based on the results, the materials' catalytic activities toward dehydrogenation of formic acid to generate hydrogen (H<sub>2</sub>) for fuel cells were determined.

#### Introduction

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To address current energy and environmental issues associated with the rapid consumption of fossil fuels, major research on alternative, clean and sustainable energy sources is continuing worldwide.<sup>1,2</sup> Among the plausible alternative energy sources and carriers that have received significant attentions and that are expected to contribute to the solutions of these issues in the future, hydrogen (H<sub>2</sub>) stands out. In fact, H<sub>2</sub> has long been considered as one of the most notable and propitious energy carriers for portable and stationary energy systems. Furthermore, successful usage of H<sub>2</sub> as a plausible energy carrier in fuel cells for transportation applications and many other commercial alternative energy systems have so far not made it into large scale applications, mainly due to the unavailability of efficient and economically feasible technologies that allow sustainable production, reliable storage, and costeffective distribution of  $H_2$ . So, the development of safe and inexpensive hydrogen storage systems is one of the major requirements to enable hydrogen energy technologies to become a reality in a wide range of applications.<sup>6,7</sup> This has, therefore, led to extensive investigations, over the last decade, of numerous types of potential chemical-based  $H_2$  storage compounds and materials.

Owing to its high stability, relatively low toxicity, high volumetric hydrogen storage density (53 g/L), and ease of portability, formic acid (FA) has recently been recognized as a good liquid phase chemical hydrogen storage medium. Furthermore, compared with H<sub>2</sub>, FA can easily be stored, transported and delivered to desired sites more economically using existing infrastructures.<sup>6-9</sup> In addition, FA can readily release H<sub>2</sub> on demand under ambient conditions in the presence of the right catalysts through the reaction: HCOOH  $\rightarrow$  H<sub>2</sub> + CO<sub>2</sub>. Moreover, FA can potentially be regenerated by catalytic hydrogenation of CO<sub>2</sub>—the greenhouse gas that is often released by power plants and other industries—using the reaction:  $H_2 + CO_2 \rightarrow HCOOH$ .<sup>10</sup> This whole process can be appealing especially if the H<sub>2</sub> needed to carry out this reaction comes from water via renewable energy-driven water electrolysis. FA can also be produced from biomass by various processes such as biomass gasification, the Fischer-Tropsch process, etc.<sup>11</sup> Hence, FA is a highly attractive hydrogen carrier for decentralized fuel cell power generation sites, hydrogen refuelling stations, large-scale renewable energy storage systems, and so forth.

To make FA-based hydrogen storage systems usable in practical fuel cells, the rate of  $H_2$ -release from FA needs to be sufficiently fast

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#### ARTICLE

though. While the dehydrogenation process of FA can be accelerated by increasing the reaction temperature, this process often leads to an undesired dehydration pathway that releases CO via the reaction: HCOOH  $\rightarrow$  H<sub>2</sub>O + CO. This reaction is undesired because one of its products, CO, is detrimental to the catalysts used in many fuel cells. Besides, the reaction does not generate the desirable product H<sub>2</sub> anyway, but rather H<sub>2</sub>O. So, it is of significant importance to develop selective catalysts that can promote only the desirable dehydrogenation pathway, besides being able to do so with high activity.<sup>6</sup> To attain this goal, a number of homogeneous and heterogeneous catalysts, which work either in the absence or in the presence of external bases, have been explored for FA dehydrogenation. Among them, heterogeneous mono- and bimetallic materials, particularly those containing Pd, such as Pd,<sup>12-16</sup> PdAg,<sup>17</sup> and AuPd<sup>16,20</sup> NPs, were found to be excellent catalysts for the release of H<sub>2</sub> from FA, in addition to being convenient to use.

We recently demonstrated that the surface functional groups around Pd NPs could boost Pd's catalytic activity toward FA dehydrogenation reaction, besides stabilizing the Pd NPs (i.e., the catalytically active sites).12 In particular, ultrasmall Pd NPs supported on primary amine-functionalized SBA-15 were found to exhibit high catalytic activity and selectivity for dehydrogenation of FA at room temperature, even in the absence of external base in the reaction mixture. Similarly, several other studies demonstrated that multifunctional heterogeneous catalysts modified with amine groups, such as Pd-Amine-MIL-12514, Au-Amine-SiO<sub>2</sub>,<sup>21</sup> and Pd/PDArGO (where PDA is 1,4-phenylenediamine)<sup>22</sup> had good catalytic activity toward FA dehydrogenation. Recently, various synthetic methods leading to ultrafine metallic nanoparticles within high surface area materials and the applications of the resulting hybrid materials for catalytic conversions of various reactions including FA dehydrogenation were reviewed by Zhu and Xu.<sup>23</sup> Meanwhile, some studies indicated that modifying the electronic properties and geometries of Pd active sites using amine-containing polymers could improve Pd's catalytic activity toward FA dehydrogenation.<sup>24</sup> Despite these interesting previous studies, the effects of different amine ligands and their structures on the size of Pd NPs as well as the materials' electronic properties and catalytic activities toward FA dehydrogenation have not yet been profoundly established.

In this contribution, a series of nanoporous silica materials modified with different types of amine groups and Pd NPs are synthesized, and the relationships among the types of amine functionalities, the Pd NPs forming in the materials, and the materials' catalytic properties toward FA dehydrogenation are elucidated. The materials include SBA-15 functionalized with different amine groups and Pd NPs, named Pd/SBA-15-Amine, where "Amine" represents primary, secondary, or tertiary amines. After investigating the structures and compositions of the materials obtained after each synthetic step, their catalytic properties are studied with particular focus being paid to the relationships among the amine functionality, the size of Pd NPs, the materials' structures, and the materials' catalytic properties. Based on the results, the roles of the amine groups and the structural features of the materials and their supported Pd NPs in catalytic formic acid dehydrogenation reaction are determined.

#### Experimental

#### Materials

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Poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic<sup>®</sup> P123) was obtained from BASF. (3-

Aminopropyl)trimethoxysilane (APTMS), ammonium, hydroxide solution (NH<sub>4</sub>OH, 28-30 %, NH<sub>3</sub> basis), formic\_1acidc\_(HCQQH), anhydrous toluene, tetraethyl orthosilicate (TEOS), methylamine solution (CH<sub>3</sub>NH<sub>2</sub>, 40 wt.% in H<sub>2</sub>O), dimethylamine solution ((CH<sub>3</sub>)<sub>2</sub>NH, 40 wt.% in H<sub>2</sub>O) and palladium(II) chloride (PdCl<sub>2</sub>) were purchased all from Sigma-Aldrich. Nmethylaminopropyltrimethoxysilane (MAPTMS) and 3-(N,Ndimethylaminopropyl)trimethoxysilane (DMAPTMS) were acquired from Gelest, Inc. Hydrochloric acid (36.5 %) was purchased from Fischer Scientific. Anhydrous ethanol was acquired from Pharmco-Aaper. Different deuterated formic acids (DCOOH and HCOOD) were purchased from Cambridge Isotope Laboratories, Inc. All the reagents were used as received without further purification.

#### Instrumentations

Thermogravimetric analyses of the materials were performed with TGA 7 (PerkinElmer) in a temperature range of 50 to 900 °C and at a heating rate of 10 °C/min in air. The N2 adsorption/desorption data for the materials were obtained with a Micrometrics ASAP 2000 instrument using N<sub>2</sub> at 77 K. Based on the data, the surface areas of the materials were calculated using the Brunauer-Emmett-Teller (BET) method. The pore volumes of the materials were determined based on the amount of  $N_2$  adsorbed at a relative pressure of 0.99. The pore size distributions of the materials were determined with the Barrett-Joyner-Halenda (BJH) method using the adsorption data in the isotherms. High-resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) images were acquired with a field emission FEI Tecnai microscope G2 F20 operating at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed with a PHI 50000 VersaProbe instrument (ULVAC PHI) operating with an Al Ka X-ray beam at a background pressure of  $6.7 \times 10^{-8}$  Pa. The spectra were calibrated using C1s's peak at 284.6 eV. The amount of Pd in the catalysts was determined by means of inductively coupled plasma-optical emission spectrometry (ICP-OES) (Varian 720ES, Agilent), and the amount of nitrogen in the materials was analyzed with an elemental analyzer (EA) (FLASH 2000, Thermo Scientific). All gaseous products generated by the catalytic reactions were analyzed by an in situ FT-IR spectrometer (Nicolet iS10, Thermo Scientific) equipped with a MCT detector and a customized gas cell. Spectral data were collected using a scan rate of 8 scans min<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. UV-Vis diffuse reflectance spectroscopy was carried out with a Cary 5000 UV-Vis spectrometer (Agilent). The reaction mixtures after catalysis were analyzed with gas chromatography (GC) using a Model 7890A gas chromatograph (Agilent Technologies) equipped with a TCD detector and two columns: Hayesep D and MS13X.

#### Synthesis of SBA-15 mesoporous silica (Ext-SBA-15)

SBA-15 was synthesized in acidic solution using Pluronic<sup>®</sup> 123 as a templating agent according to a previously reported procedure.<sup>25</sup> In a typical experiment, Pluronic<sup>®</sup> 123, HCl (12 M), TEOS, and deionized (D.I.) water were mixed with a mass ratio of 2:12:4.3:26, and stirred together at 40 °C for 24 h. The solution was then aged at 65 °C for an additional 24 h. After filtration of the solution, a solid product was recovered and washed several times with D.I. water. To remove the Pluronic<sup>®</sup> 123 templates from the resulting dried white powder product, 1.0 g of the material was taken and dispersed in a solution containing ethanol (100 mL) and diethyl ether (100 mL), and the mixture was stirred at 50 °C for 5 h. After filtering the mixture, then washing the resulting solid product with copious amount of diethyl ether and then ethanol, and letting it to

dry at 40 °C in vacuum, a surfactant-extracted powder SBA-15 mesoporous silica material, named Ext-SBA-15, was obtained.

# Synthesis of SBA-15-functionalized with three different types of amines (SBA-15-Amine, where Amine is PA, SA, or TA) (*Step I*)

To introduce different types of organoamine functional groups onto the surfaces of Ext-SBA-15, 1.0 g of Ext-SBA-15 was dispersed in anhydrous toluene (50 mL) containing 1.4 mmol of APTMS, MAPTMS, or DMAPTMS, and the mixtures were stirred at 80 °C for 6 h. The mixtures were then filtered, and the resulting solid products were washed with toluene and then ethanol, and let to dry at 40 °C in a vacuum oven. White powder products, denoted as SBA-15-PA, SBA-15-SA, and SBA-15-TA, respectively, in which PA, SA, and TA stand for primary amine (PA, -NH<sub>2</sub>), secondary amine (SA, -NHCH<sub>3</sub>), or tertiary amine (TA, -N(CH<sub>3</sub>)<sub>2</sub>) groups, were finally obtained. The three resulting amine-functionalized SBA-15 materials were generally labeled also as "SBA-15-Amine". The synthetic procedure leading to the materials and their structures are illustrated in Scheme 1.

#### Synthesis of Pd(II)/SBA-15-Amine materials (Step II)

First, tetraaminepalladium(II) complex was synthesized by mixing PdCl<sub>2</sub> (5.6 x  $10^{-2}$  µmol) with 1.0 M of ammonium hydroxide (NH<sub>4</sub>OH, 1.8 µmol NH<sub>3</sub>) and then sonicating the solution until the dark red solution associated with PdCl<sub>2</sub> turned colorless (or until complete complexation occurred). The resulting solution was added into a flask containing ethanol (1.0 mL), D.I. water (4.0 mL), and SBA-15-Amine (1.0 g), where Amine is PA, SA, or TA. The mixtures were all stirred at 80 °C for 3 h. Pd/SBA-15 was synthesized by mixing the solution of tetraaminepalladium(II) chloride, prepared above, with Ext-SBA-15 and stirring the two together at 80 °C for 3 h. The mixtures were all then filtered, and the solid products were washed with copious amounts of water and let to dry at 40 °C under vacuum. This led to different Pd(II)-anchored SBA-15-Amine materials (Pd(II)/SBA-15-Amine), as shown in *step II* in Scheme 1. The latter gave the corresponding control material Pd(II)/SBA-15.

#### Reduction to Pd (0)/SBA-15-Amine (Step III)

The Pd(II)/SBA-15-Amine and Pd(II)/SBA-15 materials prepared above were all subjected to reduction using 10 % of  $H_2/N_2$  at 250 °C for 3 h to convert the Pd(II) ions in them into Pd NPs, and then yield Pd(0)/SBA-15-Amine or Pd(0)/SBA-15 materials. Here, the respective materials obtained were named as Pd(0)/SBA-15-PA (1), Pd(0)/SBA-15-SA (2), Pd(0)/SBA-15-TA (3), and Pd(0)/SBA-15 (a control material).

#### Synthesis of additional control materials

Additional control materials containing other Pd(II) species supported on unfunctionalized (or unmodified) Ext-SBA-15 were synthesized by immobilizing three different tetraaminepalladium(II) complexes into the mesopores of amine-free Ext-SBA-15. Specifically, various tetraaminepalladium(II) complexes were synthesized by mixing PdCl<sub>2</sub> (5.6 x  $10^{-2}$  µmol) with solutions containing three different amines, namely, 1.8 µmol of ammonia  $(NH_4OH)$ , methylamine  $(NH_2CH_3)$ , or dimethyl amine  $(NH(CH_3)_2)$ . The solutions were sonicated until they turned colorless, or the desired palladium(II)-amine complexes formed. The resulting different tetraaminepalladium(II) complexes were mixed with 1.0 g of unmodified Ext-SBA-15 and stirred together at 80 °C for 3 h. This led [Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]/SBA-15, [Pd(NH<sub>2</sub>CH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]/SBA-15, and to [Pd(NH(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>Cl<sub>2</sub>]/SBA-15 materials, respectively. These control materials containing Pd(II)-amine complexes (i.e., (Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>-SBA-15, Pd(NH<sub>3</sub>CH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>-SBA-15 and Pd(NH<sub>2</sub>(CH<sub>3</sub>)<sub>2</sub>)<sub>4</sub>Cl<sub>2</sub>-SBA-15) were

prepared mainly for comparative studies of the potential effect of organoamine ligands on the electronic control www.wis/cabscoption properties of the Pd(II)-amine complexes vis-à-vis those of the corresponding SBA-15-Amine-supported Pd(II)'s species, before being subjected to reduction.

#### Catalytic dehydrogenation to release H<sub>2</sub> from FA

Catalytic FA dehydrogenation reactions were performed in a modified glass reactor (volume, 40 mL) containing an aqueous solution of FA (1.0 M, 10 mL) and the catalyst (1, 50 mg; 2, 46 mg; or 3, 43 mg). Note that different masses of catalysts were used in the three cases in order to keep the amount of N (or amine groups) in them the same (i.e., 64 µmol of N in each case, based on EA). The reactor was kept at room temperature for 15 min under  $N_2$ atmosphere, and the quantity of the gas produced by the reaction was determined using an automatic gas burette system. To examine whether or not CO formed during the reaction, a portion of the gaseous products generated by the reaction was taken and analyzed by in-situ FT-IR spectroscopy and gas chromatography (GC). Unless otherwise noted, the catalytic activities for FA dehydrogenation reaction presented here were for catalysts prepared from the same batch of Ext-SBA-15. The values of catalytic turnover frequency (TOF) were calculated using equations (1) and (2) below.

moles of hydrogen in 10 min,  $n_{H2} = P_{atm}(V_{gas}/2)/RT$  Eqn. (1)

where  $P_{atm}$  is pressure,  $V_{gas}$  is the total volume of gases, R is the gas constant, and T represents a reaction temperature in Kelvin.

Turnover frequency (TOF, 
$$h^{-1}$$
) =  $\frac{moles of hydrogen in 10 min}{(moles of metal used)*time}$  Eqn. (2)

The selectivity of the FA dehydrogenation reaction in giving  $H_2$  as a product was examined *in-situ* using a FT-IR spectrometer and quantified using equation (**3**) below.

 $H_2$  selectivity = [moles of  $H_2$ /moles of ( $H_2$  + CO)] × 100 Eqn. (3)

#### **Recyclability tests**

During the recovery of solid catalysts for recycling tests, it is common to lose a small amount of the catalysts. To minimize possible experimental errors arising from such possible loss of catalyst during the catalytic FA dehydrogenation tests, the following procedure was employed. The same amount of catalyst (50 mg of **1**, for example) was added into four different identical reactors containing aqueous solution of FA (1.0 M, 10 mL). After letting the FA dehydrogenation reaction run for 2.5 h, D.I. water (10 mL) was added into each reactor. The spent catalysts were recovered by filtration and then washed with copious amount of D.I. water. The resulting recycled catalysts were let to dry in a vacuum oven before being used in the next cycle. Typically, they were combined, and the same procedure as the ones described above was performed in three reactors this time, with each containing 50 mg of the recovered catalyst **1**.

#### Kinetic isotope effect (KIE) studies

For kinetic studies, similar catalytic dehydrogenation reactions using deuterated FA (DCOOH and HCOOD), instead of FA, were carried out. Typically, 10 mL of 1.0 M of deuterated FA and the required amount of catalyst (1, 50 mg; 2, 46 mg; or 3, 43 mg) were used. The remaining steps and characterizations were the same as those employed above.

#### Result and discussion

#### ARTICLE

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## Synthesis and characterization of amine-functionalized SBA-15 mesoporous silica

A series of SBA-15 mesoporous silica materials functionalized with primary amine (PA), secondary amine (SA), and tertiary amine (TA) were synthesized by following a procedure reported previously,<sup>12</sup> with a slight modification. In short, the surface Si-OH groups of surfactant-extracted SBA-15 mesoporous silica (Ext-SBA-15) were grafted with three different 3-aminoalkoxysilanes, namely ATPMS, MAPTMS, and DMAPTMS, in toluene at 80 °C for 6 h.

The Ext-SBA-15 was prepared by removing the Pluronic® P123 templates from the as-prepared mesostructured silica with a solvent-extraction method. Even if it does not completely get rid of the templates, this method-as opposed to calcination-was chosen for removing the templates here, because it leaves behind the much-needed (in our case), higher density of Si-OH groups. A higher density of Si-OH groups are needed in our case as they enable the grafting of a larger density of organoamine groups onto the SBA-15 material, groups that can serve as co-catalysts in formic acid dehydrogenation catalysis (vide infra). Furthermore, a higher density of organoamine groups are needed in order to load the materials with a larger density of Pd(II) ions, and thereby Pd NPs (the actual groups that can catalyze formic acid dehydrogenation reaction). Besides, a substantial amount of the remaining P123 templates after the solvent-extraction process come off of the Ext-SBA-15 material during the subsequent grafting step at 80 °C for 6 h, followed by washing, and then reduction step at 250 °C for 3 h while generating the Pd NPs. Based on TGA analysis, Pluronic® P123 is known to start to undergo thermal degradation around 250 °C;<sup>26</sup> this means, a lot of the templates are removed even at this temperature when carried out for longer time (6 h in our case). So, there are not much P123 remaining in the very final products or catalysts anyways. The catalytic activity of the materials did not seem to be compromised by the presence of the residual templates either, as described below.

During the aminoorganoalkoxysilane grafting process, the Si-OH groups of the Ext-SBA-15 materials act as nucleophiles and attack the aminoorganoalkoxysilanes, generating organoamine groups covalently attached to the surfaces of Ext-SBA-15 through Si-O-Si bonds and methanol as by-product (see step I in Scheme 1). By following this procedure, three different types of amine groups (PA, SA, and TA) were then anchored onto Ext-SBA-15 from their respective alkoxysilane precursors, resulting in three different types of amine-functionalized SBA-15 (*i.e.*, SBA-15-Amine, where "Amine" is PA, SA, or TA).

The resulting SBA-15-Amine materials (where Amine represents PA, SA or TA) as well as the control material Ext-SBA-15 were all characterized by various analytical techniques including elemental analysis (EA), thermogravimetric analysis (TGA), and  $N_2$ porosimetry. EA showed the presence of similar amount of nitrogen (ca. 2.2 - 2.5 mmol/g<sub>cat</sub>) in all of the SBA-15-Amine materials (Table 1). The TGA results of the control material Ext-SBA-15 and all the SBA-15-Amine materials are depicted in Fig. S1a. In the case of the control material, the first weight loss (of ca. 0.62 %) was observed from room temperature (RT) to 120 °C, which is due to evaporation of physisorbed water. A second weight loss (of ca. 16 %) was observed in the range of 120 °C to 700 °C, and it is most likely due to the loss of residual polymer templates and water as a result of condensation of Si-OH groups. In the case of the SBA-15-Amine materials, the TGA showed two distinct weight losses (Fig. S1a). The first weight loss was observed from RT to 120 °C and attributed to the evaporation of physisorbed water from the surfaces of the materials. In all of SBA-15-Amine materials, a weight loss due to

desorption of water (*ca.* 1.6 %) was also seen in the range of BTL to 120 °C. The second weight loss was seen in the range of 7120 °C to 700 °C, and it was due to the removal of residual polymer templates, water due to condensation of Si-OH groups, and more importantly, organoamine groups due to their combustion as: NR<sub>1</sub>R<sub>2</sub>(CH<sub>2</sub>)<sub>3</sub>SiO<sub>1.5</sub> +  $xO_2 \rightarrow$  SiO<sub>2</sub> + combustion products.<sup>27</sup> After correcting for the loss of polymer templates and condensation of water, a weight loss due to the decomposition of organoamine moieties was determined to be *ca.* 11 % for all these organoamine-functionalized materials. This result suggested that the three SBA-15-Amine materials had a similar amount of grafted organoamine moieties.

 Table 1. Textural properties of Ext-SBA-15 (one of the control materials) and the three SBA-15-Amine materials derived from it by grafting organosilanes.

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	Amount of N	BET Surface	Pore	Pore				
	(mmol/	Area	Size	Volume				
	g <sub>cat</sub> ) <sup>a</sup>	(m²/g) <sup>b</sup>	(nm)℃	(cm²/g) <sup>c</sup>				
Ext-SBA-15	N/A	378	6.4	0.48				
SBA-15-PA	2.3	200	5.1	0.23				
SBA-15-SA	2.2	195	4.4	0.19				
SBA-15-TA	2.5	237	3.3	0.17				

 $^a$  Obtained based on EA.  $^b$  Obtained based on  $N_2$  adsorption/desorption data.  $^c$  Obtained from the BJH adsorption branch of the isotherms.

Based on N<sub>2</sub> adsorption/desorption measurements, the aminefunctionalized SBA-15 generally showed lower surface areas than Ext-SBA-15 (Table 1 and Fig. S1b and S1c). Lower surface areas and pore diameters were to be expected in the former as the pores in the materials were partly occupied by surface organoamine groups, which resulted from organosilane grafting. Furthermore, the gas adsorption/desorption data of all the materials gave type IV isotherm with hysteresis loops, indicating the presence of mesoporosity or mesopores in the materials as well as the retention of the mesoporous structure in the materials after organoamine grafting. However, as organoamines were grafted and as the grafted organoamines got bulkier, the pore sizes of the materials got increasingly reduced. Notably, the average BJH pore diameters of Ext-SBA-15, SBA-15-PA, SBA-15-SA and SBA-15-TA were found to be 6.4, 5.1, 4.4, and 3.3 nm, respectively (Fig. S1c and Table 1). The materials also got concomitantly lower pore volumes (Table 1). Despite its containing bulkier grafted groups (in about the same density as the two other materials), the surface area of SBA-15-TA was found to be slightly higher than those of SBA-15-PA and SBA-15-SA. Part of the reason behind this intriguing trend may have to do with the fact that SBA-15-TA is functionalized with more non-polar groups than SBA-15-PA and SBA-15-SA. The modification of the silica surface with hydrophobic groups is known to complicate the value used for the cross-sectional area of the adsorbate molecules in the conventional BET surface area analysis of materials.<sup>28-30</sup> The degree of interaction of the non-polar adsorbate  $N_2$  with the adsorbent is of great importance in adsorption and can ultimately dictate the effective molecular area of N2 molecules occupying the surface. It was shown that the effective cross-sectional area for  $N_2$  on silica surfaces could vary between 16 to 21 Å<sup>2</sup> depending on surface modification of silica.<sup>28-30</sup> Furthermore, the adsorption isotherms for organic-modified silicas in the low relative pressure region could be less convex than those of bare silica.<sup>31</sup> Although several types of corrections to obtain the effective cross-sectional area of  $N_{\rm 2}$  were considered or developed, the BET surface area analysis, by the very nature, can not be precise, especially more for non-polar modified porous materials. So, the BET surface area calculation may have slightly over-exaggerated the value obtained for the relatively

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hydrophobic material SBA-15-TA (or catalyst **3**) compared with those of SBA-15-PA and SBA-15-SA (or catalysts **1** and **2**).

#### Synthesis and characterization of Pd(II)/SBA-15-Amine

The immobilization of Pd(II) ions into SBA-15-Amine was achieved by contacting SBA-15-Amine materials with a solution containing tetraaminepalladium(II) chloride, or [Pd(NH<sub>3</sub>)<sub>4</sub>Cl<sub>2</sub>]. The latter was generated in situ by mixing PdCl<sub>2</sub> and NH<sub>3</sub> (aq) (Part 1 in Step II in Scheme 1 and Fig. S2). To monitor the interactions between the tetraaminepalladium(II) complexes and the amine groups (i.e., PA, SA or TA) grafted onto Ext-SBA-15, all the resulting three different Pd(II)/SBA-15-Amine materials were analyzed by UV-Vis diffuse reflectance spectroscopy (Fig. 1a). The Pd(II)/SBA-15-Amine materials exhibited an absorption maximum ( $\lambda_{max}$ ) centered between ca. 285 to 300 nm, attributable to ligand-metal (L-M) charge transfer or interband transitions in the metal-amine complexes.<sup>32,33</sup> Notably also, the absorption spectra of all the Pd(II)/SBA-15-Amine materials showed bathochromic or red shifts compared with that of the control material Pd(II)/SBA-15 (whose  $\lambda_{max}$  was at *cq.* 282 nm). The extent of the shift in the absorption maxima increased as the number of methyl substituents on the nitrogen atom of the amine group was increased: i.e., Pd(II)/SBA-15-PA ( $\lambda_{max}$  = 285 nm), Pd(II)/SBA-15-SA ( $\lambda_{max}$  = 292 nm), and Pd(II)/SBA-15-TA ( $\lambda_{max}$  = 300 nm). These results implied that a ligand exchange reaction between the tetraaminepalladium(II) ([Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>) complexes and the amine moieties grafted on Ext-SBA-15 (NR<sub>1</sub>R<sub>2</sub>• ••SBA-15) occurred, ultimately leading to [Pd(NH<sub>3</sub>)<sub>3</sub>(NR<sub>1</sub>R<sub>2</sub>)]<sup>2+</sup>••SBA-15 materials (Part 2 of Step II in Scheme 1). Similar bathochromic shifts were seen in the three control materials prepared by mixing unmodified Ext-SBA-15 with different tetraaminepalladium(II) complexes, namely  $[Pd(NH_3)_4Cl_2]^{2+}$ ,  $[Pd(NH_2CH_3)_4Cl_2]^{2+}$ , and  $[Pd(NH(CH_3)_2)_4Cl_2]^{2+}$ (Fig. 1b). The corresponding UV-Vis spectra for the Pd-amine complexes in solution are shown in Fig. S3.

The red shift in the absorption band of the complexes as the number of amine groups on the amine moiety is increased is not unusual. N-methylation of amino-ligands is known to induce a marked red shift of the L-M charge transfer bands of many metal complexes comprising Pd(II), Pd(I), Cu(II) ions, etc. and amine ligands.  $^{\rm 32,33}$  This red shift is often due to the following three possible factors. 1) N-methylation of amine groups of metal-amine complexes causes an anodic shift in the redox potential, or a reduction in value of the electrode potential, of the metal ions in the complexes. 2) N-methylation of amine groups generally increases the electron density of the nitrogen donor atoms, making the amine moieties to become better  $\sigma$  donors and the metalamine complexes to show lower optical electronegativity. 3) The Nmethyl groups decrease the degree of solvation of the metal-amine complexes. In the presence of polar hydrogen bond capable solvents, the methyl groups around the amines can make the latter weaker  $\sigma$ -donors to the metal ions. As a result, tertiary amines are widely reported to be poorer  $\sigma$ -donors and poorer ligands than the corresponding primary and secondary amines.<sup>33,34</sup> This effect of Nmethylation on the  $\sigma$ -donating properties of the non-bonding electron pairs of the nitrogen atoms can further be attributed to two main factors: a) the formation of M-N-H...O hydrogen bonds to the solvent molecules make the nitrogen atoms of primary and secondary amines stronger  $\sigma$ -donors (conversely, the absence of this effect in the nitrogen atoms of tertiary amine ligands make

them weaker  $\sigma$  donors) and b) the steric hindrance due to the insertion of methyl groups within the ligand framework which can cause the elongation of the M-N bond and distortion of the coordination sphere around Pd<sup>II</sup> in the complexes. Since the spectra in our case were obtained for Pd(II)-organoamine complexes where the organoamine themselves are used as solvent or the complexes are present on dried powder materials, there is no additional effect due to the solvents. So, any possible effect due to solvents can be ruled out. This then leaves the observed red shift in the charge transfer band upon more *N*-methylation of the ligands to be exclusively due to the increasingly weakening  $\sigma$  electron-donating properties of the nitrogen atoms of the amine ligands and the anodic shift of the redox potential.<sup>33,34</sup>



Fig. 1 UV-Vis diffuse reflectance spectra of (a) Pd(II)/SBA-15-Amine materials and (b) Ext-SBA-15 immobilized with different tetraamine palladium(II) complexes ( $[Pd(NH_3)_4Cl_2]$ ,  $[Pd(NH_2CH_3)_4Cl_2]$ , and  $[Pd(NH(CH_3)_2)_4Cl_2]$ ).

# Synthesis and characterization of a series of Pd(0)/SBA-15-Amine materials/catalysts

Following the grafting of the organoamine groups and immobilization of Pd(II) ions into the Ext-SBA-15, the materials were reduced using H<sub>2</sub> gas (10/90 % of H<sub>2</sub>/N<sub>2</sub>) at 250 °C. This afforded black or greyish colored, powder SBA-15-Amine materials containing different amine groups and supported Pd NPs. The materials were named Pd(0)/SBA-15-Amine, where "Amine" is PA, SA or TA (see *Step III* in Scheme 1 and Fig. S2). The materials were characterized first by EA, ICP-OES, and N<sub>2</sub> porosimetry, and the results are summarized in Table 2 and Fig. S4. The EA and ICP-OES results indicated the presence of different amounts of nitrogen and palladium in the materials. While the amount of nitrogen in the catalysts was nearly identical (*ca.* 1.4 mmol/g<sub>cat</sub>), the amount of palladium in them varied, where **1** had 0.41 mmol/g<sub>cat</sub>, **2** had 0.11 mmol/g<sub>cat</sub>, and **3** had 0.16 mmol/g<sub>cat</sub>.

Although we used identical moles of Pd(II) precursors during the synthesis of the materials **1**, **2**, and **3**, we found that the final amount of Pd loaded in the materials varied. These differences are likely to do with the differences in hydrophobicity of the organoamine groups grafted in the materials. More specifically, the loadings of Pd in **2** and **3** were lower than that in **1** (Table 2) because of the relatively weaker ability of  $[Pd(NH_3)_4]^{2+}$  species to anchor onto SBA-15-grafted tertiary and secondary amine groups than onto SBA-15-grafted primary amine groups. In other words, the Pd(II) complexes anchor less favorably in SBA-15-SA and SBA-15-TA than in SBA-15-PA. The slightly higher amount of Pd in **3** (0.16 mmol/g) compared with that in **2** (0.11 mmol/g) is because **3** has slightly more amount of amine groups than **2**.

**Scheme 1.** Synthetic procedures leading to the different Pd/SBA-15-Amine materials/catalysts (in which "Amine" represents PA, SA, and TA) that were employed as catalysts for FA dehydrogenation.

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The N<sub>2</sub> adsorption/desorption data of the Pd(0)/SBA-15-Amine materials **1**, **2**, and **3** also gave a type IV isotherm with some hysteresis loops, again indicating that the original mesoporous structures of the materials remained intact even after they were treated at relatively high temperature in  $H_2/N_2$  to reduce the Pd(II) ions to Pd(0) (Fig. S4a). Furthermore, the BET surface areas of the three materials were found to reduce compared with their corresponding SBA-15-Amine materials (Table 2). Furthermore, these materials too showed increasingly lower average BJH pore diameter and pore volume, as the types of organoamine groups grafted in them were increasingly bulkier (Table 2 and Fig. S4b).

Next, the three Pd(0)/SBA-15-Amine materials and the control material Pd(0)/SBA-15 were all analyzed by TGA (Fig. S4c). All the Pd(0)/SBA-15-Amine materials exhibited an initial weight loss of *ca*. 0.75 % between RT to 120 °C and a second weight loss of 11% between 120 to 700 °C. The former was attributed to the loss of physisorbed water and the latter was attributed to the loss of physisorbed water and the latter was attributed to the composition of organoamine groups, residual templates and water due to condensation of Si-OH groups in the materials. In contrast, the control material Pd(0)/SBA-15 showed a weight loss of *ca*. 1.1 % in the temperature range of RT to 120 °C (due to the removal of water) and a weight loss of *ca*. 7.5 % in a temperature range of 120 to 700 °C (due to the removal of residual Pluronic polymer templates and water due to condensation of Si-OH groups). The latter value was smaller because this material did not contain organoamines, like the Pd(0)/SBA-15-Amine materials did (Fig. S4c).

**Table 2.** Textural properties and elemental compositions ofPd(0)/SBA-15-Amine materials.

	Amount	Amount	BET	Pore	Pore
	of N	of Pd(0)	Surface	Size	Volume
	(mmol/	(mmol/	Area	(nm) <sup>d</sup>	(cm <sup>2</sup> /g)
	$g_{cat})^a$	g <sub>cat</sub> ) <sup>b</sup>	(m²/g) <sup>c</sup>		d
Pd/SBA-15 <sup>e</sup>	N/A	0.32	166	8.1	0.27
1	1.3	0.41	186	7.5	0.29
2	1.4	0.11	196	4.6	0.26
3	1.5	0.16	242	4.4	0.30

<sup>a</sup>Analyzed by EA; <sup>b</sup>Analyzed by ICP-OES; <sup>c</sup>Obtained from the N<sub>2</sub> adsorption/desorption data using the BET method; <sup>d</sup> Obtained from the adsorption branch of the gas adsorption/desorption isotherm using the BJH method. <sup>e</sup> A control material made from unmodified SBA-15.

To examine the effect of the type of amine groups in the SBA-15-Amine materials on the size and size distribution of the Pd NPs, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was employed. As depicted in Fig. 2, the as-synthesized catalysts displayed well-dispersed, supported Pd NPs throughout their structures. However, the sizes of the Pd NPs were found to vary from material to material. The average size of Pd NPs in Pd/SBA-15 (Fig. 2a) was 2.5 nm, but those in catalysts **1** and **2** were almost similar in size and much smaller: 1.5 nm and 1.6 nm, respectively (Fig. 2b-c). On the other hand, the average size of Pd NPs in **3** was much bigger (2.9 nm) (Fig. 2d).

The observed difference in the size of Pd NPs formed in the different catalysts an be accounted based on the relative ability of the SBA-15-grafted organoamine ligands in stabilizing the Pd(II) complexes, and then Pd NPs, just like many other organic ligands and surfactants, such as poly(ethylene glycol) (PEG), polyvinylpyrrolidone (PVP), etc., which are used as capping agents

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to synthesize various metallic nanoparticles, do. The different amine functionalities existing in the as-prepared SBA-15 materials in our case can render different degrees of stability to the Pd species forming in the materials. In other words, the Pd(II) complexes or Pd NPs in the materials reported herein are expected to have different degrees of interaction with the different SBA-15 grafted amine ligands, and thus end up with different sizes. More specifically, compared with secondary and primary amine ligands, tertiary amine ligands are weaker  $\sigma$  electron donors to Pd(II) in solution, due to their poorer ability to undergo solvation, and consequently, form less thermodynamically stable Pd(II) complexes.<sup>33</sup> N-methylation can also lead to molecular crowding, more steric hindrance and stiffening, and elongated and relatively more distorted Pd-N bonds in the Pd(II)-amine complexes. Pd(II) has a higher tendency to impose its own geometry on the ligands as well, and this can in turn reduce the ability of the ligands to adapt to the stereochemical requirements of Pd<sup>II</sup> species well enough. Hence, Pd(II) complexes or metallic species (or Pd NPs forming from the reduction) within the pores of SBA-15 functionalized with more N-methylated amine ligands would be less stable than their unmethylated counterparts. In other words, the tertiary amine groups interact less strongly with the Pd NPs than the primary amine groups do, making the Pd NPs in the former to have greater chances to grow and form relatively bigger particles.

To elucidate the potential electronic interaction between the amine groups and the Pd NPs, X-ray photoelectron spectroscopy (XPS) was applied and the peaks associated with Pd 3d in the spectra were carefully analyzed (Fig. S5). When organoamine functional groups were present in the materials (or for Pd(0)/SBA-15-Amine materials), the peaks for  $Pd(0) 3d_{3/2}$  and  $Pd(0) 3d_{5/2}$  were shifted to lower binding energies of 340.6 eV and 335.3 eV compared with the corresponding peaks for Pd(0)/SBA-15 (341.2 and 335.7 eV, respectively). This indicated the presence of electron transfer from the amine functional groups (PA, SA, or TA) to the Pd centres, which is consistent with the results reported previously for related systems.<sup>13</sup> However, there were barely any difference among the peak positions of the three materials functionalized with organoamine groups. In other words, as the number of methyl substituent in the Pd(0)/SBA-15-Amine was varied (PA, SA, or TA), there was barely any shift in the Pd(0)  $3d_{3/2}$  and Pd(0)  $3d_{5/2}$  peak positions or binding energies.

# Catalytic activities of the materials toward FA dehydrogenation and the effects of their structures and compositions

FA dehydrogenation reaction was then carried out by placing the series of Pd/SBA-15-Amine materials (1, 2, and 3), with each containing identical amount of nitrogen (64 µmol), in 10 mL of 1 M of FA at room temperature. As illustrated in Fig. 3, among the three catalysts, 1 exhibited the highest catalytic activity. Notably also, catalyst 1 showed better activity than most of the catalysts reported recently employed at room temperature without any additives for FA dehydrogenation (Table S1). The activity of the three catalysts, as measured based on initial TOF and TON, decreased in the order of 1 (whose TOF was 355 h<sup>-1</sup>, TON value of 59) > 2 (whose TOF was 190 h<sup>-1</sup> and whose TON was 32) > 3 (whose TOF value of 70 h<sup>-1</sup> and whose TON value was 12) (Fig. 3a and 3b).

In order to probe the reasons behind the relative catalytic activity of these three catalysts, possible roles played by their structures and compositions were all taken into consideration. Recently, primary amine-functionalized mesoporous silica containing Pd NPs was found to have a good catalytic activity toward FA dehydrogenation.<sup>12</sup> The high catalytic activity of the

#### material was attributed to the transfer of electron density from the primary amine groups to the Pd NPs, and thereby 3the 7electronrichness of the Pd centers in it. Similar electron transfer process from secondary and tertiary amine groups to Pd NPs and similar peak positions for Pd 3d in XPS were also seen in catalysts 2 and 3; so, it is reasonable to expect high catalytic activity for these two materials as well. Indeed catalysts 2 and 3 also catalyzed FA dehydrogenation well enough. However, besides these electronic effects between amine groups and Pd NPs, other factors such as the size of Pd NPs can affect the catalytic activity of the materials in FA dehydrogenation. This was actually found to be the case, especially when comparing catalysts 1 and 2 with catalyst 3 (Fig. 3c). Catalyst 3 showed the lowest catalytic activity, which must largely be due to the relatively large sized Pd NPs it owned. Although catalyst 2 had similar sized Pd NPs (ca. 1.6 nm) as catalyst 1 (ca. 1.5 nm), catalyst 2 showed lower activity than catalyst 1 (Fig. 3c). This, on the other hand, suggested that the type of amine functional groups in these materials also directly or indirectly dictated the materials' catalytic activities in FA dehydrogenation. More specifically, the organoamine groups appeared to have the ability to affect the size and the quantity of Pd active sites forming in the Ext-SBA-15 material, and also exert different degrees of steric hindrances around the catalytic sites, as discussed further below. Furthermore, the organoamine groups dictated the pore diameters in the catalysts. So, the superior catalytic activity exhibited by catalyst 1 compared with catalyst 2 can be due mainly to combined effects of these (Fig. 3c). On the other hand, Pd/SBA-15's poor catalytic activity compared with catalyst 3, despite the former had smaller Pd NPs (2.5 nm) than the latter had (2.9 nm) (Fig. 3c) must have largely been an indication of the importance of electronic effect in dictating the catalytic activity of these materials, like those reported in few previous studies.14,21

Additionally, the observed trend in catalytic activity between these three catalysts may also be partly due to the presence (or absence) of methyl groups on the grafted amine moieties. The methyl groups attached to amine groups have an ability to increase the hydrophobicity of the amine ligand, and then indirectly influence the degree of formic acid (FA) dehydrogenation reaction. In other words, the mass diffusion of the hydrophilic formic acid/formate anion species into the pores of the catalysts during the initial step of the reaction would be in the order of 1 > 2 > 3. So, the hydrophobicity of the three organoamine groups should be another likely reason behind the trend in catalytic activity we observed for the three catalysts: 1 > 2 > 3.

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**Fig 2**. STEM images of different catalysts: (a) Pd/SBA-15, (b) Pd/SBA-15-PA (1), (c) Pd/SBA-15-SA (2), and (d) Pd/SBA-15-TA (3). The average size of Pd NPs in Pd/SBA15 (a) is taken from reference 13.

#### Governing factors for FA dehydrogenation over Pd(0)/SBA-15-Amine catalysts

To gain insight into the mechanism of the dehydrogenation reaction over the catalysts, the reaction was performed using HCOO-D and D-COOH, instead of FA (HCOOH). As depicted in Fig. 4, the  $k_{\rm H}/k_D$ values over catalysts **1**, **2**, and **3** obtained using HCOO-D were similar, suggesting that the Brønsted basicity of the amine functional groups in Pd(0)/SBA-15-Amine did not contribute much to the activity of the catalysts during FA dehydrogenation. On the other hand, the  $k_{\rm H}/k_D$  values obtained using D-COOH were higher than those obtained using HCOO-D, indicating that C-H bond cleavage was likely the rate-determining step for all the Pd/SBA-15-Amine catalysts under the reaction conditions employed herein. In addition, the  $k_{\rm H}/k_D$  values obtained with D-COOH increased in the order of **1** < **2** < **3**, which was in line with the catalysts' activity toward FA dehydrogenation: **1** > **2** > **3**.

These differences in catalytic activity exhibited by the series of Pd(0)/SBA-15-Amine catalysts (1, 2, and 3) may have once again originated from the differences in (i) the electronic effect, (ii) size of Pd NPs, (iii) steric effect in their tethered amine functional groups, (iv) hydrophobicity/hydrophilicity of their tethered amine functional groups, and (v) pore diameters in the materials. Given the relatively small differences in the size of Pd NPs and electronic effect a, as evidenced by XPS, among the three Pd(0)/SBA-15-Amine catalysts studied herein, the steric effect, pore diameter as well as hydrophobicity due to the organoamine groups appeared to have played more dominant roles in their catalytic properties (see further discussions below). All of these properties seem to favor the trend in the catalytic activity of the three catalysts as: 1 > 2 > 3. However, it should be noted that the better catalytic activity exhibited by Pd(0)/SBA-15-Amine, compared with Pd/SBA-15 (the control material containing no amine groups), may have also partly originated from electronic interaction between Pd NPs and amine groups, as supported by XPS (see above), as well as the ability of the

amine groups in being able to cooperatively dictate, it the reaction pathways as illustrated in Scheme 2. DOI: 10.1039/C7TA02040F



Journal Name

**Fig. 3** FA dehydrogenation over the as-synthesized catalysts: (a) volume of the produced gases  $(H_2 + CO_2)$  as a function of reaction time, (b) catalytic TOF of the reaction at 10 min, and (c) catalytic TOF as a function of size of Pd NPs on the catalysts.

Based on the results presented above, it is plausible that FA initially undergoes deprotonation due to the amine group, affording formate  $(HCO_2^-)$  and ammonium  $(NHR_1R_2)^+$  species as intermediates (Scheme 2, *Step 1*). Note that the formation of formate in the first step can also come from the chemical equilibrium between formic acid and formate ion in aqueous media  $(HCO_2H(aq) \leftrightarrow HCOO^-(aq) + H^+(aq))$ , which can lead to a small difference in the kinetic isotope effect among catalysts **1**, **2**, and **3** during dehydrogenation of HCOO-H/HCOO-D. Next, the C-H bond in the H-COO<sup>-</sup> intermediate species can then cleave at the Pd sites and generate  $CO_2$  and Pd-H species (Scheme 2, *Step 2*). Lastly, the hydridic species (Pd-H) undergoes protonation by the acidic proton of the protonated amine species to release H<sub>2</sub> (Scheme 2, *Step 3*).



**Fig. 4** Comparison of the kinetic isotope effect (KIE) of the series of Pd catalysts synthesized and studied.



**Scheme 2.** A possible reaction pathway for FA dehydrogenation over Pd(0)/SBA-15-Amine catalysts (**1**, **2**, and **3**). Note that step 1 represents the deprotonation of FA both by water and amine group. Obviously, the latter is a more dominant reaction and is also more responsible for the formation of the formate species in the

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reaction. In 1,  $R_1$  and  $R_2$  are H; in 2,  $R_1$  is  $CH_3$  and  $R_2$  is  $H_2$  and in  $3_{H_1R_2}$ and  $R_2$  are both  $CH_3$ . DOI: 10.1039/C7TA02040F

Recent detailed studies, however, have shown that the rate determining step (Step 2 of Scheme 2) can have two sequential transition states, one of which involves the rotation of formate (HCOO\*) species over the Pd NPs.35,36 So, in the as-developed catalysts reported herein, the rotation of the formate species can be the first step. This way, the Pd-H species generated by C-H bond activation can become near the acidic H atom present on NR<sub>1</sub>R<sub>2</sub>..H moiety and be able to interact with the latter, finally forming H (due to H<sup>-</sup> atom approach H<sup>+</sup>) (Scheme 3). Consequently, it is believed that the degree of rotation of the formate species adsorbed on Pd can dictate the rate of the reaction. The rotation of formate species adsorbed on 1 can be expected to have a lower activation energy than those adsorbed on 2 and 3 due to i) the less steric hindrance and ii) the better mass diffusion (due to the relatively bigger pores in 1) the former experience. On the other hand, in the catalysts, which have one or two methyl groups on their amine groups (catalysts 2 or 3), the adsorbed formate species require more energy to undergo the rotation due to the steric hindrance they experience, thanks to the methyl groups present around the N atoms of the amine groups in them (Scheme 3). These are most likely part of the reasons behind the trend in catalytic activity among catalysts 1, 2 and 3 (or 1 > 2 > 3).

#### Recyclability studies and analysis of by-products

Recyclability studies were additionally conducted on catalysts **1**, **2**, and **3** to determine their stability and reusability. Interestingly, in the case of catalyst **1**, the once and twice recycled catalysts actually showed higher catalytic activity for FA dehydrogenation than did the original catalyst (Fig. S6). In the other two cases, the catalytic activities of the catalysts toward FA dehydrogenation remained almost unchanged for, at least, up to 3 cycles. Catalyst **1**'s higher catalytic activity after the **1**<sup>st</sup> run was most likely because of the possible reduction of PdO species present on the surfaces of the Pd NPs by the H<sub>2</sub> gas produced from the formic acid dehydrogenation reaction and the subsequent formation of

Scheme 3. Schematic description of detailed mechanism of the catalytic dehydrogenation of FA over Pd/SBA-15-PA (1). Inserted in the orange and cyan boxes are Pd/SBA-15-SA (2) and Pd/SBA-15-TA (3) catalysts, respectively.



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additional catalytically active surface Pd(0) species in the sample.<sup>12</sup> This possible reduction could be relatively insignificant in for catalysts 2 and 3 because these two produced much less amount of H<sub>2</sub> compared with that produced by catalyst **1**. In other words, most of the possible PdO species present on the former two catalysts remained more likely in oxidized forms even after FA dehydrogenation reaction. Notably also, although TEM analysis of the spent-catalysts indicated that the average sizes of Pd NPs increased slightly after the 3<sup>rd</sup> cycle in all cases (for 1, from 1.5 nm to 2.3 nm; for 2, from 1.6 nm to 2.1 nm; and for 3, from 2.9 nm to 4.4 nm) (see Figure S6), the catalysts largely retained their activity, and even became more active in some cases, for the reaction.

The slight increase in the size of Pd NPs after recycling can be explained based on the weakened interaction between the Pd NPs and the grafted organoamine functional groups during the reactions. Given the fact that the adsorbed formic acid molecules undergo deprotonation with grafted organoamine groups (via Pd-HCOOH…NR<sub>2</sub>-SBA-15  $\rightarrow$  Pd-HCOO<sup>-</sup> + NHR<sub>2</sub><sup>+</sup>-SBA15; please also see Step 1 in Scheme 2), the resulting SBA-15-supported quaternary ammonium groups (-NHR2<sup>+</sup>) would barely have an ability to interact with and cap the Pd NPs like the NR<sub>2</sub> groups in NR<sub>2</sub>-SBA-15 do. As a result, the Pd NPs would have a greater chance to diffuse over the catalyst surface, aggregate with each other and grow into larger nanoparticles during catalysis. Note that the unprotonated amine groups donate electron densities into Pd NPs via Pd-N interaction, as evidenced by XPS (Figure S5 in Supporting information).

Finally, in-situ FT-IR spectroscopy was conducted and the results revealed that the reaction over the catalysts reported herein did not generate CO gas. In other words, the catalysts did not favor the undesired FA dehydration reaction (HCOOH  $\rightarrow$  CO + H<sub>2</sub>O) (Fig. S7). The absence of CO by-product during FA dehydrogenation was further confirmed by GC analysis (Fig. S8).

#### Conclusions

In conclusion, we have successfully synthesized and characterized the structures, compositions and catalytic properties for FA dehydrogenation of a series of Pd/SBA-15-Amine materials containing different types of amine groups and Pd NPs. Using the results, the relationships between amine groups and the Pd NPs forming in the materials have been investigated. The catalytic activity of the materials have been found to directly and indirectly relate to the terminal amine functional groups present in the materials. Specifically, the types of amine functional groups are found to dictate the size of the Pd NPs forming in the materials, the electronic properties in the materials, and the pore diameters and pore volumes in the materials. These have, in turn, dictated the overall degree of catalytic activities of the materials toward FA dehydrogenation. The structural and composition parameters identified for the materials in relation to their catalytic properties toward FA dehydrogenation reaction here may provide valuable guidelines for the development of other efficient catalysts to generate H<sub>2</sub> on-board for H<sub>2</sub>-powered fuel cells.

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