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## Zeolite Y Nanosheets Assembled Palladium Catalyst with High Catalytic Activity and Selectivity in the Vinylation of Thiophenes

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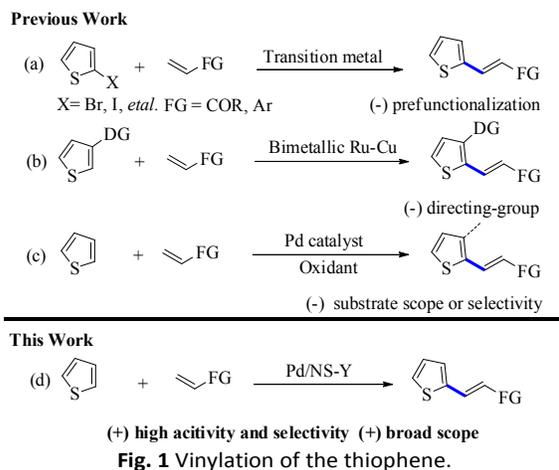
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Zeolite Y nanosheets with micro-meso-macroporous structure was synthesized, and applied to assemble Pd catalyst (Pd/NS-Y) for direct vinylation of thiophenes in high activity and selectivity, as compared to Pd(OAc)<sub>2</sub>, Pd(NO<sub>3</sub>)<sub>2</sub>, and Pd(PPh<sub>3</sub>)<sub>4</sub> catalysts. This feature should be assigned to the highly dispersed Pd<sup>δ+</sup> (δ<2) species in Pd/NS-Y that are more active than Pd<sup>2+</sup>.

Alkenylated thiophenes are very important sulfur-containing intermediates in natural products, agrochemicals and pharmaceuticals.<sup>1</sup> Generally, the alkenylated thiophenes are synthesized by the cross-coupling of the thiophenes with alkenes in the homogeneous transition-metals catalyst systems.<sup>2</sup> However, the reaction activities and the product selectivities are usually unsatisfactory. Recently, many works focus on improving the reaction performance by modifying the activities of the reactant molecule. For instance, pre-functionalizing the thiophene substrate by halogen can enhance the reaction activity.<sup>3</sup> Nevertheless, it could lead to form the stoichiometric amounts of the inorganic salts (Fig. 1a). Another strategy is use of the thiophene with incorporated directing groups or the relatively more active acrylate derivatives to improve the reaction activity and selectivity (Fig. 1b and 1c).<sup>4-6</sup> However, these routes not only limit the scope of substrate but also complicate the reaction. From view of the essence, a general and critical solution for this issue should be developing highly active and selective heterogeneous metal catalysts for the direct vinylation of thiophenes in a broad scope.

It is well known, zeolites are crystalline porous materials and widely used as supports for metal catalysts.<sup>7</sup> Especially, the unique framework structure could decorate the electronic properties of their assembled metal species, and improve its catalytic performance.<sup>8</sup> Thus, it is trigger to utilize the unique framework structure of zeolite to prepare highly active Pd catalyst for the direct vinylation of thiophenes. Herein, we first



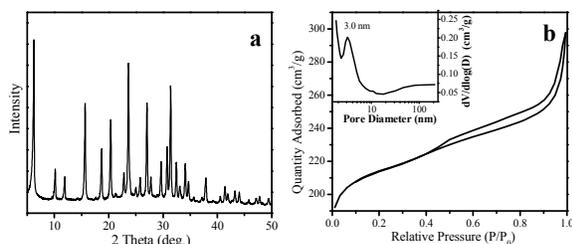
time synthesized an nanosheets of zeolite Y (NS-Y) by addition of the silane surfactant ( $[(C_2H_5O)_3SiC_3H_6N(CH_3)_2C_{18}H_{37}]Br$ , ES1<sup>†</sup>) into the zeolite Y seed solution through hydrothermal method. After assembled Pd species with NS-Y by ion-exchange of Pd(NO<sub>3</sub>)<sub>2</sub> solution, the obtained catalyst (Pd/NS-Y) showed a high activity and excellent product selectivity in the direct vinylation of thiophenes (Fig. 1d), compared to homogeneous Pd(OAc)<sub>2</sub>, Pd(NO<sub>3</sub>)<sub>2</sub>, and Pd(PPh<sub>3</sub>)<sub>4</sub> catalysts. Especially, the Pd/NS-Y catalyst afforded a broad range of reactants. The superior catalytic performance of the Pd/NS-Y catalyst could be attributed to the highly dispersed Pd<sup>δ+</sup> (δ<1) and Pd<sup>δ+</sup> (δ<2) species in the Pd/NS-Y. Moreover, the Pd/NS-Y catalyst containing meso-macroporous structure facilitates the mass transfer and further improves its catalytic performance.

Fig. 2 shows the X-ray diffraction (XRD) pattern and nitrogen sorption isotherm of the calcined NS-Y sample. The XRD pattern shows well-resolved peaks in the range 5-50° with zeolite FAU structure.<sup>9</sup> The nitrogen adsorption-desorption isotherm of the NS-Y exhibits a hysteresis loop at a relative pressure of 0.5-0.95, which is assigned to the presence of the mesoporous (Fig. 1b). Correspondingly, the mesopore-size diameter is mainly centred at 3.0 nm (insert, Fig. 1b). The sample texture parameters are shown in Table S1. NS-Y exhibits high BET and external surface area, and mesoporous volume (817 and 138 m<sup>2</sup>/g, and 0.20 cm<sup>3</sup>/g), which could benefit the mass transfer and provide abundant accessible active sites after loading of Pd.

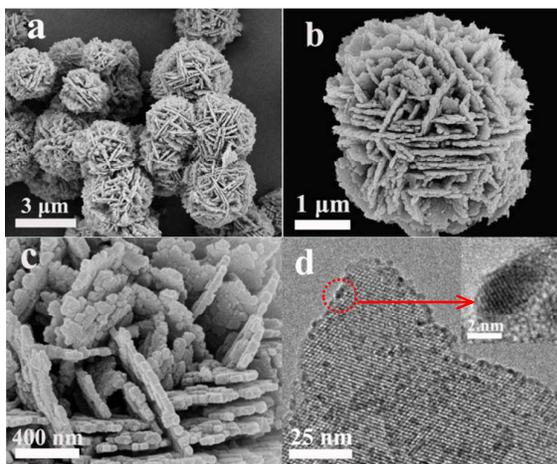
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**Fig. 2** (a) XRD pattern, and (b) nitrogen adsorption-desorption isotherm and pore size distribution (insert in Fig. 1b) of the NS-Y sample.



**Fig. 3** (a), (b) and (c) SEM images of the NS-Y sample at different resolution. (d) TEM image of the Pd/NS-Y sample.

The scanning electron microscopy (SEM) images show that the assemblies (particle size 2-5  $\mu\text{m}$ , Fig. 3a) consists of flower-shaped cards-like nanosheets (Fig. 3b), in which the zeolite nanosheets have thickness about 50 nm (Fig. 3c). In this manner, the interstice macropores could be formed in the nanosheet assemblies.<sup>10</sup> Transmission electron microscopy (TEM) images show the nanosheets with highly crystalline micropore structure (Fig. S1, ESI<sup>†</sup>). Very interestingly, the nanosheets contain intra-mesopores with the pore size of 3-8 nm (Fig. S1, ESI<sup>†</sup>). After loading of Pd, the Pd nanoparticles (1-3 nm) are highly dispersed on the outer surface of crystalline nanosheets (Fig. 3d). Combining the results of the SEM, TEM, and nitrogen sorption, it is indicated that the NS-Y exhibits a micro-meso-macroporous structure, which could facilitate the mass transfer and improve the catalytic performance of the Pd/NS-Y catalyst.

The activity of the Pd/NS-Y catalyst was first investigated by the cross-coupling of 2-methyl thiophene with butyl acrylate in the different solvents (Table 1). The Pd/NS-Y catalyst showed the highest activity by using DMSO as solvent. Compared with the homogeneous Pd(NO<sub>3</sub>)<sub>2</sub>, Pd(OAc)<sub>2</sub>, and Pd(PPh<sub>3</sub>)<sub>4</sub> catalysts (entries 8-10), the Pd/NS-Y catalyst turned out to be the most effective one. The reaction proceeded smoothly over Pd/Y, Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Pd/NS-HY catalysts (entries 11-13), while the obtained yields were much lower than that over Pd/NS-Y

**Table 1** Synthesis of alkenylated thiophenes over series catalysts under different solvents.<sup>a</sup>

Entry	Catalyst	Solvent	Yield (%) <sup>b</sup>
1	Pd/NS-Y	Ethanol	20
2	Pd/NS-Y	Water	50
3	Pd/NS-Y	Chlorobenzene	15
4	Pd/NS-Y	xylene	0
5	Pd/NS-Y	<i>n</i> -butanol	34
6	Pd/NS-Y	toluene	19
7	Pd/NS-Y	DMSO	87
8 <sup>c</sup>	Pd(NO <sub>3</sub> ) <sub>2</sub>	DMSO	64
9 <sup>c</sup>	Pd(OAc) <sub>2</sub>	DMSO	59
10 <sup>c</sup>	Pd(PPh <sub>3</sub> ) <sub>4</sub>	DMSO	54
11	Pd/Y	DMSO	70
12	Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	DMSO	73
13	Pd/NS-HY	DMSO	72
14 <sup>d</sup>	Pd/NS-Y	DMSO	81

<sup>a</sup> Unless otherwise noted, typical reaction conditions: catalyst (50 mg), solvent (1 mL), HOAc (1 mL), BQ (0.5 mmol), thiophenes (0.5 mmol), acrylates (0.25 mmol) at 60 °C; <sup>b</sup> The yields were obtained by GC analysis; <sup>c</sup> The Pd content equivalent equal to that of 50 mg Pd/NS-Y. <sup>d</sup> The reaction scale-up 100 times in an autoclave reactive to entry 7.

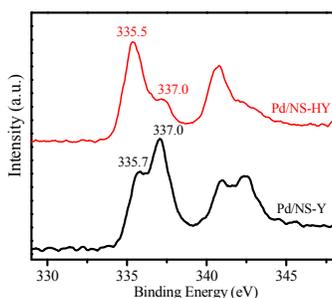
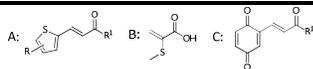
catalyst. In addition, when the reaction was scale-up to 100 times by use of the Pd/NS-Y catalyst, the obtained product yield is 81% (entry 14, Table 1).

To study on the change in the product selectivities of the Pd/NS-Y and Pd(OAc)<sub>2</sub> catalysts, the additional reactions were tested by choosing the thiophene and alkene with different substituent groups as substrates to meet the universality, and the results are summarized in Table 2 and Table S2. The main by-products in this reaction are  $\alpha$ -(methylthio)acryl derivative (B) and  $\alpha$ -functional benzoquinone (C). To our delight, the selectivity of the alkenylated thiophenes (A) over Pd/NS-Y catalyst was much higher than that of Pd(OAc)<sub>2</sub> catalyst when the electron-withdrawing alkenes were used as substrates. In addition, a high product selectivity over Pd/NS-Y catalyst was also obtained when the halogen-, methyl-substituted styrenes the electron-withdrawing alkenes were used as substrates. (Table S2, ESI<sup>†</sup>). These results indicated that the Pd/NS-Y catalyst presents superior catalytic selectivity in the direct vinylation of thiophenes.

To our knowledge, in the case of the same Pd content, the homogeneous Pd(OAc)<sub>2</sub> and Pd(NO<sub>3</sub>)<sub>2</sub> catalytic systems could provide more accessible active metal sites relative to the heterogeneous Pd/NS-Y catalytic reaction system. However, the activity of the Pd/NS-Y is much higher than that of Pd(OAc)<sub>2</sub> and Pd(NO<sub>3</sub>)<sub>2</sub>, which should be assigned to unique Pd species on the NS-Y. The X-ray photoelectron spectroscopy (XPS) analyses of the Pd/NS-Y and Pd/NS-HY show that the binding energy of Pd3d<sub>5/2</sub> is about 355.7 and 337.0 eV (Fig. 4), which are attributed to the characteristics of the Pd<sup>δ+</sup> ( $\delta < 1$ ) and Pd<sup>δ+</sup> ( $\delta < 2$ ),<sup>11</sup> respectively. This phenomenon should be assigned to the electron transfer from negatively charged framework of zeolite Y to the Pd species because of the relatively strong interaction of Pd with zeolite framework.<sup>8a</sup>

**Table 2** The product selectivities of the Pd/NS-Y and Pd(OAc)<sub>2</sub> catalysts in the vinylation of thiophenes.

Catalyst	Thiophene	Alkene	Conversion (%)	Product selectivities (%)			
				S <sub>A</sub> (%)	S <sub>B</sub> (%)	S <sub>C</sub> (%)	Other (%)
Pd(OAc) <sub>2</sub>			98	60	21	12	7
Pd/NS-Y			97	90	3	4	3
Pd(OAc) <sub>2</sub>			96	37	47	10	6
Pd/NS-Y			94	97	2	-	1
Pd(OAc) <sub>2</sub>			95	54	32	9	5
Pd/NS-Y			97	99	-	-	1
Pd(OAc) <sub>2</sub>			93	49	49	-	2
Pd/NS-Y			95	87	12	-	1

**Fig. 4** XPS spectra of Pd3d<sub>5/2</sub> in the Pd/NS-Y and Pd/NS-HY samples.

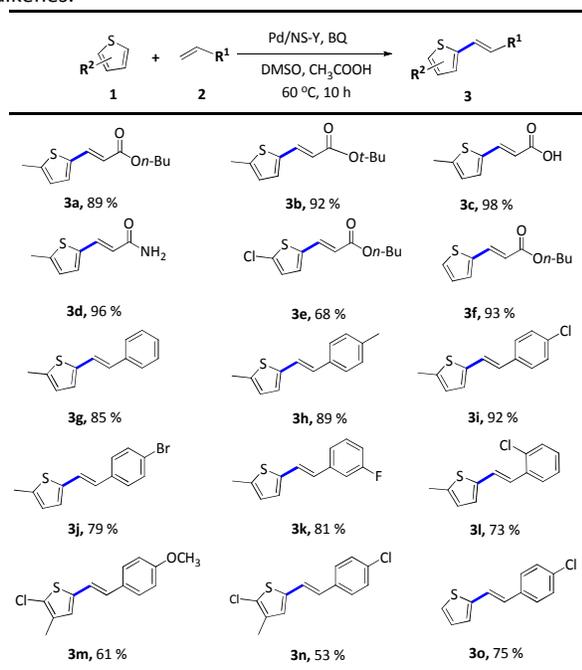
The Pd<sup>δ+</sup> (δ<2) on the NS-Y could be more active than the homogeneous Pd<sup>2+</sup> in the vinylation of thiophenes in the presence of the benzoquinone (BQ). Bras and co-workers have reported that the electron-rich Pd species easily interacted with benzoquinone (BQ) and generated a coordinated Pd, which can interact easily with electron-rich alkenes to obtain the desired product.<sup>12</sup> Further computational studies reported by Sakaki have also demonstrated that the electron-rich Pd species can easily coordinate BQ and accelerate the cross-coupling of arenes with arenes.<sup>13</sup> In our case, the highly dispersed Pd<sup>δ+</sup> (δ<1) and Pd<sup>δ+</sup> (δ<2) species on the NS-Y could coordinate BQ, resulting in the formation of the coordination of Pd species that could favour the activation of the electron-rich alkenes. The proposed reaction mechanism by the facilitation of the Pd<sup>δ+</sup> species is shown in Fig. S2.

This fact is further demonstrated by comparing the activity of the Pd/γ-Al<sub>2</sub>O<sub>3</sub> and Pd/NS-Y catalysts. Compared with NS-Y, the γ-Al<sub>2</sub>O<sub>3</sub> has a larger mesoporous surface area and mesopore volume (322 m<sup>2</sup>/g and 0.45 m<sup>3</sup>/g, Table S1, ESI<sup>†</sup>), thus, the Pd/γ-Al<sub>2</sub>O<sub>3</sub> should be more beneficial for the mass transfer than Pd/NS-Y. In addition, the Pd dispersion on the Pd/γ-Al<sub>2</sub>O<sub>3</sub> catalyst is higher than Pd/NS-Y catalyst (Fig. S3, ESI<sup>†</sup> and Fig. 3d). However, the activity of the Pd/NS-Y catalyst (87%) is much higher than that of the Pd/γ-Al<sub>2</sub>O<sub>3</sub> catalyst (73%, Table 1). This should be due to the difference in electronic property of the Pd species on the Pd/γ-Al<sub>2</sub>O<sub>3</sub> and Pd/NS-Y samples. The XPS analysis shows that the Pd species

on the γ-Al<sub>2</sub>O<sub>3</sub> are mainly Pd<sup>2+</sup> form (Fig. S4, ESI<sup>†</sup>), while Pd<sup>δ+</sup> (δ<1) and Pd<sup>δ+</sup> (δ<2) species are dominant on the NS-Y (Fig. 4). These results demonstrated that the Pd<sup>δ+</sup> (δ<1) and Pd<sup>δ+</sup> (δ<2) species are more active than Pd<sup>2+</sup> species. In addition, the meso-macroporous in the NS-Y could benefit the mass transfer for reactants, enhancing the catalytic activity. This is supported by comparison of the activity of the Pd/Y and Pd/NS-Y catalysts. The product yield over Pd/NS-Y (87%) is much higher than that over Pd/Y (70%, Table 1).

To further compare the catalytic performance of the Pd/NS-Y and Pd/NS-HY catalysts, the time dependence of the butyl acrylate conversion and the target product selectivity over Pd/NS-Y and Pd/NS-HY catalysts was examined (Fig. S5). The results show that although the Pd content and the particles size on the Pd/NS-Y (Fig. 3d) and Pd/NS-HY catalysts (Fig. S6) are similar, the activity of the Pd/NS-HY catalyst is higher than that of Pd/NS-Y catalyst. Possibly, the NS-HY with strong acidity (Fig. S7, ESI<sup>†</sup>) could favour the formation of the more active Pd<sup>δ+</sup> (δ<1) species on the Pd/NS-HY catalyst (Fig. 4), which enhances its catalytic activity. However, the catalyst with strong acidity does not benefit the formation of the target product.

The scope of the Pd/NS-Y catalyzed the vinylation of thiophenes was also examined, and the results are shown in Table 3. It is notable that all of the products presented excellent regioselectivity at the C2 position of the thiophenes with the E-configuration. To our delight, α,β-unsaturated carbonyl derivatives, with various substituents such as -On-Bu, -Ot-Bu, -OH and -NH<sub>2</sub> groups, were successfully applied to this transformation in good to high yields (**3a-3f**). Pleasingly, the styrene and 4-methyl styrene were found to be favoured in the reaction to deliver the desired products in 85 and 89% yields, respectively (**3g** and **3h**). Meanwhile, styrenes with electron-withdrawing groups at ortho-, meta- and para-positions (4-Cl, 4-Br, 3-F and 2-Cl) were also provided the corresponding products **3i-3l** in 73-93% yields. Additionally, thiophenes containing electron-withdrawing groups at C2 position also afforded the product **3m** and **3n** in relatively low yields, and the thiophene also smoothly converted into the target product **3o** in 75% yield. These results demonstrated that the Pd/NS-Y catalyst presents good compatibility with a

**Table 3** The cross-coupling reaction between thiophenes and alkenes.<sup>a</sup>

<sup>a</sup> Reaction conditions: Pd/NS-Y (50 mg), DMSO (1mL), HOAc (1mL), BQ (0.5 mmol), thiophenes (0.5 mmol), acrylates or alkenes (0.25 mmol).

broad range of functional groups.

In conclusion, a micro-meso-macroporous structured zeolite Y nanosheet assemblies was successfully synthesized, and applied to prepare Pd catalyst for direct C2-vinylation of thiophenes. Compared with homogenous Pd(OAc)<sub>2</sub>, Pd(NO<sub>3</sub>)<sub>2</sub>, and Pd(PPh<sub>3</sub>)<sub>4</sub> catalysts, Pd/NS-Y shows high activity and selectivity as well as a good compatibility with a broad range of functional groups. This could be attributed to the electron transfer from the zeolite Y framework to the Pd, resulting in formation of the Pd<sup>δ+</sup> (δ<1) and Pd<sup>δ+</sup> (δ<2) species that are more active than the Pd<sup>2+</sup> species. Additionally, the meso-macroporous in the NS-Y could facilitate the mass transfer and further improve the catalytic performance of Pd/NS-Y.

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