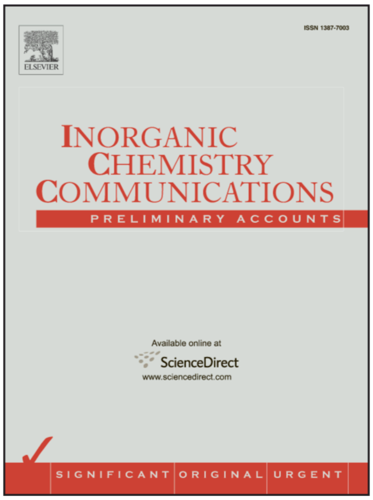

Short communication

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Short communication

Nanoporous palladium catalyzed one-pot synthesis N-alkyl amines by hydrogen transfer reaction under mild conditions

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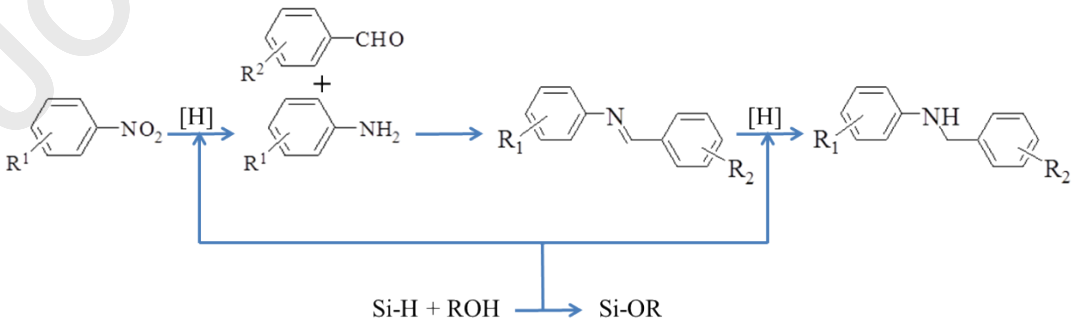
The one-pot strategy has been extensively used in organic synthesis. When using this strategy, choosing the appropriate substrate and developing an effective design decreases the reaction steps, increases efficiency, and allows the reaction to be greener and more economical [1]. A suitable catalyst allows the system to operate smoothly and under mild conditions [2-4]. The hydrogen transfer reaction is an effective approach to promote the overall strategy [5].

Due to their fundamental role in biologically active natural products, pharmaceuticals, dyes, and various organic molecules, amines have attracted increased research attention [6]. As common intermediates, N-alkyl amines (secondary amines) have been extensively studied among amine compounds. There are many different methods to synthesize N-alkyl amines [7-10]. However, expensive organic halides are conventionally used as alkylating reagents, the preparation methods are environmentally unfriendly, and secondary and tertiary amine separation has limitations [11, 12]. The hydrogenation of imines has proven to be a mild method, wherein the raw material is obtained by coupling aromatic aldehydes and aromatic amines [13, 14]. On this basis, if nitroarenes (the main precursor of aromatic amines [15, 16]) are used as the raw material instead of aromatic amines, this hydrogen-transfer-based approach would be a valuable, atom-economic, environmentally attractive, one-pot, multistep transformation [17-19]. This system involves two hydrogenation processes: reduction of nitroarenes and hydrogenation of imines. The hydrogen transfer reaction with a suitable hydrogen source may be a good choice for the one-pot reductive N-alkylation of nitroarenes. Nevertheless, the specific condition that promotes the optimal performance of the system still needs to be determined.

Selection of a suitable hydrogen source and catalyst plays an important role in the hydrogen transfer reaction. In a previous study, the oxidation of hydrosilane by ROH (water or alcohol) [20, 21] was conducted to produce active hydrogen during the reaction. This silane-based hydrogen source is widely used not only in the hydrogen transfer reaction but also in the production of molecular hydrogen on demand. With nanoporous gold (np-Au) as the catalyst, semihydrogenation of terminal and internal alkynes was realized using a np-Au/hydrosilane/water system [22]. Although the reduction of imines or ketimines could also be realized using this system [23, 24], due to the low hydrogenation activity of gold, the reaction also needed high temperature. The raw materials were aromatic amines rather than nitroarenes. Optimizing the system is essential to further develop a silane-based hydrogen source. Generally, palladium catalysts have excellent hydrogenation activities, while the reduction of nitroarenes is promoted by nanoporous Pd (np-Pd) with hydrosilane/alcohol as the hydrogen source [25]. We speculated that the np-Pd/hydrosilane/alcohol system could be a good combination for the one-pot synthesis of N-alkyl amines by reductive N-alkylation of nitroarenes under mild conditions. In this system (Scheme 1), nitroarenes with aromatic aldehydes were used as the raw material, and the oxidation of hydrosilane supplied active hydrogen. Nitroarenes were reduced to aromatic amines, which were coupled with aromatic aldehydes to obtain imines. The corresponding N-alkyl amines were obtained after the hydrogenation of imines.



Scheme 1. Schematic representation of one-pot synthesis of N-alkyl amines by reductive N-alkylation of nitroarenes with silane/alcohol as the hydrogen source.

In the present work, we demonstrate that one-pot synthesis of N-alkyl amines is realized by the hydrogen transfer reaction with the np-Pd/hydrosilane/alcohol system under mild conditions (room temperature and atmospheric pressure). Nitroarenes, aromatic amines, and imines could be the raw materials for the synthesis of N-alkyl amines. When nitroarenes and aromatic aldehydes were used as substrates, a wide range of N-alkylation amines could be obtained in high yields. This was a new attempt to use hydrosilanes/alcohol as the hydrogen source for the continuous hydrogenation system.

The catalyst was prepared by dealloying an aluminum-palladium alloy ($Al_{75}Pd_{25}$, at.%; for the preparation of the alloy, see ESI 1. General). Aluminum in the alloy was leached by sodium hydroxide (NaOH 2.5 M) at room temperature, and after 24 h, nanoporous Pd was obtained. Scanning electron microscopy (SEM) was used to observe the morphologies of np-Pd samples. As shown in Fig. 1 (a), a three-dimensional bicontinuous nanoporous structure was observed, and the ligament size was below 10 nm. The Brunner-Emmet-Teller (BET) measurements results showed that the specific surface area of the catalyst was 30.6 m^2/g, and the Barrett-Joyner-Halenda (BJH) results showed the nano-pore diameter was approximately 5 nm (see ESI Fig. S3).

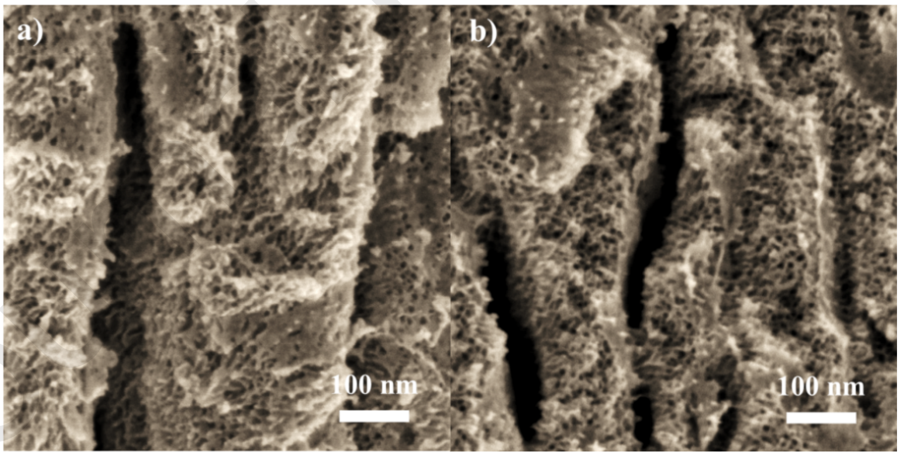
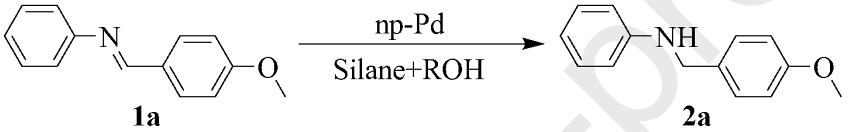


Fig. 1 (a) SEM image of dealloyed np-Pd before catalytic reaction; (b) SEM image of dealloyed np-Pd after being used eight times.

The hydrogenation of the carbon-nitrogen double bonds (C=N) was first tested. The imine N-(4-methoxybenzylidene)aniline ($4\text{-}CH_3\text{-}O\text{-}Ph\text{-}CH{=}N\text{-}Ph$, **1a**) was chosen as the raw material, with np-Pd as the catalyst. Triethylsilane (Et_3SiH) and methanol (MeOH) acted as the hydrogen source, while methanol was used as the solvent. During the reaction, minimal gas was generated, and the active hydrogen reacted with C=N. After 2.5 h, the corresponding N-alkylation amine N-(4-methoxybenzyl)aniline (4-CH_3-O-Ph-CH_2-NH-Ph, **2a**) was obtained in high yield at room temperature and atmospheric pressure (Entry 1, Table 1). Minimal aniline (2%) was found by HPLC, which indicated that the carbon-nitrogen double bond (C=N) may break during the reaction. The main product and oxidation product of silane were purified by column chromatography. These results illustrated that the np-Pd/hydrosilane/alcohol system could meet the requirement for imine reduction.

Table 1. Reduction of N-(4-methoxybenzylidene)aniline (4-CH_3-O-Ph-CH=N-Ph, **1a**) with different hydrosilane/alcohol hydrogen sources.



Entry [a)]	Silane	ROH	Time/h	Yield/%
1	Et_3SiH	MeOH	3	97
2	Et_3SiH	EtOH	6	96
3	Et_3SiH	*i*PrOH	6	77
4	$(EtO)_3SiH$	MeOH	3	95
5 [b)]	$(Me_2SiH)_2O$	MeOH	6	87
6	$PhMe_2SiH$	MeOH	4	93
7	Ph_2MeSiH	MeOH	6	92

a) Reactions were performed using the catalyst (0.1 mmol), **1a** (1.0 mmol), silanes (3.0 mmol), and ROH (4.0 mL) at room temperature. b) silanes (1.5 mmol)

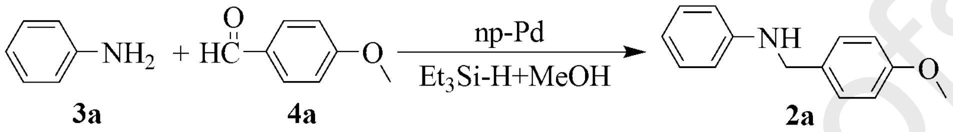
To optimize the hydrogen source, different combinations of hydrosilane and alcohol were tested. The reduction was complete with ethanol but the reaction time was long (Entry 2, Table 1). Due to the low reaction rate between isopropyl alcohol (*i*PrOH) and Et_3SiH under the reaction conditions, the hydrogenation was slow with 77% yield. Meanwhile, the C=N bond breaking reaction increased, and the yield of aniline reached 10% (Entry 3, Table 1). When triethoxysilane ($(EtO)_3SiH$) was used with a long reaction time, the yield reached 87% (Entry 4, Table 1). Additionally, 1,1,3,3-

tetramethyldisiloxane (($(Me_2SiH)_2O$), which contains two Si-H bonds in one molecule, had qualitative efficacy similar to that of triethylsilane (Entry 5, Table 1). When aromatic silanes such as dimethylphenylsilane ($PhMe_2SiH$) and dimethylphenylmethoxylsilane (Ph_2MeSiH) were used in the system, the reaction proceeded smoothly. Due to the steric hindrance of the benzene ring the yield was slightly decreased (Entries 6 and 7, Table 1). Therefore, the Et_3SiH/MeOH component with low steric hindrance showed high reactivity in this system and was a suitable hydrogen source combination for the following reactions.

To further understand the hydrogen transfer process, the effect of reactant quantity was studied. First, the influence of imines was tested. As shown in Fig. S2a, the reaction rate was linearly dependent on the concentration of imines. As shown in Fig. S2b, no evident changes in the reaction rate were observed with the dosage of Et_3SiH increased from 2.0 mmol to 5.0 mmol. It can be speculated that the hydrogen-producing reaction was fast on the nanoporous palladium surface, and the hydrogen source provided enough hydrogen for the reduction reaction. The activation of the C=N bond and hydrogenation was the rate-limiting step. Different imines as substituents were tested (see ESI Table S1). Through these results, we speculated that the substituent on the carbon side of benzene was crucial to the hydrogenation of the C=N bond, which is similar to the findings of a previous study [26].

Then, aromatic amines instead of imines were used as raw materials. In our design, imines could be obtained smoothly by the thermodynamically feasible reaction between aniline ($Ph-NH_2$, **3a**) and 4-anisaldehyde ($4-CH_3O-Ph-CHO$, **4a**). Imine **1a** could be reduced to the corresponding secondary amine **2a**. As shown in Table 2, when equal dosages of **3a** and **4a** were added into methanol with Et_3SiH simultaneously (Method A), the yield was only 64%. When **3a** and **4a** were reacted without hydrosilanes, the yield of imines was above 95%. This means that the reduction of **4a** to 4-anisyl alcohol inhibited the production of imines and negatively affected the yield. When excess **4a** was added, the yield of **2a** increased as the ratio of **4a** increased (Entries 2 and 3, Table 2). This illustrates that excess **4a** caused the coupling between **3a** and **4a** to proceed smoothly. In another Method (B), **3a** and **4a** were added first, and Et_3SiH was added after the imines were generated completely (after approximately 2.5 h). Compared with Method A, under this condition, imines were obtained without interference and were then hydrogenated. With Method B, the yield could reach 90%, and with increased dosage of **4a,** the yield increased to 94%. However, when the ratio increased from 1:1.25 to 1:1.5, the yield did not increase significantly.

Table 2. Synthesis of N-(4-methoxybenzyl)aniline from aniline and 4-anisaldehyde.



Entry	Ratio (**3a** : **4a**)	Method	Time/h	Yield/%
1	1 : 1	A	5	64
2	1 : 1.25	A	5	91
3	1 : 1.5	A	5	92
4	1 : 1	B	6	90
5	1 : 1.25	B	6	94
6	1 : 1.5	B	6	94

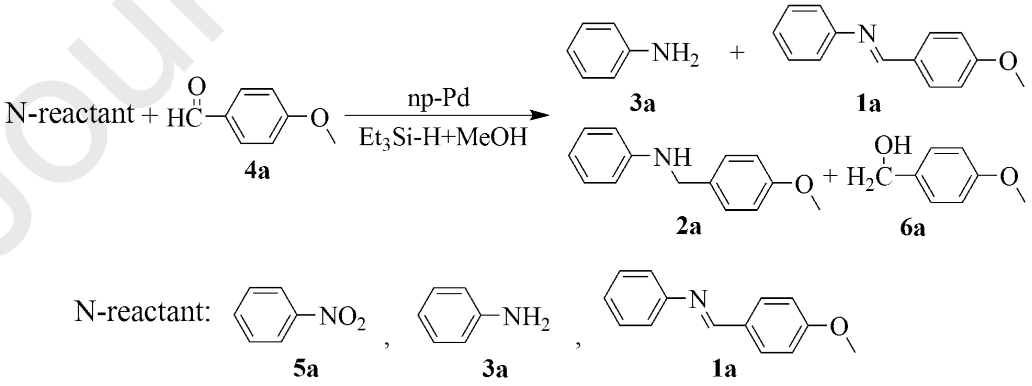
a) Reactions were performed using the catalyst (0.1 mmol), aniline (1.0 mmol), 4-anisaldehyde (1.0 mmol ~1.5 mmol), Et_3SiH (3.0 mmol), and MeOH (4.0 mL) at room temperature. In Method A, Et_3SiH was added simultaneously with other reactants; in Method B, Et_3SiH was added after 2.5 h.

Different aromatic amines and aromatic aldehydes (1:1.25) were then investigated as raw materials. As shown in Table S2, when substituted aromatic aldehydes (2-HO-, 4-CH_3-) were used, the reactions took place smoothly, and the yield of the corresponding N-alkylation amine was high. In particular, the yield from Method B was above 96% (Entries 2 and 4, Table S2). When aniline (**3a**) and benzaldehyde (**4d**) were used, the yields were 50% and 79% with Methods A and B, respectively (Entries 5 and 6, Table S2). The yield of substituted aromatic amine **3b** was low even with Method B (Entries 7 and 8, Table S2). Using the substituted aromatic aldehyde **4c** led to improved yields (Entries 9 and 10, Table S2). It is worth noting that the substituent group on the aromatic amine may have led to difficulties in the formation of the carbon-nitrogen double bond

(C=N) during the reaction.

On this basis, the synthesis of N-alkyl amines was carried out using nitroarenes as raw materials. When nitrobenzene (**5a**) and 4-anisaldehyde (**4a**) were added simultaneously, the yield of N-(4-methoxybenzyl)aniline (**2a**) was only 52% (Entry 1, Table 3). Although the conversion of nitrobenzene into aniline was close to 100%, 4-anisaldehyde was also reduced rapidly. After such reduction, the amount of **4a** that should react with **3a** to obtain imines would be low. The results showed that the catalyst had similar selectivity for nitro and aldehyde groups, thus the nitroarenes should be reduced primarily. The reduction of imine **1a** was tested with 4-anisaldehyde (**4a**). Although 4-anisaldehyde could be reduced, when **1a** was present, the main product was N-alkyl amines (Entry 2, Table 3). This result proved that the C=N bond was primarily reduced, while the reduction of C=O was inhibited in this system. When **3a** and **4a** were both present, the imine could be generated rapidly with excess **4a**. Although 4-anisaldehyde was reduced, **2a** was also obtained in high yield (Entry 2, Table 3). On these bases, when nitroarenes were used, Et_3SiH was added two separate times. The first was when nitroarenes were added to reduce $-NO_2$, and aromatic aldehydes were subsequently added to the system. The second was after imines appeared to reduce the N=C bond, and the target product was obtained. Under this condition, the yield of **2a** could reach 94% (Entry 4, Table 3).

Table 3. The reaction between 4-anisaldehyde and different reactant.



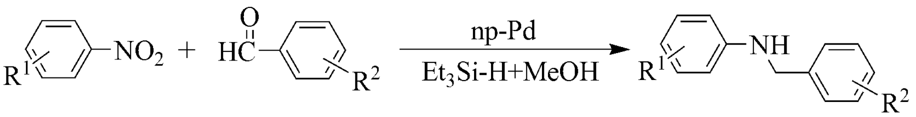
Entry	Reactant	Time/h	Yield of **3a** /%	Yield of **1a** /%	Yield of **2a** /%	Yield of **6a** /%
1	**5a**	6	39	9	52	50

2	**1a**	3	2	/	97	5
3	**3a**	5	/	4	91	20
4[b)]	**5a**	7	4	1	94	20

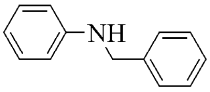
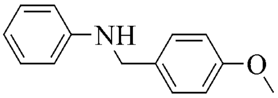
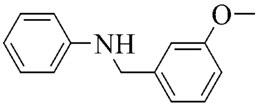
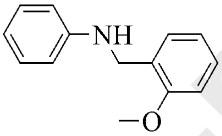
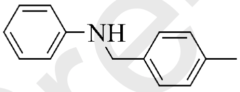
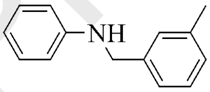
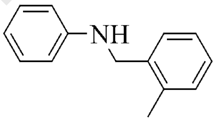
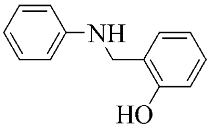
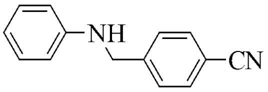
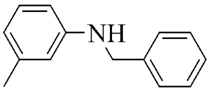
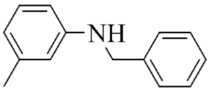
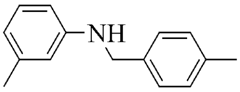
a) Reactions were performed using the catalyst (0.1 mmol), 4-anisaldehyde **4a** (1.25 mmol), MeOH (4.0 mL), N-reactant (1.0 mmol), Et_3SiH (8.0 mmol). b) **5a** (1.0 mmol) with Et_3SiH (5.0 mmol) for 2h, then **4a** (1.25 mmol) was added for 2 h. Lastly, Et_3SiH (3.0 mmol) was added again.

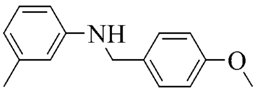
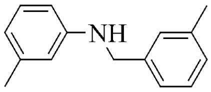
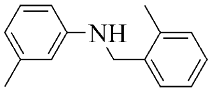
Different nitroarenes and aromatic aldehydes were used to synthesize N-alkyl amines under the condition that Et_3SiH was added twice. As shown in Table 5, a wide range of N-alkylation amines were obtained in high yields. No substituted nitrobenzene and benzaldehyde proceeded smoothly, and the yield of **2b** was similar to that when aniline was used (Entry 1, Table 4). Then, aromatic aldehydes with different substituents were tested, and not only electron-donating groups (methyl, methoxyl, and hydroxy) but also electron-withdrawing groups (nitrile) on aromatic aldehydes could achieve the reaction. For the reaction between 2-, 3-, and 4-anisaldehyde (the same substituent but different positions) and nitrobenzene, the yields were all above 85%. Moreover, 4-anisaldehyde (94%) showed the highest activity, and the yield of 3-anisaldehyde (85%) was lowest (Entries 2-4, Table 4). Similar results were obtained for 2-, 3-, and 4-tolualdehyde. For this reaction, 3-tolualdehyde showed the lowest activity, while 2-tolualdehyde had the highest yield (Entries 5-7, Table 4). When salicylaldehyde was used, the yield reached 92% (Entry 8, Table 4). For 4-cyanobenzaldehyde, the electron-withdrawing group did not affect the activity, and the unsaturated nitrile bond was not hydrogenated (Entry 9, Table 4). When substituted nitroarenes were reacted with the unsubstituted benzaldehyde, the yield was 48% (Entry 10, Table 4). However, increasing the ratio of benzaldehyde would lead to the yield reaching 70% (Entry 11, Table 4). The yield increased significantly when substituted nitroarenes were reacted with substituted benzaldehyde. Different aromatic aldehydes could make the reaction with substituted nitroarenes proceed smoothly (Entries 12-15, Table 4).

Table 4. Synthesis of N-alkyl amines from different nitroarenes and aromatic aldehydes.



5 **4** **2**

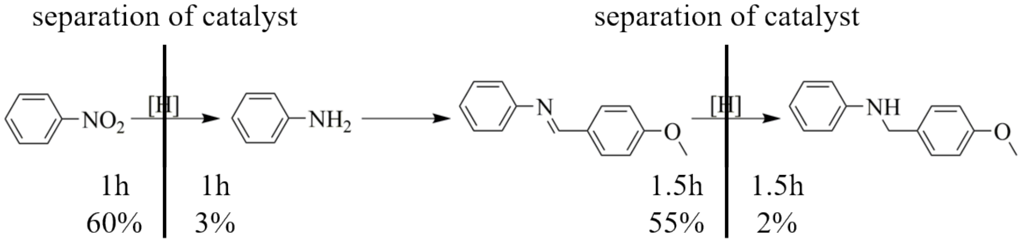
Entry	R^1	R^2	Product	Time/h	Yield/%
1	H-	H-		6	84
2	H-	4-CH_3O-		7	94
3	H-	3-CH_3O-		7	85
4	H-	2-CH_3O-		6	92
5	H-	4-CH_3-		6	92
6	H-	3-CH_3-		6	86
7	H-	2-CH_3-		5	95
8	H-	2-HO		5	92
9	H-	4-CN-		7	98
10	3-CH_3-	H-		5.5	48
11[b)]	3-CH_3-	H-		5.5	70
12	3-CH_3-	4-CH_3-		8	85

13	3-CH_3-	4-CH_3O-		8	89
14	3-CH_3-	3-CH_3-		8	78
15	3-CH_3-	2-CH_3-		8	80

a) Reactions were performed using the catalyst (0.1 mmol), nitroarenes **2** (1.0 mmol), Et_3SiH (5.0 mmol), and MeOH (4.0 mL) at room temperature for 2 h. Then aromatic aldehydes **4** (1.25 mmol) was added for 2 h. Lastly, Et_3SiH (3.0 mmol) was added again.

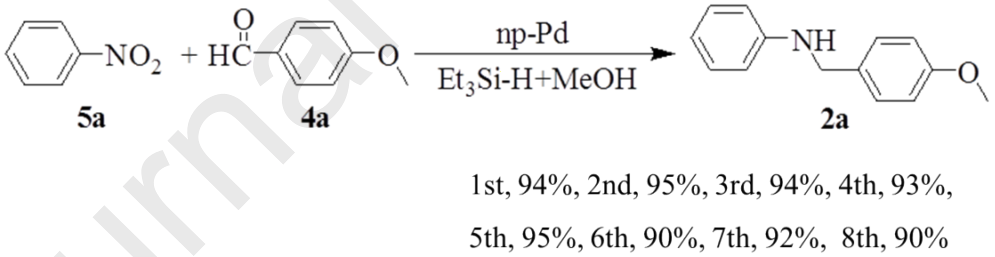
b) Aromatic aldehydes **4** (2.0 mmol) were added.

To explain the stability of np-Pd, we carried out the following experiments. In the reduction of nitrobenzene, after Et_3SiH was added to the reaction system for 1 h, the np-Pd was separated from the system by filtration. Furthermore, the conversion of nitrobenzene was measured to reach 60% by high performance liquid chromatography analysis (HPLC analysis). The filtrate remained without the catalyst for an additional 1 h, and further consumption of nitrobenzene amounted to 3%. The second experiment was conducted in another system; the reduction of nitrobenzene was completed, and N-(4-methoxybenzylidene)aniline was obtained. After Et_3SiH was added to the reaction system for 1.5 h, the catalyst was filtered from the reaction mixture. In this experiment, the yield of N-(4-methoxybenzyl)aniline (**2a**) was measured to be 55% by HPLC analysis. The filtrate remained without the catalyst for an additional 1.5 h, and further yield of N-(4-methoxybenzyl)aniline amounted to 2%. Then, the solution without the catalyst was analyzed by inductivity coupled plasma atomic emission spectroscopy (ICP-AES). The concentration of palladium in the filtrate was lower than the detection limit (< 0.02 ppm). According to a previous study [20], these results showed that the leaching of palladium was minimal, and the majority of the catalytic activity originated from the heterogeneous nanoporous palladium.



Scheme 2. Stability studies of nanoporous palladium.

The cycling experiment was used to further test the recycling capacity and reusability of the catalyst. The catalyst was separated by filtration after the reaction. After rinsing with acetone without other purification, the dried catalyst was reused. The catalyst could be reused at least eight times with the yield maintained above 90% (Scheme 3). As shown in Fig. 1b, although ligament size coarsened, the catalyst recovered after eight times of recycling also retained a three-dimensional bicontinuous nanoporous structure. To better understand the coarsening phenomenon, BET and BJH calculations were performed. The BET results showed that the specific surface area of the used catalyst was 25.4 m^2/g which was decreased slightly from 30.6 m^2/g. Moreover, the BJH results showed that the pore diameter was also approximately 5 nm (see ESI Fig. S2).



Scheme 3. Reusability studies of np-Pd. Reactions were performed using the catalyst (0.1 mmol), **5a** (1.0 mmol), Et_3SiH (5.0 mmol), and MeOH (4.0 mL) at room temperature for 2 h. Then, **4a** (1.25 mmol) was added for 2 h. Lastly, Et_3SiH (3.0 mmol) was added again.

In summary, the one-pot synthesis of N-alkyl amines was realized with nanoporous palladium as the sustainable catalyst and silane/alcohol as the hydrogen source. Imines, aromatic amines, and nitroarenes could be used as raw materials. A series of N-alkyl amines was obtained in considerable yield under mild conditions. Np-Pd could be reused at least eight times. The results described here provide further evidence that nanoporous Pd is a suitable choice to promote and develop a clean and efficient reaction. Further studies to extend the scope of the np-Pd catalytic hydrogen transfer system are in progress in our laboratory.

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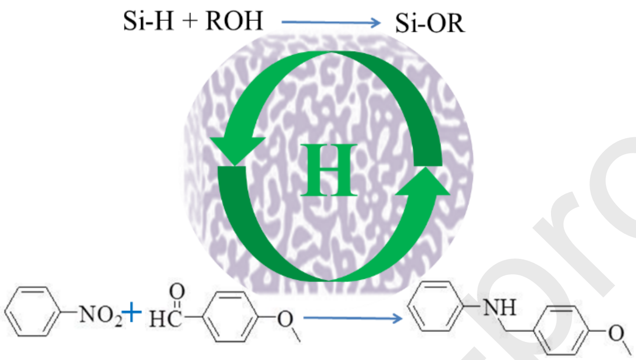
Highlights

Np-Pd/hydrosilanes/alcohol system was used for one-pot hydrogen transfer reaction.

One-pot synthesis N-alkyl amines was realized with green hydrogen source.

Stability, recycling capacity and reusability of catalyst was proved.



One-pot synthesis N-alkyl amines was realized by using nanoporous palladium as sustainable, heterogeneous catalyst and silane/alcohol as hydrogen source.

Keywords: Nanoporous palladium, Hydrogen transfer reaction, One-pot reaction, N-alkyl amines

Yang Cao: Data curation. Zhiwen Li: Conceptualization, Methodology, Investigation, Writing-Original draft preparation, Writing-Reviewing and Editing. Cao Hou: Investigation. Xiaoqun Cao: Project administration.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: