

# One-by-one hydrogenation, cross-coupling reaction, and Knoevenagel condensations catalyzed by PdCl<sub>2</sub> and the downstream palladium residue†

Cite this: DOI: 10.1039/c3gc40991k

Received 26th May 2013,  
Accepted 24th June 2013

DOI: 10.1039/c3gc40991k

www.rsc.org/greenchem

Hu Wang,<sup>a</sup> Li Li,<sup>a</sup> Xing-Feng Bai,<sup>a</sup> Wen-Hui Deng,<sup>a</sup> Zhan-Jiang Zheng,<sup>a</sup> Ke-Fang Yang<sup>\*a</sup> and Li-Wen Xu<sup>\*a,b</sup>

A novel catalyst-economic strategy with a recovered palladium catalyst was successfully applied for multi-task and maximum reuse in different types of one-by-one downstream reactions, from catalytic hydrogenation to Suzuki and Sonogashira-type cross-coupling reactions, Knoevenagel condensations, and *trans*-Knoevenagel-like condensations.

Over the past decades there has been an increased emphasis on the development of novel strategies for environmentally benign chemical processes and green chemistry.<sup>1</sup> Especially for catalytic processes, one important and practical aspect of research towards more sustainable and green processes is the development of one-pot, recyclable or multi-task catalysts that provide high selectivity and activity in various chemical reactions.<sup>2</sup> However, it is a challenge to retain or raise their selectivities and activities after several cycles. The decrease of the catalytic activity of recovered catalysts is unavoidable in many cases.<sup>3</sup> The synthetic application of the resulted deactivated metal catalyst should be considered as an alternative and urgent topic in sustainable synthetic chemistry. To the best of our knowledge, there are few examples focused on the multi-task and maximum reuse of a deactivated metal catalyst in different downstream reactions,<sup>4</sup> which would be a novel strategy or concept for catalyst-economic processes and sustainable chemistry.<sup>5</sup>

Regarding the maximum utilization of the deactivated catalyst, the concepts of recycling and multi-task reuse of transition-metal-based catalysts for various reactions would provide many advantages, such as energy economy and being waste-free. Now for the first time we describe our efforts to advance sustainable synthetic methods by designing a novel

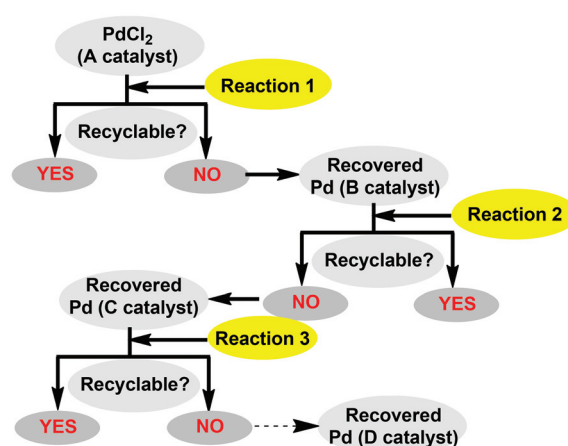


Fig. 1 Multi-task and maximum reuse of recovered catalyst in different types of downstream reactions.

catalyst-economic strategy with recovered palladium catalyst for multi-task and maximum reuse in different types of downstream reactions, from catalytic hydrogenation to cross-coupling reactions and Knoevenagel condensations (Fig. 1), which are synthetically useful transformations in organic chemistry.

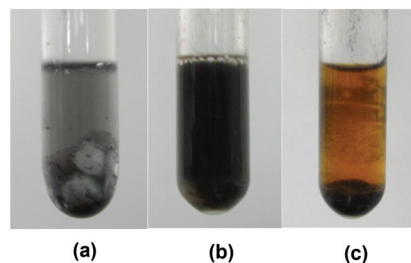
Initially, we hypothesized that a Pd catalyst immobilized on soluble cross-linked polysiloxane, which is well recognized from environmental and economical points of view, could be easily separated from the product and reused. Although several encapsulated and cross-linked molecular catalysts in polysiloxane (PMHS) gels have been reported by several groups in the past years,<sup>6</sup> in which the self-encapsulated Pd, Ru and Pt catalysts exhibited excellent catalytic activity in hydrogenation, alkene isomerization, and atom-transfer radical cyclization, we found that a palladium catalyst encapsulated in small amounts of polysiloxane gel (PMHS) was not easily recycled for the next transformation. Nearly complete immobilization is absolutely necessary for the recovery of the catalyst for an economically viable process with expensive palladium catalysts. Therefore, the removal or reuse of the palladium@PMHS residue from the products is not an easy task in fact. We were

<sup>a</sup>Key Laboratory of Organosilicon Chemistry and Material Technology of Ministry of Education, Hangzhou Normal University, Hangzhou 310012, P. R. China.  
E-mail: liwenxu@hznu.edu.cn; Fax: +86 2886 5135; Tel: +86 2886 5135

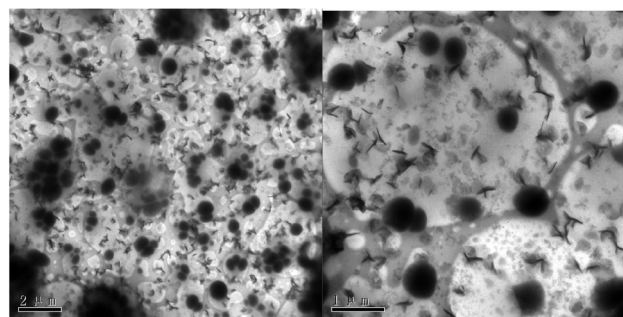
<sup>b</sup>State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, P. R. China.  
E-mail: licpxuhw@yahoo.com

†Electronic supplementary information (ESI) available. See DOI: 10.1039/c3gc40991k

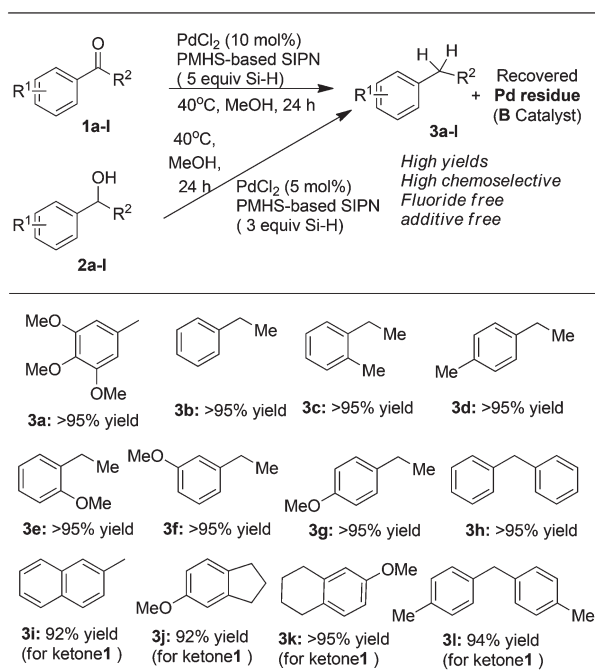
interested in the usage of PMHS-based semi-interpenetrating network (PMHS-SIPN) for the support of palladium, which would guarantee the success of recycling and reusing the palladium catalyst in downstream reactions. The semi-interpenetrating networks (SIPNs) of polymethylhydrosiloxane (PMHS) and polyacrylate (PA) is a white solid containing a lot of reactive Si-H moieties and it is prepared *via* the cobalt-catalyzed polymerization of acrylates under mild conditions, in which cobalt acetate ( $\text{Co}(\text{OAc})_2$ ) is utilized as an effective catalyst in the presence of *p*-toluenesulfonic acid ( $\text{TsOH}$ ) for the cross-linking reaction (see ESI†).<sup>7</sup> Inspired by previous work on the palladium-catalyzed deoxygenated reduction of aromatic ketones in the presence of PMHS,<sup>8</sup> we utilized this reduction reaction to encapsulate  $\text{PdCl}_2$  in the PMHS-based semi-interpenetrating networks (PMHS-SIPNs). In fact, as well as the development of a novel strategy for the immobilization of the Pd catalyst, a synthetically useful fluoride-free deoxygenation reaction of aromatic ketones and benzyl alcohols was also established. Both reactions were performed under optimized conditions (at 40 °C, in MeOH, with suitable amounts of  $\text{PdCl}_2$  catalyst and PMHS-SIPN) to ensure complete conversion. As shown in Scheme 1, both aromatic ketones and benzyl alcohols were transferred to the corresponding alkanes in excellent yields.<sup>9</sup> Notably, the selectivities and isolated yields of all these substrates shown in Scheme 1 were excellent in terms of the desired alkane products, in which no alcohol intermediate was detected for these ketone substrates. Therefore, the one-pot preparation of Pd@silicone-based SIPNs (Fig. 2 and 3) combined with the high yield synthesis of alkanes in the deoxygenated reduction finished simultaneously, which not only makes it an attractive and practical alternative to the previous



**Fig. 2** The desired supported palladium residue formed at the end of the deoxygenated reduction: (a) 1 min; (b) after 1 h; (c) after 24 h.



**Fig. 3** TEM images of the recovered palladium catalyst embedded in the silicone-based SIPN (**B** catalyst) at the end of the deoxygenated reduction.

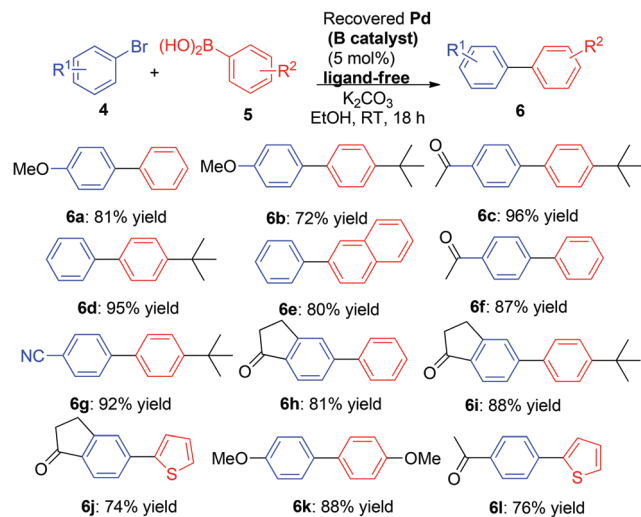


**Scheme 1**  $\text{PdCl}_2$  (**A** catalyst)-catalyzed deoxygenated reduction of aromatic ketones or benzylic alcohols.

process of utilizing aryl chlorides as additives and large amounts of KF as an activator of the PMHS, but also leads to the successful immobilization of the palladium residue without loss of catalyst after the reaction. Notably, the resulting palladium residue is a jelly-like solid not soluble in general solvents, such as methanol, chloroform, *etc.*<sup>9b</sup> Consequently, for the next transformations, the use of this palladium catalyst embedded in the silicone-based material is required. Thus, to utilize the recovered palladium catalyst embedded in the silicone-based SIPNs (**B** catalyst), the development of various palladium-catalyzed transformations, with the exception of reductions, is highly desirable.

The palladium-catalyzed Suzuki reaction is the most important and efficient strategy for the construction of unsymmetric biaryl compounds. Numerous strategies with palladium catalyst systems have been designed to promote the highly practical Suzuki cross-coupling reaction.<sup>10</sup> Inspired by these results, we wished to investigate the catalytic activity of the recovered palladium in ligand-free Suzuki cross coupling reactions.

Fortunately, on the basis of numerous screening experiments, we found that the cross coupling reaction of bromobenzene and 4-*tert*-butylphenylboronic acid took place smoothly in ethanol at room temperature to give the biaryl compound **6d** in excellent yield (95%). Under the same conditions (5 mol% of Pd), the Suzuki reaction of different aryl bromides and boronic acids was studied using the recovered palladium-catalyst. As shown in Scheme 2, the cross-coupling reactions using aryl bromides that have a methoxyl, carbonyl, and cyanide group proceeded smoothly under these conditions, exhibiting a wide functional group tolerance. Thus,



**Scheme 2** Suzuki reaction in the absence of ligand using the recovered palladium-catalyst (**B** catalyst).

the present palladium catalyst system was proved to be useful in Suzuki cross-coupling reactions, which also provides a simple method for Suzuki cross-coupling reactions of aryl bromides at room temperature.

During the course of this work, and to gain insight into the multi-task application of the recovered palladium catalyst, we also wanted to examine the palladium-catalyzed Sonogashira coupling reaction due to its importance in organic synthesis.<sup>11</sup> Traditionally, the Sonogashira reactions were promoted by both palladium and copper catalysts, thus it was necessary to develop a copper-free and mild process for the synthesis of alkynes. Encouraged by the above findings in the Suzuki cross-coupling reaction, we sought to ascertain whether the recovered palladium catalyst could also be utilized in the Sonogashira reaction in the absence of copper salts. We then determined the reaction conditions in the palladium-catalyzed Sonogashira reaction. Under the general conditions (5 mol% Pd catalyst, 2 equiv. of  $K_2CO_3$ , in EtOH, at 60 °C), the cross coupling reaction of 1-chloro-4-iodobenzene and 1-ethynylbenzene was first explored using the same recovered palladium residue (**B** catalyst) generated from the previous reduction as the catalyst. Interestingly, this Sonogashira coupling reaction was completed easily, and an excellent yield of the desired diaryl alkyne (**9d**) was obtained (92%). The recovered palladium catalyst could be reused three times (entries 1–3, Table 1). However, the next study on the scope of the palladium-catalyzed Sonogashira reaction with various alkynes and substituted iodobenzenes met serious problems.

Under copper-free conditions in water or ethanol, most of the alkynes did not react with the substituted iodobenzenes and this palladium-catalyzed Sonogashira reaction resulted in poor yields in most cases (<10% GC conversion, entries 4–7 of Table 1). Fortunately, the observation that the Sonogashira reaction of 1-chloro-4-iodobenzene with various terminal alkynes was complete into the corresponding diaryl alkynes in high yields, prompted us to investigate the effect of the

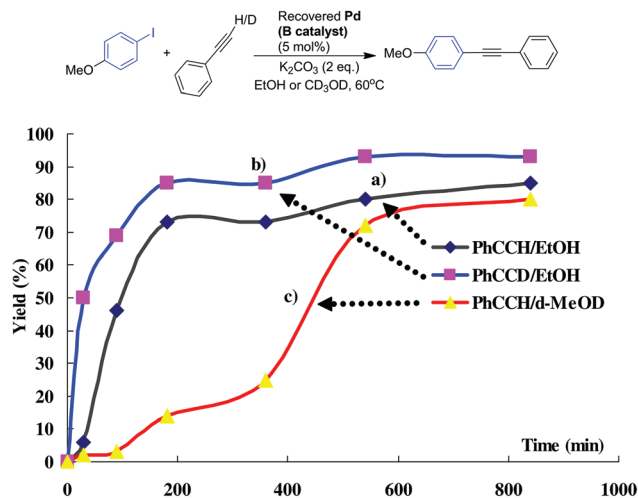
**Table 1** Recovered palladium (**B**) catalyzed Sonogashira reaction: Optimization of reaction conditions

Entry	R <sup>1</sup>	Solvent	Additive (10 mol%)	Yield <sup>a</sup> (%)
1	<i>p</i> -Cl	EtOH	None	92
2	<i>p</i> -Cl	EtOH	None	77 <sup>b</sup>
3	<i>p</i> -Cl	EtOH	None	49 <sup>c</sup>
4	<i>p</i> -OMe	H <sub>2</sub> O	None	Trace
5	<i>p</i> -OMe	EtOH	None	Trace
6	<i>p</i> -F	EtOH	None	Trace
7	H	EtOH	None	Trace
8	<i>p</i> -F	EtOH	PhCl	87
9	<i>p</i> -OMe	EtOH	PhCl	92
10	H	EtOH	PhCl	88
11 <sup>d</sup>	H	EtOH	—	72 (22) <sup>f</sup>
12 <sup>d</sup>	H	EtOH	PhCl	16 (84) <sup>f</sup>
13 <sup>e</sup>	H	EtOH	—	26 (74) <sup>f</sup>
14 <sup>e</sup>	H	EtOH	PhCl	12 (84) <sup>f</sup>
15	H	Toluene	PhCl	18
16	<i>p</i> -OMe	EtOH	PhCl <sup>g</sup>	92
17	<i>p</i> -OMe	EtOH	PhCl <sup>h</sup>	96

<sup>a</sup> Isolated yield. Trace refers to <10% GC yield. <sup>b</sup> The recovered Pd (**B**) catalyst was recycled and reused in the second cycle. <sup>c</sup> The recovered Pd (**B**) catalyst was recycled and reused in the third cycle. <sup>d</sup> The palladium catalyst was PdCl<sub>2</sub> without any support. <sup>e</sup> The palladium catalyst was Pd(OAc)<sub>2</sub> without any support. <sup>f</sup> Byproduct 1,1,2-triphenylethene was detected and the yield is given in parentheses. <sup>g</sup> 5 mol% PhCl was used. <sup>h</sup> 50 mol% PhCl was used.

chloride group in this cross-coupling reaction. Thus we hypothesized that the chloride group on the aromatic ring of substrate **7** may play an important role in the acceleration of the copper-free Sonogashira coupling reaction. To gain further insight into the requirements for the chloro-group, we examined the palladium-catalyzed Sonogashira reaction in the presence of 10 mol% of chlorobenzene. Surprisingly, we found that the Sonogashira coupling reaction of chloro-free aryl halides or terminal alkynes proceeded smoothly in high yields (Table 1, entries 8–10, 87–92% yield). Thus, we focused on the effect of chlorobenzene on the catalytic activity of other palladium catalysts. As shown in Table 1 (entries 11–14), the addition of PhCl improved the catalytic activity of PdCl<sub>2</sub> and Pd(OAc)<sub>2</sub> largely, and the next arylation of the Sonogashira product (1,2-diphenylethyne) occurred smoothly to give 1,1,2-triphenylethene as the major product. There are no obvious differences with low or large amounts of PhCl (Table 1, entries 16 and 17) because both 5 mol% and 50 mol% gave excellent yields (92% and 96% yield respectively).

Notably, the importance of methanol and ethanol was revealed by the solvent effect; the use of toluene resulted in poor conversions and the reaction rate showed the accelerating effect of ethanol (Fig. 4). Hence, we hypothesized that the addition of PhCl would be beneficial to the promotion of the catalytic cycle of Pd(0) with oxidative addition–reductive elimination. Although the true mechanism is unclear at present, we suggest that the enhancement of the catalytic activity in the

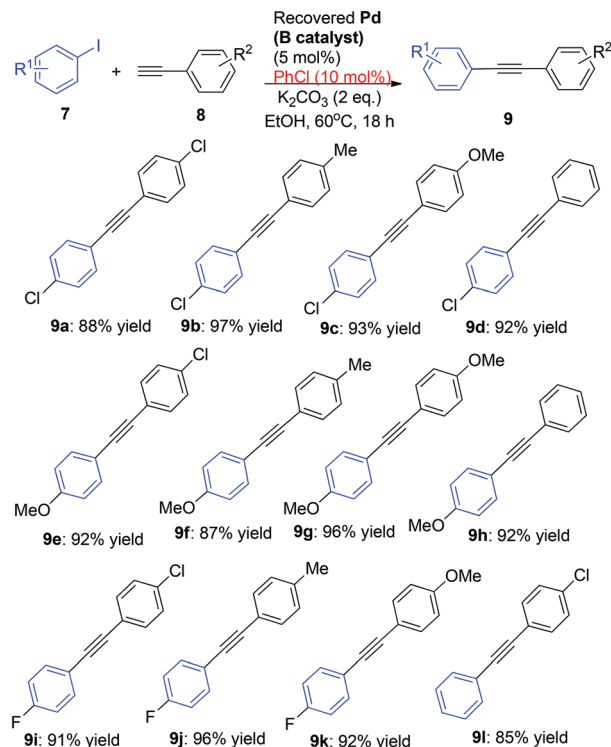


**Fig. 4** Plot of yield versus time (min) showing the different reaction rates in the PhCl-activated Sonogashira reaction of 1-iodo-4-methoxybenzene with (a) 1-ethynylbenzene (◆) in EtOH; (b) deuterium-modified 1-ethynylbenzene (PhCCD, ■) in EtOH; (c) 1-ethynylbenzene (▲) in d-MeOD.

palladium-catalyzed Sonogashira reaction may be due to the formation of an activated chloropalladium species derived from the oxidative addition of palladium to chlorobenzene.<sup>12</sup> Although the halide effects in transition metal catalysis have been studied in oxidations and reductions,<sup>13</sup> to the best of our knowledge, there is no report of chlorobenzene serving as a catalyst activator in the palladium-mediated Sonogashira cross-coupling reaction.

The general applicability of the present Sonogashira reaction using the recovered palladium-catalyst was demonstrated by expanding it to different alkynes and substituted iodobenzenes. As illustrated in Scheme 3, the palladium-catalyzed Sonogashira reaction of various substrates gave the desired diaryl alkynes in excellent isolated yields in the absence of ligand and copper salts. These results are particularly interesting and useful in view of the fact that the recovered palladium could be applied in the synthesis of conjugated diaryl alkynes and diaryls *via* a simple ligand-free and copper-free Sonogashira reaction under mild conditions, as well as the Suzuki cross-coupling reaction. Notably, no byproducts, such as triarylethenes, were detected in this reaction under the optimized conditions, thus it could be regarded as a clean and environmentally benign C–C bond formation reaction because of the easy separation of the catalyst and the one-pot reaction without additives and side-products.

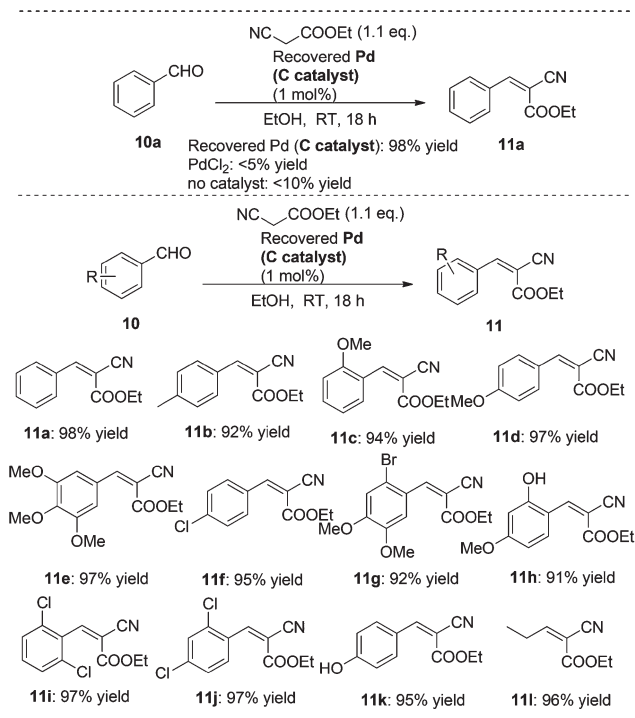
After the Suzuki and the Sonogashira reactions, the palladium residue can be separated by simple filtration and washed with water.<sup>14</sup> Although the recovered palladium residue (C catalyst)<sup>15</sup> can be recycled several times in the Sonogashira reaction, we were interested in the down-stream processing of palladium black. Regarding the basic conditions in the upstream Suzuki or Sonogashira reactions and the poor catalytic activity of the recovered palladium (C catalyst) in the Suzuki reaction, we next turned our attention to the Knoevenagel condensation of aldehydes and active methylenes, which is a



**Scheme 3** Recovered palladium (B catalyst)-catalyzed Sonogashira reaction in the absence of ligand and copper salts.

powerful and frequently used reaction for the formation of carbon–carbon double bonds.<sup>16</sup> Under our optimized conditions, only 1 mol% of palladium residue (C catalyst) could promote the Knoevenagel condensation of various aldehydes and ethyl 2-cyanoacetate successfully with complete conversion at room temperature (Scheme 4).

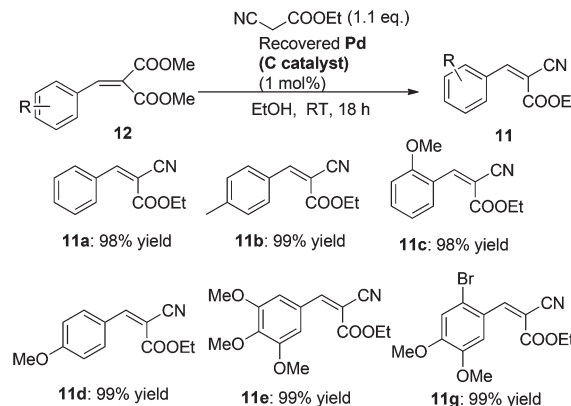
On the basis of the experimental results and the EDS spectra of the recovered palladium residue (C catalyst), the encapsulated palladium and potassium salt on the silicone material was found to be the true catalyst in this reaction. In the controlled experiment, the use of PdCl<sub>2</sub> as catalyst without a base resulted in almost no conversion in the Knoevenagel condensation of benzaldehyde and ethyl 2-cyanoacetate. And the use of catalytic amounts of K<sub>2</sub>CO<sub>3</sub> (10 mol%) as a base catalyst led to only a moderate yield (70%) under similar reaction conditions. Interestingly, the addition of a catalytic amount of K<sub>2</sub>CO<sub>3</sub> (10 mol%) as well as 1 mol% of PdCl<sub>2</sub> gave the desired product in excellent yield (95%). All these experimental results revealed that the support of semi-interpenetrating networks (SIPNs) with cross-linked organosilicon material and polyacrylate (PA) had been changed completely after the palladium-catalyzed cross-coupling reaction, including the Suzuki and Sonogashira reactions. The hydrolysis of the ester group of polyacrylate (PA) with basic K<sub>2</sub>CO<sub>3</sub> could possibly occur to form the supported potassium salt (see IR spectra in ESI†). Thus, the organosilicon and polyacrylate-containing supported potassium and palladium material is a cooperative catalyst in the Knoevenagel reaction and the Knoevenagel-type



**Scheme 4** Recovered palladium (C catalyst)-catalyzed Knoevenagel condensation in the absence of base.

condensation. Also, it is not excluded that some unidentified effect of traces of potassium carbonate played an important role in keeping the high catalytic activity. As shown in Scheme 4, we have established that the recovered palladium residue (C catalyst) could be applied to mediate Knoevenagel condensations in excellent yields. Notably, it turned out that catalyst recycling could be carried out for at least ten consecutive experiments under the same reaction conditions (see ESI<sup>†</sup>), which allows the reuse of the recovered palladium (C catalyst) in certain transformations to be possible. Our work also shows that the concept of multi-task and maximum reuse of the recovered catalyst in different types of downstream reactions can be a valuable tool for environmentally benign chemical processes and waste-free green chemistry. Thus, it provides economic potential for the technical and comprehensive application of expensive and supported palladium catalysis.

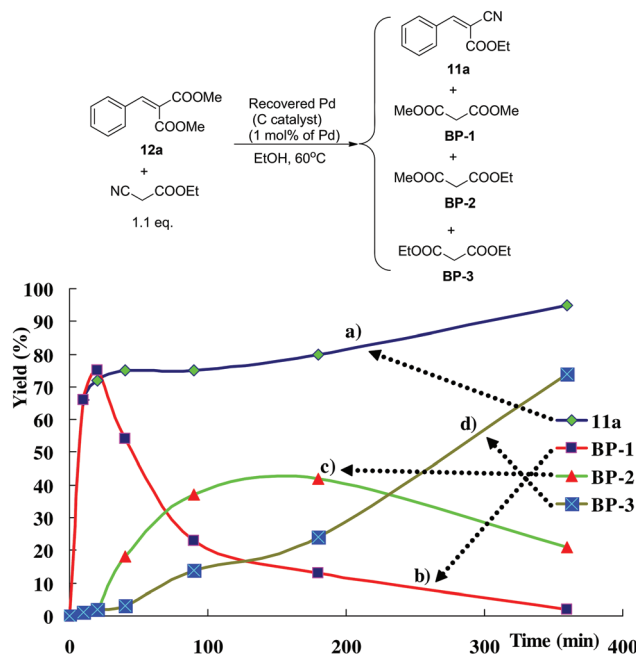
During the study of the palladium residue (C catalyst)-catalyzed Knoevenagel condensation of aldehydes and active methylenes, we found that dimethyl 2-benzylidenemalonate (12a) could be converted to benzaldehyde and dimethyl malonate in the presence of the palladium residue (C catalyst) under the Knoevenagel reaction conditions. Unexpectedly, we found that an interesting Knoevenagel-like transformation occurred in the reaction of dimethyl 2-benzylidenemalonate (12a) and ethyl 2-cyanoacetate, which resulted in the corresponding product 11a, an  $\alpha,\beta$ -unsaturated carbonyl compound, in excellent yields (Scheme 5). Similarly to *trans*-esterification, this Knoevenagel-like or *trans*-Knoevenagel transformation provided an interesting exchange of functional groups. We



**Scheme 5** Recovered palladium (C catalyst)-catalyzed Knoevenagel-like condensation.

have also found the recovered palladium catalyst residue (C catalyst) in this *trans*-Knoevenagel reaction can play a dual role because of the *trans*-esterification of dimethyl malonate with EtOH (solvent). As shown in Fig. 5, we determined the yield of all side-products (BP-1, 2, 3) as well as the desired product 11a, which showed that the *trans*-esterification of dimethyl malonate led to the formation of ethyl methyl malonate and diethyl malonate invariably. On the other hand, the reaction of the *trans*-Knoevenagel-like condensation should occur similarly to the mechanistic procedure of the *trans*-esterification as both reactions required the use of EtOH.

In summary, we have developed a sustainable and catalyst-economic concept for the multi-task and maximum reuse of



**Fig. 5** Plot of yield versus time (min) showing the different reaction rates in the *trans*-Knoevenagel transformation of dimethyl 2-benzylidenemalonate with ethyl 2-cyanoacetate: (a) the desired product 11a (◆); (b) dimethyl malonate (BP-1, ■); (c) ethyl methyl malonate (BP-2, ▲); (d) diethyl malonate (BP-3, ▣).

recovered palladium catalyst in different types of downstream reactions (Fig. 1). This has been the first systematic investigation focused on the multi-task and comprehensive utilization of limited and recovered transition metal catalyst, which provide a novel and environmental benign strategy for the reuse of deactivated catalyst. Especially, it was shown that all the model transformations with palladium as the catalyst, from simple PdCl<sub>2</sub> to the recovered palladium residue, were carried out successfully under exceptionally mild conditions. On top of the advantages of multi-task and maximum reutilization of expensive palladium catalysts, the corresponding new palladium catalyst systems in related reactions provide the following merits: (i) a simple and high-yield method for the deoxygenated reduction of aromatic ketones or benzylic alcohols with the solid, reactive, and functional hydrosilane (Si-H)-containing material; (ii) a ligand-free and simple Suzuki process for the synthesis of diaryls; (iii) a copper-free and ligand-free Sonogashira coupling of aryl halides and terminal alkynes; (iv) the first example of chlorobenzene serving as an activating additive in Pd-mediated cross-coupling reactions; and (v) an efficient Knoevenagel condensation and Knoevenagel-like or *trans*-condensation were demonstrated with the reused palladium residue. In addition, all these reactions could be carried out in environmentally friendly ethanol. More importantly, we have developed various procedures for the preparation of alkanes, diaryls, aryl alkynes, and  $\alpha,\beta$ -unsaturated carbonyl compounds respectively under mild conditions with a single palladium catalyst. In view of the established utility of the recovered palladium in various downstream reactions, we anticipate that this concept of multi-task and maximum reuse catalysis (MTMRC) of expensive metal catalyst as well as related catalysts and reactions will find wide application and offer the possibility for the development of synthetic applications of waste or deactivated transition metal catalysts for organic transformations.

The authors gratefully thank the financial support of the National Natural Science Foundation of China (NSFC, no. 51203037 and 21173064), Zhejiang Provincial Natural Science Foundation of China (Q12B020037), and Program for Excellent Young Teachers in Hangzhou Normal University (HNUEYT, JTAS 2011-01-014).

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- (a) The isolated yields given in this scheme are the average value of three runs, and the yields of the reduction reaction with ketones provided in Scheme 1 are the same as those of alcohols. There is no difference between the two types of substrates (b) The amount of palladium in the silicone-based IPN material before and after the reaction was determined by graphite furnace atomic absorption spectrometry. It was found that there are no obvious differences

- on the amount of palladium before and after reaction (1.74%). The SEM picture and XPS of the palladium@silicone-based PN material have been provided in the ESI.†
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