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Mizoroki–Heck reaction over palladium nanoparticles supported on WO_3

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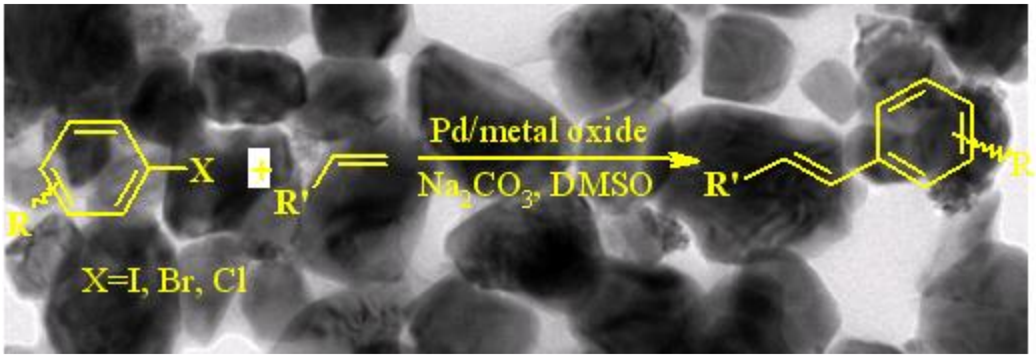
Graphical abstract



Highlights

1) Palladium nanoparticles supported on WO_3 were synthesized.

2) Excellent yield has been achieved.

3) Recoverability and reusability of catalysts were studied.

Abstract

Palladium nanoparticles supported on metal oxide WO_3were synthesized and the physicochemical properties of compounds were characterized by X-ray diffraction (XRD), X-ray absorption near edge spectroscopy (XANES) at O and Pd K-edges, energy dispersive X-ray analysis (EDX), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The catalytic activity of compounds in the carbon–carbon coupling reactions of aryl halides with olefins (Mizoroki–Heck reaction) was studied. The catalyst can be easily separated from the reaction mixture and reused after washing without reduction in activity.

***Keywords**:* nanostructures; chemical synthesis; X-ray diffraction; transmission electron microscopy (TEM); catalytic properties

1. Introduction

Mizoroki–Heck reactions as an efficient method for carbon–carbon bond formation are one of the most useful transformations in organic synthesis that tolerates various functional groups, such as ketones, esters, amides, ethers or heterocyclic rings [1-5]. Heck coupling reactions are generally catalysed by soluble palladium (Pd) complexes containing various ligands in organic solvents and, more recently, as well as in aqueous media [6-12]. Many of these homogeneous catalytic processes, which are the first choice of chemists because of their high activity and selectivity, however these are not easy to handle, difficult to separate, and have limited reuse potential often due to contamination with final products or formation of metal-complexes [13-16]. Catalyst separation and reusability are a critically important issue for the sustainable development of any catalytic process [17, 18].Therefore, heterogeneous catalysis is gaining increasing importance in the production of fine chemicals and pharmaceuticals and in chemical technology due to its definite technical advantages, namely production processes, competitiveness and economy. To enhance the reusability of catalysts, the nano-Pd catalysts are commonly immobilized onto inorganic or organic supports [19-27]. This type of catalysis provides high reaction rate and high turnover numbers (TON) and often affords high selectivities and yields. In these reactions, activity mainly depends on the nature of the support used for the reaction [28]. From earlier works the support is known to affect the electronic density at the surface of palladium and their catalytic properties for Heck reactions [28]. Augustine and O'Leary took into consideration a number of oxide-based catalysts and found that support effects are observed only in the coupling of 4-nitrobenzoylchloride that was relatively slow over Pd/MgO in comparison with both Pd/SiO_2 and Pd/Al_2O_3 [29, 30].

The present work focuses on the model reaction of bromobenzene with styrene catalysed by palladium nanoparticles supported on WO_3 as a support. The palladium nanoparticles supported on WO_3 was prepared and various analytical methods such as. XRD, XANES, SEM, EDX and TEM were utilized to characterize the nanoparticles.

2. Experimental details

2.1. Materials

Chemicals and solvents were purchased from Merck and Fluka and used without further purification. WO_3 nanoparticles were synthesized according to our previous published procedure [31].

2.2. Synthesis of supported palladium nanoparticles

Supported palladium nanoparticles were prepared by an impregnation method using $Pd(OAc)_2$ as a source for Pd. The required amount of $Pd(OAc)_2$, to give 5wt% Pd loading, was mixed and was pulverized with support. Methanol (20 mL) was added to the mixture of $Pd(OAc)_2$ and support. This mixture was mechanically stirred to ensure the homogeneous distribution of $Pd(OAc)_2$ over the supports. After stirring, CH_3OH was evaporated under vacuum using a rotary evaporator. After impregnation, Pd(0) nanoparticles were obtained by reduction of the Pd(II)/WO_3 with hydrazine hydrate.

2.3. General Procedures for the Heck Reaction

A flask was charged with 0.003g of catalyst along with an appropriate amount of aryl halide (1.0 mmol), olefin (1.1 mmol), Na_2CO_3 (2.0mmol), and DMSO (2 mL) and a magnetic stir bar. The mixture was heated to 120°C with stirring for a specified period of time. After the reaction mixture was cooled to room temperature, H_2O (5 mL) was added and the product was extracted with diethyl ether (2×10 mL). The aqueous solution was separated from the organic layer. The diethyl ether solution was dried over $CaCl_2$, and evaporated to dryness under reduced pressure to afford the desired product, which was then washed with hexane (3×5 mL). The purity of the compounds was checked by GC and NMR and yields are based on the aryl halide.

3. Results and Discussion

3.1. Catalyst characterization

XRD patterns were recorded for WO_3 and supported palladium nanoparticles to determine structure and phase formation of Pd nanoparticles supported on WO_3 (Fig. 1). The XRD patterns of the Pd/WO_3 showed only peaks of WO3 support (monoclinic) [31]. No peaks attributed to Pd were observed in the pattern of catalyst. Also no characteristic peaks of impurities for both WO_3 and Pd/WO_3 are detected in the patterns demonstrating that the samples have high phase purity.

XANES spectra are just a finger print for a specific molecule and hence a powerful tool to investigate the electronic structure of a material. According to the dipole selection rule, the O K-edge spectra are due to transitions from atomic-like 1*s* state to unoccupied bound and free states with *p*-character, which experience some relaxation in the presence of the 1*s* core-hole positive charge. The O K-edge spectra reflect also the shape of the density of metal *d*-states, due to a hybridisation between the metal *d* and oxygen 2*p* orbitals. The normalised oxygen K-edge XANES of compounds are shown in Fig. 2. The O K-edge XANES patterns of the WO_3 and sample containing palladium nanoparticles supported on WO_3 showed clear peaks of WO_3 support (monoclinic). The results of XANES data analysis are in agreement with those reported previously [32, 33]. Despite some changes in intensity of peaks, no shift in the position of the absorption edge was observed for WO_3 and supported palladium nanoparticles. These results show that Pd-nanoparticles are only supported on WO_3 and matrix of it remains same.

The information about the surface of WO_3 and sample containing palladium nanoparticles supported on WO_3 was obtained by the scanning electron microscopy (SEM) image as presented in Fig.3. The SEM image shows particles with diameters in the range of nanometers.

Transmission electron microscopy (TEM) images of the catalysts show that Pd nanoparticles are formed and dispersed on the WO_3 with a size about 50-100 nm (Fig. 4).

3.2. Catalytic effects

Initially, the reaction of bromobenzene with styrene was chosen as a model reaction in the presence of Pd/WO_3 catalyst. All reactions were performed under air without any additive. Results are summarized in Table 1. In order to understand the effect of catalyst amount on the catalytic reactivity, the first, catalyst screening of the reaction was carried out. When the amount of Pd/WO_3 catalyst was increased from 0.001 to 0.005g, the yield of product increased drastically from 49 to 68% (entries 1–5). With a further increase of catalyst to 0.006 g, the yield of *trans*-stilbene remains almost constant (entry 6). Because of lower amount of Pd loading, we chose 0.005 g of Pd/WO_3catalyst for further experiments. Then effects of various bases and solvents were investigated (entries7–17). It appeared that $Na_2CO_3$and K_2CO_3gave better results than any other bases with 68% and 65% of yields, respectively. In case of solvents, using DMSO as a solvent provided excellent results. As shown in table 1 (entry 18), the catalytic activity of the system decreased dramatically when Pd/WO_3 was replaced by WO_3 support.

Although the temperature-dependent curves in Fig. 5a confirm very low *trans*-stilbene yield in low temperatures (r.t.-60 °C), a significant growth in the product yield is observed at higher temperatures. Moreover performing the reaction at 100°C caused lower conversions than120 °C. Also, with an increase in the reaction time from 1 to 5h, the yield of *trans*-stilbene shows a significant increase from 54 to 70%. Further increase of the reaction time to 6h shows no effect on the yield of *trans*-stilbene (Fig. 5b).

On the basis of the optimized reaction conditions, the coupling reactions between a range of aryl halides and olefins were carried out in the presence of palladium nanoparticles supported on

WO3, Na_2CO_3 as a base, and DMSO as a solvent at 120°C. As shown in Table 2, aryl iodides with a variety of electron-rich and electron-poor substituent proceeded smoothly, giving the coupling products in good to excellent yields. The reactivity of aryliodides with electron-withdrawing substituent was higher than those with electron donating substituent. Furthermore, steric hindrance due to the ortho substituents on the aryliodides affected the reaction progress and therefore aryliodides substituted with methoxy group at ortho position were less reactive to the coupling reaction than the para derivative.

It is worth noting that the most electron-poor aryl bromide, 4-acetylbromobenzene, showed a good reactivity and was successfully coupled with olefins in good to excellent yields (entries 9-12). However, the Heck coupling of bromobenzene due to the strong C-Br bond compared to C-I bond was rather difficult to proceed under the same reaction conditions (entries 13-16).

In final, a further set of experiments were carried out to check the reusability of the Pd/WO_3 for the Heck reaction at 120 °C for 5 h. For each recycle, the catalyst was recovered from reaction mixture by filtration, washed 2-3 times with distilled water and ethyl ether repeatedly, dried at 50 °C for half an hour, and reused for the next run. As shown in Fig. 7, yield slightly decreased due to the loss of catalyst activity after the catalyst was reused four times, which might be caused by catalyst agglomeration in the catalytic process.

By comparing of the SEM images of the fresh and recycled Pd/WO_3 catalyst, it was found that the recycled catalyst show signs of support agglomeration after repeated of the Heck reaction (Fig. 8a). Also the comparison of the XANES patterns of the fresh and reused catalyst signifies that some structural changes have occurred in the reused catalyst. The first intense peak at 531 eV in the O K-edge spectrum of fresh Pd/WO_3 is related to oxygen $2p$(O) states in the $5d(t_{2g})$ conduction band due to $5d(t_{2g})$(TM)–2p(O) interaction. XANES spectra for used Pd/WO_3 are modified and shifted for main-peak/edge, which indicating a change in the WO_3 matrix (Fig. 8b). To further confirm the electronic structure of Pd-supported WO_3, XANES measurement at Pd K-edge is performed as shown in Figure 8(c) for fresh and used Pd/WO3.The line shapes of the normalized NEXAFS indicate that Pd in the fresh catalyst is totally metallic while the used catalyst is mixed state of Pd metallic and Pd-O with very low concentration of Pd in compared to the fresh catalyst [34, 35]. Also the EXAFS Fourier transform results in Fig. 8c shows that Pd metallic particle size in reused Pd/WO_3 is relatively very small than that in fresh Pd/WO_3. Thus, support agglomeration, structural changes, oxidation of Pd metallic to Pd^{II} and leaching of Pd are primarily responsible for the reduction in Pd/WO_3 catalytic activity upon its repeated use.

4. Conclusions

The palladium nanoparticles supported on WO_3were successfully synthesized and characterized by XRD, XANES, NEXAFS, SEM, EDX and TEM. This new material was found to be an effective catalyst for the carbon–carbon coupling reactions of aryl halides with olefins (Mizoroki–Heck reaction). This coupling reaction is an efficient way to prepare styrene derivatives, which are important chemicals for many applications. Effects of catalyst amount, solvent, base and temperature effects, reaction time and nature of supports on the yield of Heck reaction were also studied. The high efficiency and use of only catalyst without any additives make the method useful and attractive for the Heck reaction. Finally, a further set of experiment was carried out to check the reusability of the Pd/WO_3 catalyst for the Heck reaction under air.

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Appendix A. Supplementary data

Experimental characterization data for Heck coupling products are available in the Supplementary Data.

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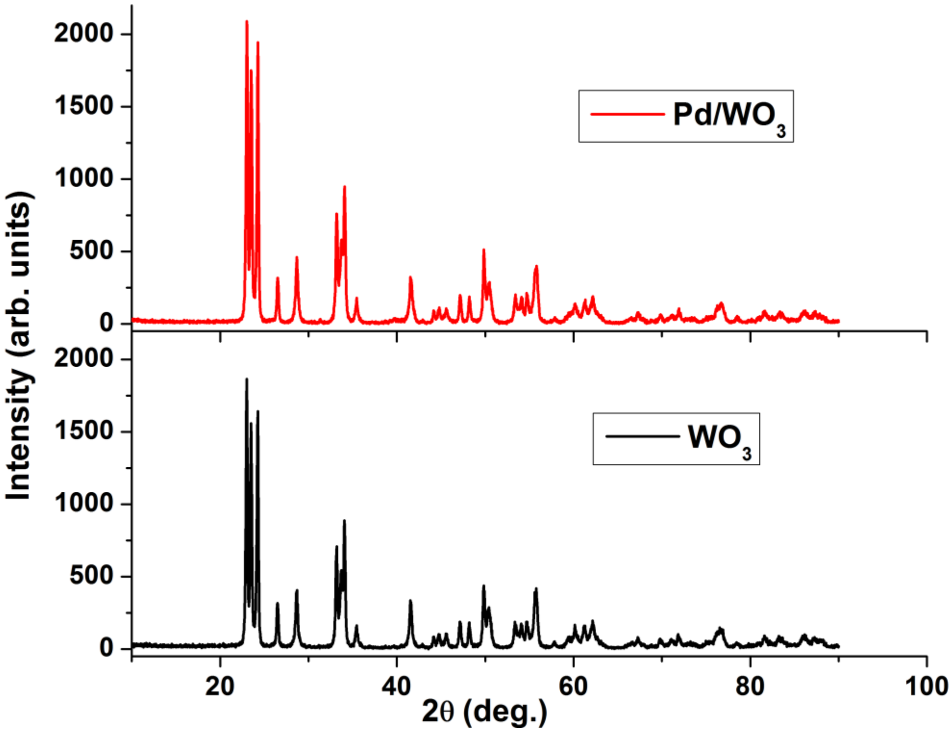


Fig. 1. XRD pattern of WO_3 and sample containing palladium nanoparticles supported on WO_3

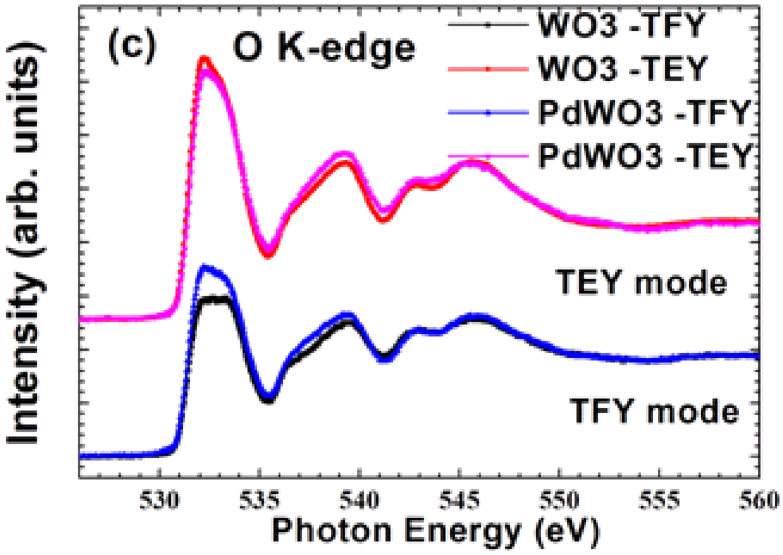


Fig. 2. O K-edge XANES patterns of WO_3 and sample containing palladium nanoparticles supported on WO_3

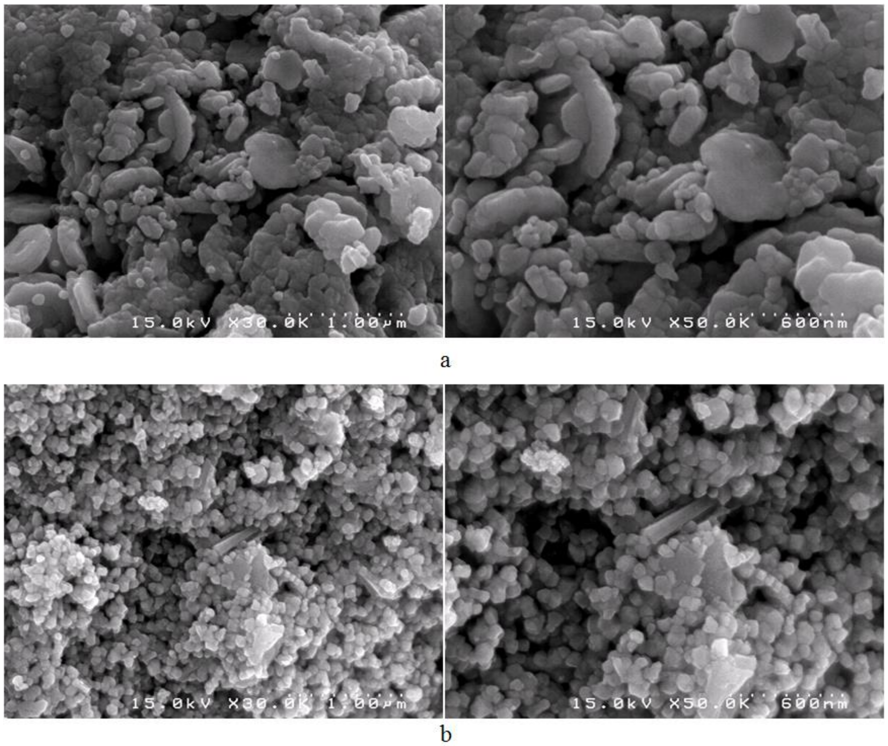


Fig. 3. SEM images of: a) WO_3; b) Pd/WO_3

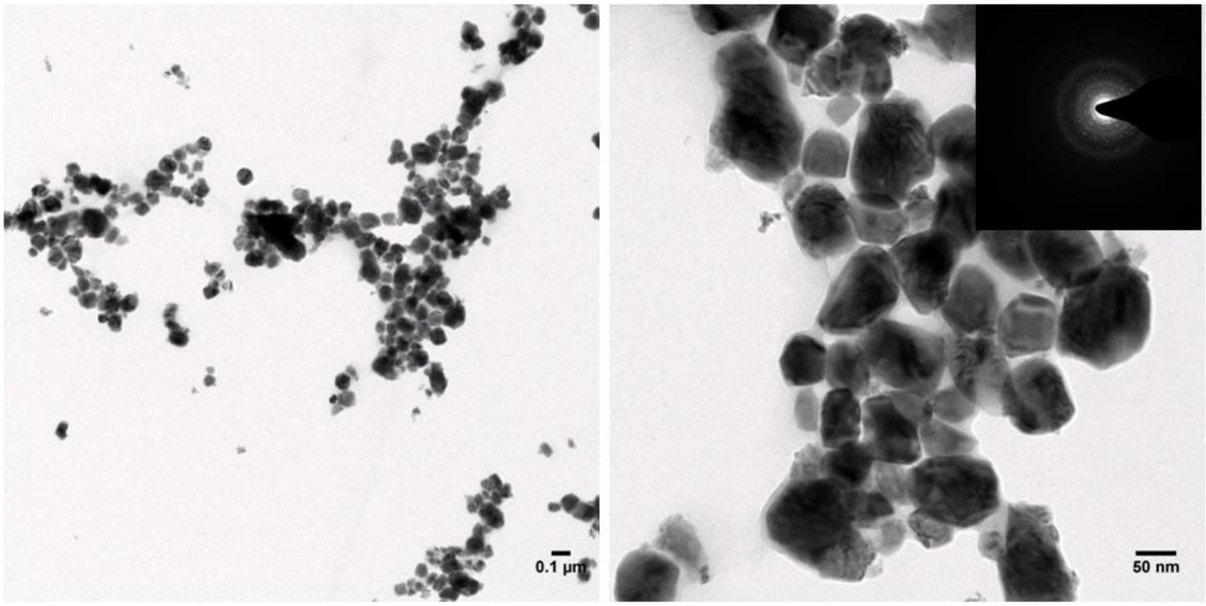


Fig. 4.TEM images of sample containing palladium nanoparticles supported on WO_3

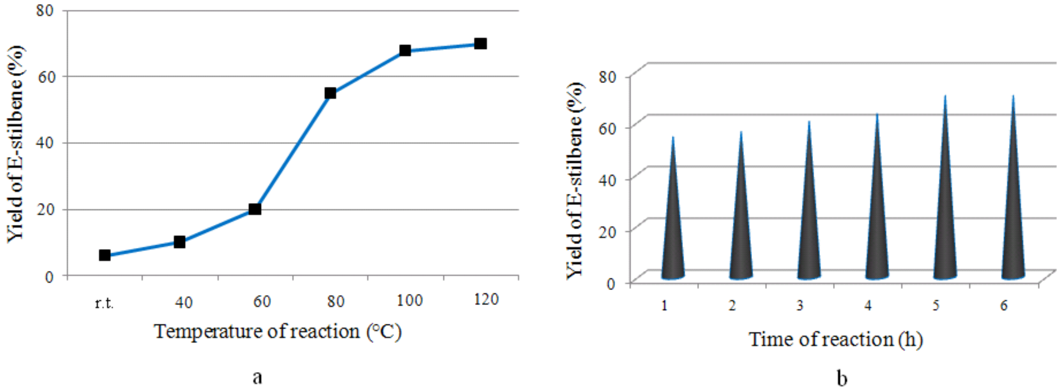


Fig. 5. Effects of (a) the temperature of reactionand; (b) the time of reactionon the Heck reaction in presence of Pd/WO_3 as a catalyst

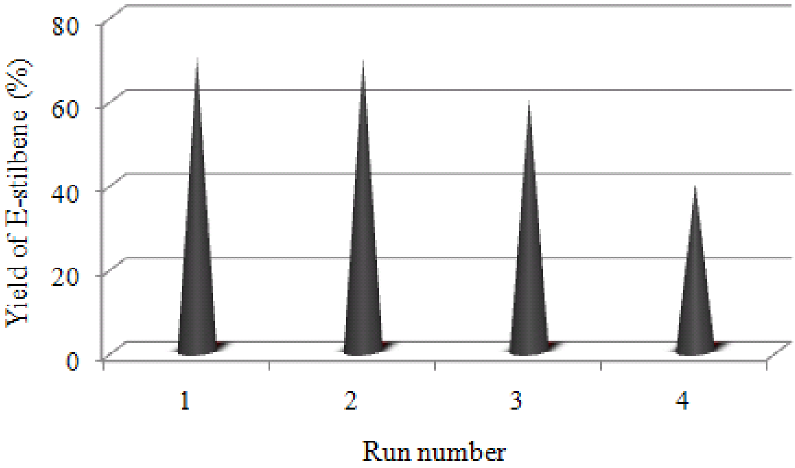


Fig. 7. Recycling studies of the catalyst Pd/WO_3 for the Heck reaction

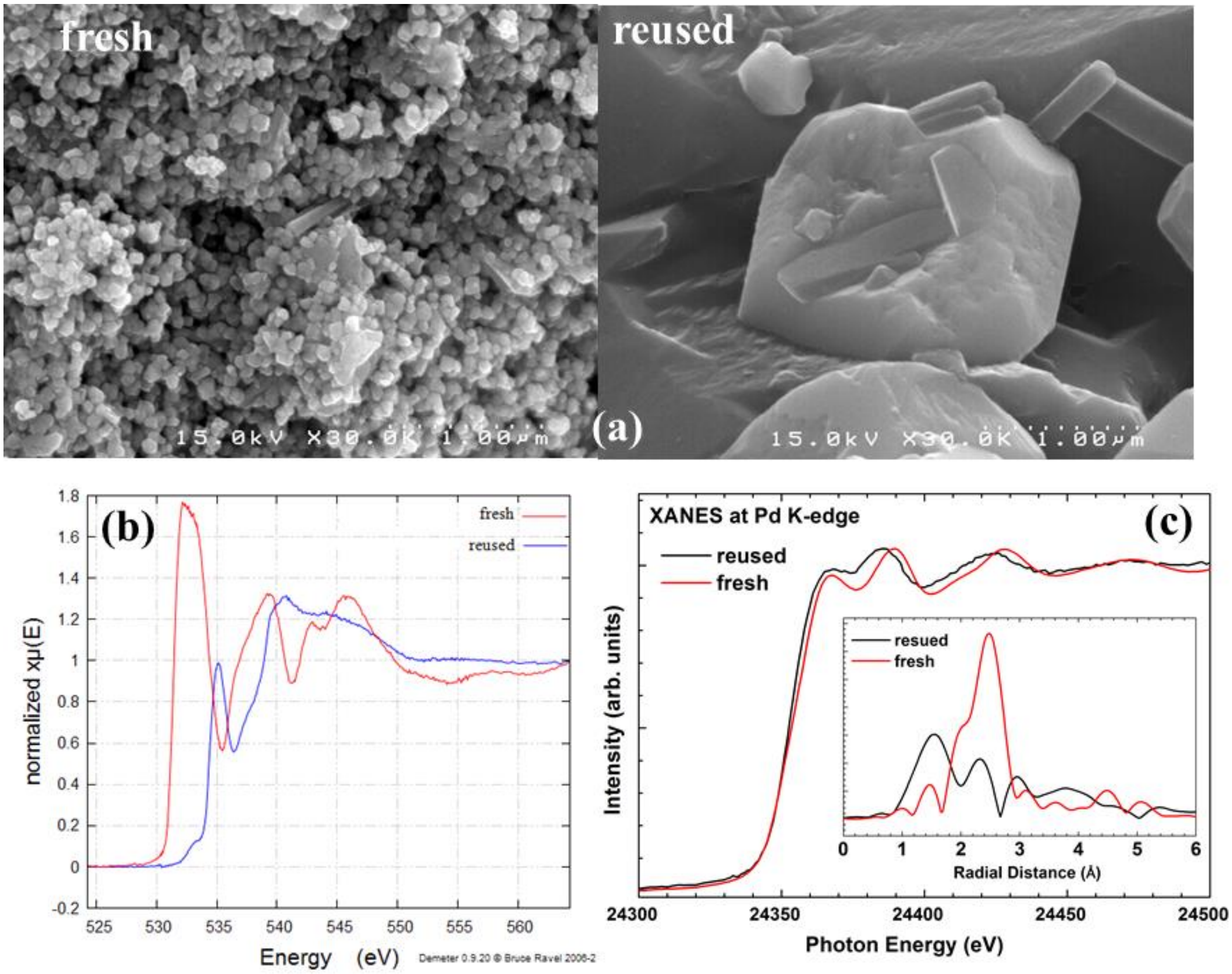


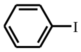
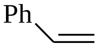
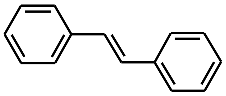
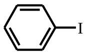
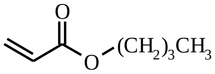
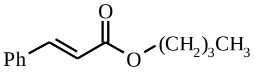
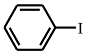
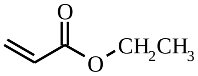
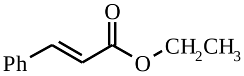
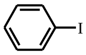
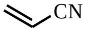
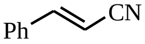
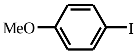
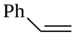
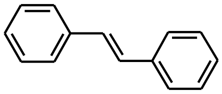
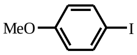
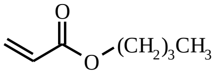
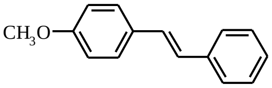
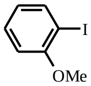
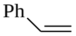
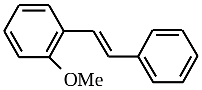
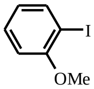
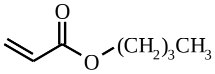
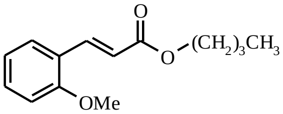
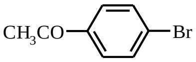
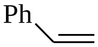
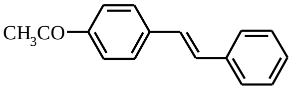
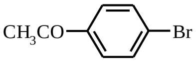
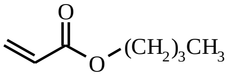
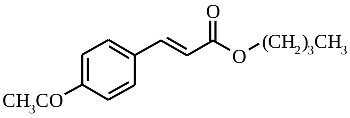
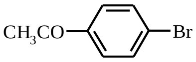
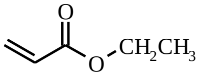
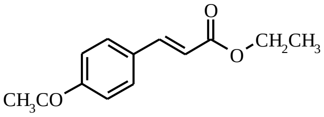
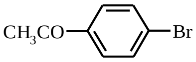
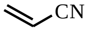
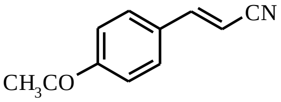
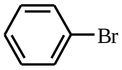
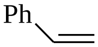
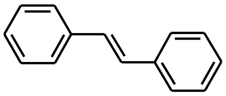
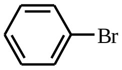
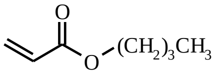
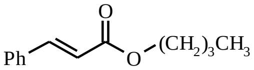
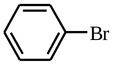
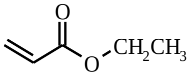
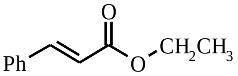
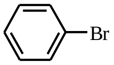
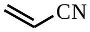
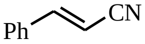
Fig. 8. a) SEM images; b) XANES patterns; c) Pd K-edge NEXAFSand EXAFS fitting of fresh and reused catalyst, Pd/WO_3.

Table 1.The Effect of various conditions on the Heck reaction.[a]

Entry	Amount of catalyst	catalyst	Base	Solvent	Temperature (°C)	Time (h)	Yield (%)[b]
1	0.001	Pd/WO_3	Na_2CO_3	DMSO	100	5	49
2	0.002	Pd/WO_3	Na_2CO_3	DMSO	100	5	53
3	0.003	Pd/WO_3	Na_2CO_3	DMSO	100	5	59
4	0.004	Pd/WO_3	Na_2CO_3	DMSO	100	5	61
5	0.005	Pd/WO_3	Na_2CO_3	DMSO	100	5	68
6	0.006	Pd/WO_3	Na_2CO_3	DMSO	100	5	65
7	0.005	Pd/WO_3	K_2CO_3	DMSO	100	5	65
8	0.005	Pd/WO_3	Na_3PO_4	DMSO	100	5	63
9	0.005	Pd/WO_3	NH_3	DMSO	100	5	7
10	0.005	Pd/WO_3	NaOAc	DMSO	100	5	15
11	0.005	Pd/WO_3	KOH	DMSO	100	5	8
12	0.005	Pd/WO_3	Na_2CO_3	H_2O	100	5	5
13	0.005	Pd/WO_3	Na_2CO_3	CH_3OH	100	5	25
14	0.005	Pd/WO_3	Na_2CO_3	CH_3CN	100	5	25
15	0.005	Pd/WO_3	Na_2CO_3	DMF	100	5	53
16	0.005	Pd/WO_3	Na_2CO_3	H_2O/DMSO	100	5	47
17	0.005	Pd/WO_3	Na_2CO_3	H_2O/DMF	100	5	40
18	0.005	WO_3	Na_2CO_3	DMSO	100	5	0

[a]Reaction conditions: 1.0 mmol of aryl halide, 1.2 mmol of olfins, 2 mmol of base. [b] Isolated yield

Table 2. Heck reaction between aryl halides and olefins in presence of Pd/WO$_3$ as a catalyst.[a]

Entry	Ar-X	Olefins	Products	Yield (%)[b]
1				96
2				96
3				95
4				93
5				94
6				95
7				89
8				91
9				83
10				85
11				85
12				88
13				70
14				43
15				41
16				48

[a] Reaction conditions: 1.0 mmol of aryl halide, 1.2 mmol of olefins, 2 mmol of Na$_2$CO$_3$, 120 °C, 5h.

[b] Isolated yield