Journal of Organometallic Chemistry 900 (2019) 120916

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Pd nanoparticles stabilized on the Schiff base-modified boehmite: Catalytic role in Suzuki coupling reaction and reduction of nitroarenes

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ARTICLE INFO

Article history:
Received 31 July 2019
Received in revised form
24 August 2019
Accepted 26 August 2019
Available online 27 August 2019

Keywords:
Boehmite
Pd NPs@Sch-boehmite
Catalytic reduction
Biaryls
Nitroarenes

ABSTRACT

Palladium nanoparticles (Pd NPs) were decorated on Schiff base-modified boehmite (Sch-boehmite) particles via a simple method without deploying any additional reducing agents and their structure was confirmed by different characterization methods. The ensuing Pd NPs@Sch-boehmite was evaluated as a retrievable catalyst for multiple cycles in Suzuki cross-coupling reactions with extensive substrate tolerance to produce biaryls in high yields within 6 min, and the reduction of 2-nitroaniline (2-NA) and 4-nitrophenol (4-NP) at room temperature in 3–4 min, respectively. Moreover, Pd NPs@Sch-boehmite catalyst could be conveniently recovered and reused multiple times.

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1. Introduction

There is growing interest in nanotechnology due to its applicability in various fields such as material science, medicine, chemistry, biology, biotechnology and physics [1–8]. The design of metal nanoparticles (MNPs) have gained popularity owing to their outstanding properties and important usages in different applications; especially as catalyst in both, fundamental academic research and industrial applications [9,10]. A wide variety of MNPs such as Cu, Ni, Au and Ag have been applied for various organic reactions [11–14]. Among these, Pd NPs have a major catalytic role due to their ability to catalyze different catalytic reactions under heterogeneous and homogeneous conditions [15]. However, one of the most important problems in preparation of Pd NPs is aggregation and their adverse effect on catalytic performance of nanoparticles [16,17], besides, the cost of Pd NPs for their practical application. On the other hand, the recovery and reusability of catalysts are important features for the sustainable process improvement. These shortcomings can be resolved by selecting ideal support materials which have large surface area, excellent stability, high porosity with good accessibility and endowed with versatile functional groups for strong interaction with metal ion. Therefore, it is highly desirable pursuit to develop an effective support for the immobilization of Pd NPs. Consequently, different supports such as mesoporous silica, graphene, zeolite and carbon have been used for the preparation of MNPs and their reuse [18–21]. Among them, aluminum oxides have a particular edge compared to other supports because their significant properties like eco-friendly nature, low cost, durability against chemicals, non-toxicity and thermal stability [22]. Boehmite surface as an aluminum oxide hydroxide (γ-AlOOH) particle is surrounded by additional hydroxyl groups which easily allows chemical modifications [23]. In view of its outstanding properties, boehmite can be an ideal stabilizer for supporting Pd NPs on nanoscale dimensions; their performances can be evaluated in the catalytic reduction of toxic nitroarenes and also for the preparation of biaryls via Suzuki cross-coupling reaction.

Biaryls are versatile organic compounds which are applied in the preparation of various pharmaceuticals, agrochemicals, natural compounds and other useful materials [24,25]. Pd-catalyzed Suzuki coupling reactions are one the prominent synthetic pathway to synthesize biaryl compounds [26,27]. Since the discovery of Suzuki reactions, different Pd catalysts have been prepared and utilized as

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https://doi.org/10.1016/j.jorganchem.2019.120916
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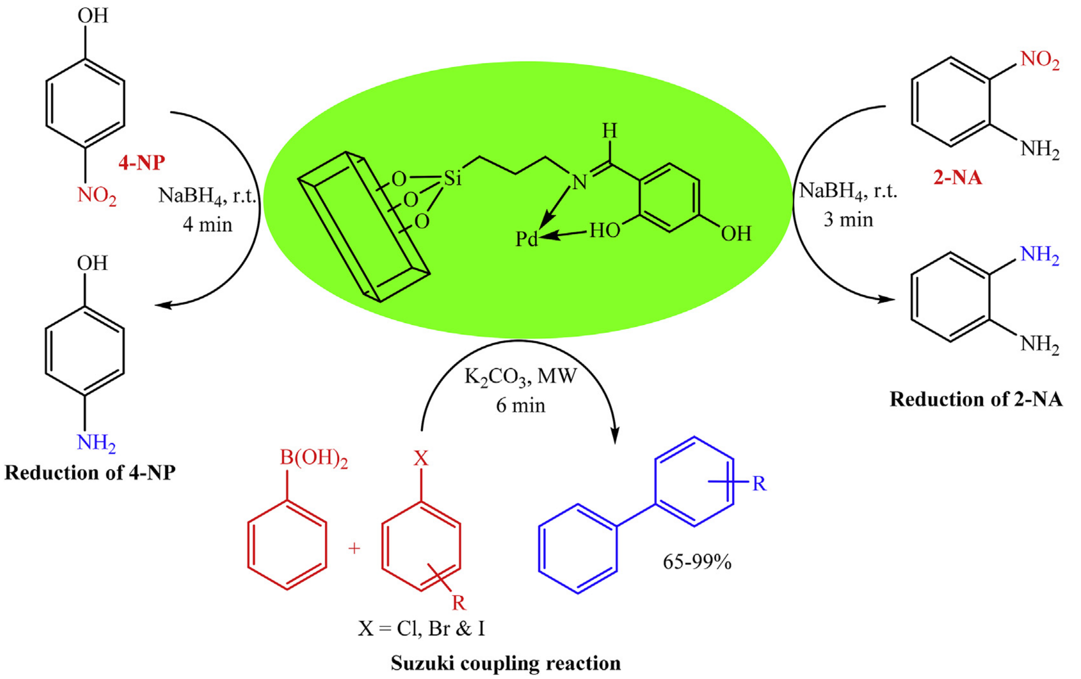
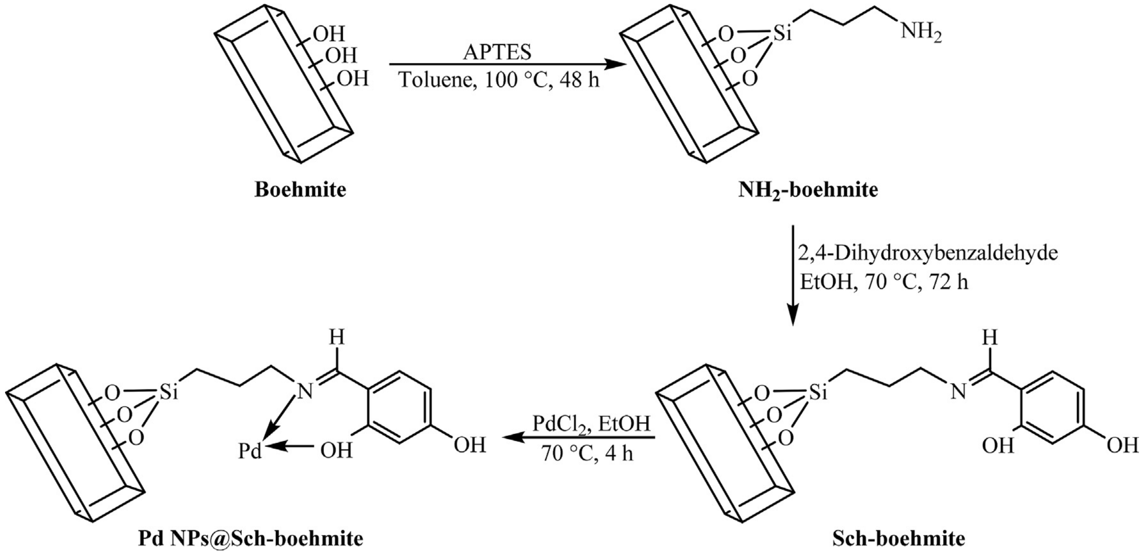
catalysts for production of biaryls via Suzuki coupling reactions [27–29]; their general use in homogeneous catalyst systems have some disadvantages in large-scale applications such as recycling of catalyst, purification of the desired product and higher operational cost [30]. Moreover, the Pd residues in the product stream are a serious concern in the pharmaceutical and medical industries for toxicity reasons. Heterogeneous catalysts on different solid supports have provided the solution and hence the need for heterogeneous Pd NPs or Pd complexes which have high catalytic activity with the ability to recycle and reuse.

Nitroarenes have been extensively used in industrial applications, are known as organic contaminants responsible for skin irritation, kidney, liver and nervous system damage [31–34]; due to their biological and chemical stability, their degradation in waste water streams is a formidable challenge. As an example, 4-nitrophenol (4-NP), a significant industrial pollutant, affects public human health and ecosystem when it is released into the environment due to its high toxicity and chemical stability [35,36], the other environmental contaminant being 2-nitroaniline (2-NA) which negatively affects both, human and aquatic life even at very low concentration in water, due to its mutagenic and carcinogenic effects [37,38]. However, these hazardous materials have high resistance to microbial degradation and their elimination from the environmental is challenging [39]. Consequently, the safe removal of both nitro compounds and related organic dyes is essential for the ecosystem and human health and various techniques have been



Scheme 1. Preparation of Pd NPs@Sch-boehmite and its application in the reduction of 4-NP, 2-NA and also Suzuki cross-coupling reaction.



Scheme 2. Schematic illustration of the preparation of Sch-boehmite.

applied for their removal [37,40]. Among the used techniques, catalytic reduction of these pollutants using catalyst and $NaBH_4$ is one of the most effective method because it provides easy operation, mild reaction conditions and relatively low cost [41,42]. Therefore, catalysts with high activity are vital for the effective removal of these substances.

In our ongoing efforts of designing Pd heterogeneous catalysts, we have now prepared highly active Pd NPs on Schiff base-modified boehmite (Pd NPs@Sch-boehmite) and evaluated their catalytic prowess for the synthesis of biaryls and reduction of 2-NA and 4-NP by $NaBH_4$ (Scheme 1). We found that versatile Pd NPs@Sch-boehmite catalyst showed good activity for these reactions within a short reaction time.

2. Methods

2.1. Instrument and reagents

Functional groups of samples were verified by PerkinElmer 100 FT-IR spectrophotometer. X-ray pattern of boehmite particles, and Pd NPs@Sch-boehmite were recorded by Rigaku smart lab system. The surface profiles of boehmite particles, and the catalyst were obtained using FEI Quanta 450 FEG. Thermal analysis was recorded with EXSTAR S11 7300 under nitrogen atmosphere. GC-MS, model of Agilent GC-7890 A-MS 5975 was used for the characterization of biaryls. The reduction of nitroarenes was checked using Genesys 10S UV-VIS.

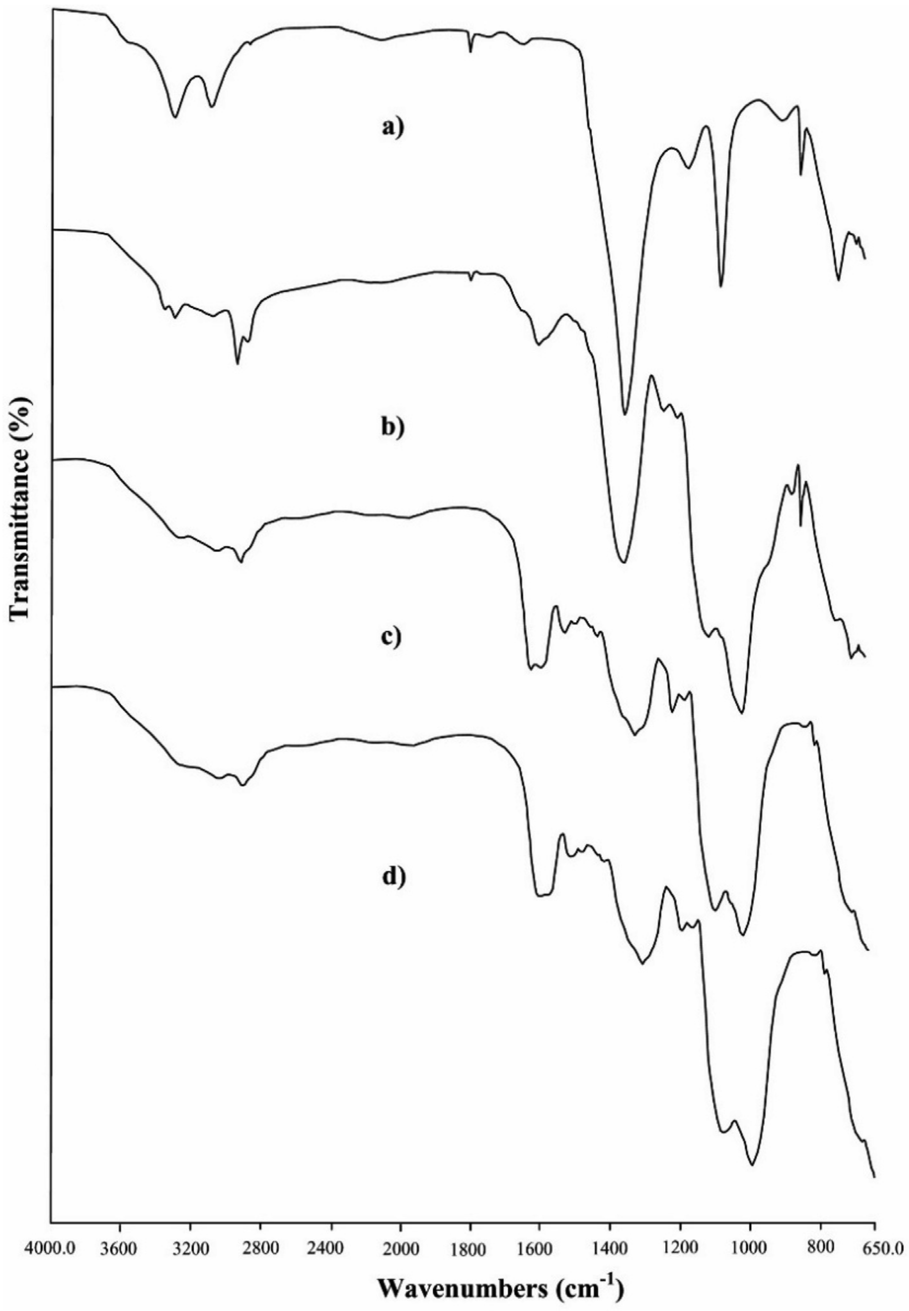


Fig. 1. FT-IR spectra of (a) boehmite particles, (b) NH_2-boehmite, (c) Sch-boehmite and (d) Pd NPs@Sch-boehmite catalyst.

2.2. Fabrication of boehmite particles

The boehmite NPs were prepared according to previously reported study [23]. Briefly, 50 mL of solution of NaOH (6.49 g) was added drop by drop to 30 mL of $Al(NO_3)_3 \cdot 9H_2O$ solution (20 g) and stirred at 25 °C and then the mixture was sonicated for 3 h. Finally, the resulting boehmite precipitate was separated, rinsed with H_2O and then dried at 220 °C for 4 h for further use in the preparation of NH_2-boehmite.

2.3. Fabrication of NH_2-modified boehmite particles (NH_2-boehmite)

Boehmite particles (2 g) and 4 mL of (3-aminopropyl)triethoxysilane (APTES) was mixed with anhydrous toluene (40 mL) and heated at 100 °C for 48 h (Scheme 2). Then, NH_2-boehmite particles were collected, washed with H_2O and dried for usage in the preparation of Sch-boehmite.

2.4. Fabrication of Schiff base-modified boehmite particles (Sch-boehmite)

NH_2-boehmite (1 g) and 1 g of 2,4-dihydroxybenzaldehyde was placed into the 30 mL of EtOH and heated at 70 °C for 72 h (Scheme 2). The imine formation was confirmed by FT-IR analysis. Finally, the formed Sch-boehmite was collected and washed with hot EtOH and dried and deployed in the preparation of Pd NPs@Sch-boehmite.

2.5. Fabrication of Pd NPs@Sch-boehmite

Sch-boehmite (0.5 g) was mixed with $PdCl_2$ (0.05 g) in EtOH (20 mL) and heated at 70 °C for 4 h for reduction of Pd(II) to Pd NPs (Scheme 2). It was observed that the reaction mixture turned to dark color during this time. Finally, Pd NPs@Sch-boehmite was collected by filtration, washed with H_2O and dried to use in further catalytic reactions.

2.6. General fabrication of biaryls using Pd NPs@Sch-boehmite under solvent-free conditions

In a Schlenk tube, $PhB(OH)_2$ (1.8 mmol), aryl halide (1.0 mmol), Pd NPs@Sch-boehmite (0.005 mol%) and K_2CO_3 (3.5 mmol) were irradiated in a microwave oven for 6 min. The used catalyst was separated from the reaction mixture by filtration for the next cycle of catalytic reaction after completion of the reaction. The ensuing reaction mixture was extracted with H_2O/toluene (1:2 v/v) and the organic phase was concentrated via evaporation under reduced pressure to obtain the desired biaryls which were then identified by GC/MS analyses.

2.7. Reduction of 2-NA and 4-NP by Pd NPs@Sch-boehmite

The freshly prepared $NaBH_4$ (0.05 M, 0.1 mL) was added to 1 mL of 4-NP solution (1.25×10^{-4} M) or 2-NA (1×10^{-4} M) and stirred for 1 min. Then, 1 mg of Pd NPs@Sch-boehmite was transferred into solution and the resulting mixture was stirred at ambient temperature until completion of catalytic reduction. The reaction progress was followed by UV–Vis spectrometer during this time period. It was observed that yellowish colors of the solutions turned to colorless after the catalytic reduction. Finally, Pd NPs@Sch-boehmite was collected from reaction media and washed with H_2O for regeneration and reuse in the next cycle of catalytic reaction.

3. Results and discussion

3.1. Nanocatalyst characteristics

The characterization of the Pd NPs@Sch-boehmite was performed by FT-IR (Fourier-Transform Infrared), FE-SEM (Field Emission Scanning Electron Microscopy), TG/DTG (thermogravimetric-differential thermal analysis), EDS (Energy Dispersive X-ray Spectroscopy) and XRD (X-ray Diffraction) techniques.

FT-IR spectra of boehmite particles, NH_2-boehmite, Sch-boehmite and also Pd NPs@Sch-boehmite are shown in Fig. 1. Boehmite particles FT-IR spectrum showed two strong peaks at

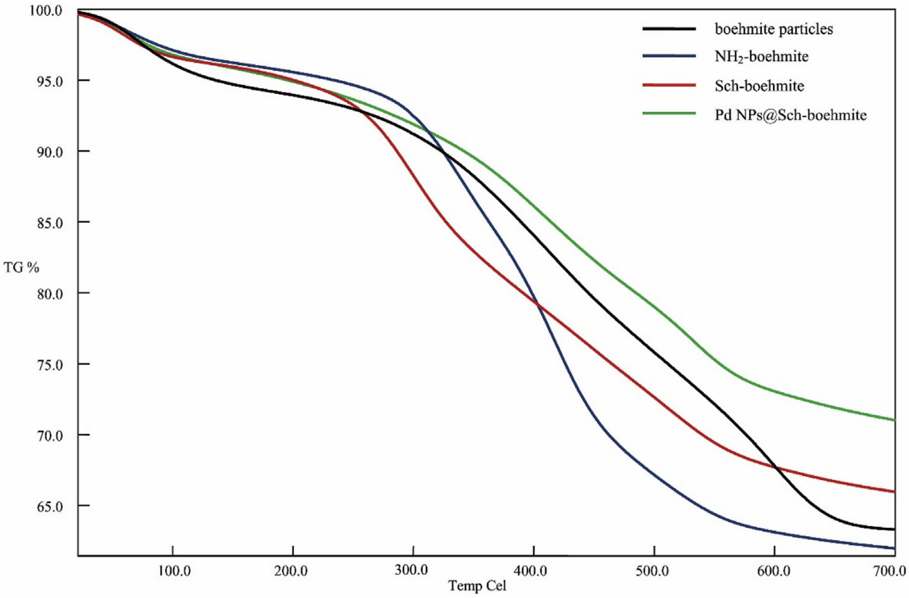


Fig. 2. TG/DTG spectra of boehmite particles, NH_2-boehmite, Sch-boehmite and Pd NPs@Sch-boehmite catalyst.

3293 and 3080 cm^{-1} representing stretching of OH bonded to Al [43]. The peak at 1342 cm^{-1} is associated to nitrate stretch vibration. The bands at 1160 and 1065 cm^{-1} correspond to symmetrical bending vibrations of OH—OH hydrogen binding [44]. The peak at 725 cm^{-1} is linked to vibration of Al—O [22]. The small peaks at 1788 and 834 cm^{-1} can be explained by nitrate impurities [45]. FT-IR results of boehmite particles is in accord with previous studies, confirming the successful synthesis of boehmite. When NH_2-boehmite FT-IR spectrum was examined, beside characteristic peaks of boehmite nanoparticles, newer peaks appeared at 3353 and 3292 cm^{-1} (N—H asymmetrical and symmetrical stretching), 2929 and 2864 cm^{-1} (aliphatic C—H stretching), 1592 cm^{-1} (NH_2 deformation vibration), and 1006 cm^{-1} (Si—O stretching) [46,47]. These important peaks affirmed that the amino groups were successfully grafted on to boehmite. When compared to FT-IR spectra of Sch-boehmite with NH_2-boehmite, a new peak appeared at 1635 cm^{-1} which is confirming formation of Schiff base. Additionally, we observed two peaks at 1605 and 1539 cm^{-1} which were attributed to stretching of C=C aromatic ring. These bands showed that Schiff base formation was successfully performed. There is a significant change in the Pd NPs@Sch-boehmite catalyst FT-IR spectrum when compared to Sch-boehmite. However, it was observed that the functional bands shifted to a lower wavelength which can be explained by interactions of Sch-boehmite and palladium ions.

Thermal durability of boehmite particles, NH_2-boehmite, Sch-boehmite and Pd NPs@Sch-boehmite catalyst were examined and their TGA diagrams are provided in Fig. 2. While degradation temperature maximum (T_{max}) of boehmite particles was recorded as 407.5 °C, T_{max} of NH_2-boehmite, and Pd NPs@Sch-boehmite were recorded as 327 °C and 295 °C, respectively. TGA diagram of Pd NPs@Sch-boehmite catalyst indicated that it was stable up to 404.4 °C. This result revealed that Pd NPs@Sch-boehmite catalyst are more durable than its support.

Fig. 3 displays FE-SEM images of boehmite particles and Pd NPs@Sch-boehmite catalyst which revealed their cubic orthorhombic structures; surface of boehmite particles were covered with Pd NPs. As seen in Fig. 3c, Pd NPs were quite homogeneously dispersed and their average particle size was determined to be 30 nm. Additionally, EDS analyses were carried out for every chemical modifications and it was found that chemical alterations were successfully accomplished (Fig. 4).

XRD analyses of boehmite particles and Pd NPs@Sch-boehmite catalyst (Fig. 5) were performed and the indicated peaks corresponding to the characteristic peaks of boehmite particles were confirmed (Fig. 5a). In case of Pd NPs@Sch-boehmite catalyst, it contains a series of peaks at 39.1°, 45.4° and 66.26° which can be ascribed to diffraction from the (1 1 1), (2 0 0) and (2 2 0) planes of face centered cubic of Pd NPs on the boehmite surface [11,48,49].

3.2. Catalytic studies of Pd NPs@Sch-boehmite

3.2.1. Fabrication of biaryls via suzuki cross-coupling reaction

An efficient method is presented for the formation of biaryls via microwave (MW)-assisted Suzuki coupling reaction of phenylboronic acid with aryl halides. Initially, Pd NPs@-Sch-boehmite was evaluated as heteregeonus catalyst for the biaryls preparation. The catalytic tests were performed under greener solvent-free conditions using MW irradiation. To find the ideal reaction parameters, different parameters such as catalyst loading and base-type were studied on *p*-iodide anisole and phenylboronic acid as the model reactants; highest reaction yield was attained with 0.005 mol% Pd NPs@-Sch-boehmite catalyst, 6 min reaction time and K_2CO_3 as base. To assess the functional group tolerance, a range of aryl halides were used (Table 1) and the Pd NPs@-Sch-boehmite catalyst converted aryl iodides to desired biaryls with excellent reaction yields (entries 1—6); 1-iodo-3-nitrobenzene was converted to corresponding product with reaction yield of 94%. On the other hand, excellent yields were achieved when aryl bromides were applied as the substrate (entries 7—15); 4-bromobenzonitrile afforded outstanding reaction yield of 98%. Based on the encouraging findings, the scope of Pd NPs@-Sch-boehmite was expanded for aryl chlorides which have strong C—Cl bond and good yields were obtained (Table 1, entries 16—21). The reaction was tolerated by diverse functional groups such as nitro, methyl, methoxy, amino, and nitrile functionalities; the nature of the substituent on the ring of aryl halides did not affect the reaction time, even for compounds

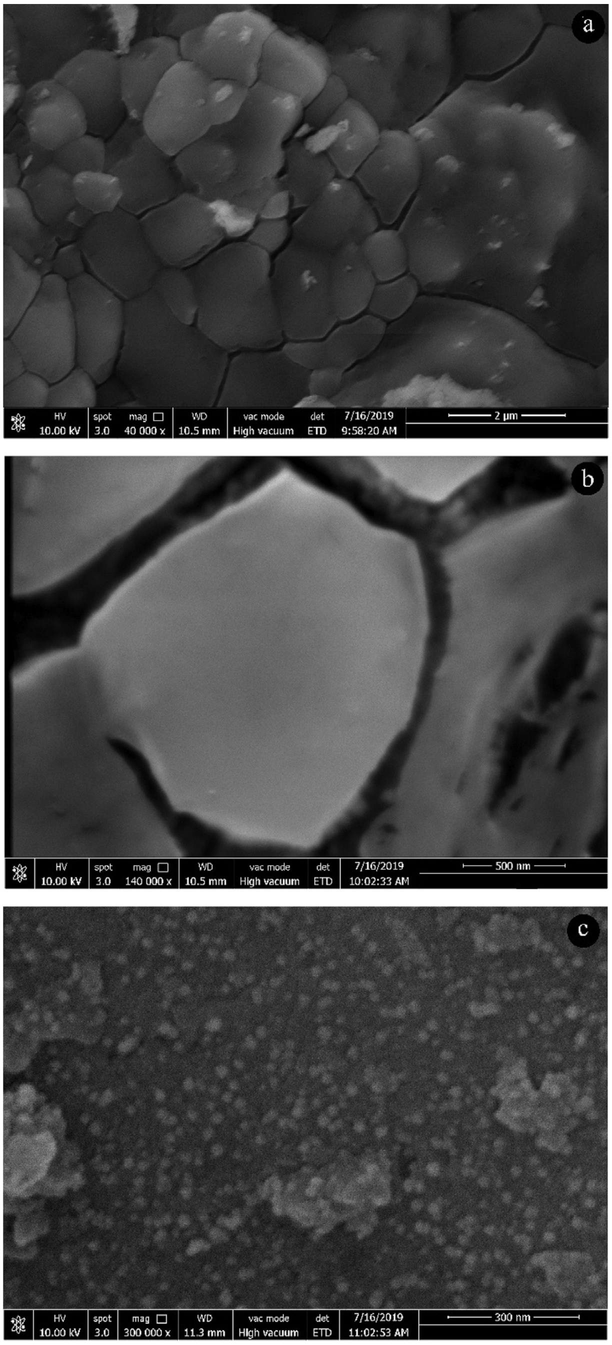


Fig. 3. FE-SEM images of boehmite particles (a, b) and Pd NPs@Sch-boehmite catalyst (c).

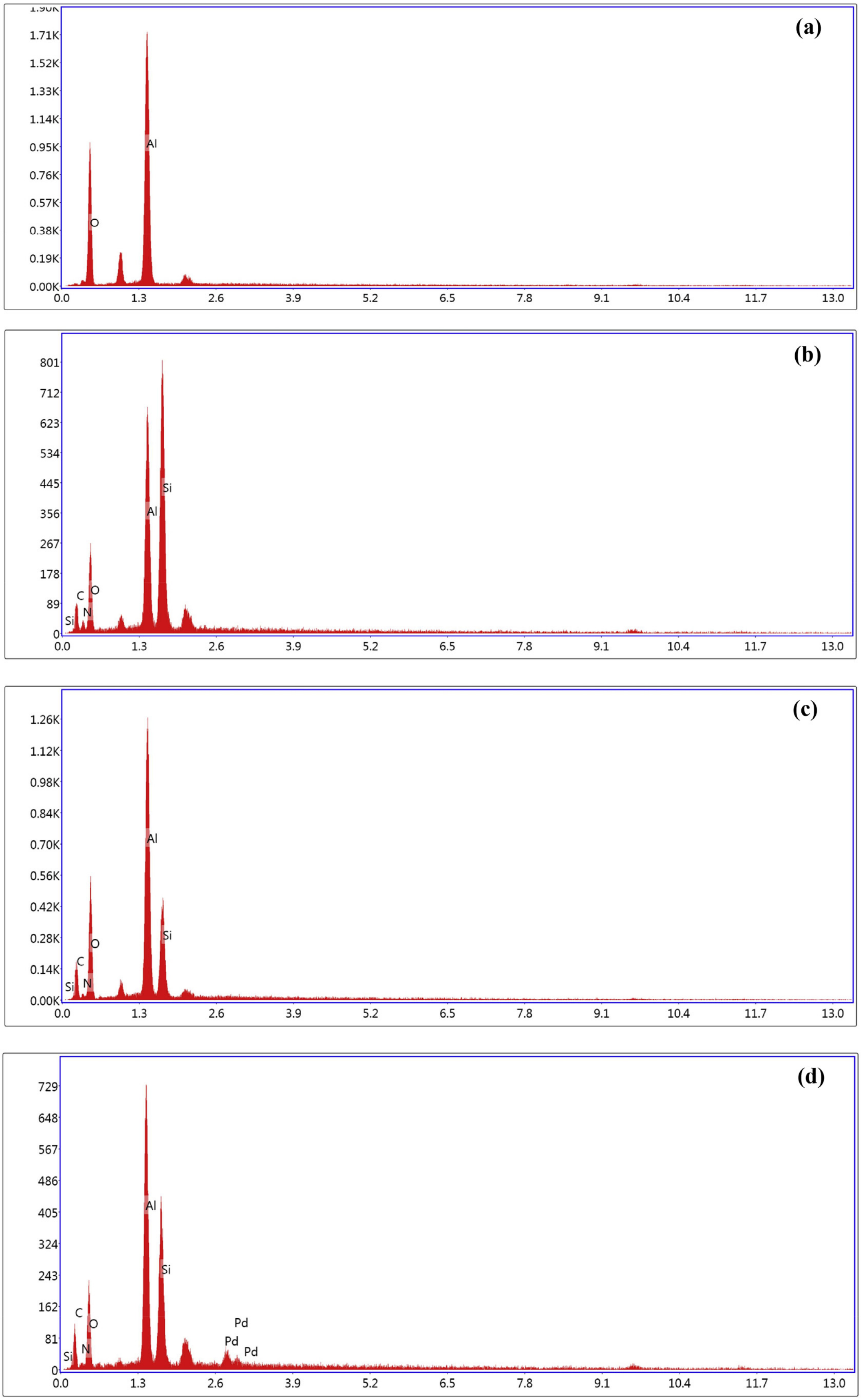


Fig. 4. EDS spectra of boehmite particles (a), NH_2-boehmite (b), Sch-boehmite (c) and Pd NPs@Sch-boehmite catalyst (d).

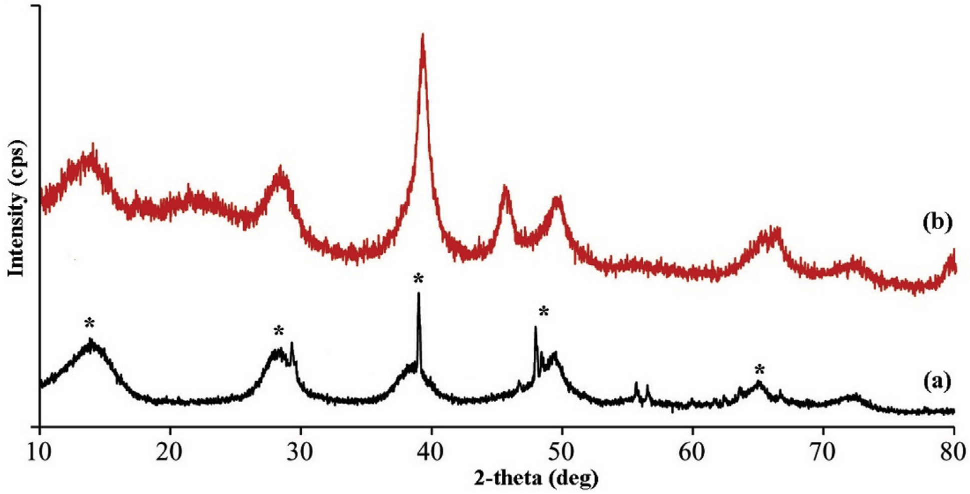
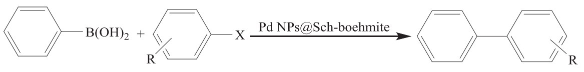


Fig. 5. XRD patterns for boehmite particles (a) and Pd NPs@Sch-boehmite catalyst (b).

Table 1
Pd NPs@Sch-boehmite catalyzed fabrication of biaryls.



Entry	X	R	Yield (%)
1	I	4-NH_2	85
2	I	3-NO_2	94
3	I	4-OMe	99
4	I	2-Me	72
5	I	3-Me	75
6	I	4-Me	80
7	Br	2-OMe	86
8	Br	3-OMe	92
9	Br	4-OMe	96
10	Br	4-NO_2	99
11	Br	3-NO_2	90
12	Br	4-CN	98
13	Br	4-NH_2	80
14	Br	3-Me	75
15	Br	4-Me	78
16	Cl	2-OMe	69
17	Cl	3-OMe	72
18	Cl	4-OMe	76
19	Cl	3-NO_2	81
20	Cl	4-CN	86
21	Cl	4-Me	65

Reaction conditions: 1.0 mmol aryl halide, 1.8 mmol $PhB(OH)_2$, 3.5 mmol K_2CO_3, Pd NPs@Sch-boehmite catalyst (0.005 mol%), 6 min, 400 W.

bearing the ortho-substituents (Table 1, entries 4,7,16). These conclusions showed that Pd NPs@-Sch-boehmite possesses good catalytic effect for most halides.

3.2.2. *Pd NPs@Sch-boehmite catalyzed reduction of 2-NA and 4-NP*

Among the reduction reactions, the reduction of toxic nitroarenes is one of the most crucial and are generally performed using MNPs themselves or supported MNPs. The versatility of Pd NPs@Sch-boehmite catalyst, was also evaluated for the aqueous room temperature catalytic reductions of 2-NA and 4-NP using $NaBH_4$ at room temperature. The reactions were followed by UV–Vis spectroscopy as it is known that 4-NP has typical absorption band about at 300 nm and with addition of $NaBH_4$ as a reducing agent, shifting of the absorbance band occurs from 300 to 400 nm because of the 4-nitrophenolate ion (4-NPT) formation. Additionally, it is expected that complete disappearance of the band at 400 nm occurs with reduction of 4-NP (Fig. 6a). In the absence of Pd NPs@Sch-boehmite or $NaBH_4$, no reduction occurred indicating that presence of reducing agent and catalyst are essential for the 4-NP reduction. Following the Pd NPs@Sch-boehmite addition, strong band at 400 nm decreased and it vanished after 4 min (Fig. 6a). Additionally, a new band was observed at about 300 nm which affirms the formation of 4-aminophenol (4-AP) as the reaction solution becoming colorless. The Pd NPs@Sch-boehmite is acting as a redox catalyst via the electron relay effect between donor BH_4^- acceptor and nitro group. These results revealed that reduction of 4-NP was completely performed in 4 min

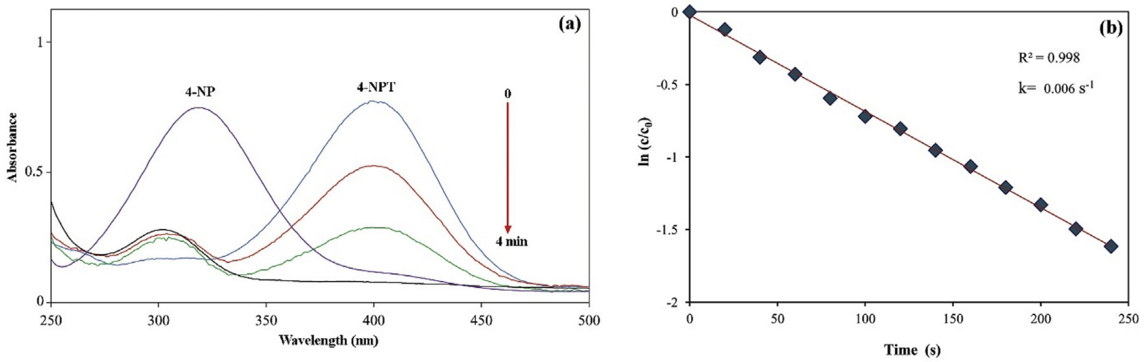


Fig. 6. UV–Vis spectra for the reduction of 4-NP to 4-AP using Pd NPs@Sch-boehmite catalyst (a) and linear dependence between time and ln (c/c_0) (b).

Table 2
Pd NPs@Sch-boehmite-catalyzed reduction of 4-NP compared to reported catalysts.

Entry	Reaction conditions	Time	Ref.
1	Au@PZS@CNTs	16 min	[50]
2	Fe_3O_4@C@Pt	60 min	[51]
3	GA-Pt NPs	8 h	[52]
4	HMMS$-NH_2-$Pd	60 min	[53]
5	NAP-Mg-Au(0)	7 min	[54]
6	PdCu/graphene	1.5 h	[55]
7	Cu NPs	2 h	[56]
8	Polymer-anchored Pd(II) complex	5.5 h	[57]
9	Pd-FG	12 min	[58]
10	KCC-1/Au	12 min	[59]
11	Au/graphene hydrogel	720 s	[60]
12	p(AMPS)-Ni composite	5.5 h	[61]
13	p(AMPS)-Co composite	28 min	[62]
14	Resin-Au NPs	20 min	[63]
15	Ag NPs@MWCNTs-polymer composite	5 min	[64]
16	$FeNi_2$ alloy nanostructure	60 min	[65]
17	Pd NPs/GNs	15 min	[66]
18	Ni@Pd/MIL-101	2 h	[67]
19	AgNC-1	2 h	[68]
20	Au-GO	30 min	[69]
21	Pd NPs@Sch-boehmite	4 min	This work

by Pd NPs@Sch-boehmite which was much shorter than reported catalysts documented in the literature (Table 2).

Catalytic ability of Pd NPs@Sch-boehmite was also investigated for the reduction of 2-NA to 2-phenylenediamine at room temperature using $NaBH_4$. As seen in Fig. 7, 2-NA displayed two characteristic bands at about 283 and 410 nm without Pd NPs@Sch-boehmite. After the addition of the catalyst to the reaction media, the band intensity at 410 nm gradually decreased and disappeared completely in 3 min; also the band at 283 nm shifted to 290 nm with reaction time and the yellowish reaction solution turned to colorless. Figs. 6b and 7b showed a linear correlation between reaction time (t) and ln (c/c_0) in 2-NA and 4-NP reduction using Pd NPs@Sch-boehmite. These catalytic systems follow pseudo first-order kinetic, because $NaBH_4$ concentration is higher than 4-NP and 2-NA, and rate constants were determined via following equation:

$$\ln (c/c_0) = -kt$$

where, c_0 and c are 4-NP and 2-NA initial and final concentrations, respectively at selected reaction time (t), and also k (s^{-1}) is the reaction rate. Rate constants were calculated as 0.006 s^{-1} and 0.0027 s^{-1}, respectively.

Also, the catalytic ability of the Pd NPs@Sch-boehmite is compared with reported catalysts in the recent years in the formation of 4-AP and preparation of 4-methoxybiphenyl; better performance is observed by Sch-boehmite-based catalyst (Tables 2 and 3). The synthesized Pd NPs@Sch-boehmite could perform reactions in higher yields and in shorter time duration. On the other hand, compared with the reported works, aryl chlorides could be use in our method for Suzuki coupling reaction, which is rather uncommon.

3.2.3. *Catalyst recyclability*

Catalyst reproducibility is a very important factor for use in industrial and commercial applications and therefore, recyclability study for Pd NPs@Sch-boehmite was undertaken. At the end of the reactions, Pd NPs@Sch-boehmite was separated from the reaction media, washed with water, and directly reused for the next successive runs. The Pd NPs@Sch-boehmite could be recycled for eight cycles by providing 82% yield in the coupling reaction of $PhB(OH)_2$ and *p*-iodide anisole. Additionally, we determined that Pd NPs@Sch-boehmite could be reused seven times for 4-NP and 2-NA reduction with not significant loss of its activity (yields: 92 and 88%,

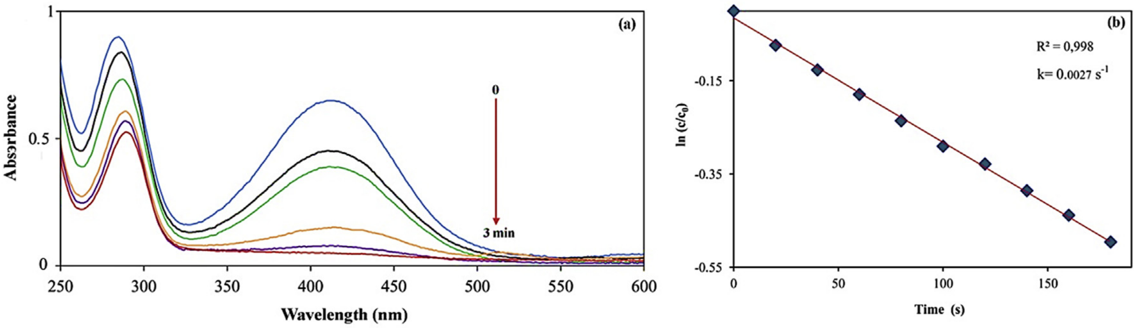


Fig. 7. UV−Vis spectra for the reduction of 2-NA using Pd NPs@Sch-boehmite catalyst (a) and linear dependence between ln (c/c_0) and time (b).

Table 3
Pd NPs@Sch-boehmite-catalyzed preparation of 4-methoxybiphenyl from reaction of $PhB(OH)_2$ with 4-bromoanisole compared to reported catalysts.

Entry	Reaction conditions	Temp. (°C)	Time	Yield (%)	Ref.
1	OCMCS-3aPd	100	48 h	97	[70]
2	Pd NPs@CMC/AG	60, US	30 min	94	[71]
3	CL-Gly-Pd	MW, 400 W	7 min	94	[72]
4	Pd-1/FSG	100	12 h	86	[73]
5	pEVPBr-Pd	90	9 h	68	[74]
6	$Pd(OAc)_2$, polymer-supported ferrocenylphosphine	110	6 h	67	[75]
7	PS-PEG600-NHC-Pd	50	12 h	76	[76]
8	Pd-PVP	90	24 h	89	[77]
9	Agarose hydrogel supported Pd nanoparticles	80−100	5 h	80	[78]
10	Polymer-supported Pd−NHC complex	50	12 h	68.5	[79]
11	Fe_3O_4-Pd	50	12 h	90	[80]
12	Pd NPs@Sch-boehmite	MW, 400 W	6 min	96	This work

respectively). The palladium catalyst leaching was also checked by ICP-OES assay after the reusability tests and only about 1% of palladium leaching was determined for each recycling run.

4. Conclusions

We have developed a simple method for the preparation of a highly effective and reusable Pd NPs supported on Schiff base-modified boehmite particles. Interestingly, the Pd NPs@Sch-boehmite catalyst displayed good catalytic ability for the synthesis of biaryls under solvent-free conditions from aryl halides comprising iodides, bromides and chlorides and accommodated an array of substituents on diverse substrates. Further, its high activity for 4-NP and 2-NA reduction was discerned; complete reduction occurred within 3–4 min. Moreover, Pd NPs@Sch-boehmite catalyst could be reused for many cycles in all these catalytic reactions because of its heterogeneous nature. This salient feature also facilitated both, the ease of purifying of the final product and no formation of by-product in the reactions. The synthesis of Pd NPs@Sch-boehmite was economical in view of the low catalyst loading. The designed versatile catalyst Pd NPs@Sch-boehmite may find additional useful applications in catalysis and we anticipate that the Sch-boehmite support may provide an ideal platform for the immobilization of MNPs such as Au, Pt and Cu, and will stimulate the discovery of highly efficient and low-cost earth-abundant catalysts for chemical transformations.

Conflicts of interest

Authors declare no conflict of interest.

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