

Palladium Supported On Ethylenediaminetetraacetic Acid Functionalized Cellulose: Synthesis, Characterization, And Its Application In Carbon–Carbon Cross-Coupling Reactions

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Abstract

Through the esterification of cellulose (Cell) with ethylenediaminetetraacetic dianhydride, ethylenediaminetetraacetic acid-functionalized cellulose (Cell-EDTA) was conveniently obtained. Furtherly a novel and efficient Cell-EDTA-supported palladium catalyst (Pd@Cell-EDTA) was easily prepared via coordination of Cell-EDTA with PdCl₂. The as-prepared Pd@Cell-EDTA was fully characterized by inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectra (FTIR), energy-dispersive spectroscopy (EDS), scanning electron microscopy, transmission electron microscopy (SEM), thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) techniques. Then Pd@Cell-EDTA were successfully exerted as catalysts in Suzuki reactions and Sonogashira reactions. Due to the interactions of carboxylic groups, nitrogen atoms, and hydroxyl groups on cellulose, the Pd complex showed excellent activity towards these carbon-carbon cross-coupling reactions. The catalyst recycling experiment for Suzuki model reaction showed that the catalyst can be reused at least five times without significant losing its catalytic performance. The present cellulose-based Pd@Cell-EDTA catalyst offers the salient features of wide application, excellent catalytic activity, good reusability, tolerance of broad scope of substrate, and environmental benign.

Introduction

The Pd-catalyzed cross-couplings such as Suzuki, Heck, Sonogashira, Stille, and Buchwald-Hartwig reactions have been recognized as one of the most versatile and powerful tool for building carbon-carbon and carbon-heteroatom bonds (Biffis et al. 2018), and therefore, have attracted great interest in the chemicals, materials, pharmaceuticals, agrochemicals, and industrial communities (Rayadurgam et al. 2021; Devendar et al., 2018). Over the last decade, great effects made on homogeneous and heterogenous Pd catalysts for these types of cross-couplings have been surveyed (Phan et al. 2006). Among various homogeneous and heterogenous, from a catalysis perspective, heterogeneous Pd catalysts have received increasing attention because of their certain advantages with respect to economy and sustainability, which is based on good catalytic activity, easy separation, excellent reusability and good stability (Phan et al. 2006; Taladriz-Blanco et al. 2013). In more recent years, the seeking of novel heterogeneous Pd catalytic system to replace existing homogeneous ones has been ongoing. Generally, a number of different supports, namely metal oxides (Phan et al. 2006; Taladriz-Blanco et al. 2013), synthetic polymers (Phan et al. 2006; Taladriz-Blanco et al. 2013), carbon materials (Gholinejad et al. 2013), and metal organic frameworks (MOFs) (Luo et al. 2019) have been widespread used as support materials for heterogenization of Pd catalysts and shown to be highly efficient for cross-coupling reactions with the added benefits of catalyst recovery and reusability. However, not many of them are biodegradable, economical, widely naturally available. Moreover, the functional groups or ligands on these supports are not conveniently available in many cases for modulating the catalytic active sites, thus decreases its catalytic activity. Thus, it is essential that the exploitation for biopolymers modification. The functionalized bio-degradable and bio-derived polymers are designated as supports,

which create more anchoring sites to capture Pd for the preparation of highly efficient catalysts. Recently, biopolymer (Ahmad et al. 2021; Nasrollahzadeh et al. 2020) like cellulose, chitosan, starch, alginate, and protein as support materials specially used for Pd immobilization are gaining momentum because they are being renewable and biodegradable, as well as have a large number of various surface functional groups such as hydroxyl, amino, and/or carboxylic groups.

Recently, celluloses are emerging as support materials with the aim to use in heterogeneous catalysis. Celluloses are naturally abundant, low-cost, non-toxic biodegradable materials consisting of long chain of β -anhydro-D-glucopyranose units (AGU) with three hydroxyl groups per AGU, and thereby provides suitable interaction sites (hydroxyl group, $-OH$) for metal ion adsorption. The widely investigated catalysts are still Pd catalyst directly deposited on cellulose. Cellulose impregnated with Pd was the first report of using cellulose as a support in Heck and Sonogashira couplings (Reddy et al. 2006; Xu et al. 2006). Then, this method was furtherly improved by Morres et al. (Cirtiu et al. 2011). Unfortunately, pristine cellulose has a low adsorption capacity as well as variable physiochemical stability. Thus, this deposited Pd catalysts are inevitably deactivated by the Pd aggregation or leaching during the course of reaction. To surmounted these drawbacks, it is highly desirable to develop novel strategy to fabricate the functionalized cellulose supported Pd catalyst. Based on the advantage of abundant reactive hydroxyl groups, various organic groups/ligands can be easily grafted on cellulose chain, flexibly offering binding sites for Pd immobilization, which not only make the catalyst exhibit superior catalytic activity but also guarantee the good stability and reusability. More recently, several surveys highlighted the latest progress on cellulose-supported Pd catalysts in organic reactions (Ahmad et al. 2021; Kamel et al. 2021; Kumbhar et al. 2015).

Ethylenediaminetetraacetic acid (EDTA) is a non-toxic, cost-effective, and commonly used metal chelating agent in analytical chemistry due to its strong chelating ability to metal ions (Jiang et al. 2019). Thus, it is of great interesting to graft this efficient chelate onto supportive materials as sorbents. Several reported works have used EDTA modified cellulose (Cell-EDTA) to removal heavy metals, such as the adsorption of Cu^{2+} , Sr^{2+} , Pb^{2+} , Cd^{2+} , and others (Kahovec et al. 1980; d'Halluin et al. 2017; Cheng et al. 2019). However, its use as a support for catalytic applications has yet explored up to the present time.

Inspired by the preponderance of cellulose and EDTA, it should be reasonably considered Cell-EDTA as an appealing material for immobilization of Pd catalyst. Herein, in this article, ethylenediaminetetraacetic acid (EDTA) have been successfully grafted onto the cellulose and furtherly used it to anchor Pd catalyst (Pd@Cell-EDTA). The as-prepared Pd@Cell-EDTA catalyst was fully characterized and explored as a heterogeneous catalyst for Suzuki reactions and Sonogashira reactions. The critical role of the Pd@Cell-EDTA becomes apparent when compared to the significantly poorer Pd deposition on pristine cellulose. The multiple contributions are (1) cellulose is an organic biopolymer, environmentally friendly, and sustainable resource support material; (2) the EDTA multidentate ligands were introduced; (3) the chelation of Pd(0)/Pd(II) and confined growth of Pd(0) nanoparticles (NPs) were achieved after partial reduction by hydroxyl groups of cellulose; (4) the activity of the Pd catalyst were modulated by EDTA

ligand; (5) the phenylboronic acids was activated *via* esterification of phenylboronic acid with hydroxyl groups of cellulose; and (6) the catalyst is easily recovered and reused for several times.

Experimental Part

Materials and instrumentations

Microcrystalline cellulose and all other chemicals were obtained from commercial sources and used as received without further purification.

The elemental palladium content of the catalyst was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) using X Series 2 instrument. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Fisher Scientific K-Alpha instrument. Fourier transform infrared spectra (FTIR) were collected on a Nicolet 6700 spectrophotometer in KBr pellet within the spectral range of 4000 – 400 cm^{-1} at 2 cm^{-1} resolution and 32 scans. Scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) were conducted with a Zeiss Sigma 500 instrument. Transmission electron microscopy (TEM) was obtained with a Philips Tecnai instrument. Thermogravimetric analysis (TGA) and derivative thermogravimetric analysis (DTG) were performed on a Netzsch STA449 under a nitrogen atmosphere from 30 to 800°C in a 50 $\text{mL}\cdot\text{min}^{-1}$ N_2 flow and a ramp rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$. Gas chromatography (GC) was performed on a Shimadzu GCMS-QP2020. ^1H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were obtained with a Bruker Avance instrument with CDCl_3 as solvent and TMS as internal standard. HRMS was determined by using Agilent 6545 Q-TOF MS.

Preparation of EDTA dianhydride

To a solution of ethylenediaminetetraacetic acid (EDTA, 12.5 g) in pyridine (22 mL) was added Ac_2O (20 mL). After being stirred for 24 h at 70°C, the resulting mixture was cooled to room temperature and filtered. The collected solid was successively washed with Ac_2O and diethyl ether and dried in vacuum to give EDTA dianhydride.

Procedure for the pretreatment of microcrystalline cellulose

Microcrystalline cellulose (5.0 g) was dispersed in a freshly prepared aqueous NaOH solution (10 w/w%, 200 mL). This mixture was then stirred for 24 h at ambient temperature and then filtered. The collected cellulose samples were washed with EtOH and dried under high vacuum to give light yellow activated microcrystalline cellulose.

Procedure for the preparation of Cell-EDTA and Pd@Cell-EDTA

The Cell-EDTA was prepared according to the procedure described elsewhere (Kahovec et al. 1980; d'Halluin et al. 2017; Cheng et al. 2019) with a modification. Activated microcrystalline cellulose (3.7 g) was immersed in DMF (200 mL) and successively treated by EDTA dianhydride (10.3 g) followed by

pyridine (20 mL). The mixture was stirred at 70°C for 24 h and filtered. The collected solid was washed successively with DMF, EtOH and ethyl acetate and finally dried in vacuum to give Cell-EDTA composite.

Then, 1.8 g Cell-EDTA (1.8 g) was added in a pre-prepared PdCl₂ and NaCl solution (0.5g/0.5g, 30 mL) and continued stirring at room temperature for 24 h and then filtered. The collected yellowish solid was successively washed with distilled water, ethyl acetate, dichloromethane, and then dried under high vacuum to afford Pd@Cell-EDTA catalyst.

General procedure for Pd@Cell-EDTA catalyzed Suzuki reaction

A mixture of aryl halide (1.0 mmol), arylboronic acid (1.2 mmol), K₂CO₃ (2.0 mmol), and a catalytic amount of Pd@Cell-EDTA (0.05 mol% of Pd) was stirred in 2 ml 78% EtOH at 78 °C in a sealed vessel for the specific time indicated by TLC. A certain amount of ethyl acetate was added to the vessel after the completion of reaction to extract the product and separate the catalyst. The catalyst was washed with ethyl acetate (3×5ml) adequately and dried at 50 °C for the next run. The filtrate was washed with brine and then the organic layers were separated, the organic phase was dried over anhydrous Na₂SO₄. After evaporation of solvent by using a rotary evaporator, the residue was isolated by column chromatography on silica gel to give the desired pure product. All the products are known and their ¹H NMR and ¹³C NMR data were identical to those reported in the literature.

General procedure for Pd@Cell-EDTA catalyzed Sonogashira reaction

Pd@Cell-EDTA catalyst (0.1 mol %) was added to a mixture of aryl halide (1 mmol), terminal alkyne (1.2 mmol), and K₂CO₃ (2.0 mmol) in 2 mL of MeOH. The reaction was heated in an oil bath at 65°C and tracked by TLC. Upon the reaction accomplished, adequate ethyl acetate was added to the flask to extract the product and separate the catalyst. The target pure product was obtained by column chromatography after removal of organic solvent using a rotary evaporator. All the products are known and their ¹H NMR and ¹³C NMR data were in accordance with those reported literature.

Results And Discussion

Synthesis and characterization of catalyst

The synthetic route to prepare Pd@Cell-EDTA catalyst was outlined in Scheme 1. In the presence of acetic anhydride, EDTA is dehydrated into EDTA dianhydride. Meanwhile, the microcrystalline cellulose is activated by 10% sodium hydroxide solution, converting its hydroxyl group into alkoxide to enhance its nucleophilicity. Thanks to the presence of abundant reactive hydroxyl groups in pre-activated cellulose, EDTA can be easily grafted onto the surface of microcrystalline cellulose successfully through the esterification reaction with EDTA dianhydride in the presence of pyridine in DMF. This reaction allows introducing carboxylic and amine functional groups that present high ability to form Pd complexes. Furtherly, Pd@Cell-EDTA catalyst was prepared by coordination of Pd²⁺ with Cell-EDTA. According to previous data (Busch et al. 1956), Pd(II) salts react with EDTA easily in water to form square complexes

containing one ligand residue per Pd atom. EDTA is used as tetradentate ligand which coordinates with two nitrogen atoms and two carboxylic groups. Pd(0) was formed by the partly reduction of Pd (II) by the hydroxyl group of cellulose (Seyednejhad et al. 2019). The Pd content in fresh Pd@Cell-EDTA catalyst was determined by ICP-AES to be 0.11 mmol/g.

Then, various analytical techniques including XPS, FTIR, EDS, SEM, TEM, TGA, and DGT were performed to identify the components, structures, and morphology of Pd@Cell-EDTA catalyst.

XPS is used to confirm the components and oxidation state of elements present in the Pd@Cell-EDTA catalyst. Figure 1 showed the XPS survey scan spectra of the typical elements in the binding energy range of 0-1400 eV and high-resolution spectra of N_{1s} and Pd_{3d} of catalyst. It was found that Pd, C, N and O elements were the predominate species in Fig. 1a. Two peaks centered at 400.75 and 399.63 eV in Fig. 1b corresponding N_{1s} (Nolting et al. 2007), which can be ascribed to the N element in EDTA and indicate that EDTA has been successfully grafted onto cellulose chain. According to Fig. 1c, two valence states of Pd in the catalyst can be observed. XPS spectra indicated the presence of both Pd(II) and Pd(0) phases. The peak at 338.42eV corresponds to Pd (II) while 336.82eV corresponds to Pd (0) (Lin et al. 2017) which may be formed by the reduction of Pd (II) by the hydroxyl group of cellulose (Seyednejhad et al. 2019). Pd (0) can also be stabilized by EDTA owing to its vacant orbital, which effectively prevent Pd (0) from aggregating into palladium black and thus losing activity.

The FTIR of microcrystalline cellulose (curve a) and Pd@Cell-EDTA (curve b) in the range of 4000 – 500 cm^{-1} are presented in Fig. 2. Compared with the spectra of microcrystalline cellulose, a new peak appeared at 1742 cm^{-1} in the spectra of Pd@Cell-EDTA, which is corresponded to the carboxylic group in EDTA (d'Halluin et al. 2017), furtherly indicating that EDTA has been successfully grafted onto microcrystalline cellulose. Besides, the characteristic absorption peaks at 1431 cm^{-1} and 1639 cm^{-1} are respectively assigned to the symmetric and asymmetric stretching vibration of carboxylate groups (Lin et al. 2017; Zhang et al. 2016).

In order to have a further insight into the morphology of the catalyst, the SEM and TEM images of Pd@Cell-EDTA composites were depicted in Fig. 3. As can be seen in Fig. 3a-d, the catalyst was composed of micron-scale fibers with very rough surface, which provides a wide contact area between the reactants and catalyst. With more high magnification, it can be clearly observed in TEM images (Fig. 3e) that the catalyst was composed of quasi-spherical nanoparticles and the average diameter of these nanoparticles was about 30 nm as shown in histogram of nanoparticle sizes (Fig. 3f).

The distribution of Pd has important impact on the catalytic activity. To adequately analyse the elemental distribution of Pd@Cell-EDTA catalyst, SEM element mapping images are exhibited in Fig. 4. The elemental mappings conclusively evidence the existence of C, O, N, and Pd elements and their homogeneously dispersion throughout the catalyst.

EDS analysis shown in Fig. 5 was performed to determine the element content in Pd@Cell-EDTA catalyst. The results showed that the contents of each element in the catalyst were C: 53.74%, N: 3.44%, O: 42.65%, and Pd: 0.16%. From the content of carbon and nitrogen, the approximate ratio of cellulose to EDTA in the catalyst can be calculated. Set the amount of cellulose as n_{Cell} and the amount of EDTA as n_{EDTA} , then there are:

$$\text{C: } 12 \times 6 \times n_{\text{Cell}} + 12 \times 10 \times n_{\text{EDTA}} = 53.74$$

$$\text{N: } 15 \times 2 \times n_{\text{EDTA}} = 3.44$$

It can be worked out that $n_{\text{Cell}} = 0.55$, $n_{\text{EDTA}} = 0.11$, and $n_{\text{EDTA}} : n_{\text{Cell}} = 5:1$, which indicating that about every five cellulose units can graft one EDTA molecule. Considering that each cellulose unit has three hydroxyl groups, the degree of substitution of EDTA between cellulose chain is 6.7%.

In order to test the thermodynamic stability of Pd@Cell-EDTA, TGA and corresponding DTG analyses of were performed and presented in Fig. 6. As can be seen in the curse of TGA (curse a), there is a slightly weight loss below 100 °C originated from the removal of physical adsorptive moisture. The catalyst exhibited a sharp loss in mass at nearly 250 °C in the curse of DTG (curse b), probably related to the decomposition of the cellulose macromolecule chain (Das et al. 2010). This result indicated that Pd@Cell-EDTA has a good thermal stability from room temperature to 250 °C and suitable for most organic catalytic reactions since they are usually carried out below 200 °C. Moreover, due to the remaining of palladium, there is still a small weight of the residue at the higher temperature.

Application of Pd@Cell-EDTA in Suzuki reactions

To search the optimal reaction conditions for Suzuki reactions, iodobenzene (1.0 mmol) and phenylboronic acid (1.2 mmol) was selected as model substrates and various conditions were systematically explored (Supplementary materials, Table S1). The optimized reaction condition for the Suzuki model reaction was set at the usage of iodobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), and 0.05 mol % of Pd under 2 ml 78% EtOH at 78 °C.

Obtaining the optimal reaction conditions, various iodobenzene and phenylboric acid were investigated to further examined the generality and limitation of this methodology. The results were generalized in Table 1. It can see that either electron-withdrawing or electron-donating groups of iodobenzene and phenylboric acid has no obvious effect on the reaction. Most of the substrates afforded high yields and only the reaction of 4-methyliodobenzene with 4-methoxyphenylboric acid gives a moderate yield of 77% (Table 1, entry 5). It indicates that this catalytic system has good universality and tolerance of various substrate. Additionally, it was worth noting that 2-iodothiophene can also obtain high yields (Table 1, entry 16), which meant this catalyst was compatible of a wide scope of substrates.

Application of Pd@Cell-EDTA in Sonogashira reactions

In order to further explore the application universality of Pd@Cell-EDTA, Sonogashira reactions had been performed in the presence of Pd@Cell-EDTA catalytic system to prepare corresponding diphenylacetylene. The model reaction of iodobenzene (1.0 mmol) and phenylacetylene (1.2 mmol) was exerted to search of the optimal reaction conditions (Supplementary materials, Table S2). To conclude, the optimal condition for model reaction involved the usage of iodobenzene (1.0 mmol), phenylacetylene (1.2 mmol), K_2CO_3 (2.0 mmol), and 0.10 mol % of Pd of catalyst in 3 mL MeOH at 70 °C. It is worth mentioning that there was no copper salt using as a co-catalyst in this catalytic system neither nitrogen protection device, indicating that Sonogashira reaction can also run smoothly without copper, which can effectively avoid copper-induced oxidative self-coupling of alkynes, *i.e.*, the Glaser reaction (Sindhu, et al. 2014).

The generality of the Pd@Cell-EDTA catalyst for the Sonogashira reaction was explored *via* using structurally diverse iodobenzene and phenylacetylene with the optimized conditions, and the results are summarized in Table 2. Most of substrates bearing with electron-donating or electron-withdrawing groups produced the expected product in good to excellent yields. However, when iodobenzene bearing with a strong electron-donating groups, such as 4-methoxyiodobenzene as the reactant, the yield decreases significantly (Table 2, entries 11–13), which is in line with the reported literature that iodophenene with electron-donating group has higher E_{HOMO} (Highest Occupied Molecular Orbital energy), thus the intermediate after oxidation addition is more stable and difficult to conduct the subsequent reaction (an der Heiden et al. 2008). Fortunately, 1-octyne as the reactant also achieved in good yields, making enlarge the scope of substrates in this catalytic system.

Recyclability and heterogeneity test of Pd@Cell-EDTA in Suzuki reactions

For the purpose of practical application, the recyclability of the Pd@Cell-EDTA composites was evaluated by repetitive experiment on the Suzuki model reaction under the afore-mentioned optimal condition. The results shown in Fig. 7 demonstrated that the catalyst could be effectively recycled for more than 5 consecutive runs without significant dropping its catalytic activity.

To further investigated the homogeneity/heterogeneity of Pd@Cell-EDTA catalysts, hot filtration test was performed similarly using the Suzuki model reaction. First, the model reaction was carried out at 78 °C for 5 min, at that point the solid catalyst was filtered off. The left reaction mixture was allowed to react for another 25 min at reaction temperature. The product yields were obtained in 52% (5 min) and 65% (30 min), respectively. Only a slight increase in the product yield was observed from 52–65%, suggesting that the catalysis was characteristically heterogeneous in nature.

Explanation of the superior catalytic performance of Pd@Cell-EDTA on carbon-carbon cross-couplings

The highly catalytic activity of the synthesized Pd@Cell-EDTA catalyst towards carbon-carbon cross-couplings presumably due to the synergic effect of EDTA and hydroxyl groups of cellulose. The electron-donation of nitrogen and carboxylic groups of EDTA to Pd facilitates the electronic charge transfer, resulted in a highly negatively charged Pd center, which makes Pd more electron rich for facile oxidative

addition of aryl halide, and hence significantly enhanced the catalytic activities for Suzuki, Heck, and Sonogashira reactions (Rai et al. 2016; Wang et al. 2017). It should be note that, to Suzuki reaction, the catalyst has superior catalytic performance with very low Pd loading (0.05 mol% of Pd). The activity of the catalyst can be attributed to the coordination of EDTA with Pd and the activation of phenylboronic acid *via* esterification of hydroxyl groups of cellulose (Zhai et al. 2015; Oshima et al. 1999). The reported works demonstrated the cyclic phenylboronate ester have better reactivity in Pd-catalyzed Suzuki reaction (Delaney et al. 2020; Nichele et al. 2009). The suggested synergic effect for Suzuki reaction depicted in Fig. 8.

Comparison of catalytic activity of Pd@Cell-EDTA in Suzuki reaction with other reported catalysts

To illustrate the advantages of Pd@Cell-EDTA catalyst, other previously reported Pd catalysts have been compared in Table 3 using the Suzuki model reaction as a reference. The comparative results demonstrate that Pd@Cell-EDTA has some outstanding merits over other solid Pd catalysts in terms of low catalyst loading, short reaction time and excellent yield.

Conclusions

An easy method for the fabrication of Pd@Cell-EDTA catalyst has been developed through the esterification reaction of microcrystalline cellulose with ethylenediaminetetraacetic dianhydride and then anchor Pd *via* coordination with Pd(II) solution. This as-prepared catalyst was well characterized by ICP, XPS, FTIR, EDS, SEM, TEM, TGA and DTG analyses. It was proven that Pd@Cell-EDTA was a highly efficient catalyst for Suzuki reactions and Sonogashira reactions. The outstanding features of excellent catalytic activity, wide application, tolerance of broad scope of substrate, good reusability and environmental benign in this catalytic system make it potential and competitive for practical applications.

Declarations

Ethics Declarations

Conflict of interest

Authors have no conflict of interest.

Animal and human rights

There is no animal research content in this paper.

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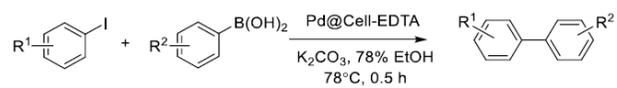
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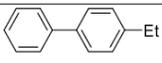
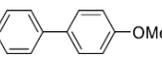
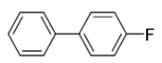
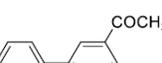
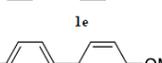
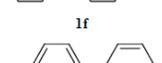
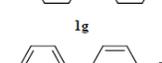
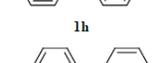
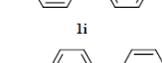
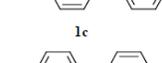
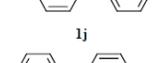
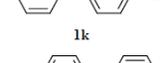
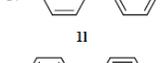
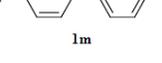
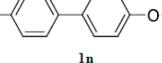
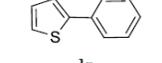
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Tables

Table 1 Pd@Cell-EDTA-catalyzed Suzuki reactions to synthesis of various biphenyl ^a

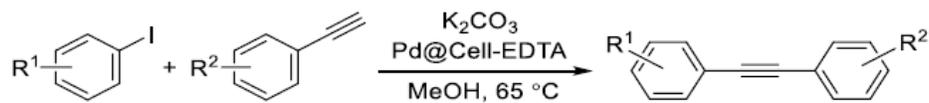


Entry	R ¹	R ²	Product	Yield ^b / %
1	H	4-Et	 1b	97
2	H	4-MeO	 1c	99
3	H	4-F	 1d	99
4	H	3-COCH ₃	 1e	99
5	4-Me	4-MeO	 1f	77
6	4-Me	H	 1g	92
7	4-Me	F	 1h	95
8	4-MeO	4-Et	 1i	99
9	4-MeO	4-H	 1j	88
10	4-MeO	4-F	 1k	89
11	4-Cl	4-MeO	 1l	98
12	4-Cl	H	 1m	99
13	4-Cl	F	 1n	94
14	4-F	4-OCHMe ₂	 1o	91
15	4-F	4-F	 1p	90
16		H	 1r	99

^aReaction conditions: iodobenzene (1.0 mmol), phenylboronic acid (1.2 mmol), catalyst (0.05 mol%), K₂CO₃ (2.0 mmol), 78% EtOH (2 mL), 78 °C.

^bIsolated yield.

Table 2 Pd@Cell-EDTA-catalyzed Sonogashira reactions to synthesis of various diphenylacetylene ^a



Entry	R ¹	R ²	Time / h	Product	Yield ^b / %
1	H	4-Cl	3		73
2	H	4-MeO	3		99
3	H	<i>n</i> -octyne	2		78
4	4-Me	H	2		93
5	4-Me	4-MeO	2		88
6	4-Me	<i>n</i> -octyne	3.5		83
7	4-CF ₃	H	2		97
8	4-CF ₃	4-Cl	2		98
9	4-CF ₃	4-MeO	2		87
10	4-CF ₃	<i>n</i> -octyne	2		96
11	4-MeO	H	3.5		50
12	4-MeO	4-Cl	7		N. R.
13	4-MeO	4-MeO	2		86

^a Reaction conditions: iodobenzene (1.0 mmol), phenylacetylene (1.2 mmol), base (2.0 mmol), catalyst (0.10 mol%), 65 °C.

^b Isolated yield.

Table 3 Comparison between Pd@Cell-EDTA and other reported Pd-catalysts using the Suzuki model reaction as a reference ^a

Entry	Catalyst(mol%)	Solvent	Temp. (°C)	Time (h)	Yield (%)	Ref.
1	Pd@Cell-EDTA (0.050)	EtOH/H ₂ O	78	0.5	99	this work
2	OCMCS-SB-Pd(II) (0.46)	EtOH/H ₂ O	50	2	96	(Dong et al. 2021)
3	Pd NPs@CNCC (1.0)	EtOH/H ₂ O	80	2	95	(Wang et al. 2020)
4	FLA-Pd (0.05g)	H ₂ O	reflux	1	93	(Nasrollahzadeh et al. 2019)
5	Fe ₃ O ₄ @SiO ₂ -4-AMTT-Pd(II) (0.1)	H ₂ O	50	3.5	68	(Hajipour et al. 2018)
6	Pd NPs (1.0)	H ₂ O	100	12	85	(Nasrollahzadeh et al. 2015)
7	NHC-Pd/GO-IL (0.1)	EtOH/H ₂ O	60	2.5	92	(Movahed et al. 2014)
8	PdNPs@chitosan (0.10)	TBAB	90	5	97	(Cotugno et al. 2014)
9	Pd (II)-SBA-16 (0.5)	EtOH/H ₂ O	80	2.5	100	(Wei et al. 2013)
10	Starch-Pd ⁰ NPs (0.10)	DMF/H ₂ O	80	0.5	97	(Liu et al. 2010)

^a Suzuki reaction using bromobenzene and phenylboronic acid as substrates.

Figures

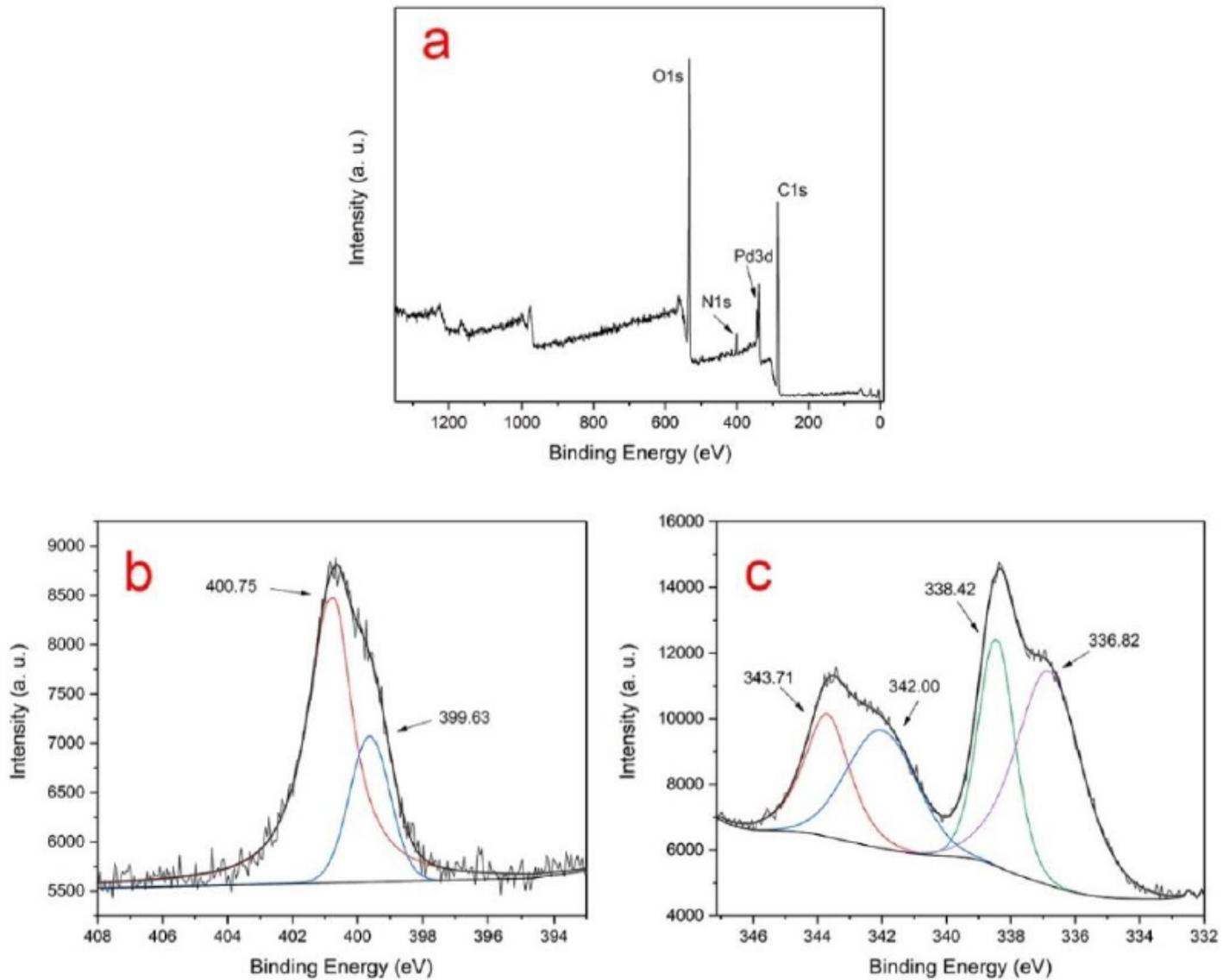


Figure 1

The survey scan of XPS (a) and high-resolution spectra of N1s (b) and Pd3d (c)

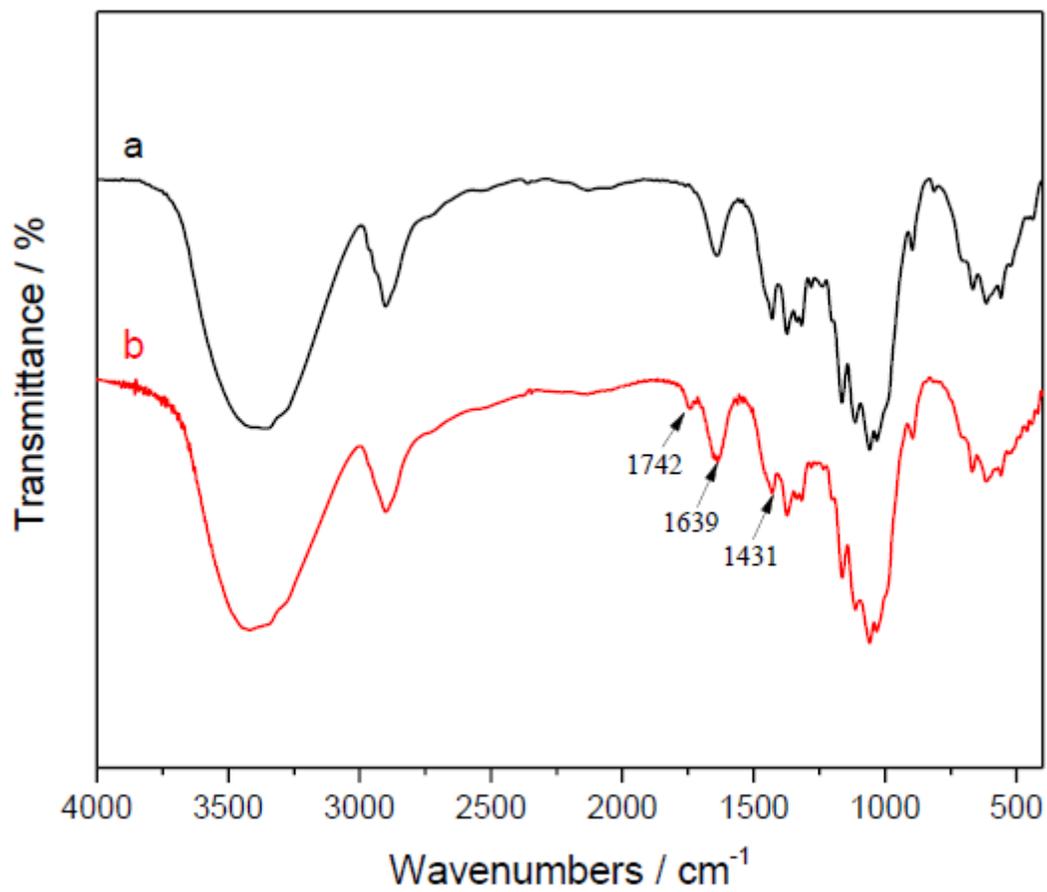


Figure 2

The FTIR spectra of microcrystalline cellulose (a) and Pd@Cell-EDTA (b)

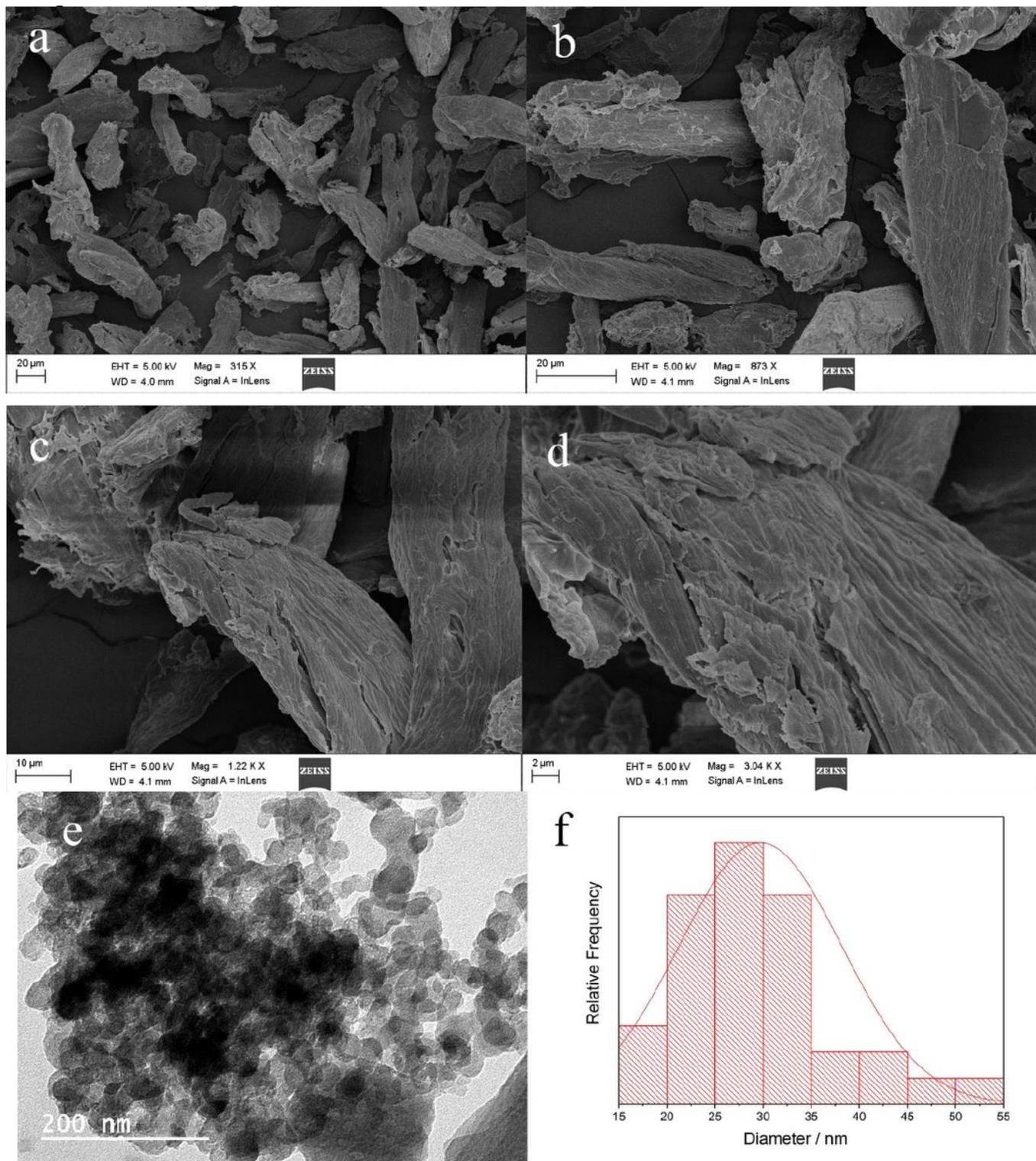


Figure 3

SEM (a, b, c, d) and TEM (e) images and nanoparticles diameter histogram (f) of Pd@Cell-EDTA catalyst

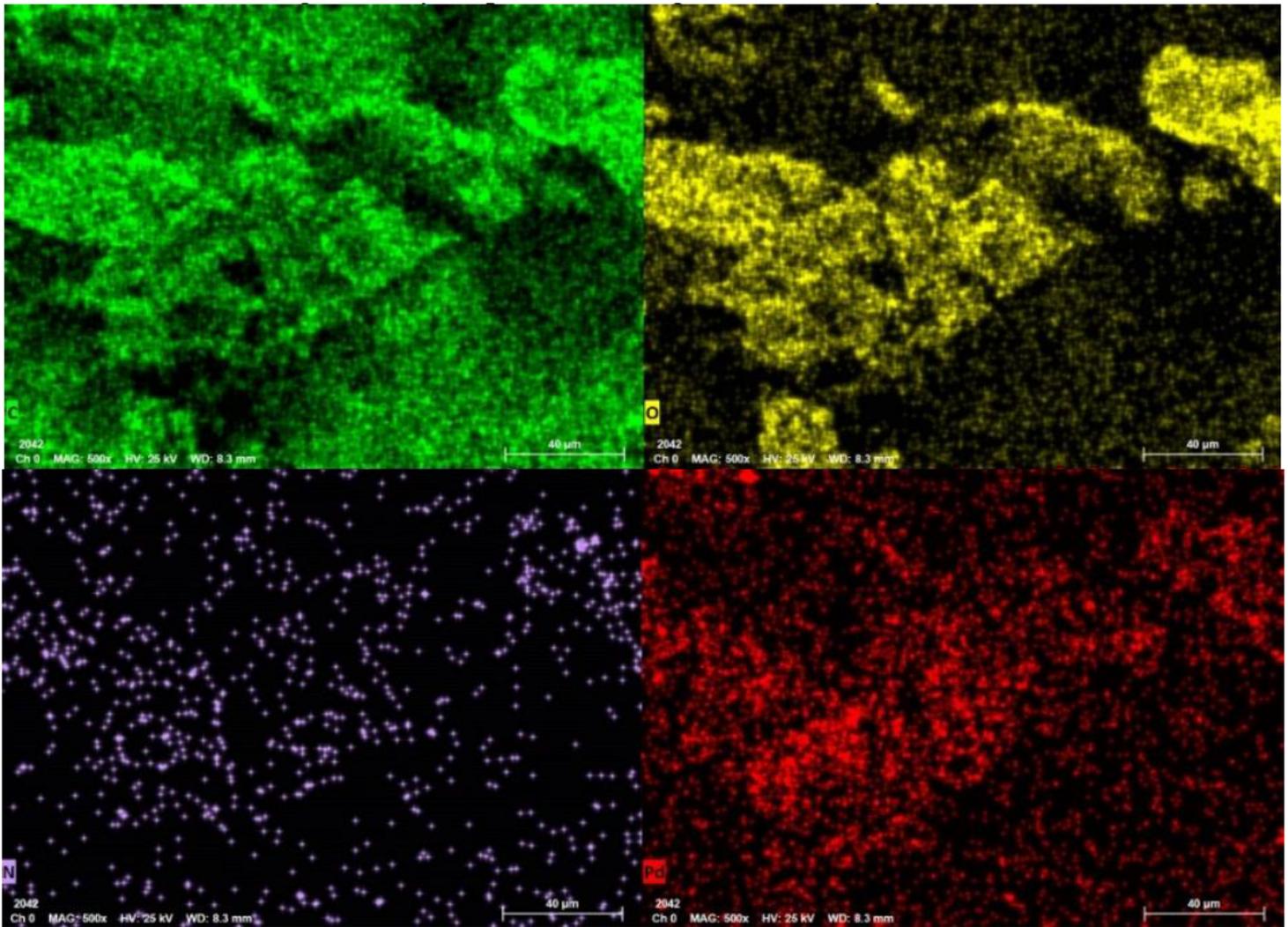


Figure 4

SEM corresponding elemental mapping images of Pd@Cell-EDTA catalyst

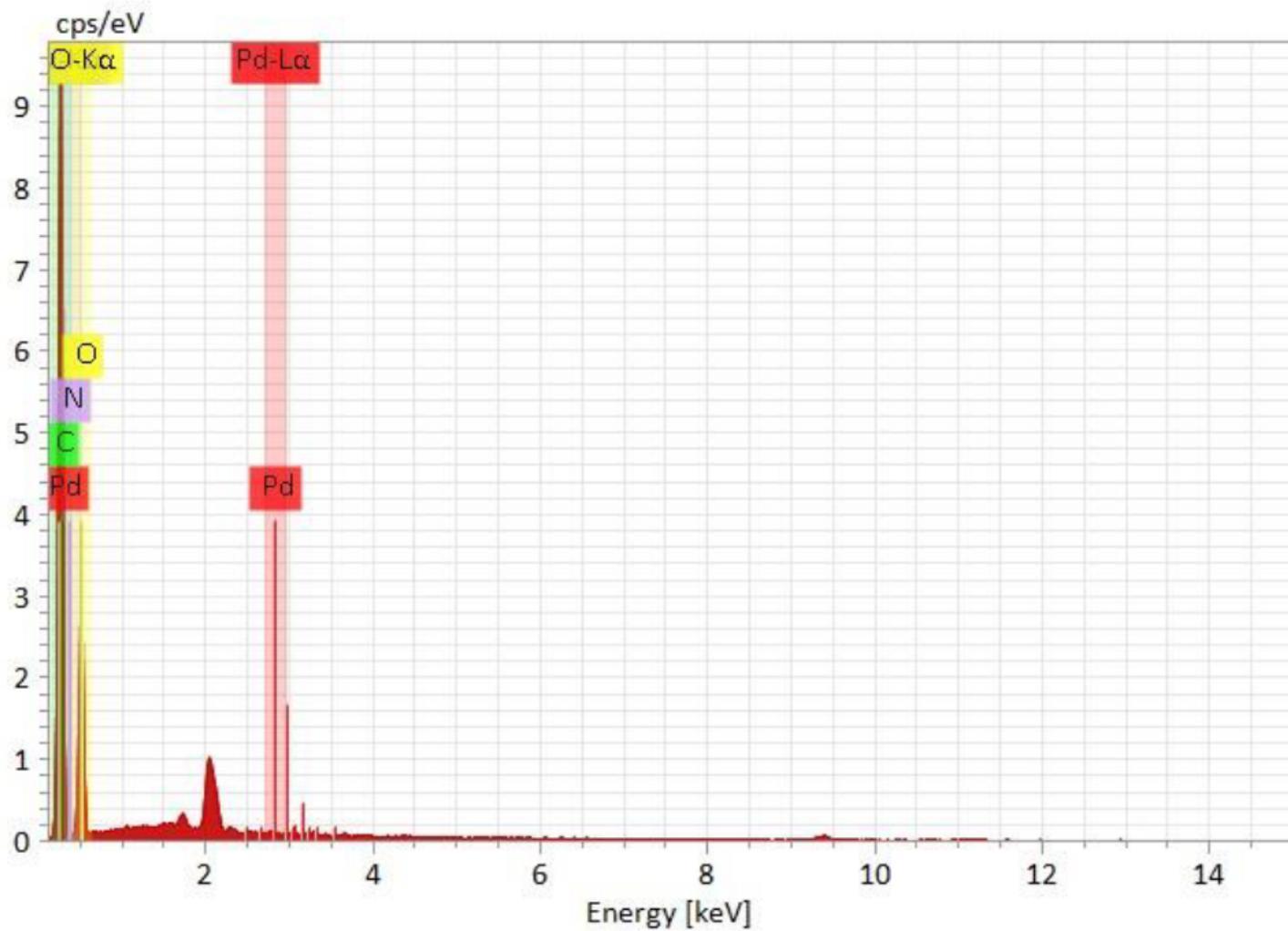


Figure 5

The EDS element analysis of Pd@Cell-EDTA catalyst

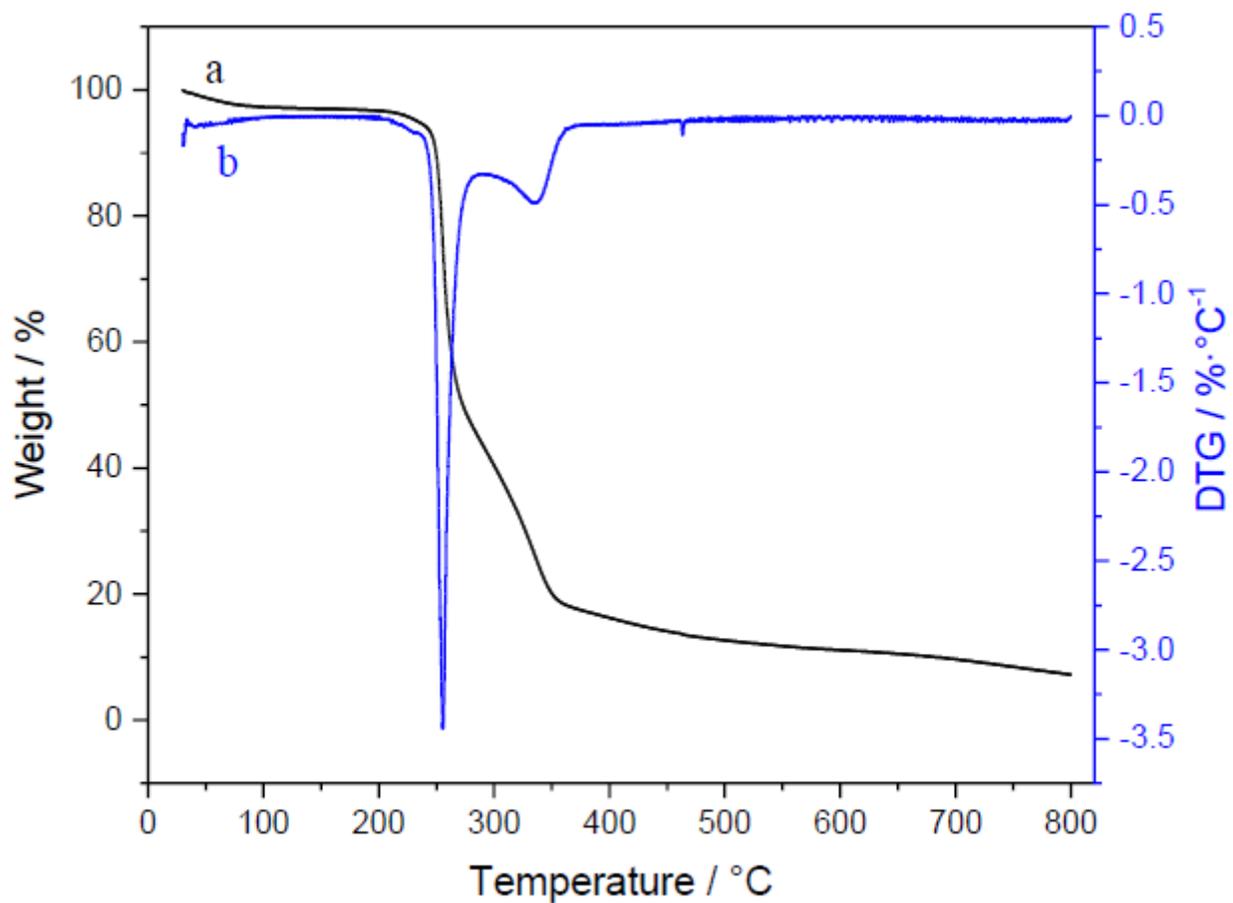


Figure 6

The TGA (a) and DTG (b) curves of Pd@Cell-EDTA catalyst

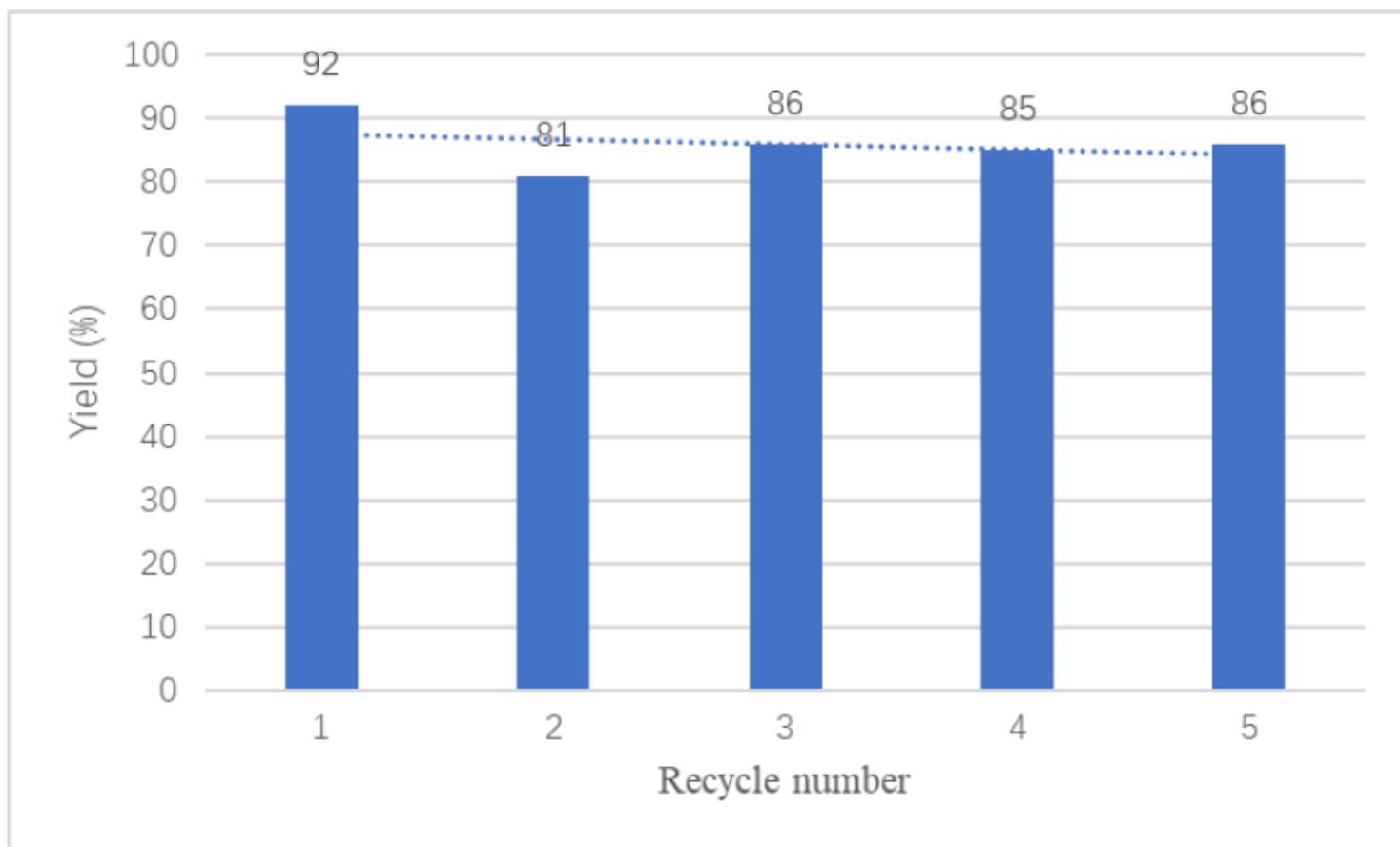


Figure 7

Recycling of Pd@Cell-EDTA in Suzuki reaction

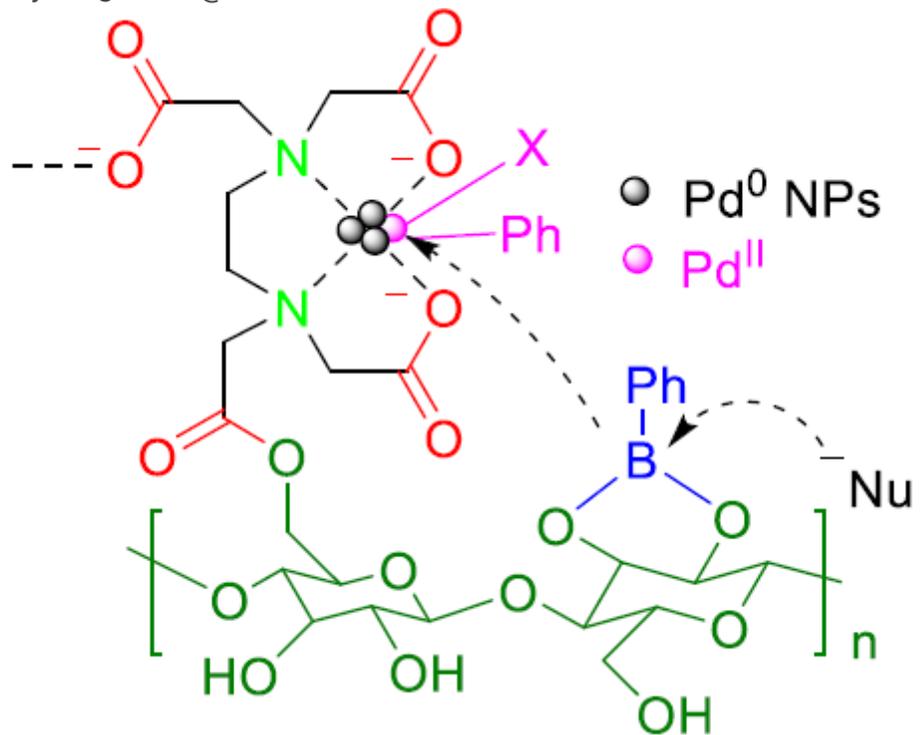


Figure 8

The suggested activation model of Pd@Cell-EDTA for Suzuki reaction

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme1.png](#)
- [PdCellEDTAsupplementarymaterial.docx](#)