



## Research paper

## Pd supported on Cu-doped Ti-pillared montmorillonite as catalyst for the Ullmann coupling reaction

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## ABSTRACT

The preparation and characterization of Pd/montmorillonite supported catalysts and their application in the O-, N-, and S-arylation through Ullmann coupling reaction were reported. The catalysts consisted of Pd supported on raw montmorillonite and on a Cu-doped Ti-pillared montmorillonite, and were prepared via impregnation of the clay supports with a Pd-precursor by the incipient wetness method. The catalysts were found to be effective and gave good to excellent yield in the arylation reactions. The catalyst based on the PILC was reusable and gave good yield up to three cycles of reaction.

## 1. Introduction

The C–C bond forming reactions constitute an important class of reactions in organic chemistry for the preparation of a number of complex compounds of pharmaceutical interest. Smectites and their modified forms have been used as supports for supported catalysts in many organic reactions such as Diels–Alder, oxidation, reduction, acetalation, among others. In particular, Pillared Clays (PILC) have been used themselves or supporting active phases for several organic reactions (Gil et al., 2010; Bergaya and Lagaly, 2013; Vicente et al., 2013).

Palladium has been demonstrated as the most effective metal in constructing C–C bonds. Palladium-catalyzed C–C coupling reaction involving aryl halide has made critical impact on organic synthesis (Sarkar et al., 2017; Tian et al., 2017). Pd-catalyzed homogeneous C–C coupling reactions are common but with a number of disadvantages such as formation of complexes with groups in the catalysts, contamination of the products with Pd, that may lead to toxicity and affect the conductivity among other properties. Heterogeneous version of Pd-catalysts for C–C bond forming reactions are fewer due to difficulty in the synthesis, stability, activity, the cost of ligands, such as bulky tertiary phosphines, and difficulties associated with the separation of the ligands and their degradation products, as phosphine oxides. Thus, catalysts as polymer-supported macrocyclic Schiff base palladium complex (He and Cai, 2011), Pd supported on dendrimers (Ricciardi et al., 2015), Pd nanoparticles supported on amino functionalized metal-organic framework (MOF) (Huang et al., 2011) have been

reported. Recently, a magnetically separable Fe<sub>2</sub>O<sub>3</sub> supported palladium catalyst, whose synthesis involved the use of linkers and a multistep synthetic procedure, has been reported (Heidari et al., 2017). The preparation of these catalysts involves multistep reactions and the chemicals used for the synthesis of catalyst are expensive.

Practical applications of clay mineral supported Pd materials have increased due to the simplest method of preparation, economically affordable, and reusability. For example, Pd supported on PILC catalysts have been used for destruction of chlorinated VOC (Aznárez et al., 2015; Michalik-Zym et al., 2015), while Bouazizi et al. (2016) have prepared Pd nanoparticles through incorporation of Boltorn polyol dendrimer H30 in montmorillonite, finding high affinity towards hydrogen. In the specific field of organic synthesis, Varadwaj et al. (2014) reported the preparation of an organo-functionalized clay mineral supported Pd catalyst, using it in Suzuki–Miyaura and Ullmann coupling reactions; Pd supported on a montmorillonite previously functionalized with APTES silane has been used for the carbonylative Sonogashira reaction of aryl diiodides and for the synthesis of dibenzoylmethane (Chavan et al., 2015); a Pd supported on halloysite-dicationic-triazolium catalyst has been used for Suzuki cross-coupling reaction (Massaro et al., 2015); and catalysts composed of Pd nanoparticles immobilized on laponite have been employed for the synthesis of resveratrol (Heck–Mizoroki C–C cross-coupling reaction) (Martínez et al., 2016).

In this context, a Pd-catalyst supported on Cu-doped Ti-pillared montmorillonite has been prepared, and its catalytic activity on the Ullmann O-, N- and S-arylation of amines and phenols has been

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investigated.

## 2. Experimental

### 2.1. Materials

The clay mineral used in this work was a raw montmorillonite from Cheto, Arizona, USA (The Clay Minerals Repository, where this sample is denoted as SAZ-1). The natural clay mineral was purified before its use by dispersion–decantation, separating the fraction lower than 2  $\mu\text{m}$ . Its cation exchange capacity was 0.67 meq/g, its basal spacing 13.60 Å and its BET specific surface area 49  $\text{m}^2/\text{g}$ . It is remarkable that the CEC, determined by saturation with  $\text{NH}_4^+$  followed by Kjeldahl titration, was smaller than that usually reported for this reference clay, about 0.90 meq/g. The purified solid clay was designated as “Mt”. Aryl halides and substituted phenols were obtained from Sigma Aldrich. Solvents used were of analytical grade and were purified by standard methods prior to use.

### 2.2. Preparation of Cu-doped Ti-pillared montmorillonite

Preparation of Cu-doped Ti-pillared montmorillonite has been reported elsewhere (González-Rodríguez et al., 2015, where this sample was denoted MtTiCu10). Among the solids there reported, the Cu-doped Ti-pillared montmorillonite was selected for this work because of its low acidity and the presence of Cu, an attractive element for catalysis of organic reactions. Briefly, Ti-polycation solution was prepared by slow addition, under vigorous stirring, of  $\text{TiCl}_4$  (doped with  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Cu}^{2+}/\text{Ti}^{4+}$  ratio 10:90) to absolute ethanol, until a homogeneous yellowish solution was obtained. This solution was added to a solution of glycerin in distilled water. The new mixture was maintained under stirring for 3 h, and then it was dropwise added to a previously prepared montmorillonite aqueous dispersion, using a Ti/montmorillonite ratio of 40 mmol/g and aging under magnetic stirring at room temperature for 18 h. Then, the solid was separated by centrifugation, washed by dialysis for 48 h, dried overnight at 70 °C and finally calcined at 500 °C for 2 h at a heating of 1 °C/min. This solid was denoted as MtTi500.

### 2.3. Preparation of Pd-supported catalysts

Both the parent Mt and the solid pillared with Ti doped with Cu were used as supports. These solids were impregnated with palladium (5% Pd), using Pd(II) acetate as precursor, dissolving in acetone, and impregnating the solids by the incipient wetness method. Then, the solids were dried, and calcined at 500 °C for 2 h, leading the final catalysts. These solids were denoted as MtPd500 and MtTiPd500, when derived from the raw or the pillared Mt, respectively.

### 2.4. Characterization of the solids

Element chemical analyses were carried out at Activation Laboratories Ltd., in Ancaster, Ontario, Canada, using inductively coupled plasma-atomic emission spectrometry (ICP-AES). FT-IR spectra were recorded in the 450–4000  $\text{cm}^{-1}$  range in a PerkinElmer Spectrum-One spectrometer by the KBr pellet method. X-ray diffraction (XRD) patterns were recorded between 2 and 65° (2 $\theta$ ) over non-oriented powder samples, at a scanning speed of 2°/min, by using a Siemens D-500 diffractometer, operating at 40 kV and 30 mA, and employing filtered Cu  $K_\alpha$  radiation ( $\lambda = 1.5418$  Å). Textural properties were determined from nitrogen (Air Liquide, 99.999%) adsorption data, obtained at –196 °C using a Micrometrics Gemini VII 2390 t, Surface Area and Porosity apparatus. Specific surface area was obtained by the BET method ( $S_{\text{BET}}$ ), external surface area ( $S_{\text{ext}}$ ) and micropore volume ( $V_p$ ) by means of the t-method, and the total pore volume ( $V_t$ ) from the nitrogen adsorbed at a relative pressure of 0.95 (Sing et al., 1985;

Rouquerol et al., 1998).

### 2.5. General procedure of arylation reaction

A mixture of the various substrates, such as phenol, amine, pyrrole (1.2 mmol), 4-nitrochlorobenzene (1 mmol), base  $\text{K}_2\text{CO}_3$  (1.2 mmol) and DMF (3  $\text{cm}^3$ ) were taken in a 25  $\text{cm}^3$  RB flask. 20 mg of catalyst was added to the reaction mixture and heated up to 110 °C for the required time. The progress of the reaction was monitored by thin-layer chromatography (TLC). After completion of the reaction, the catalyst was filtered and washed with dichloromethane. The filtrate was diluted with water and again extracted with dichloromethane and the organic layer was dried over anhydrous sodium sulfate. Further purification of the product was carried out by column chromatography using petroleum ether and ethyl acetate as solvents. The products were confirmed by FT-IR and  $^1\text{H}$  NMR spectral methods; FT-IR was recorded by the KBr pellet method using a JASCO FT-IR spectrometer in the range of 400–4000  $\text{cm}^{-1}$ , while  $^1\text{H}$  NMR spectra were recorded on a Bruker 400 MHz instrument using TMS as internal standard (see Fig. S1, Supplementary Data). Melting points were determined using a digital melting point apparatus.

## 3. Results and discussion

### 3.1. Characterization of the catalyst

The chemical water-free composition of the raw clay mineral was  $\text{SiO}_2$ : 69.08%;  $\text{Al}_2\text{O}_3$ : 19.71%;  $\text{Fe}_2\text{O}_3$ : 1.75%;  $\text{MnO}$ : 0.05%;  $\text{MgO}$ : 6.91%;  $\text{CaO}$ : 2.09%;  $\text{Na}_2\text{O}$ : 0.07%;  $\text{K}_2\text{O}$ : 0.07%;  $\text{TiO}_2$ : 0.26%, while the composition of the pillared Mt support was, also in water-free basis, as follows:  $\text{SiO}_2$ : 55.53%;  $\text{Al}_2\text{O}_3$ : 15.97%;  $\text{Fe}_2\text{O}_3$ : 1.44%;  $\text{MnO}$ : 0.01%;  $\text{MgO}$ : 5.34%;  $\text{CaO}$ : 0.10%;  $\text{Na}_2\text{O}$ : 0.03%;  $\text{K}_2\text{O}$ : 0.04%;  $\text{TiO}_2$ : 21.12%;  $\text{CuO}$ : 0.41%, showing clearly the incorporation of Ti as pillaring species and Cu as doping species (although in lower amount than that targeted in the pillaring solution), and the removal of Ca as the main exchangeable element (González-Rodríguez et al., 2015). For the Pd-catalysts, as they were prepared by a method that did not involve filtration steps, it was assumed that 5% Pd was incorporated.

The structure of montmorillonite was maintained after impregnation and calcination (see Figs. 1 and S2); all the characteristic peaks of montmorillonite were observed after the impregnation treatment. The basal spacing of Mt500 solid was 9.57 Å, while for the pillared MtTi500 solid, it was 16.49 Å. The impregnated solids showed similar basal

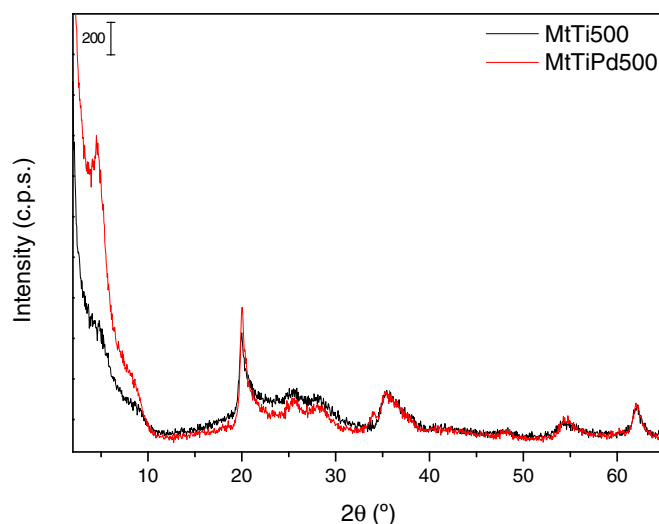


Fig. 1. X-ray diffractograms of the doped PILC support and the impregnated solid, both calcined at 500 °C.

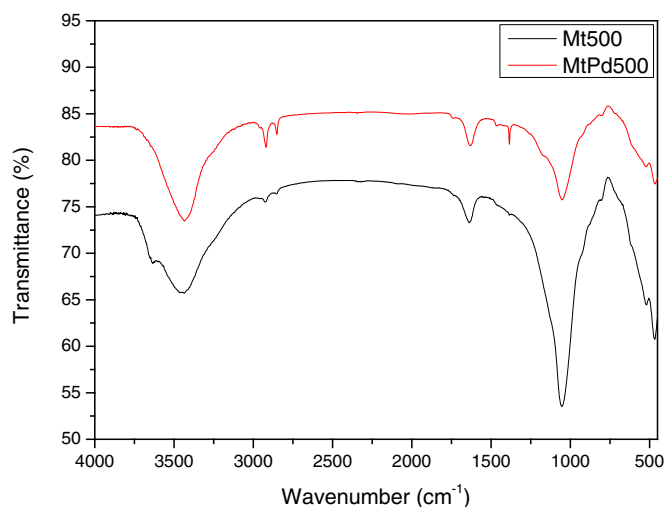
**Table 1**  
Textural properties of the supports and the catalysts, all calcined at 500 °C.

	$S_{\text{BET}}$ (m <sup>2</sup> /g)	$S_t$ (m <sup>2</sup> /g)	$V_{\mu}$ (cm <sup>3</sup> /g)	$V_{\Sigma}$ (cm <sup>3</sup> /g)
Mt500	49	49	0.000	0.103
MtTi500	329	135	0.108	0.136
MtPd500	80	64	0.009	0.104
MtTiPd500	89	69	0.012	0.158

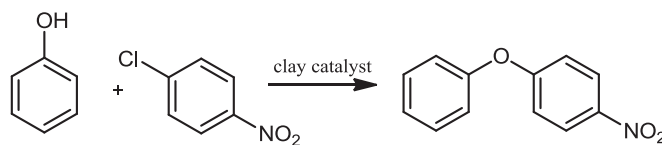
spacings. No peaks from Pd-species were detected in the impregnated solid. Besides, in the case of the raw Mt, the Pd-containing solids showed less intense reflections, but when the doped-PILC was used as support, the impregnation clearly favored the ordering of the layers, 001 reflection became more intense, probably the solid was ordered during the wetness impregnation and although it was then calcined, it maintained a best ordering that the support.

The nitrogen adsorption-desorption isotherms (see Fig. S3) are typical of layered solids, corresponding to type II (IUPAC classification), with a type H4 hysteresis loop at high relative pressure ( $p/p^0$ ) values, typical for solids with narrow slit pores (Sing et al., 1985). The loop closed at a relative pressure lower than 0.4, being reversible below this relative pressure. Both catalysts showed similar BET specific surface area, 80 and 89 m<sup>2</sup>/g, micropore volume, 0.009 and 0.012 cm<sup>3</sup>/g, and total pore volume, 0.104 and 0.158 cm<sup>3</sup>/g (see Table 1). It is remarkable that the impregnation caused a strong decrease of surface area and porosity in the case of the pillared clay mineral, associated with the occupancy of the porosity by Pd species. However, in the case of the parent clay mineral, the textural properties slightly developed during the impregnation, probably due to the removal under calcination of the acetate anions from the precursor and eventually some acetone molecules retained after the impregnation process. In any case, both Pd-supported solids showed acceptable BET specific surface area, which reinforce their potentiality as catalysts.

The FT-IR spectra of the supports and the impregnated solid were similar (see Fig. 2 for Mt500 and MtPd500), but two important differences were observed. The first one was the disappearance of the hydroxyl band near 3600 cm<sup>-1</sup> after impregnation, which strongly suggested its interaction with the Pd precursor during this process. Two effects from the precursors were also observed, C–H stretching vibrations close to 2900 cm<sup>-1</sup> and a sharp peak from the acetate group near 1400 cm<sup>-1</sup>. This indicated the permanence of these anions even after the calcination at 500 °C, although in very small amount.



**Fig. 2.** FT-IR spectra of the Mt500 support and the impregnated solid, both calcined at 500 °C.



**Scheme 1.** O-arylation of phenol with 4-nitrochlorobenzene.

**Table 2**  
Screening of the catalyst for O-arylation of phenol and 4-nitrochlorobenzene.

Entry	Catalyst	Yield (%)
1	MtTiPd500	97
2	MtTi500	48
3	MtPd500	76
4	SiO <sub>2</sub>	48 <sup>a</sup>
5	ZnO	45 <sup>a</sup>
6	TiO <sub>2</sub>	47 <sup>a</sup>
7	CeO <sub>2</sub>	87 <sup>a</sup>

Reaction conditions: 4-Nitrochlorobenzene (1 mmol), phenol (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (1.2 mmol), DMF (3 cm<sup>3</sup>), Catalyst: 20 mg, Temperature: 110 °C, time: 2 h.

<sup>a</sup> Results from Agawane and Nagarkar (2011).

### 3.2. Catalytic performance

#### 3.2.1. Catalyst screening

Three solids were tested for the O-arylation of phenol and 4-nitrochlorobenzene (see Scheme 1), namely the supported Pd/pillared Mt catalyst, MtTiPd500, and the two references: Pd/raw Mt, MtPd500, and the pillared Mt, MtTi500 (see Table 2); and some bibliographic results were also included (see Entries 4–7).

MtTiPd500 showed the best behavior, with higher yield than the other solids. The results indicated that both the pillaring procedure and, mainly, the incorporation of Pd exerted a positive effect on the catalytic behavior. Compared to the bibliographic results available for common metal oxide catalysts, MtPd500 also showed higher catalytic performance and CeO<sub>2</sub> is the only oxide with a relatively close behavior in DMSO as solvent and base KOH. Choudhary et al. (1992) have reported that bimetallic catalysts showed better activity than monometallic ones in the C–C coupling reaction, and this conclusion was also valid for the present catalysts, the system composed of Pd-Cu-Ti-montmorillonite was much more active than the other systems. The enhanced catalytic performance should be reasonably ascribed to the involvement of Ti and Cu in assisting Pd in the oxidative addition and reductive elimination steps.

#### 3.2.2. Effect of the solvent

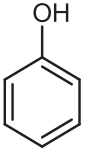
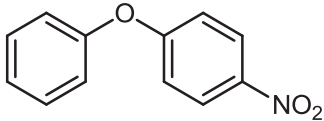
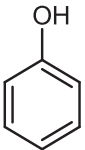
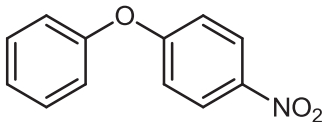
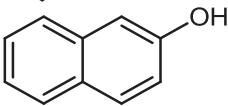
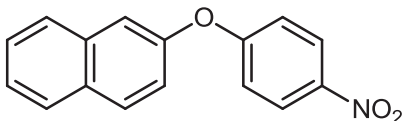
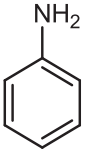
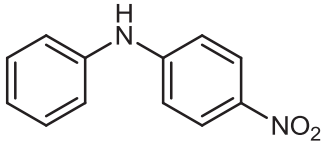
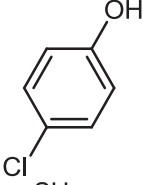
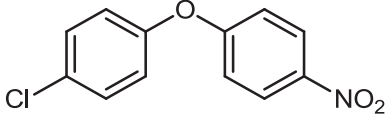
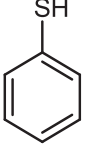
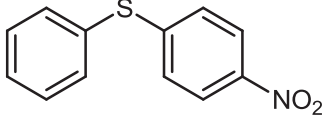
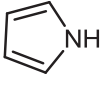
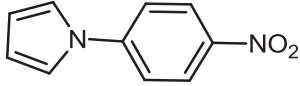

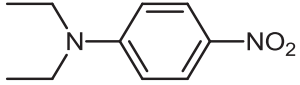
The effect of the solvent was also studied selecting phenol and 4-nitrochlorobenzene as substrates, at 100 °C, and using MtPd500 as catalyst. Various solvents with several properties were considered (see Table 3). The best results were obtained for DMF, which was selected as the solvent of choice for further studies. DMF is known to be a good reducing agent for metals (Layek et al., 2013), which seemed to influence the yield more than other properties of the solvents. It was

**Table 3**  
Effect of solvent for O-arylation of phenol.

Entry	Solvent	Yield (%)
1	DMF	97
2	DMSO	92
3	Dioxane	76
4	Toluene	48
5	Water	–

Reaction conditions: 4-Nitrochlorobenzene (1 mmol), phenol (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (1.2 mmol), solvent (3 cm<sup>3</sup>), catalyst: 20 mg, temperature: 110 °C, time: 2 h.

**Table 4**  
Yield of arylation of various substrates with 4-nitrochlorobenzene.<sup>a</sup>

Entry	Substrate	Product	Time (h)	Yield (%)
1			2	97
2			3	94
3			4.5	76
4			4	62
5			2	86
6			2.5	76
7			7	78
8			10	40

Reaction conditions: 4-Nitrochlorobenzene (1 mmol), phenol (1.2 mmol), K<sub>2</sub>CO<sub>3</sub> (1.2 mmol), DMF (3 cm<sup>3</sup>), catalyst: 0.02 g. Temperature: 110 °C, time: 2 h.

<sup>a</sup> In Entry 2, the substrate is 4-nitroiodobenzene.

significant that the reaction did not occur in water, the most polar solvent used, which suggested a possible influence of the polarity, although a tendency yield vs. polarity was not observed for other solvents.

### 3.2.3. Effect of the substrates

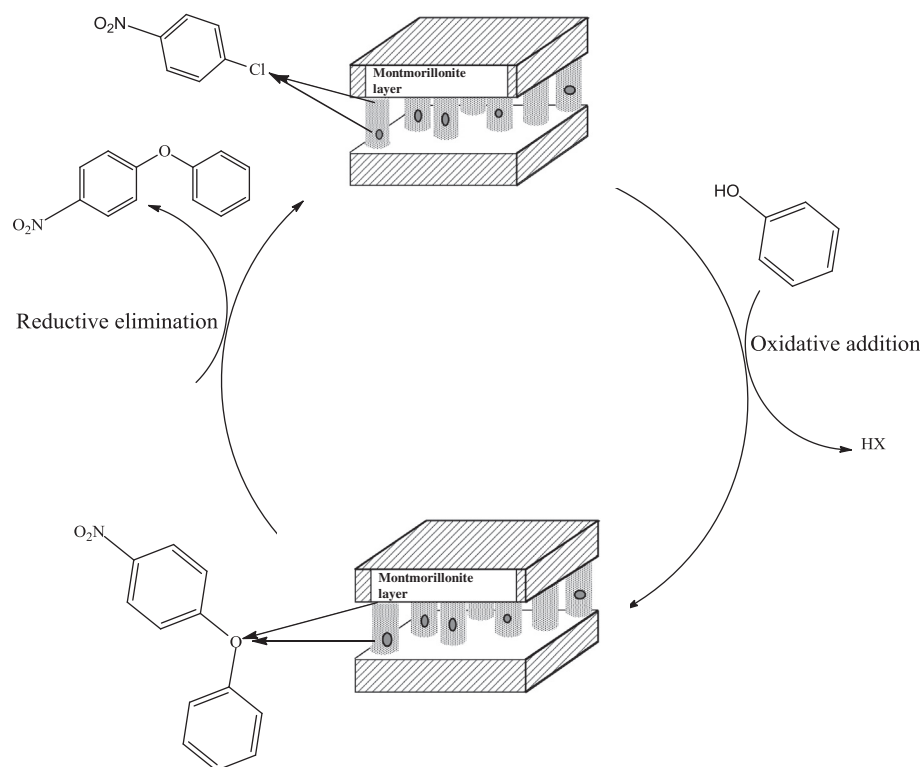
Various substrates were considered for the arylation with 4-nitrochlorobenzene, substrates such as phenol, naphthol, aniline or thiophenol, containing O-, N-, and S-atoms (see Table 4). Both the electron donating and electron withdrawing groups on the phenol ring afforded good arylation yields. O-arylation showed best yields than N- and S-reactions, although the yields obtained for thiophenol and pyrrole were satisfactory. Electron withdrawing groups in the ortho and para positions increased the rate of nucleophilic aromatic substitution reaction; the nitro group in the para position of 4-nitrochlorobenzene was found to influence the yield of reaction for all the substrates. Differences in the yield may be ascribed to the differences in the stability of the phenoxide formed by the different substrates.

With these results, a tentative mechanism for the reaction can be

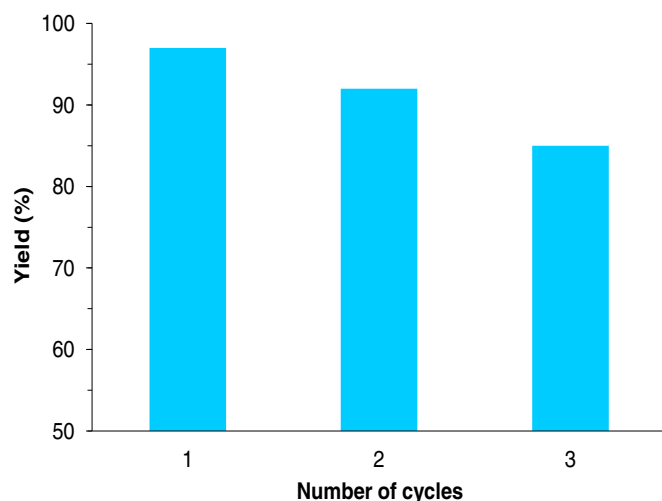
proposed (see Scheme 2). First, the nitro halogenated molecule was adsorbed on the surface of the catalyst interacting with Pd and Cu particles forming an intermediate, a loose complex catalyst-nucleophile. DMF acted as a solvent, while the metals present on the surface of montmorillonite may participate in the reaction, Cu and Pd particles taking part in the redox cycle and Ti pillars probably assumed a co-operative effect giving acidity, although not evidences of such roles were available. Oxidative addition of phenol occurred in the second step, which upon reductive elimination resulted in the final product.

### 3.2.4. Recycling studies

The recyclability of the catalyst was studied for three cycles. After the reaction, the catalyst was separated by filtration followed by washing with dichloromethane, dried in an air oven at 40 °C and used for a successive run. A moderate loss in activity was observed during each cycle (Fig. 3). This suggested that the catalyst may be reused, although the regeneration step should be improved, as the washing with dichloromethane and the drying steps seemed to damage the catalyst.



**Scheme 2.** Mechanism proposed for the O-arylation reaction on the montmorillonite catalyst.



**Fig. 3.** Recyclability of MtTiPd500 catalyst on the Ullmann coupling reaction. Reaction conditions: 4-Nitrochlorobenzene (1 mmol), phenol (1.2 mmol),  $K_2CO_3$  (1.2 mmol), DMF (3  $cm^3$ ), Catalyst: 20 mg, Temperature: 110 °C, Time: 3 h.

#### 4. Conclusions

Recyclable catalysts composed of Pd supported on montmorillonite or Cu-doped Ti-pillared montmorillonite have been prepared. The catalysts were found to be active for arylation of phenol. The catalyst based on the pillared clay mineral was found to be reusable with a moderate loss in activity. The mechanism proposed for the reaction involved the impregnated Pd and also the Cu doping the support.

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#### Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.clay.2017.12.037>.

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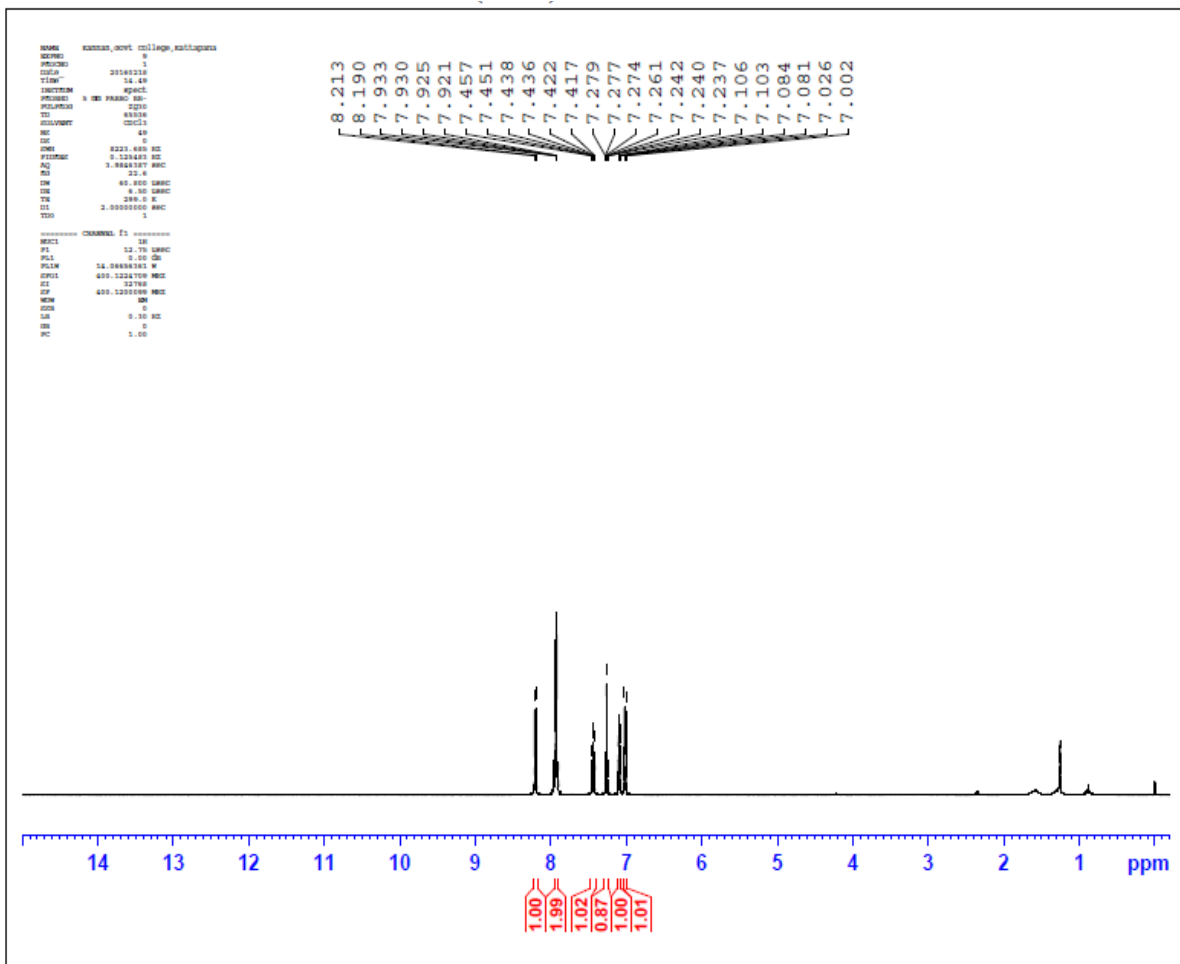
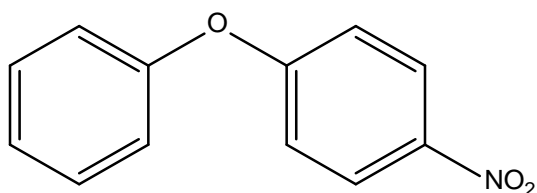
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# SUPPLEMENTARY MATERIAL

## Pd supported on Cu-doped Ti-pillared montmorillonite as catalyst for the Ullmann coupling reaction

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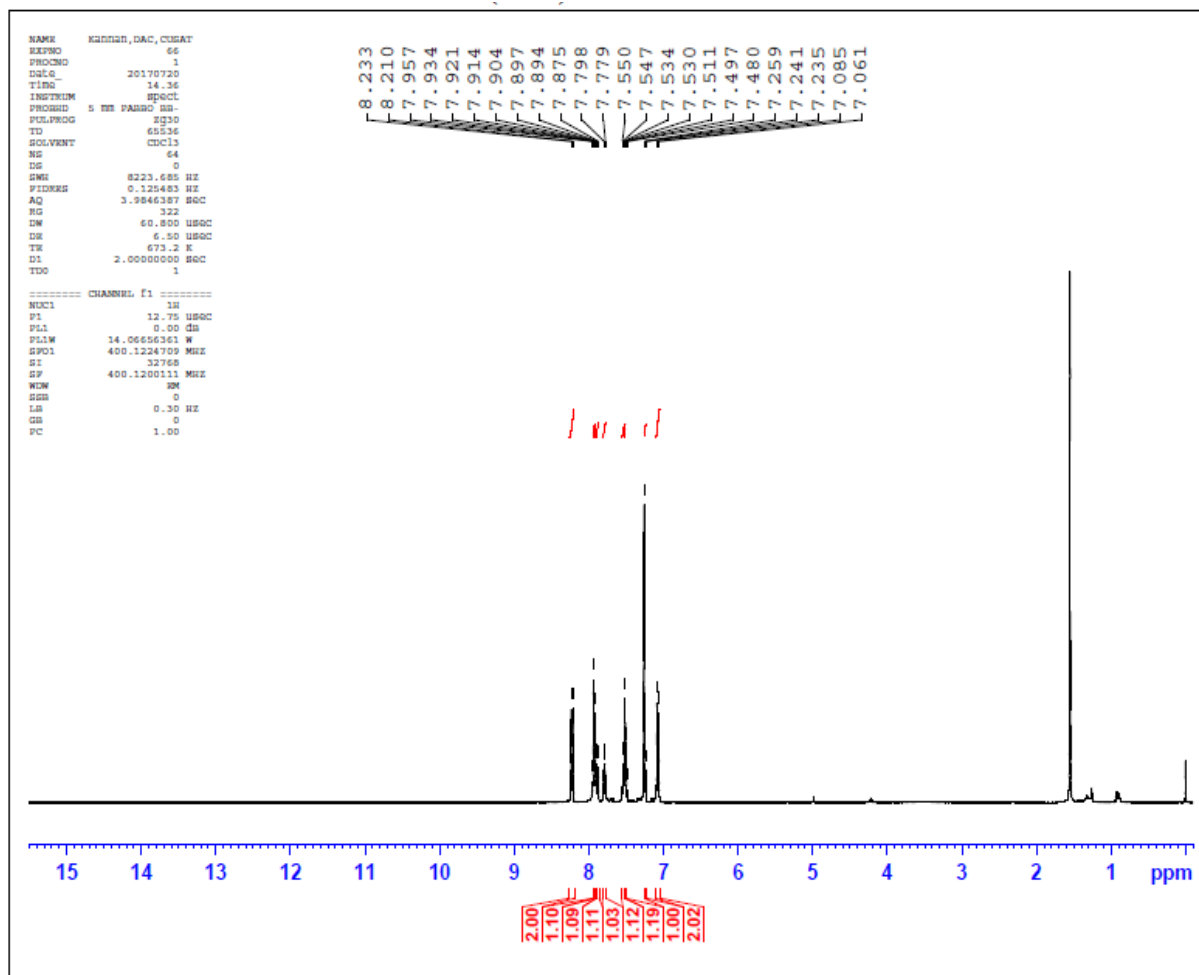
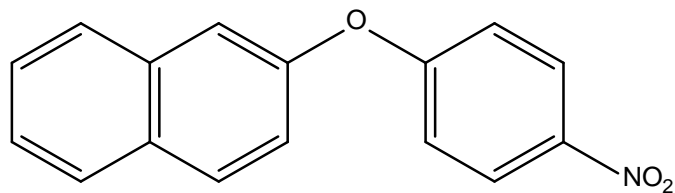
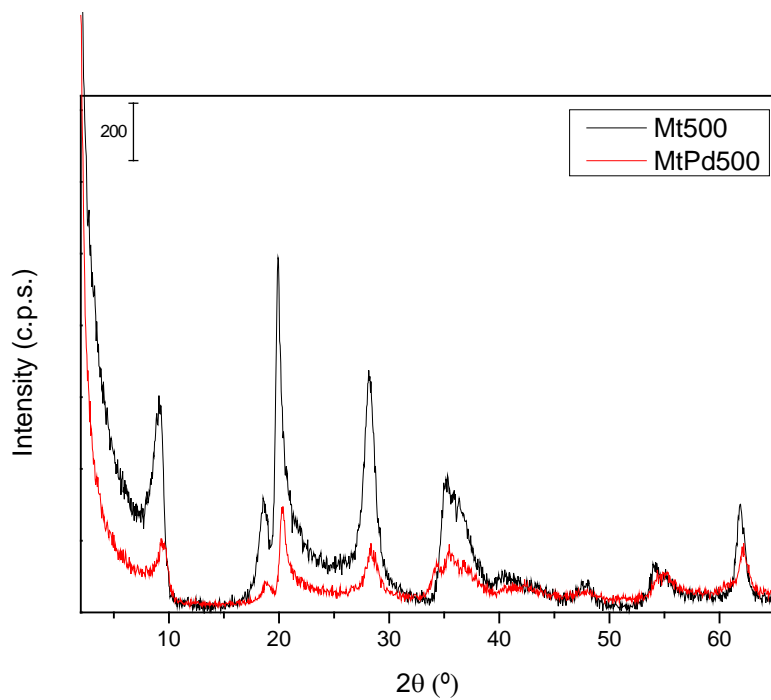
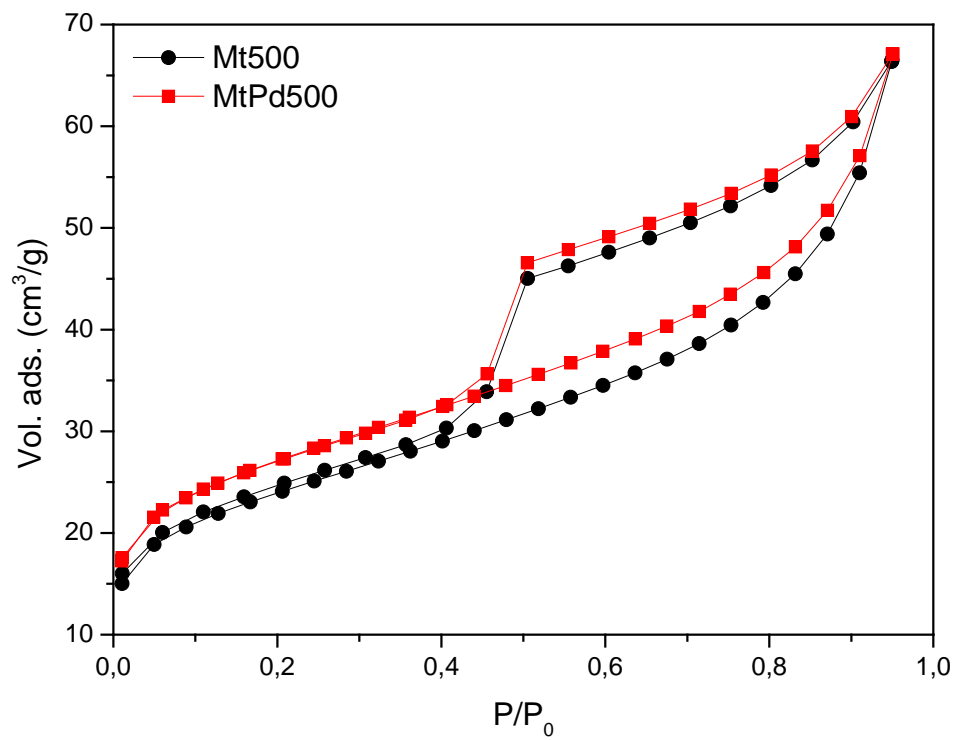


Fig. S1. <sup>1</sup>H NMR Spectral Data of Selected Products (400 MHz, CDCl<sub>3</sub>).





**Fig. S2.** X-ray diffractograms of the raw Mt support and the impregnated solid, both calcined at 500°C.



**Fig. S3.** Nitrogen adsorption and desorption isotherm of catalyst.