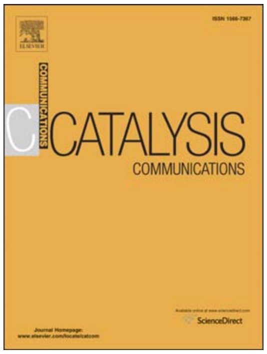

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Incorporation of TiO_2 coating on a palladium heterogeneous nanocatalyst. A new method to improve reusability of a catalyst

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Abstract

To improve the reusability of a modified chitosan supported palladium catalyst (MC-Pd) it was coated with 50 wt% $TiO_2$and in this way the MC-Pd@TiO_2catalyst was prepared. The catalyst was characterized with different techniques. Activity ofthe catalyst was studied in the Suzuki cross-coupling reactions. The reusability of the catalyst was tested and the results indicated that after 10 runs, in the presence of MC-Pd catalyst the reaction yield decreased to 70% while it was 95% for the coated catalyst. After 10 runs, the Pd leached from MC-Pd catalyst was 20% and for the MC-Pd@TiO_2 catalyst was less than 4%.

*Keywords:*Palladium; Nanocatalyst; TiO_2; Suzuki reaction; Leaching.

1. Introduction

One of the main problems in the use of metal heterogeneous catalysts is leaching of the metalfrom surface of the used supports which leads to reduced efficiency of the reaction after a few cycles [1-3]. In the other words, the reusability of these catalysts decreases after several cycles of reaction. In this study, we introduce a novel method to improvereusability of a heterogeneous catalyst, for the first time. For this purpose, we synthesized a heterogeneous palladium (Pd) catalyst and then coated it with titanium dioxide by using titanium tetra n-butoxide, as precursor.It was expected that the leaching of palladium from the coated catalyst should be reduced compared to the uncoated catalyst.

Chitosan as a natural biopolymer, has many advantageous such as biodegradability, biocompatibility, non-toxicity, good mechanical strength and insolubility (in many organic solvents) which make it an environmental friendly support for the synthesis of heterogeneous catalysts [4,5]. In this study, we used chitosan and modified itchemically in two steps and then immobilized palladium nanoparticles on it. In this way a heterogeneous palladium catalyst was synthesized and it was utilized in Suzuki coupling reaction.

C-C coupling reactions like Suzuki and Heck reactions are frequently used for the preparation of intermediate compounds in the synthesis of fine chemicals [6-8]. Due to the main advantages of Suzuki coupling reaction it was chosen as a model reaction for this research [9].

Our main goal in presenting this research was to introduce a novel method for improvingthe reusability of a heterogeneous palladium catalyst. Forreducing of palladium leaching from the synthesized catalyst, it was coated by titanium dioxide, a porous inorganic coating, and its reusability was compared to the uncoated catalyst.

2. Experimental

2.1. Materials

Chitosan powder (MW = 100,000–300,000, deacetylation degree ≥90%) was purchased from Acros Organics. Methyl acrylate, diethylenetriamine, methanol, ethanol, n-hexane, titanium(IV) n-butoxide, Aryl halides, phenylboronic acid, palladium chloride and potassium carbonate obtained from Merck. All chemicals, reagents and solvents were synthetic grade, and used without any extra purification.

2.2. Characterization techniques

FTIR spectra were recorded by FTIR spectrophotometer (Jasco 680-plus) using KBr pellets.

X-Ray diffractionanalyses were performed using a diffractometer with Cu anode (Philips X’pert, Netherland).

Morphology of the catalyst was evaluated by transmission electron microscopy (TEM) images obtained in a JEM 2100Fmicroscope operated with an accelerating voltage of 200 kV.

The surface morphology of the samples was observed by field emission scanning electron microscopy (TESCAN MIRA3) with energy dispersive X-ray (EDX) spectrometer.

The metal content of the catalysts was determined with Perkin Elmer USA, Optima 7300D inductively coupled plasma (ICP) atomic emission spectrometer (AES).

TGA curve of the catalyst was obtained under a nitrogen atmosphere at a sample heating rate of 10 °C min^{-1} using BAHR-STA/TGA-503.

Adsorption–desorption isotherms of nitrogen at 77.3 K were measured using aNOVAWin2, version 2.2 (Quantachrome instruments) and surface area was measured by the BET equation [10].

2.3. Synthesis of modified chitosan

The procedure for synthesis of a similar modified chitosan (ChitMA) has been previously described [11] (supplementary data). The final biopolymer renamed hereafter as MC (see Scheme 1S in supplementary data).

2.4. Preparation of the MC-Pd catalyst

For this purpose, 1 g of MC powder was dispersed in 50 mL ethanol and an aqueous solution of $PdCl_2$ (10 mL, 0.56 mmol) was added dropwise to the reaction mixture. To obtain the Pd^0 nanoparticles on the support, an aqueous $NaBH_4$ solution was slowly added under vigorous stirring at room temperature.

2.5. Preparation of the MC-Pd@TiO_2 catalyst

A porous coating of TiO_2 was created around the MC-Pd catalyst according to the following procedure:initially, 0.1 g of the catalyst was dispersed in 20 mL of n-hexane under vigorous stirring (800 rpm) at room temperature. Then a calculated amount of $Ti(O\text{-}nBu)_4$ (50wt% TiO_2 relative to the catalyst) dissolved in 5 mL of n-hexane and was added dropwise to the mixture. After 1 h of stirring, the $Ti(O\text{-}nBu)_4$ was hydrolysed with a few drops of DI water. After 24 h, the reaction mixture was filtered and dried. In this way, the MC-Pd@TiO_2 catalyst was prepared (Scheme 1).

Scheme 1.

3. Results and discussion

3.1. FTIR spectra

Infrared spectra of Chit (a), ChitMA (b), ChitMAD (c), MC-Pd (e) and MC-Pd@TiO$_2$ (f) are shown in Fig. 1. In the chitosan spectrum (Fig. 1a), a broad peak in the range of 3000–3600 cm^{-1} is distributed to the stretching vibrations of O─H and N─H bonds. The peaks appeared at 1650 and 1590 cm^{-1} could be attributed to the C=O stretching vibration of residual acetamido groups exist in the chitosan, and the bending vibration of N─H bonds, respectively [12]. Also the peaks in the region of 1000-1300 cm^{-1} are ascribed to the stretching vibrations of C─O─C bridges and C─O bonds related to primary and secondary alcohols [13]. Compared to the chitosan spectrum, a new peak appears at 1725 cm^{-1} in the ChitMA spectrum (Fig. 1b) that could be due to the stretching vibration of the ester groups which were formed through the reaction with the methyl acrylate. The disappearance of the peak at 1590 cm^{-1}, related to N─H bending vibration, indicates that the reaction occurred on the chitosan amino group. Moreover, the peak at 800 cm^{-1} could be attributed to the rocking bending motion of the methylene group in the methyl acrylate. For the ChitMAD spectrum, as shown in Fig. 1c, the main difference observed is the decrease of the peak at 1725 cm^{-1} due to the egression of the OCH$_3$ from the ester groups through the reaction with diethylenetriamine. Moreover, an increase in the intensity of the peaks at the region of 2800-3000 cm^{-1}could be related to methylenic groups of the diethylenetriamine. In this spectrum, the peak at 1155 cm^{-1}that is attributed to the stretching vibrations of C─N bonds, was shifted to the lower wavenumbers (1123 cm^{-1}) in the MC-Pd catalyst spectrum (Fig. 1d), which indicates that palladium was coordinated with the amine ligands [14,15]. As can be seen, in the spectrum of the MC-Pd@TiO$_2$ catalyst (Fig. 1e) the appearance of a broad peak in the range of 450-600 cm^{-1} is assigned to the vibration of Ti─O─Ti bonds [16].

Fig. 1.

3.2. TG and XRD analysis

The thermogravimetric curve of the MC-Pd@TiO$_2$ catalyst is shown in Fig. 2S in supplementary data. An initial weight loss of 4wt% between 100 and 130 °C was observed. This weight lost can be attributed mainly to the loss of water bound or trapped in the sample. The second stage started at 250 °C and continued up to 450 °C with a mass loss of about 15wt% that can be attributed to decomposition of the modified chitosan [12,17].

Fig. 2 shows the X-ray diffraction patterns of MC, MC-Pd and MC-Pd@TiO_2samples. The wide peak at 20° in MC is attributed to its partial crystalline feature [18].As can be seen in the XRD pattern of the MC-Pd catalyst, the sharp peaks at 40.1°and 46.5° assigned to the characteristic peaks of Pd^0 [19-21]. Clearly, after coating of the MC-Pd catalyst by amorphous TiO_2, the intensity of characteristic peak were decreased. According to the equation used by Baran et al.[13], we calculated lower crystallinity values for these samples compared to chitosan (see Fig.2S in supplementary data). This confirms chemically modification and metal ion coordination.

Fig. 2.

3.3. FESEM-EDX

The FE-SEM images of the synthesized catalysts are shown in Fig. 3. The images of the MC-Pd catalyst (Fig. 3a) show chitosan sheets that by modification with methyl acrylate and diethylenetriamine tolerated some defects and roughness on the surface which make it more porous. These morphological changes could be attributed to structural modification of chitosan. In addition, Pd nanoparticles appear as bright dots over the surface [22]. After coating the MC-Pd catalyst with a porous TiO_2 the morphology of the sheets has changed in a way that one could imagine that the sheets were decorated with a layer of TiO_2. In the other words, the morphology of the MC-Pd@TiO_2 presented clearly a uniform coating of porous TiO_2 on the surface of the MC-Pd catalyst (Fig. 3b). By formation a shell of TiO_2 around the MC-Pd catalyst, one would expect to observe a decrease in the leaching of the Pd from the surface. Additionally, to confirm the presence of the metals in synthesized catalysts, EDX spectra of them were recorded (see Fig. 3S in supplementary data).

Fig. 3.

3.4. TEM analysis

TEM images of the MC-Pd@TiO_2catalyst showed that Pd nanoparticles exist as dark-gray spots, with a diameter range of 2-10 nm (Fig. 4). As can be seen, the Pd nanoparticles were homogeneously dispersed on the surface of the modified chitosan and no obvious aggregation was observed. The results indicated that created functional groups on the modified chitosan plays an important role in improving the dispersion of Pd nanoparticles [7,23].

Fig. 4.

3.5. ICP-OES measurements

The palladium loading level in the MC-Pd catalyst was measured by inductively plasma-atomic emission spectrometry (ICP-AES). The content of loaded palladium was 0.52 mmol/g.

3.6. N_2 adsorption–desorption isotherms

The N_2 adsorption–desorption isotherm of the MC-Pd@TiO_2 catalyst is presented in Fig. 4S in supplementary data. The catalyst has a specific surface area of 129.18 m^2/g and exhibits a type IV adsorption–desorption isotherm which could be classified as a mesoporous solid, according to the IUPAC definition. Moreover, this isotherm shows an H1 hysteresis loop. This shape of hysteresis of isotherm were reported for solids consisting of particles crossedby nearly cylindrical channels or made by aggregates (consolidated) or agglomerates (unconsolidated) of spherical particles. In this case, pores can have uniform size and shape [24,25].

3.7. Catalytic studies

In this section, we have tested the catalytic activity of the synthesized catalysts for the Suzuki cross-coupling reaction. The influence of various reaction parameters such as base, solvent, time, temperature and the amount of catalyst on the reaction were tested for the two catalysts, separately (see Tables S1 and S2 in supplementary data).

3.8. Reusability of the catalysts

To reach our main goal in this research, the reusability of the catalysts was examined in the related optimum conditions for 10 cycles. At the end of reactions, the catalysts were simply recovered from the reaction media by filtration, washed with ethanol and water, dried at roomtemperature, and then reused for the next run. The results demonstrated that in the case of the MC-Pd catalyst after 10 cycles, the yield of reaction decreased to 70% while it was 95% for the MC-Pd@TiO_2 catalyst (see Fig.6S in supplementary data).In order to investigate the leaching of Pd during the reaction in our catalytic system, we measured the remaining amount of palladium in the catalysts after 10 cycles by ICP-AES. The results indicated that in the case of the MC-Pd catalyst, palladium leaching was 20% while it was <4% for the MC-Pd@TiO_2 catalyst. To interpret this difference in the microscopic scale, one could imagine that the TiO_2 coating, compresses the structure of modified chitosan that leads to more coordination of its free ligands to the palladium, so leaching of palladium would be more difficult.According to obtained results, due to better reusability of the MC-Pd@TiO_2 catalyst, finally it was selected as the optimum catalyst despite its longer time of reaction.

3.9. Suzuki cross-coupling reaction of various aryl halides

In the optimized conditions, the Suzuki cross-coupling reactions of various aryl halides were carried out using the MC-Pd@TiO_2 catalyst. The results are summarized in Table 1 [26].

3.10. Mercury poisoning test

Mercury poisoning test were conducted with the model reaction in the optimum conditions (Table 1, entry 1) by MC-Pd@TiO_2. This model reaction was done for 2.5 h without any mercury and yield for catalyst was 55%. Then, 300 molar equivalents of mercury, relative to the Pd catalyst, was added in to the reaction medium and stirred for another 2.5 h. After the allowed time the expected product was obtained with lower yield (52%). This test showed that the reaction mechanism fallows a heterogeneous pathway (Table 1, entry 11) [27].

4. Conclusion

In this research, we introduced a novel method to promote the reusability of a heterogeneous catalyst for the first time. This method is simple, applicable and cost-effective. The results indicated that by using a simple coating one could decrease leaching of palladium or probably any other metal catalyst from the synthesized heterogeneous catalyst.The proposed method can be a promisingalternative approach for the preparation of metal heterogeneous catalysts that arefrequentlyused in the industrial reactions. In this way, could economically save expensive metals such as Pd, Pt and Au in the heterogeneous catalysts.

Acknowledgments

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Scheme 1. Overall schematic of MC-Pd and MC-Pd@TiO_2 catalysts.

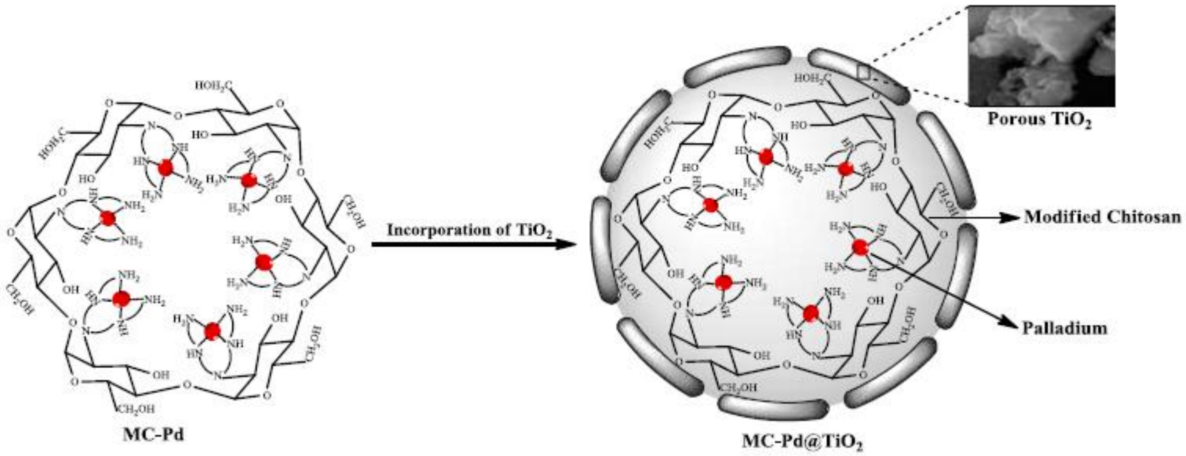


Fig. 1. FT-IR spectra of Chit (a), ChitMA (b), ChitMAD (c), MC-Pd (d) and MC-Pd@TiO$_2$ (e).

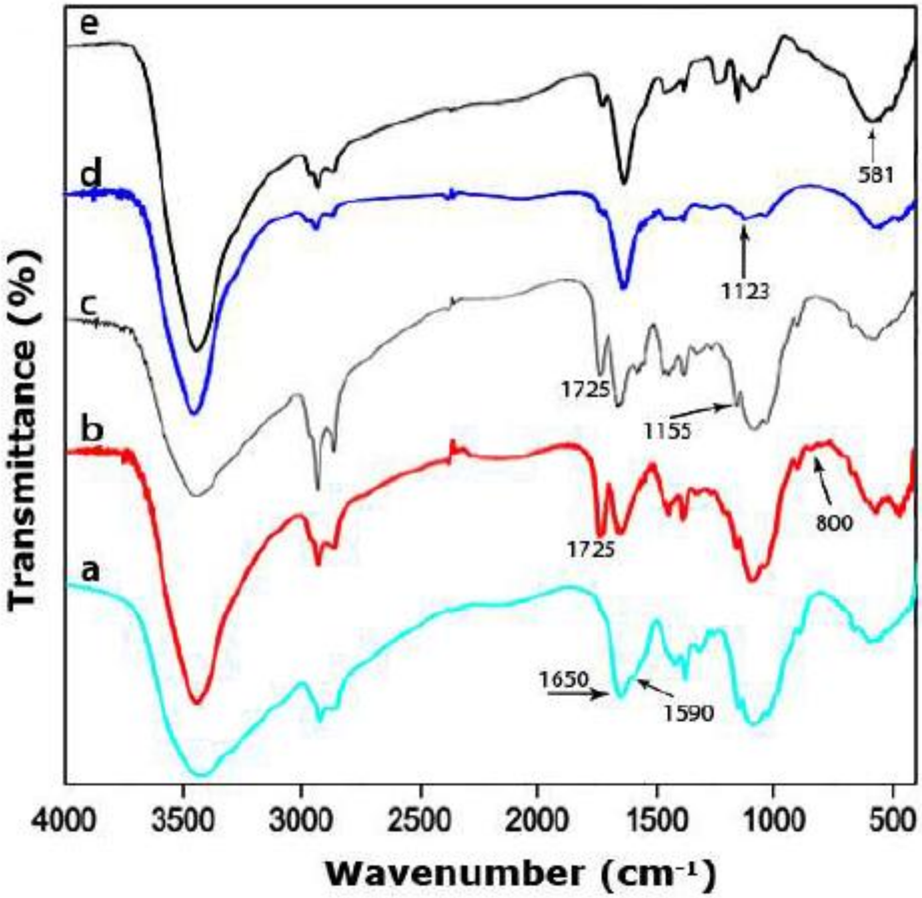


Fig. 2. (a) XRD patterns of MC, MC-Pd and MC-Pd@TiO$_2$.

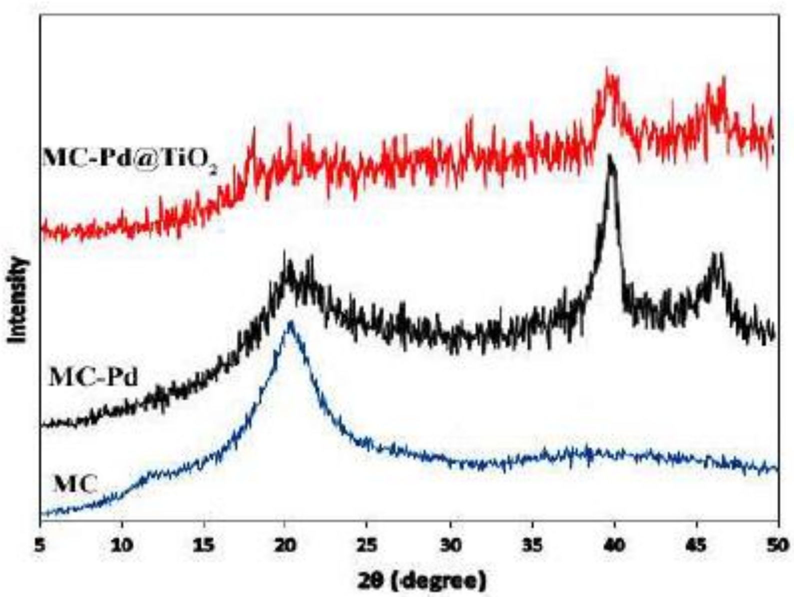


Fig. 3. FESEM images of MC-Pd (a) and MC-Pd@TiO_2 (b).

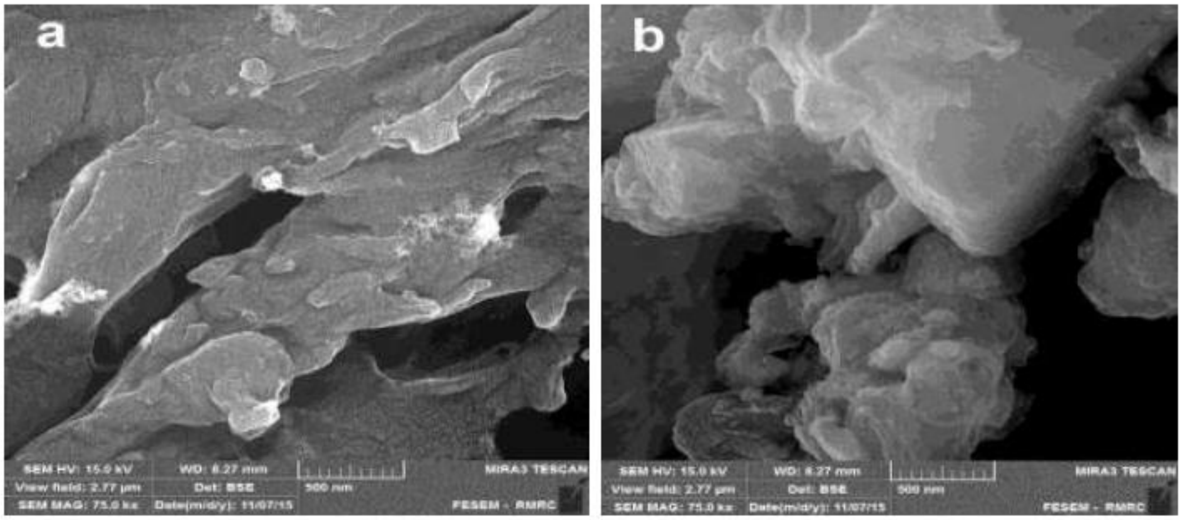


Fig. 4. TEM image of MC-Pd@TiO$_2$.

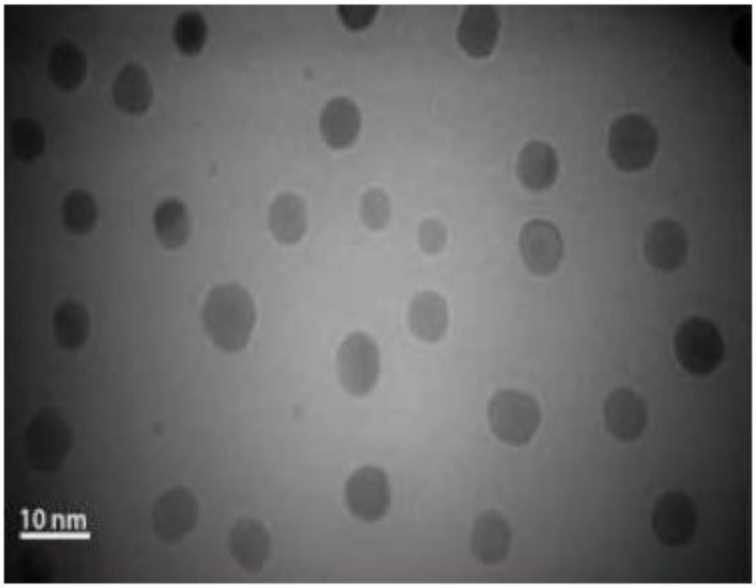
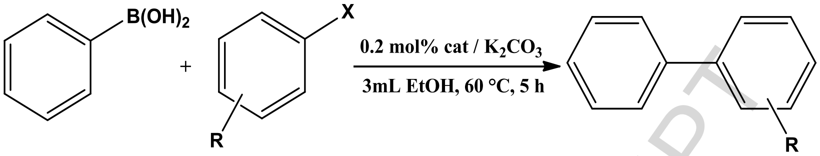


Table 1. Suzuki cross-coupling reaction of various aryl halides with phenylboronic acid catalyzed by MC-Pd@TiO$_2$**.**



Entry	Aryl halide	Yield (%)	TON	TOF
1	1-iodo-4-nitrobenzene	100	500	100
2	Iodobenzene	93	465	93
3	1-iodo-3-nitrobenzene	96	480	96
4	1-iodo 4-metoxybenzene	90	450	90
5	Bromobenzene	80	400	80
6	4-bromoacetophenone	90	450	90
7	4-bromobenzaldehyde	91	455	91
8	1-bromo-4-metoxybenzene	82	410	82
9	Chlorobenzene	25	125	25
10	1-chloro-4-nitrobenzene	46	230	46
11[a]	1-iodo-4-nitrobenzene	52	260	52

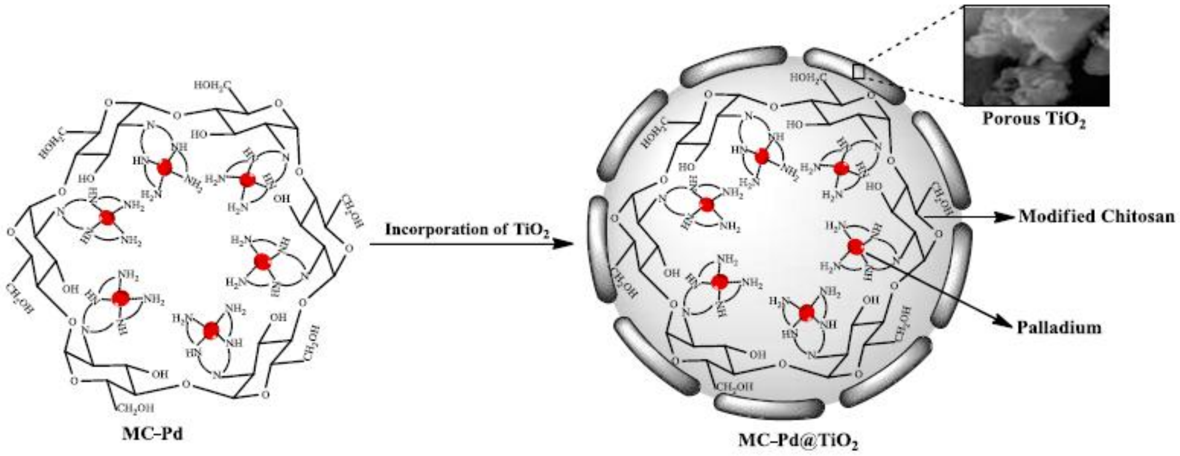
Reaction conditions; the catalyst (0.2 mol%), aryl halide (0.1 mmol), phenylboronic acid (0.11 mmol), K$_2$CO$_3$ (0.3 mmol), ethanol (3 ml) and time (5 h).

TON: (turnover number, yield of product/per mol of Pd)

TOF: (turn over frequency, TON/time of reaction)

[a] In the presence of excess Hg (Hg:Pd = 300:1)

Graphical abstract



Highlights

- Incorporation of TiO_2enhanced the reusability of MC-Pd catalyst.
- After 10 runs, the Pd leached from MC-Pdcatalyst was less than MC-Pd@TiO_2catalyst.
- The proposed method can be a promising approach for preparation of catalysts.