

## FULL PAPER

# Immobilization of a Pd(II) complex on hydrophilic graphite oxide and its catalytic investigation in the Heck coupling reaction

Ágnes Mastalir<sup>1</sup>  | Martin Hancsárik<sup>1</sup> | Tamás Szabó<sup>2</sup>

<sup>1</sup>Department of Organic Chemistry, University of Szeged, Szeged, Dóm tér 8, H-6720, Hungary

<sup>2</sup>Department of Physical Chemistry and Materials Science, Szeged, Rerrich Béla tér 1, H-6720, Hungary

**Correspondence**

Ágnes Mastalir, Department of Organic Chemistry, University of Szeged, H-6720 Szeged, Dóm tér 8, Hungary.  
Email: mastalir@chem.u-szeged.hu

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Tetraamminepalladium(II) chloride monohydrate was heterogenized on hydrophilic graphite oxide (GO), synthesized by Brodie's method. Two samples, with Pd contents of 2% and 5%, referred to as Pd2 and Pd5, respectively, were prepared by a simple and scalable impregnation method and tested as catalysts in the Heck coupling reaction of styrene and bromobenzene. The reactions were carried out at 423 K for 3 hr by applying Na<sub>2</sub>CO<sub>3</sub> as a base and *N*-methylpyrrolidone or dimethylformamide (DMF) as a solvent. The Pd complexes heterogenized on graphene oxide platelets proved to be highly active and selective catalysts, and Pd2 was more efficient than Pd5. The effect of quaternary ammonium salts (tetrabutylammonium bromide and tetrabutylammonium chloride, TBAC) as modifiers and that of an ionic liquid (1-butyl-3-methylimidazolium bromide, bmim) was studied and the highest conversions were obtained when TBAC was employed. The selectivity for the formation of the main product, *E*-stilbene, was in the range 91–96%. Catalyst recycling was investigated and the extent of leaching was found to depend on the solvent. DMF proved to be a highly feasible reaction medium because both catalysts could be recycled five times in this solvent without any significant loss of activity. A hot filtration test was performed and gave evidence that leaching of the active Pd species did not take place under the above reaction conditions. These results substantiate the fact that simple cationic Pd species can be efficiently immobilized on pristine GO surfaces without the requirement of the functionalization of GO with nitrogen-containing mono or multidentate ligands as binding sites.

**KEYWORDS**

graphite oxide, Heck reaction, hot filtration test, recycling, tetraalkyl ammonium salt

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## 1 | INTRODUCTION

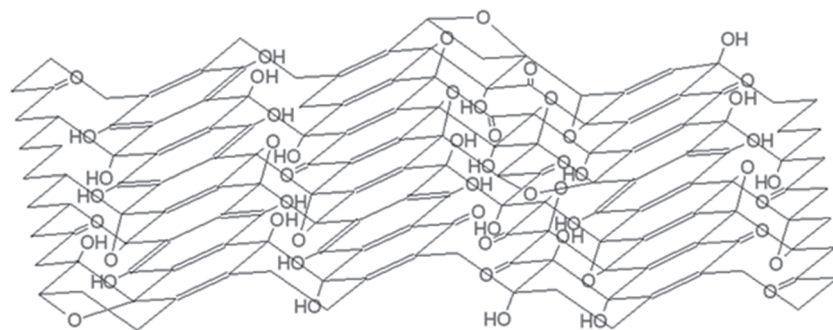
Graphite oxide (GO) was first synthesized in the 1850s via the controlled oxidation of graphite using strong oxidizing agents such as  $\text{KClO}_3$  and  $\text{HNO}_3$ . GO is a layer-structured compound that contains a hexagonal network of carbon layers, characteristic of graphite, but without its conjugated bond structure.<sup>[1]</sup> GO is also regarded as a pseudo two-dimensional solid in bulk form, with strong covalent bonding within the layers and weak hydrogen bonding between the layers.<sup>[2,3]</sup> The lamellar structure of GO contains randomly distributed aromatic regions, together with aliphatic regions and oxygen-containing functional groups, including hydroxyl, epoxy, and carboxyl groups, embedded in the carbon layers.<sup>[4]</sup> During its preparation, GO should be handled with care and dried at low temperature to prevent decomposition, which may occur at elevated temperatures.<sup>[5]</sup> The elemental composition of GO depends on the nature of pristine graphite, its particle size, and the preparation conditions. As related to the complex structure of this material and the lack of suitable analytical techniques to be applied for characterization, the exact composition and the precise chemical structure of GO have not yet been determined and are the subject of further investigations.<sup>[1,6,7]</sup> However, most structural models<sup>[2,6–11]</sup> agree that cyclic ether, alcoholic hydroxyl, and carboxyl groups are covalently attached to the carbon skeleton which, depending on the degree of oxidation, may contain unoxidized aromatic regions over the graphene oxide platelets. These structural features are shown in a representative model in Figure 1.

Recently, the dependence of the physicochemical properties of GO on the synthesis method has been highlighted<sup>[12]</sup> and considerable sample-to-sample variations were also demonstrated.<sup>[13]</sup> However, all sorts of graphene oxides are hydrophilic materials. The spacing between the GO sheets is responsive to the water content of the environment: interlayer distances of ca. 0.6 nm characteristic of dry samples<sup>[2,14]</sup> can be doubled on full hydration from vapor,<sup>[10,15]</sup> while in slightly basic solutions GO

undergoes swelling and exfoliation, which results in the formation of a colloidal solution.<sup>[10,12]</sup> GO is an excellent host material for the intercalation of long-chain aliphatic hydrocarbons, surfactants, transition metal ions, alcohols, and polymers.<sup>[4,16]</sup> Intercalated GO nanocomposites can be utilized for the fabrication of thin films, in photochemical reactions, and may also be applied to control the aggregation state of organic dyes.<sup>[4,17]</sup> More recently, surfactant-intercalated GO materials<sup>[18]</sup> have been synthesized and employed as support materials of catalytically active Pd complexes and nanoparticles.<sup>[19–22]</sup>

Heterogenized palladium species have been tested as catalysts in various coupling reactions,<sup>[23–25]</sup> including the Heck reaction, considered to be one of the most efficient procedures for the formation of C–C bonds.<sup>[26–29]</sup> In the conventional Heck reaction, Pd(II) or Pd(0) complexes are used in solution as homogeneous catalysts.<sup>[26–31]</sup> The application of heterogeneous Pd catalysts and Pd complexes immobilized on solid materials has also been found to be beneficial, as these samples can be easily handled, recovered, and recycled.<sup>[32–34]</sup> While GO as a support material was often demonstrated to be highly feasible as a support of Pd nanoparticles (NPs) in catalytic Heck reactions,<sup>[35–39]</sup> there is only a handful of studies that report on the application of GO related to the Heck-coupling processes as a host for Pd species dispersed on the molecular level.<sup>[40–44]</sup> These studies employ at least one, but typically a few,<sup>[40,41]</sup> organic reactions to immobilize the palladium centers on the surface of graphene oxide nanosheets. The idea in these studies is the anchorage of nitrogen-containing molecules such as aminoguanidine,<sup>[40]</sup> 5,10,15,20-tetrakis-(4-hexyloxyphenyl)-porphyrin,<sup>[44]</sup> 1-(2,6-diisopropylphenyl)-3-(propyltrimethoxysilyl)imidazol-2-ylidene,<sup>[43]</sup> and sulfophthalocyanine<sup>[42]</sup> over the GO plates acting as ligands for the coordination of Pd(II) ions.

With the motivation of finding suitable, less complicated pathways for the decoration of pristine graphene oxide surfaces with Pd species, we intended to use only one of the simplest precursors, tetraamminepalladium(II)



**FIGURE 1** The structural model of GO proposed by Szabó et al.<sup>[8]</sup>

chloride. In this study, we show that a very simple impregnation method based on ion exchange affords catalysts of high activity and selectivity in the Heck coupling reaction of styrene and bromobenzene, while maintaining efficient binding of the reaction centers on the carbonaceous support in the presence of different solvents. Catalyst recycling was investigated and the effect of modifiers (quaternary ammonium salts and an imidazolium salt) on the catalytic performance was also studied.

## 2 | EXPERIMENTAL

### 2.1 | Materials

The graphite used for the synthesis of GO was an SGA 20 Kropfmühl AG product (Hauzenberg, Germany). NaClO<sub>3</sub>, fuming HNO<sub>3</sub> (99.5%), tetraaminepalladium(II) chloride monohydrate (98%), styrene (>99%), bromobenzene (BrB, 99%), tetrabutylammonium bromide (TBAB, >99%), tetrabutylammonium chloride (TBAC, >97%), Na<sub>2</sub>CO<sub>3</sub>, and 1-butyl-3-methylimidazolium bromide (bmim, >97%) were purchased from Sigma Aldrich (Budapest, Hungary). *N*-methyl-pyrrolidone (NMP, >99%) was an Alfa Aesar product (Heysham, England) and dimethylformamide (DMF, 99.5%) was obtained from VWR Chemicals (Leuven, Belgium).

### 2.2 | Synthesis of GO

GO was synthesized according to Brodie's method.<sup>[45]</sup> First, 2 g of graphite was placed in a two-necked flask and 17 g of NaClO<sub>3</sub> was added. The flask was placed into an ice bath and equipped with a reflux condenser and a dropping funnel containing 12 ml of fuming HNO<sub>3</sub>. This was added dropwise to the graphite–NaClO<sub>3</sub> mixture under cooling and magnetic stirring. On the addition of HNO<sub>3</sub>, the mixture underwent swelling and a greenish suspension was formed. The reaction mixture was left under stirring for 20 hr, and then 8 ml of HNO<sub>3</sub> was added in 40 min. The flask was subsequently placed into a steam bath and heated at 333 K for 6 hr. Following this procedure, GO was obtained. The product was first washed with 200 ml of ultrapure distilled water and then by 40 ml of 3 M HCl five times. The resulting solid was a light brown powder, which was centrifuged at 3000 rpm and then purified by dialysis performed by ion-exchanged water. As GO is sensitive to light, the final product was stored as an aqueous suspension in a refrigerator. The zeta potential of GO in aqueous suspension

(at 1 mM ionic strength) was characterized by a Malvern NanoZS Instrument (Malvern, Worcestershire, England) and found to be  $-35 \pm 5$  mV, confirming that the dispersed graphene oxide particles are negatively charged.

### 2.3 | Catalyst preparation

The catalysts were synthesized by impregnation. Tetraaminepalladium(II) chloride monohydrate was dissolved in 1 ml of distilled water and the solution was added to the aqueous GO suspension under stirring, which was maintained for 24 hr. The product was subsequently filtered under vacuum by a Büchner funnel. The wet solid was spread on a glass plate and dried at 298 K. The dry solid was collected and stored in a desiccator until use. Two samples with Pd loadings of 2% and 5% were synthesized, denoted as Pd2 and Pd5, respectively.

### 2.4 | Catalytic reaction

The reactions were performed in 5 ml glass pressure tubes, equipped with magnetic stirrers, heated in an oil bath. For each reaction, the mass of catalyst was 10 mg and the reactant (BrB):Pd ratio was 1000:1. As compared to bromobenzene, styrene was applied in excess ( $n = 1.2n_{\text{BrB}}$ ), as well as Na<sub>2</sub>CO<sub>3</sub> as a base ( $n = 1.4n_{\text{BrB}}$ ). When Pd2 was used as a catalyst, the reaction mixture consisted of 198  $\mu$ l of bromobenzene, 259  $\mu$ l of styrene, and 279 mg of Na<sub>2</sub>CO<sub>3</sub>. When Pd5 was used, the amounts of the reactants and the base were increased by a factor of 2.5, according to the Pd loading. The amount of the modifier (TBAB, TBAC or bmim) was  $n = n_{\text{BrB}}/5$  for each reaction. After addition of the solvent (1 ml of NMP or DMF), the sealed glass tubes were placed into a preheated oil bath and the reaction mixtures were subjected to magnetic stirring. The reactions were performed at 423 K for 3 hr. Afterwards, the reaction mixtures were cooled down to room temperature, diluted with 5 ml of diethyl ether and filtered on a layer of alumina to remove any residual Pd catalyst. The clean filtrates were analyzed using a Hewlett Packard (Agilent Technologies, Santa Clara, California, USA) 5890 gas chromatograph equipped with a DB-5 capillary column and a flame ionization detector. For a typical run, the initial temperature was 353 K, the heating rate was 10 K/min and the final temperature was 473 K, maintained for 10 min. The product analysis was completed by gas chromatography–mass spectrometry (GC-MS) measurements using an Agilent (Agilent, Santa Clara, USA) 6890 N GC and an Agilent 5973 mass selective detector operated under the same conditions.

### 3 | RESULTS AND DISCUSSION

#### 3.1 | Catalyst heterogenization

Impregnation of the GO support with tetraaminepalladium(II) chloride from aqueous media resulted in complete decoloration of the solution of the yellow-colored Pd complex at both Pd loadings of 2 and 5 wt%. Likewise, the Pd content of the filtrate was spectrophotometrically undetectable. These findings confirm that the complex divalent cations are completely adsorbed at the surface of the negatively charged GO sheets, substantiating that an ion-exchange process takes place between the dissolved precursors and dispersed nanoplatelets. It is noteworthy that such a strong adsorption of palladium(II) ions is possible only by simple electrostatic interaction, and there is no need for the preliminary creation of a reactive monolayer of chelating ligands over the basal surfaces of the solid host. The first study of the catalytic Heck reaction using a Pd-complex anchored GO catalyst was reported by Ma'mani et al.<sup>[40]</sup> Their novel heterogeneous catalyst showed high activity and easy catalyst recovery with minimal leaching after the catalytic run. However, the large difference between the amount of Pd precursor added in the synthesis (10 mmol PdCl<sub>4</sub><sup>2-</sup>/1 g solid) and that actually found in the catalyst (0.9 mmol/g) implied that more than 90% of the Pd salt was lost during catalyst preparation. Thus, the present immobilization technique provides a substantial improvement of the catalyst deposition in economic terms compared to the recent efforts relying on the

surface complexation reactions of the relatively expensive palladium species.

#### 3.2 | Catalytic studies

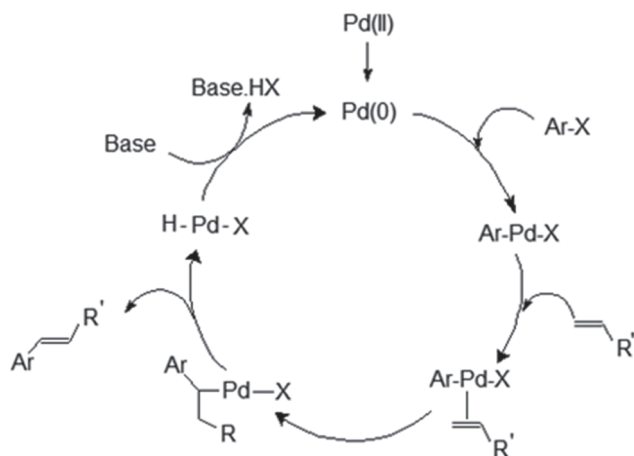
The generally accepted mechanism of the Heck reaction is shown in Figure 2.

In the first reaction step, an organic halide reacts with the active Pd catalyst via oxidative addition. The reactant alkene is then coordinated to Pd and forms an alkene complex. In the next step, insertion of the alkene group into the Pd–R bond takes place, which results in the formation of an alkyl complex. This is decomposed through  $\beta$ -elimination and the product is formed, a substituted alkene. Meanwhile, a Pd hydride complex is obtained, which is transformed into the active Pd species via reductive elimination. It is essential to apply a base in the reaction to neutralize the acid formed in the final reaction step.

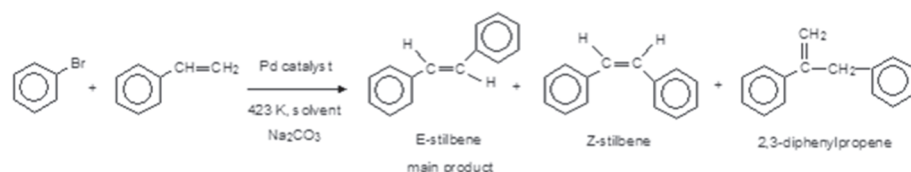
In the Heck coupling reaction of styrene and bromobenzene, the main reaction product was the thermodynamically most stable stereoisomer *trans*-1,2-diphenylethylene (*E*-stilbene), formed by  $\beta$ -coupling of the reactants. Small amounts of *cis*-1,2-diphenylethylene (*Z*-stilbene) and 2,3-diphenylpropene, formed by  $\alpha$ -coupling, may also be obtained as by-products (Figure 3).

The catalytic activities of the heterogenized Pd complexes Pd 2 and Pd 5 were investigated by using different solvents. Figure 4 shows the results obtained for Pd2 by applying either NMP or DMF as a solvent.

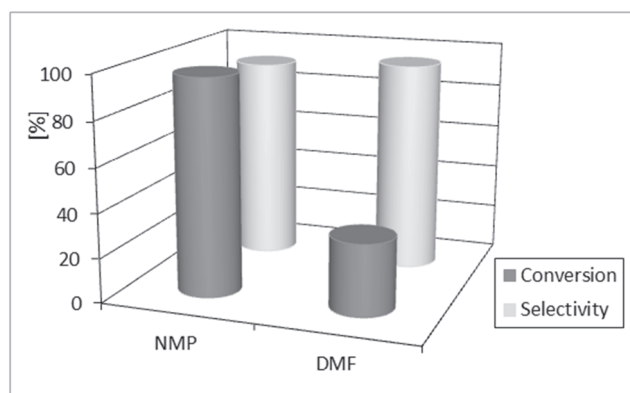
As can be seen in Figure 4, the solvent has a substantial effect on the catalytic activity. When NMP was used, a conversion of 97% was determined, which decreased to 32% when the solvent was DMF. A similar difference was obtained for the catalyst with higher Pd loading (Figure 5). In this case, the conversions were found to be lower, which suggested that the active site distribution of Pd2 was more favorable for the Heck coupling reaction. The low Pd loading of Pd2 may give rise to the formation of an enhanced amount of small and monodispersed Pd particles, which may have a beneficial effect on the catalytic performance. A similar experience has been found for the Heck coupling reactions of bromoarenes by applying silica-supported Pd catalysts in the presence of an ionic liquid.<sup>[34]</sup> Nevertheless, the effect of NMP was clearly more favorable in the reaction performed using Pd5.



**FIGURE 2** The mechanism of the Heck coupling reaction



**FIGURE 3** The Heck reaction of styrene with bromobenzene

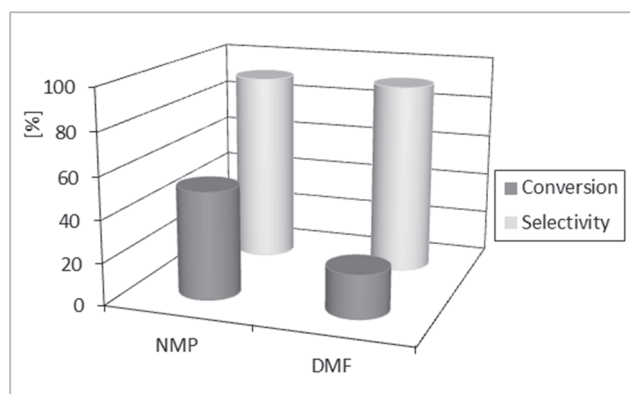


**FIGURE 4** Conversion and selectivity values in the Heck reaction of styrene and bromobenzene using Pd2 as a catalyst

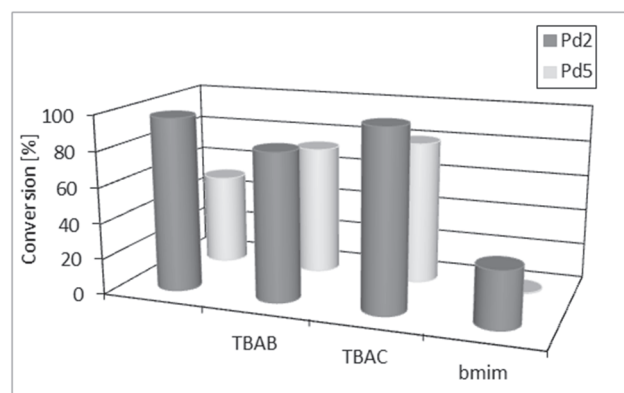
On the other hand, the selectivities for the formation of the main product, *E*-stilbene, were hardly affected by the solvent, as they varied between 91% and 95% for all the reactions.

### 3.3 | Effect of the modifiers

Quaternary ammonium salts have been found to be highly efficient at enhancing the catalytic activity and selectivity in Heck reactions. In particular, the effects of tetraalkylammonium bromide and chloride have been studied, which may also be regarded as phase transfer catalysts. These compounds tend to accelerate the reaction by providing more contact between the components of the complex reaction mixture.<sup>[46–49]</sup> Ionic liquids have also received much attention recently as environmentally friendly materials that have been favorably applied in various organic reactions as additives, reaction media or novel liquid catalysts.<sup>[50–52]</sup> In the present study, the effect of TBAB, TBAC, and bmim on the Heck coupling



**FIGURE 5** Conversion and selectivity values in the Heck reaction of styrene and bromobenzene using Pd5 as a catalyst

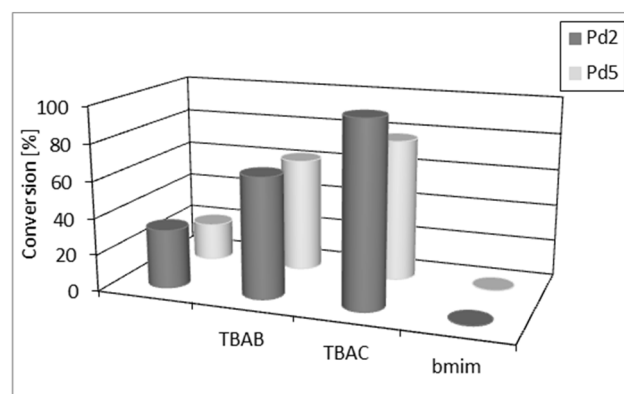


**FIGURE 6** The effect of modifiers on the Heck coupling reaction of styrene and bromobenzene in NMP

reaction was investigated. The results obtained using NMP as a solvent are displayed in Figure 6.

As can be seen in Figure 6, the effect of the modifier was more pronounced for the catalyst with the higher Pd loading (Pd5). For Pd2, the conversion obtained in the absence of modifier was already very high (97%), and no appreciable increase was anticipated. In fact, a slight decrease was observed for TBAB, whereas in the presence of TBAC the conversion was increased to 100%. In contrast, the initial conversion of 51%, obtained for Pd5, was considerably enhanced in the presence of both TBAB and TBAC, which proved to be highly efficient in the reaction, unlike the ionic liquid, which decreased the conversions for both samples. The same reactions were also performed using DMF as a solvent and the results are shown in Figure 7.

As shown in Figures 4 and 5, the conversions in DMF were much lower than those in NMP. Accordingly, the effect of the modifiers proved to be more significant when DMF was used. It was found that both TBAB and TBAC increased the conversions to an appreciable extent and



**FIGURE 7** The effect of modifiers on the Heck coupling reaction of styrene and bromobenzene in DMF

similar trends were obtained for both catalysts. Under such conditions, the application of TBAC proved to be more favorable as it afforded complete conversion when Pd2 was used as a catalyst. Likewise, the conversion observed for Pd5 (77.5%) displayed a several-fold increase compared to the original conversion (21%). In contrast, the addition of the ionic liquid was found to block the reactions completely for both catalysts. It may be ascertained that the application of quaternary ammonium salts proved to be highly beneficial for the conversion and their effect strongly varied with the solvent. The effect of TBAC was found to be more beneficial, as its application resulted in full conversions in both solvents when Pd2 was used as a catalyst. On the other hand, the modifiers exerted hardly any effect on the selectivity of the formation of the main product, which varied in the range 91–96%, irrespective of the solvent.

### 3.4 | Catalyst recycling

The recycling of the heterogenized catalysts was investigated in both NMP and DMF. After the first reaction had been completed, the reaction mixture was cooled to room temperature and diluted by diethyl ether. After sedimentation, the supernatant was removed and the residual solid was washed by diethyl ether three times. Then the solvent was removed by a rotary evaporator and the recovered catalyst was used as previously. All the catalysts were subjected to five consecutive runs.

Figures 8 and 9 show the results obtained using NMP as a solvent for the recycling of Pd2 and Pd5, respectively.

As shown in Figure 8, the catalytic activity of Pd2 declined gradually. Up to the fourth run, only a moderate decrease was observed, followed by a more pronounced loss of activity after the fifth application. Nevertheless, the product selectivities remained unchanged (91–92%).

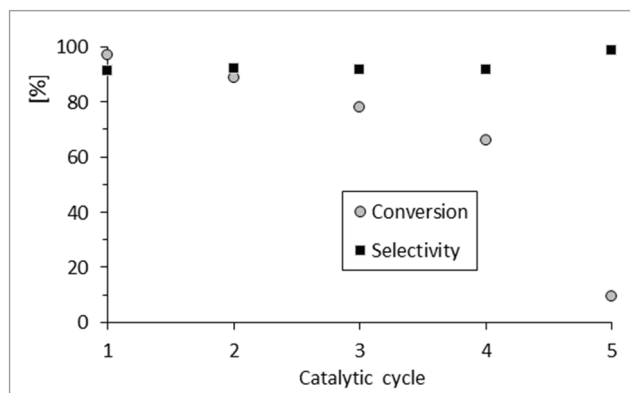


FIGURE 8 Recycling of Pd2 in NMP

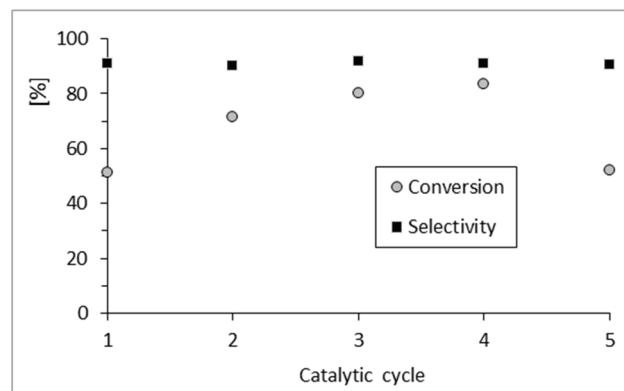
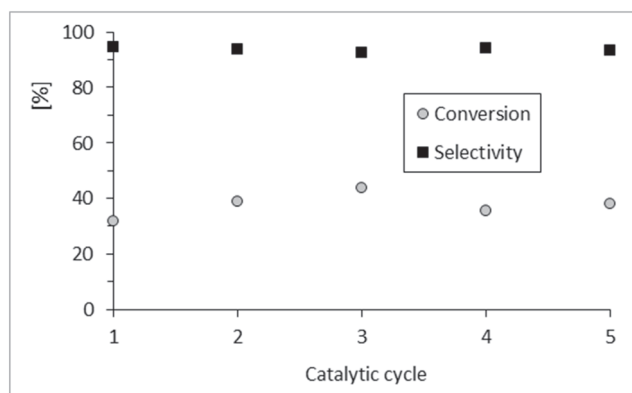


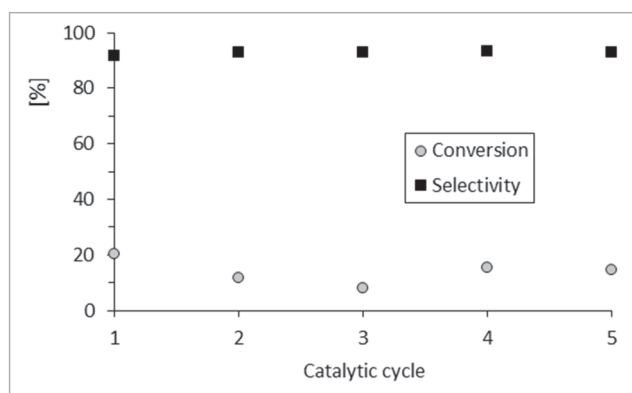
FIGURE 9 Recycling of Pd5 in NMP

In contrast, an unexpected increase in activity was found for the recycling of Pd5 (Figure 9). The highest conversion (84%) was determined after the fourth run and then the activity dropped considerably. The conversion obtained after the fifth run was the same as that observed for the first application (52%), which implies that no activity loss took place in up to five repeated runs. Irrespective of the variation in the conversion, the product selectivities were nearly constant and very similar to those obtained for Pd2 (Figure 8). It may therefore be ascertained that Pd5 could be more efficiently reused than Pd2, which suffered a significant loss of activity by the fifth application. The unusual increase in conversion observed for Pd5 during recycling may be attributed to a structural change in the catalyst. It is reasonable to assume that under the reaction conditions the hexagonal network of GO was transformed into turbostratic carbon with a rather irregular structure in which the layers are folded or crumpled and there is no stacking between them.<sup>[53,54]</sup> The formation of a less ordered structure of the support material may provide enhanced access for the reactants to the active Pd species and thereby tends to contribute to improved catalytic performance.

On the other hand, the decrease in conversion observed for Pd2 may be related to leaching and redeposition of the active Pd species on the surface of GO. As reported previously for heterogeneous Pd catalysts participating in the Heck reaction, the catalytically active species are formed as soluble Pd complexes via coordination with the solvent (NMP or DMF). When the reactants are consumed, the complexes decompose and Pd particles are redeposited on the surface of the support material.<sup>[55,56]</sup> This kind of redeposition may be less efficient on repeated applications, considering that the dissolved Pd species may be redeposited not only on the bare surface of the support, but also on the surface of the Pd particles remaining on the support, which may give



**FIGURE 10** Recycling of Pd<sub>2</sub> in DMF



**FIGURE 11** Recycling of Pd<sub>5</sub> in DMF

rise to particle aggregation.<sup>[33,34]</sup> As reported previously, leaching and redeposition of the Pd particles have often been accompanied by a decrease in the metal surface area. Under the reaction conditions, heterogenized Pd complexes may also undergo *in situ* reduction, which transforms the active Pd complex into metallic Pd particles with reduced activities.<sup>[27]</sup>

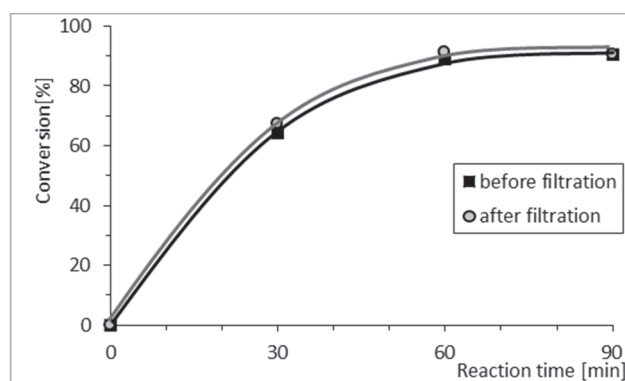
The data collected for the recycling of the catalysts in DMF are shown in Figures 10 and 11.

As mentioned above (Figures 4 and 5), the conversions observed in DMF were considerably lower than those in NMP, which tends to form a more favorable coordination interaction with the active Pd species. As shown in Figures 10 and 11, the results obtained for the catalysts with different Pd loadings were rather similar, as there was no significant variation in the conversions in up to five repeated runs. This indicates that both catalysts could be reused several times without any appreciable loss of activity. Similarly, the selectivities obtained in NMP remained unchanged for repeated applications. For the formation of *E*-stilbene, the highest selectivities were determined for Pd<sub>5</sub> (93–95%).

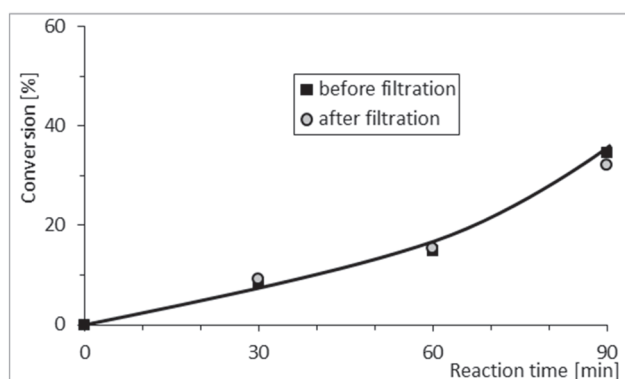
### 3.5 | Hot filtration test

The development and application of reusable heterogeneous catalysts in the Heck coupling reactions have been the subject of numerous studies. Under certain reaction conditions, leaching of the supported Pd particles has also been observed.<sup>[57–59]</sup> Information on the active Pd species in solution can be obtained by the hot filtration test. This is also called the split test, and is typically performed by interrupting the reaction at a low conversion and then carrying it on after catalyst removal. If no further conversion is detected in the catalyst-free solution phase, the leaching of Pd may be excluded.<sup>[24,60]</sup>

In the present study, leaching was investigated as follows: the reaction was interrupted at 30 min and then the filtrate was collected from the hot reaction mixture. The reaction was conducted for another 150 min using the filtrate in the absence of the solid catalyst. Parallel reactions were also performed using filtrates obtained after 60 and 90 min reaction times and the total reaction time was 3 hr in all cases. The filtrates collected after 30, 60, and 90 min were analyzed by GC, as well as those obtained after 3 hr. The hot filtration test was performed for Pd<sub>2</sub>, which proved to be a more active catalyst than



**FIGURE 12** Hot filtration test of Pd<sub>2</sub> in NMP



**FIGURE 13** Hot filtration test of Pd<sub>2</sub> in DMF

Pd5. The results obtained in NMP and DMF are shown in Figures 12 and 13, respectively. The conversion determined for the original reaction mixtures after the reaction times of 30 min, 60 min and 90 min are depicted in Figures 12 and 13. These data were compared with those obtained at the same reaction times, determined by using the filtrated reaction mixtures, obtained after removal of the catalyst.

As can be seen in Figures 12 and 13, the conversions obtained in NMP were considerably higher than those in DMF, which is in line with our previous observations (Figures 4 and 5). Further, different trends were obtained for the two solvents. More importantly, the conversions obtained after 3 hr were nearly the same as those observed after shorter reaction times, the differences being within the range of experimental error. This implies that after catalyst removal, the filtrates contained no appreciable amounts of dissolved Pd particles and hence leaching of the Pd particles may be excluded. This may be established for both solvents, indicating that under the current experimental conditions Pd2 may be regarded as a truly heterogeneous catalyst.

## 4 | CONCLUSIONS

GO was synthesized and employed as a support material for the immobilization of tetraamminepalladium(II) chloride monohydrate. Two samples with different Pd loadings, Pd2 and Pd5, were prepared by impregnation and employed as catalysts in the Heck coupling reaction of styrene and bromobenzene, for which the main product was *E*-stilbene. The solvent was found to exert a crucial effect on the catalytic performances of both samples and the application of NMP was more favorable than that of DMF. The utilization of the quaternary ammonium salts TBAB and TBAC as additives proved to be highly beneficial in terms of the conversions and only slightly affected the selectivity of the main product, which varied between 91% and 96%. The best performance was obtained by using Pd2 as a catalyst and TBAC as a modifier, affording complete conversions in both solvents. Catalyst recycling studies performed in NMP revealed that Pd5 could be more efficiently reused than Pd2, whereas in DMF both catalysts could be recycled five times without any appreciable loss of activity. In order to gain more information on the soluble Pd species in solution, a hot filtration test for Pd2 was carried out. Experimental evidence indicated that leaching of the Pd particles could be excluded and hence Pd2 may be regarded as a truly heterogeneous catalyst. Whereas recently developed heterogenized catalysts have been prepared by using relatively complicated synthesis

steps involving potentially toxic reaction residues, often at high excesses of the expensive palladium precursors, the present impregnation procedure is facile and relatively cheap because it does not rely on preliminary functionalization protocols.

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## ORCID

Ágnes Mastalir  <https://orcid.org/0000-0002-8038-4635>

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