

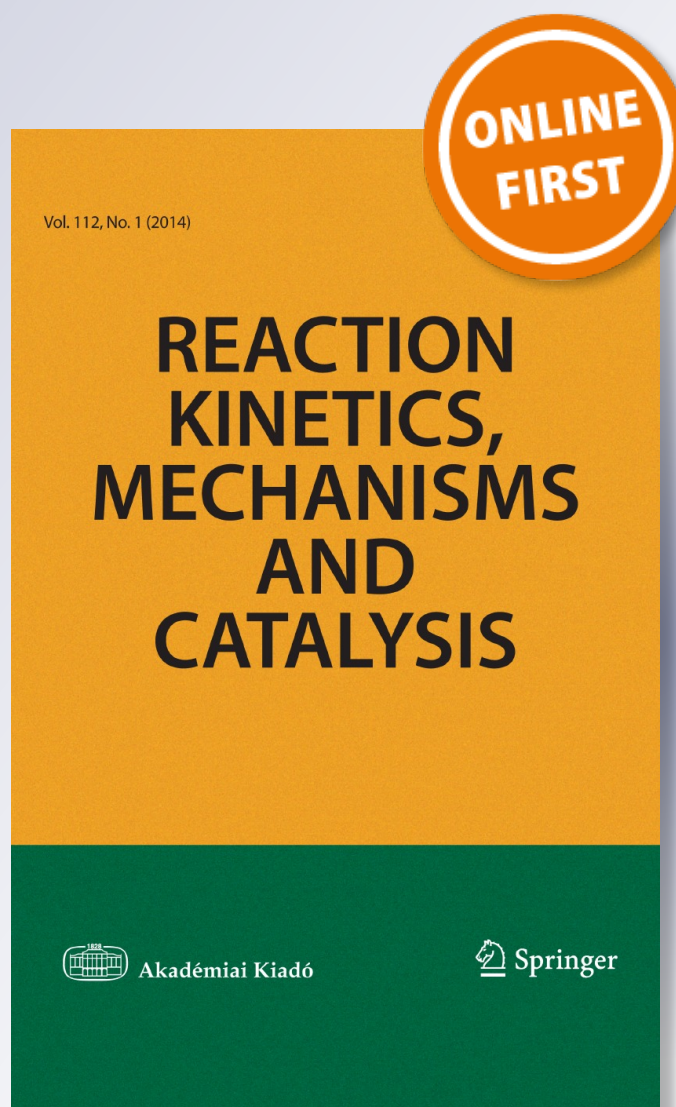
*Catalytic investigation of PdCl<sub>2</sub>(TDA)<sub>2</sub> immobilized on hydrophobic graphite oxide in the hydrogenation of 1-pentyne and the Heck coupling reaction*

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**Reaction Kinetics, Mechanisms and Catalysis**

ISSN 1878-5190

Reac Kinet Mech Cat  
DOI 10.1007/s11144-014-0735-x



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# Catalytic investigation of $\text{PdCl}_2(\text{TDA})_2$ immobilized on hydrophobic graphite oxide in the hydrogenation of 1-pentyne and the Heck coupling reaction

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Received: 17 December 2013 / Accepted: 22 May 2014  
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**Abstract** A Pd(II) complex with chloride and tridecylamine ligands ( $\text{PdCl}_2(\text{TDA})_2$ ) was immobilized on graphite oxide modified with the cationic surfactant octadecyltrimethylammonium bromide ( $\text{C}_{18}\text{TABr}$ ). Samples with different Pd loadings were synthesized and tested for the liquid-phase hydrogenation of 1-pentyne and the Heck coupling reactions of styrene–bromobenzene and styrene–iodobenzene. For the hydrogenation of 1-pentyne, the catalytic performance was found to be affected by the pretreatment procedure. For the Heck coupling reactions, the  $\text{PdCl}_2(\text{TDA})_2/\text{GO}$  samples proved to be highly efficient catalysts. The catalytic activity was found to depend on the Pd loading for both reactions.

**Keywords** Graphite oxide ·  $[\text{PdCl}_2(\text{TDA})_2]$  · Immobilization · Alkyne hydrogenation · Heck reaction

## Introduction

Graphite oxide (GO) is an oxygen-rich carbonaceous material, which may be produced by the controlled oxidation of graphite. GO is a two-dimensional solid, with strong covalent bonding within the layers and weaker interlayer contact between intercalated water molecules [1–4]. One of the most recent models of GO, which represents a modified version of the original Hofmann model [5] describes a

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GO layer as a random distribution of flat aromatic regions with unoxidized benzene rings and other regions of alicyclic six-membered rings with tertiary hydroxyl and epoxide groups. The graphene oxide sheets are terminated with carboxyl groups [6, 7]. Unlike most lamellar compounds of graphite, GO cannot be characterized by a definite empirical formula, as GO is a nonstoichiometric compound and its composition depends on the synthesis conditions [4, 8]. Furthermore, GO is strongly hygroscopic and decomposes above 333 K [3]. GO is also a hydrophilic material, which may be readily dispersed in water to form stable colloidal suspensions [2, 3, 8]. As the GO lamellae are capable of parallel orientation, self-assembled films can be prepared from diluted dispersions [9, 10]. As a result of liquid sorption, GO readily undergoes swelling and disaggregation [2]. GO also possesses an excellent intercalation ability and cation exchange capacity and therefore a large number of intercalated GO materials have been synthesized and investigated. The intercalation of alkyltrimethylammonium ions resulted in the formation of organophilic GO materials, which may be applied in organic dyes or in photochemical reactions [11–13]. In the present study, hydrophobic GO was utilized as a host material for the immobilization of  $\text{PdCl}_2(\text{TDA})_2$ , which has been previously applied for alkyne hydrogenation [14].  $\text{PdCl}_2(\text{TDA})/\text{GO}$  samples with different Pd loadings were synthesized and investigated as catalysts for the liquid-phase hydrogenation of 1-pentyne and the Heck coupling reaction.

## Experimental

### Immobilization of $\text{PdCl}_2(\text{TDA})_2$ over hydrophobized graphite oxide

Graphite oxide was synthesized by Brodie's method [15].  $[\text{PdCl}_2(\text{TDA})_2]$  ( $\text{TDA} = \text{NH}_2(\text{CH}_2)_{12}\text{CH}_3$ ) was prepared by the reaction of  $\text{PdCl}_2$  with tridecylamine (TDA) in toluene, in a glass equipment with agitation under reflux and an argon atmosphere at 353 K for 4.5 h. For the synthesis of  $[\text{PdCl}_2(\text{TDA})_2]$ , the molar ratio  $\text{TDA}/\text{PdCl}_2 = 2$  was used. The pure  $[\text{PdCl}_2(\text{TDA})_2]$  complex was obtained in the solid phase after purification by column chromatography [16].

The hydrophobization of GO was performed by applying the cationic surfactants dodecyltrimethylammonium bromide ( $\text{C}_{12}\text{TABr}$ ) and octadecyltrimethylammonium bromide ( $\text{C}_{18}\text{TABr}$ ). 2 g of GO was measured and 400 ml of distilled water was added. The pH was adjusted to 9.8 by using an  $\text{NH}_4\text{OH}$  solution and the suspension was left under stirring overnight. The surfactant was dissolved in distilled water, the pH was adjusted to 10.8 and the surfactant solution was mixed into the GO suspension. The suspension was stirred for 4 h and then filtered. The solid was dried at room temperature and stored in a desiccator.

As revealed in Fig. 1, the GO sample modified by  $3 \text{ mmol g}^{-1} \text{ C}_{18}\text{TABr}$  was found to have the highest interlamellar spacing ( $>3.3 \text{ nm}$ ), indicating that intercalation of the surfactant molecules between the GO layers took place. Accordingly, this sample was selected for further investigations. The GO sample hydrophobized by  $3 \text{ mmol g}^{-1} \text{ C}_{18}\text{TABr}$  was subsequently swollen in toluene for 24 h and impregnated with a toluene solution of  $\text{PdCl}_2(\text{TDA})_2$ . The suspension was

left under stirring for 24 h, then the solid was filtered and the supernatant was analyzed by UV–Vis spectroscopy, in order to determine the Pd complex concentrations. The suspension was spread over a glass plate and then the solvent was evaporated.

### Catalytic hydrogenation

The liquid-phase hydrogenation of 1-pentyne was investigated in an automated hydrogenation apparatus. The reactions were performed at 298 K and  $10^5$  Pa, by using 5 mg of catalyst and a reactant: Pd (R: Pd) ratio of 1,000. The standard pretreatment of the catalyst (P1) included flushing of the sample with  $H_2$  and then the sample was subjected to static  $H_2$  for 60 min. After evacuation,  $H_2$  was re-introduced and  $1\text{ cm}^3$  of toluene was injected into the reactor. Pretreatment was completed in toluene under stirring for 45 min. The reactions were performed under efficient stirring (1,400 rpm) to eliminate mass transport limitations. For additional measurements, the pretreatment procedure was modified in a way that the sample was left in toluene under stirring for 24 h (P2). During the measurement, the hydrogen consumption was recorded as a function of reaction time. The reaction rates were determined from the slopes [17] and the product mixtures were analyzed by a Hewlett Packard 5890 gas chromatograph, equipped with a HP1 capillary column and FID, by using heptane as an internal standard. For the hydrogenation of 1-pentyne, the only product was 1-pentene, overhydrogenation or isomerization was not observed.

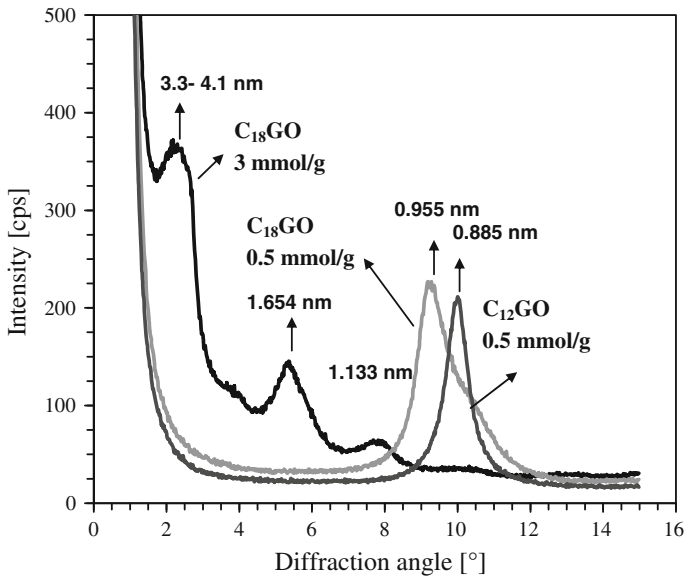
### The Heck coupling reaction

The Heck coupling reaction (Fig. 2) [18–21] was investigated for the reactants styrene–bromobenzene and styrene–iodobenzene by applying the reactant: Pd ratio (R: Pd) = 1,000 and 1,200, as referred to the halogenated compound and styrene, respectively. The reactions were carried out by using  $2.5\text{ cm}^3$  of N-methylpyrrolidone as a solvent and an excess of  $Na_2CO_3$  (1.4 equiv. vs. bromobenzene) as a base.

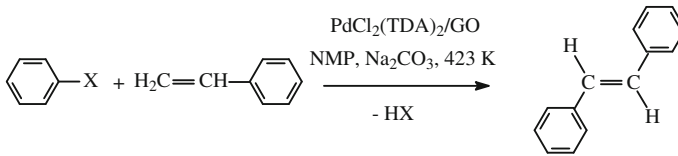
The reactions were performed under magnetic stirring at 423 K for 3 h. Then the product mixture was filtered, diluted by diethylether and the diluted solution was analyzed by a HP 5890 gas chromatograph, by using a HP1 capillary column, FID and dodecane as an internal standard. Analysis was performed in the temperature range 100–180 °C. The catalysts could be readily recovered and reused in 5 consecutive cycles without significant leaching and loss of the catalytic activity (<6 %).

## Results and discussion

For the liquid-phase hydrogenation of 1-pentyne, the reaction rates and the conversions were determined [22] after 25 min of reaction time and the results were summarized in Table 1. After standard pretreatment (P1), the initial rates were found to decline considerably as the reactions progressed (Fig. 3). This may be



**Fig. 1** XRD patterns of organophilic GO samples



**Fig. 2** The Heck coupling reaction

attributed to the appearance of interlamellar Pd species, which participated in the reactions as active sites. Similar experiences have been made for GO-intercalated Pd nanoparticles [23, 24].

The highest conversion was observed for the sample with the lowest Pd content. Both the reaction rates and the conversions exhibited a decreasing trend as the Pd loading increased (Table 1). The low conversions obtained for the samples with the highest Pd loadings suggested limited access for the reactants to the active sites, which resulted in moderate hydrogenation activities. The results suggested the predominance of interlamellar active sites in the above reaction, as the catalytic behaviour of the samples proved to be essentially different from those of conventional supported Pd catalysts.

In order to investigate the effect of pretreatment on the catalytic performance, a modified procedure was applied: the catalyst was subjected to static  $\text{H}_2$ , then the solvent was introduced and the sample was left under stirring for 24 h. Following this procedure (P2), the hydrogenation of 1-pentyne was found to proceed with constant rate for all the samples and enhanced conversions were observed (Fig. 3).



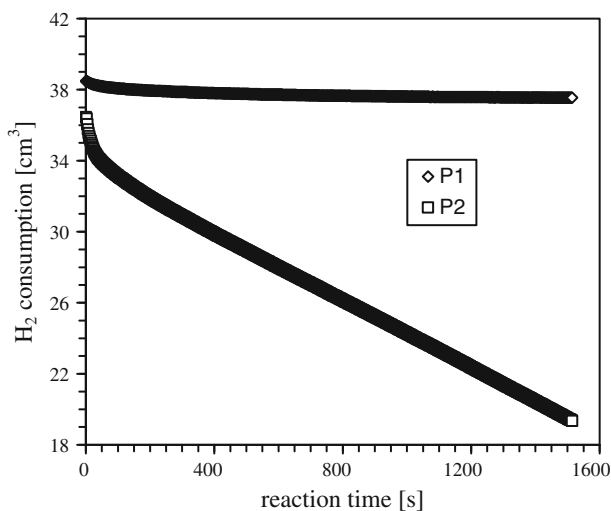
**Table 1** Liquid-phase hydrogenation of 1-pentyne over PdCl<sub>2</sub>(TDA)<sub>2</sub>/GO samples

Catalyst <sup>a</sup>	Reaction rate (cm <sup>3</sup> H <sub>2</sub> min <sup>-1</sup> g Pd <sup>-1</sup> ) <sup>b</sup>	Conversion (%) <sup>b</sup>	Reaction rate (cm <sup>3</sup> H <sub>2</sub> min <sup>-1</sup> g Pd <sup>-1</sup> ) <sup>c</sup>	Conversion (%) <sup>c</sup>
0.1 % Pd/GO	1,081	34.7	1,824	47
0.5 % Pd/GO	765	18.9	1,548	24
1 % Pd/GO	538	12.5	1,982	29
2 % Pd/GO	397	8.9	1,436	34
5 % Pd/GO	298	6.5	2,290	59

<sup>a</sup> T = 298 K, p = 10<sup>5</sup> Pa, R:Pd = 1,000, t = 25 min

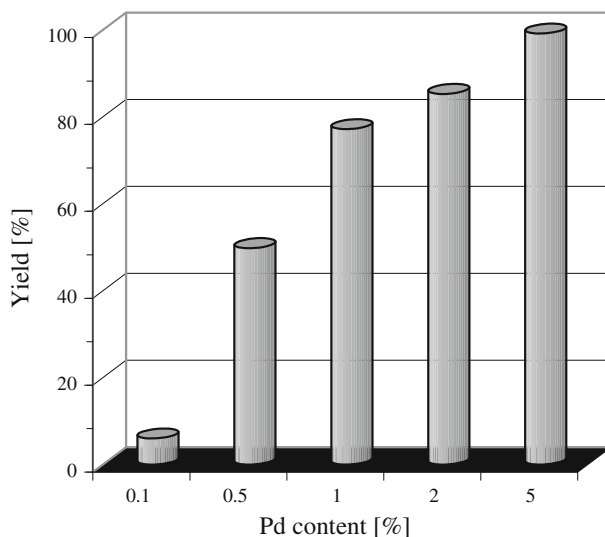
<sup>b</sup> Pretreatment: static H<sub>2</sub>, 60 min, static H<sub>2</sub> and solvent, 45 min

<sup>c</sup> Pretreatment: static H<sub>2</sub> and solvent, 24 h

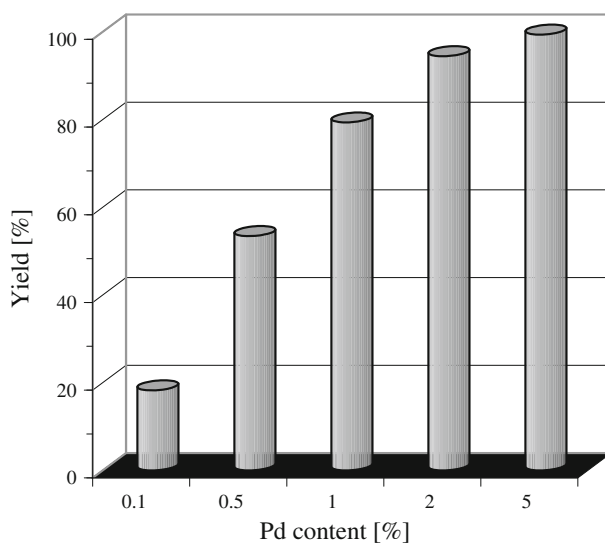


**Fig. 3** Liquid-phase hydrogenation of 1-pentyne over PdCl<sub>2</sub>(TDA)<sub>2</sub>/GO (5 % Pd/GO). P1 standard pretreatment, P2 pretreatment in toluene under H<sub>2</sub> for 24 h

The most pronounced increase in the conversion was obtained for the sample with the highest Pd loading, which proved to be the most efficient catalyst after P2. The difference between the reaction rates may be interpreted in terms of the swelling ability of the host material. Given the excellent intercalation and swelling ability of graphite oxide, it may be assumed that a considerable amount of the active Pd species was intercalated between the graphite oxide layers and hence such species were inaccessible for the reactants after standard pretreatment (P1). However, a prolonged exposure of the sample in toluene (P2) gave rise to an enhanced swelling of the host material, which was found to increase the catalytic performance by providing more access to the intercalated Pd species. It may also be suggested that P2 afforded partial reduction of the PdCl<sub>2</sub>(TDA)<sub>2</sub> complex, which contributed to an enhanced catalytic performance. For the sample with the lowest Pd loading (0.1 %



**Fig. 4** Yield of the coupling product in the Heck reaction of styrene and bromobenzene



**Fig. 5** Yield of the coupling product in the Heck reaction of styrene and iodobenzene

Pd/GO), the difference in the conversions, obtained after P1 and P2, was less substantial, indicating that the interlamellar Pd content of this sample was insignificant.

The yields for the products of the Heck coupling reactions of styrene with bromobenzene and iodobenzene are displayed in Figs. 4 and 5, respectively.



It may be established that the  $\text{PdCl}_2(\text{TDA})_2/\text{GO}$  samples displayed a marked catalytic activity for the Heck coupling reaction and an increase in the Pd content resulted in an enhanced catalytic performance. In both reactions, the most efficient catalysts were the samples with the highest Pd loadings, for which complete conversions were obtained and the main reaction product (Fig. 2) was formed with a selectivity of 100 %. On repeated applications, the catalytic activities of the immobilized Pd complexes were found to be maintained up to 5 catalytic runs. It may be established that the  $\text{PdCl}_2(\text{TDA})_2/\text{GO}$  samples were powerful catalysts in the Heck coupling reactions. Furthermore, the activities of the samples with higher Pd loadings exceeded those reported for some of the conventional heterogeneous Pd catalysts under similar experimental conditions [25–28]. The results obtained for the reaction of iodobenzene and styrene were similar to those obtained by Tamami and Ghasemi, for a Pd catalyst supported on cross-linked polyacrylamide [29]. Accordingly, the  $\text{PdCl}_2(\text{TDA})_2/\text{GO}$  samples may be regarded as heterogenized homogeneous catalysts [21, 30, 31] which combine the advantages of homogeneous Pd complexes (high activity and selectivity) with those of supported Pd catalysts (easy recovery and recycling). The complete understanding of the catalytic cycle and the role of Pd in the Heck coupling reaction is still a big challenge, which requires further investigations [32, 33].

## Conclusions

Graphite oxide was hydrophobized with cationic surfactants and the sample modified with  $3 \text{ mmol g}^{-1} \text{ C}_{18}\text{TABr}$  was selected as a support material for the immobilization of  $\text{PdCl}_2(\text{TDA})_2$ .  $\text{PdCl}_2(\text{TDA})_2/\text{GO}$  samples with different Pd loadings were prepared by impregnation and the catalytic activities were investigated in the hydrogenation of 1-pentyne and the Heck coupling reaction. The samples displayed moderate to medium activities for 1-pentyne hydrogenation. Modification of the pretreatment procedure was found to exert a beneficial effect on the catalytic performance. For the Heck coupling reaction, the  $\text{PdCl}_2(\text{TDA})_2/\text{GO}$  samples proved to be active and selective catalysts and the sample with the highest Pd loading exhibited the best catalytic performance.

**Acknowledgments** Financial support by the TÁMOP-4.2.2.A-11/1/KONV-2012-0047 project and the 103191 OTKA NN Grant is gratefully acknowledged.

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