Reductive Ullmann Coupling of Aryl Halides by Palladium Nanoparticles Supported on Cellulose, a Recoverable Heterogeneous Catalyst

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Palladium nanoparticles supported on cellulose were prepared without using any reducing agent and used as a highly efficient catalyst for the Ullmann reductive coupling of aryl halides in the presence of zinc, in a water-alcohol mixture as solvent in air. The obtained palladium nanoparticles were characterized by scanning electron microscopy (SEM), FTIR, thermogravimetric analysis (TGA) and ICP-AES analysis. The synthesis of biaryls from chloroarenes was performed by this catalyst with good yield. The catalyst remains stable up to 75 °C and can be recovered and reused several times without loss of activity.

Key words: Ullmann C–C Coupling, Aryl Halides, Palladium Nanoparticles, Cellulose Support, Recoverable Catalyst

Introduction

Green chemistry focuses on the design of chemical processes to reduce generation of wastes [1]. Green methods are based on two main ideas, choice of solvent and using heterogeneous catalytic reactions. Heterogeneous catalytic reactions, as selective as possible, are superior to the homogenous ones because of their reusability advantages [2]. The choice of solvent as the main component of a reaction system is very important. The appropriate solvent in green chemistry is water which is safe, nontoxic, cheap, odorless and accessible everywhere, but with limited chemical compatibility [3]. There is much attention to develop new methods and technologies to perform reactions in water by the use of co-solvents [4], phase transfer catalysts [5], surfactants [6], cyclodextrines [7], and ionic derivatization [8].

The Ullmann reaction [9], which is often considered as a simple homocoupling reaction, has been used for the biaryl synthesis. In the classical method, copper, high temperature and aryl iodides or bromides are used for the reaction, and dimethylformamide is considered as a suitable solvent as (i) it can stand up to high temperatures, (ii) its polarity accelerates the reaction, and (iii) the products can be easily isolated and purified using this solvent [10]. Unfortunately, the yield of the reaction by copper is low, and the reaction is sensitive to air and water. The classical Ullmann reaction is restricted to electron-deficient aryl halides and is not effective for chloroarenes which are readily accessible in large scales compared to other haloarenes [11]. The recent trend was to perform this reaction under mild conditions with less sensitivity to water or air [12]. This has led to perform the Ullmann coupling variant, catalyzed by nickel or palladium [13]. Palladium-catalyzed carbon-carbon bond forming reactions are among the most selective and effective reactions in organic synthesis [14, 15]. Homogeneous Ullmann homocoupling of aryl halides catalyzed by palladium complexes have been reported by Rawal et al. [16]. Pd/C-catalyzed Ullmann coupling reactions in the presence of reducing agents like zinc [17], hydrogen [18], sodium formate [19], triethylamine [20], alcohols [21], and indium [22] have been developed especially in recent years. Bamfield et al. synthesized biaryls in moderate yields from haloarenes by using sodium formate as reducing agent [19]. Various chloro- and bromobenzenes can form biaryls via Pd/C-catalyzed Ullmann coupling by using hydrogen as reducing agent in the presence of a small amount of PEG-400 and sodium hydroxide [18]. Zinc has been used as a reducing agent in the Ullmann coupling of haloarenes, catalyzed by Pd/C in aqueous acetone under air atmosphere in water in the presence of crown ethers [23]. The yields were high, but only iodo- and bromoarenes could be used in the latter method, also the separation of crown ethers made the process uneconomical [24]. Zinc-mediated Ullman-type coupling could be implemented with chloroarenes when the reaction was performed in liquid carbon dioxide [25]. In a two-phase system (like oil-water microemulsion) under phase-transfer catalyst conditions, biaryls were obtained in excellent yields. However, the difficulty of

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the product purification still remains as a challenging problem [26].

Nowadays, due to its cheapness, availability, chemical inertness, thermal stability and insolubility in most organic solvents as well as water, the application of cellulose as the catalyst support is increasing [27]. Recently, the preparation of palladium nanoparticles supported on cellulose or cellulose nanocrystallites have been reported [28, 29]. The Pd(0)-supported catalyst was prepared by reducing Pd(II) with hydrazine hydrate and used for Suzuki coupling of aryl halides and aryl boronic acids [28]. The Pd(0) catalyst on nanocrystalline cellulose was also prepared by reduction of Pd(II) by hydrogen and used in Heck coupling [29].

In this study palladium nanoparticles supported on cellulose were prepared, and the catalytic performance and the reusability of the catalyst were studied by performing the homocoupling of haloarenes.

Results and Discussion

Catalyst characterization

Scanning electron micrographs were recorded with a Hitachi S4160 instrument. SEM images indicated the formation of palladium nanoparticles on the surface of cellulose (Fig. S-1; Supporting Information; see note at the end of the paper for availability). The Pd nanoparticles seem to be deposited homogeneously on the surface of cellulose.

To determine the thermal stability of the catalyst, thermogravimetric analysis (Fig. S-2) was run from ambient temperature up to 600 °C. The sample was heated at the rate of 20 °C min⁻¹ under the flow of nitrogen. Up to 200 °C the thermal weight loss of the cellulose support was negligible, and the catalyst showed good thermal stability. A decline in the weight of catalyst was observed from 220 °C to 300 °C. This result was confirmed by the thermogravimetric dW/dT curve (Fig. S-3).

The FT-IR spectra indicate the chemical and thermal stability of palladium supported on cellulose under the reaction conditions. The negligible differences in the FT-IR spectra show that the catalyst is stable under the coupling reaction conditions.

An ICP-AES analysis of the catalyst was performed to determine the amount of active palladium particles supported on the cellulose. The catalyst was dissolved in concentrated HNO₃, diluted with distilled water and subjected to the ICP-AES analysis. The concentration of palladium particles in the catalyst is 0.00416 g (0.039 mmol) per 1 g of catalyst.

It is well demonstrated that sodium dodecyl sulfate (SDS) gives stability to the aqueous dispersion of cellulose molecules in water when the catalyst is synthesized. The adsorption of surfactant on the cellulose surface increases the wetting behavior and interfacial adhesion of cellulose, leading to better dispersion in water [30].

Catalyst testing for Ullmann homocoupling

To test the catalytic activity of palladium nanoparticles supported on cellulose, the coupling reaction of iodo-, bromo- and chlorobenzene were studied as model systems in the presence of zinc. To do this, a mixture of water-alcohol was used as solvent system. The palladium particles supported on cellulose represent an efficient and economical catalyst for the Ullmann reaction in water with zinc with no sensitivity to air. Under the reaction conditions, biaryls were synthesized from chloroarenes with good yields with no need to add any additive or using harsh conditions (Scheme 1).

The reaction was performed with substituted aryl halides as well. It seems that substituents in the *ortho* position lower the reaction rate and yield due to steric hindrance. The results are summarized in Table 1.

The coupling reaction by the prepared catalyst is applicable for chloroarenes but it needs more catalyst (7-10 mol-%) and high temperature. In the coupling reduction of aryl halides bearing carbonyl groups (entry 9 and 11 in Table 1), the use of zinc will end up in the reduction of the carbonyl group. In this case, hydrazine in basic media was used as a reducing agent to hinder the reduction of ester groups.

The reaction rate went up with increasing temperature but the stability of the particles on the cellulose support was decreased. The stability of the catalyst was studied as a function of reaction temperature. Up

Ar-X
$$Pd(0)$$
 supported on cellulose Ar-Ar
Zn, H₂O-alcohol Ar-Ar

X= I, Br, Cl

Scheme 1. Ullmann homocoupling of aryl halides.

Entry	Substrate	Product	Temp. (°C)	Yield ^a (%)	Melting point (°C)	
					found	reported
1		Ph	25	94	66-68	68.2 [31]
	\bigcirc	\bigcirc				
2	Br	Ph	25	96	66-68	
	\bigtriangleup	\bigtriangleup				
3	Ċ	Ph	70	83	65-68	
	\bigcirc	\bigcirc				
4	-		40	93	69-71	70-71 [32]
	Br	, N				
		<u> </u>				
5		OMe	50	88	174–176	175–176 [33]
	Br	\square				
	\bigcirc	\bigcirc				
	ОМе	OMe				
6		Me	50	92	117-120	118–120 [34]
	Ŗr	\square				
	\square	\square				
	Me	Me				
7		Me	70	79	117-120	
	CI	Ý				
	\square	\square				
	Me	Me				
8	-		90	56	59-62	61-63 [35]
	CI	CI				
0			70	78	70 72	72 73 [36]
9	Ŗr	MeOOC	70	78	10-12	72-75[50]
	COOMe	COOMe				
10	\checkmark	\sim	40	86	154-157	158 [37]
	Br					
	()					
11	D-		70	79	151-154	154 [38]
	Br COOMe	MeOOC COOMe				
	\bigvee					

Table 1.	Ullmann homocoupl	ling of different	haloarenes using	Pd nanor	particles supported	l on cellulose ((4 - 10 mol-%).
			(

^a Isolated yields.

to 75 °C good stability was observed, and the catalyst could be recovered and reused several times without loss of activity. At temperatures above 80 °C, stability and reusability of the catalyst decreased.

Conclusion

Palladium nanoparticles supported on cellulose could be used as effective and economical catalyst for

the Ullmann reductive coupling of haloarenes in the presence of zinc as reducing agent and water-alcohol mixtures as solvent in the presence of air. The prepared catalyst was used for the Ullmann coupling of chloroarenes. Good stability and recovery of the catalyst was observed at temperatures below 75 °C.

Experimental

Catalyst preparation

Microcrystalline cellulose (1 g) and sodium dodecyl sulfate (SDS) (0.23 g) were added to a solution of $PdCl_2$ (0.017 g) in water (50 mL), and the mixture was refluxed for 4 h. The reaction mixture was cooled to room temperature, and the precipitated particles were filtered and washed several times with distilled water. The particles were dried in air and grinded in a mortar to be used for the Ullmann reaction.

Ullmann homocoupling

To a mixture of haloarene (2 mmol) and zinc (0.39 g, 6 mmol) in distilled water (20 mL) and ethanol (2 mL) was

- [1] I. T. Horvath, P. T. Anastas, *Chem. Rev.* 2007, 127, 2167–2168.
- [2] C. Li, Chem. Rev. 2005, 105, 3095-3166.
- [3] C. C. Tzschucke, C. Market, W. Bannwarth, S. Roller, A. Hebel, R. Haag, *Angew. Chem. Int. Ed.* **2002**, *41*, 3964–4000.
- [4] F. Amoroso, S. Colussi, A. Dell Zotto, J. Llorca, A. Trovarelli, *Catal. Commun.* 2011, 12, 563–567.
- [5] B. K. Allan, K. N. Singh, Synthesis 2011, 1125-1131.
- [6] P. Ghosh, A. Mandal, *Catal. Commun.* **2011**, *12*, 744 747.
- [7] J. A. Imaonigie, D. H. Macartney, *Inorg. Chem.* 1993, 32, 1007–1012.
- [8] J. F. W. Keana, A. P. C. Morat, J. J. Volwerk, J. Org. Chem. 1983, 48, 2661–2666.
- [9] F. Ullmann, J. Bielecki, Chem. Ber. 1901, 34, 2174– 2185.
- [10] A. P. Degnan, A. I. Meyers, J. Am. Chem. Soc. 1999, 121, 2762–2769.
- [11] J. Hessan, M. Sevignon, C. Gozzi, E. Schulz, M. Lemaire, *Chem. Rev.* 2002, 102, 1359–1470.
- [12] F. E. Ziegler, I. Chliwner, K. W. Fowler, S. J. Kanfer, S. J. Kuo, N. D. Sinha, J. Am. Chem. Soc. 1980, 102, 790-798.
- [13] T. D. Nelson, R. D. Crouch, Org. React. 2004, 63, 265–555.

added the catalyst (2 g of cellulose, 0.00832 g, 0.078 mmol of palladium). The mixture was stirred at the temperature given in Table 1, and the reaction progress was monitored by TLC. After the completion of the reaction, the mixture was filtered, and the catalyst was washed with diethyl ether several times. Recovered catalyst was grinded by mortar immediately after initial drying to be used in the next run. The filtrates were extracted using diethyl ether; the organic solvent was dried over sodium sulfate and evaporated under reduced pressure. All products were recrystallized from suitable solvents and characterized by melting points, ¹H NMR and IR spectroscopy.

Supporting information

SEM photographs, TGA and thermogravimetry curves of the palladium nanoparticles supported on cellulose are given as Supporting Information available online (DOI: 10.5560/ZNB.2013-3048).

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- [14] Y. Q. Zhang, X. W. Wei, R. Yu, Catal. Lett. 2010, 135, 256–262.
- [15] A. Kamal, V. Srinivasulu, B. N. Seshadri, N. Markandeya, A. Alarifi, N. Shankaraiah, *Green Chem.* 2012, 14, 2513–2522.
- [16] D. D. Hennings, T. V. Iwama, H. Rawal, Org. Lett. 1999, 1, 1205 – 1208.
- [17] N. Ple, A. Turck, K. Couture, G. Queguiner, *Tetrahe*dron **1994**, 50, 10299 – 10308.
- [18] M. B. Goldfinger, K. B. Crawford, T. M. Swager, J. Am. Chem. Soc. 1997, 119, 4578–4593.
- [19] A. Arcadi, A. Burini, S. Cacchi, M. Delmastro, F. Marinelli, B. Pietroni, *Synlett* **1990**, 47.
- [20] Y. Han, A. Roy, A. Giroux, *Tetrahedron Lett.* 2000, 41, 5447–5451.
- [21] D. Gittis, S. Mukhopadhyay, G. Rothenberg, Y. Sasson, Org. Proc. Res. Dev. 2003, 7, 109–114.
- [22] M. Rottländer, P. Knochel, Synlett 1997, 1084-1086.
- [23] S. Ventrakaman, C. J. Li, Org. Lett. 1999, 1, 1133– 1135.
- [24] S. Ventrakaman, C. J. Li, *Tetrahedron Lett.* 2000, 41, 4831–4834.
- [25] J. Li, Y. Xie, H. Jiang, M. J. Chen, Green Chem. 2002, 4, 424–425.
- [26] C. J. Z. Jiang, J. Cai, Colloids. Surf. A 2007, 305, 145-148.

- [27] L. Zhou, J. He, J. Zhang, Z. He, Y. Hu, C. Zhang, H. He, J. Phys. Chem. C 2011, 115, 16873-16878.
- [28] N. Jamwal, R. K. Sodhi, P. Gupta, S. Paul, Int. J. Biol. Macromol. 2011, 49, 930–935.
- [29] C. M. Cirtiu, A. F. D. Briere, A. Moores, *Green Chem.* 2011, 13, 288–291.
- [30] N. Karousis, G. E. Tsotsou, F. Evangelista, P. Rudolf, N. Ragoussis, N. Tagmatarchis, J. Phys. Chem. C 2008, 112, 13463-13469.
- [31] W. F. Newhall, E. J. Elvin, L. R. Knodel, Anal. Chem. 1954, 26, 1234–1236.
- [32] W. H. F. Sasse, Org. Synth. 1966, 46, 5.

- [33] J. Bergman, R. Carlsson, B. Sjoberg, Org. Synth. 1977, 57, 18.
- [34] L. F. Elsom, A. Mckillop, E. C. Taylor, Org. Synth. 1976, 55, 48.
- [35] J. J. Dobbie, J. J. Fox, A. J. H. Gauge, J. Chem. Soc. Trans. 1911, 99, 1615–1620.
- [36] R. B. Hill, R. L. Sublett, H. G. Ashburn, J. Chem. Eng. Data 1963, 8, 233–234.
- [37] K. R. Wilson, R. E. Pincock, J. Am. Chem. Soc. 1975, 97, 1474–1478.
- [38] J. I. Kim, G. B. Shuster, J. Am. Chem. Soc. 1992, 114, 9309–9317.