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# Preparation of supported Palladium Catalysts using Deep Eutectic Solvents

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Abstract: Deep eutectic solvents (DESs) dissolve metal salts or oxides and are used as solvent and carbon source for the preparation of supported palladium catalysts. After dissolving of the palladium salt in the DES, the pyrolysis of the mixture under nitrogen atmosphere yields catalytically active palladium on supporting material composed of carbon, nitrogen and oxygen (CNO) by a simple single step preparation method without further activation. The catalysts were characterized by SEM and XPS microscopy, XRD, BET and CHNS/O elementary analysis. The amount of functional groups on the surface of the supporting material was determined by Boehm titrations. Moreover, the activity of the prepared catalysts was evaluated in the hydrogenation of linear alkenes and compared with a commercial Pd/C catalyst.

Supported palladium catalysts, like palladium on activated carbon, find extensive use in chemical synthesis for a wide variety of reactions ranging from the reduction of alkynes, alkenes, aldehydes, ketones, nitro groups, nitriles and imines to carbon-carbon bond formation reactions like the Sonogashira, Heck or Suzuki cross coupling reactions.<sup>[1]</sup> Supporting materials, like activated charcoal, are used for a fine distribution of metals on a large surface and for the stabilization of small metal particles.<sup>[2]</sup> Thereby, catalytically active atoms are better accessible than in comparable metal bulk materials.<sup>[3]</sup> Another advantage of activated carbon as a supporting material is the facile recovery and recycling of the precious metals by oxidation of the carbon after use.<sup>[4]</sup>

Conventionally, several steps are necessary for the preparation of these catalysts. The surface of the activated charcoal produced by either steam or chemical activation is loaded by ionic adsorption of a metal salt forming uniformly impregnated catalysts, which is subsequently dried and reduced to the metallic form. <sup>[2, 5]</sup>

We report here a simple single step method for the preparation of supported metal catalysts using deep eutectic solvents (DESs). A great advantage over the conventional impregnation method is that all kinds of metal precursors or mixtures of them can be easily supported in different ratios. Moreover, the properties of the supporting material can be influenced by the deep eutectic solvent. DESs<sup>[6]</sup>, which are defined as a fluid, composed of two or three components<sup>[7]</sup>, which are able to selfassociate by hydrogen bond interactions to form an eutectic mixture with a melting point lower than that of each individual component,[8] are prepared using cheap and abundant non-toxic starting materials.<sup>[9]</sup> The solubility of metal compounds, especially of metal oxides<sup>[10]</sup> and the fact that several DESs show a high carbon content renders them well-suited starting materials for catalyst preparation. All components are stirred under heating to an adequate temperature until a homogeneous, clear liquid has formed.[11] This liquid serves as solvent for the palladium precursor and the subsequent pyrolysis of the mixture yields the active catalyst without further activation. Moreover, the prepared catalysts can be easily reused after a filtration and washing step. The supporting material (CNO) consists of carbon,

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nitrogen and oxygen, which is already loaded with the metal.<sup>[12]</sup> Our initial studies began with the preparation of a deep eutectic solvent consisting of 40 w% D-glucose and 60 w% urea, the dissolution of palladium(II) acetate in the mixture and the subsequent pyrolysis in a round-bottom flask (Figure 1a).



**Figure 1.** Overview of the preparation of palladium supported catalysts using DES: DES production, dissolution of Pd(OAc)<sub>2</sub>, pyrolysis using the flask (a) or nozzle (b) method and finally, the Pd/CNO catalyst prepared.

To improve the relatively lowly active Pd/CNO catalyst obtained (Table 1, entry 2), a nebulization apparatus was constructed for the preparation of smaller particles and thus of a larger surface (Figure 1b). This theory could be verified by BET measurements The catalysts prepared by nozzle show a four times greater surface (38.89 ± 1.18 m<sup>2</sup>/g) compared to the catalysts produced by flask method (10.14 ± 0.48 m<sup>2</sup>/g), whereas the surface of a commercial activated charcoal is still much hiaher (800 - 1200 m<sup>2</sup>/g<sup>[2]</sup>). Nevertheless, the activity to surface ratio is noticeably better. In the case of the catalyst prepared by nozzle, the time to reach complete conversion is only three times as high compared to a commercial Pd/C catalyst (10 w% Pd loading, Sigma Aldrich); even though the surface of the supporting material was approximately 25 times lower Figure 2).



Figure 2. Activity comparison of a commercial catalyst Pd/C and the catalysts prepared by nozzle or flask method.

A strong dependency of the catalyst activity on the preparation temperature was determined as well. It could be shown, that 440 °C was the optimum preparation temperature for the

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catalysts prepared by a urea - D-glucose DES for simple hydrogenation reactions with 1-dodecene **1** as test substrate (Table 1). A threefold faster conversion was observed using catalysts prepared by nozzle method at 440 °C (Table 1, entry 6) compared to the catalyst prepared by flask method at a lower temperature (Table 1, entry 2).

 $\label{eq:table_table_table} \ensuremath{\textbf{Table 1}}. \ensuremath{\mbox{ Comparison of catalysts prepared at different temperatures and by different methods.}$ 

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Entry	Conditions	Time [min]	Conversion [%] <sup>a)</sup>	
1	10 w% Pd/C (Sigma Aldrich), 1 mmol 1	25	100	
2	10 w% Pd, flask, 420 °C, 1 mmol <b>1</b>	230	100	
3	10 w% Pd, nozzle, 250 °C, 1 mmol <b>1</b>	60	5	
4	10 w% Pd, nozzle, 380 °C, 1 mmol <b>1</b>	90	36	
5	10 w% Pd, nozzle, 420 °C, 1 mmol <b>1</b> 90 59			
6	10 w% Pd, nozzle, 440 °C, 1 mmol 1	70	100	
7	10 w% Pd, nozzle, 470 °C, 1 mmol <b>1</b>	90	94	
8	10 w% Pd, nozzle, 500 °C, 1 mmol <b>1</b>	90	93	

<sup>a)</sup> Conversion determined by GC-MS analysis; the reactions were carried out with 1 mmol 1-dodecene 1 and 25 mg catalyst in 5 mL MeOH.

Additionally, a deep eutectic solvent dependency of the optimum preparation temperature for the catalysts was observed. In general, the preparation temperature for the catalysts with the highest activity ranged between 440 and  $510^{\circ}$ C.

Table 2. Overview of the DES dependent optimum preparation temperature.

DES System	optimum temperature [° C]
choline chloride - D-sorbitol	470
choline chloride - vanillin	440
choline chloride - D-fructose	490
choline chloride - D-glucose	460
urea - D-glucose - D-fructose	470
urea - D-fructose	510
urea - D-glucose	440
N,N'-dimethylurea - vanillin	450
N,N'-dimethylurea - D-fructose	480
N,N'-dimethylurea - lignin	480

SEM-BSE investigations, indicated a better distribution of the palladium on the surface of the catalyst prepared by nozzle at 440 °C (Figure 3c) compared to the catalyst prepared at a lower temperature, shown in Figure 3b, or by flask method (Figure 3a), which explain the different activities of the catalysts.



Figure 3. SEM investigation (BSE mode) of the Pd/CNO catalysts; a) prepared by flask; b) prepared by a nozzle at 420  $^{\circ}$ C c) prepared by nozzle at 440  $^{\circ}$ C; magnification is 500:1.

This result was confirmed by X-ray photoelectron spectroscopy (XPS), whereby the metal loading on the surface of the catalysts was determined exemplarily for urea - D-fructose based catalysts (Figure 4) prepared by nozzle or flask method at the DES dependent optimum temperature 490 °C. The catalysts

prepared by nozzle show with 13.5 w% again a higher palladium amount and thus a better distribution on the top surface layer, while 6.4 w% palladium were found at the catalyst surface prepared by flask method.



Figure 4. XPS analysis of urea - D-fructose based catalysts prepared by a) nozzle or b) flask method at 490 °C.

Considering the supporting material more precisely, SEM-EDX investigations and CHNS/O measurements offered different compositions based on the used DES and preparation temperature. The hydrogen bond acceptors (urea, N,N'-dimethylurea and choline chloride) influence the nitrogen content of the support, while the temperature affects the carbon content.

Table 3. Functional groups on the surfac	e of the supporting material based on
urea - D-glucose DES were determined b	y Boehm titrations.

	т [°С]	250	380	420	440	470	500
round- bottom flask	n (basic) [µmol/g]	364.0	934.1	1023.2	968.5	967.7	899.0
	n (acidic) [µmol/g]	537.6	979.6	1083.8	1036.5	868.0	770.1
nozzle	n (basic) [µmol/g]	404.6	1139.9	1121.8	1019.8	888.7	707.6
	n (acidic) [µmol/g]	227.3	1074.9	967.0	902.3	654.0	419.4
com. activated carbon	n (basic) [µmol/g]	505.9					
	n (acidic) [µmol/q]	587.9					

The amount of functional groups on the surface of the supporting materials based on urea - D-glucose DES were determined by Boehm titrations (Table 3).<sup>[13]</sup> For each preparation temperature of the supporting material a different number of functional groups are available. Using the nozzle method, for all temperatures the amount of basic groups is higher than the amount of acidic groups. Using the round-bottom flask method, this behavior can be observed only at higher temperatures (470 and 500 °C), while it is the other way around for temperatures up to 440 °C. Moreover, much more functional groups on the surface could be found in comparison to a commercially available activated carbon at temperatures above 300 °C.

Table 4. Reproducibility tests using urea - d-glucose based Pd/CNO prepared by nozzle at 440  $^\circ\text{C}.$ 

reproducibility	conversion after 60 min [%]
1 <sup>st</sup> preparation	92 %
2 <sup>nd</sup> preparation	96 %
3 <sup>rd</sup> preparation	89 %

In addition, the preparation of the catalysts at different times using the same conditions give relevant information about the reproducibility of the method. The urea - d-glucose based Pd/CNO catalysts were prepared three times at 440 °C by nozzle and Table 4 shows, that it is possible to reproduce the catalyst activity using this method.

In conclusion, the reported protocol shows the preparation of a Pd/CNO catalyst by a simple single step method based on deep eutectic solvents, to the best of our knowledge, for the first time. In contrast to the commercial Pd/C, the catalyst activity can be influenced by many preparation parameters regarding the desired application field. It has to be investigated, if the preparation temperature depends on the used substrates as well and a further characterization of the supporting material is necessary to understand the preparation mechanism in more detail.

#### **Experimental Section**

#### Chemicals

Commercial reagents and used chemicals were purchased from Sigma Aldrich, Acros, TCI, VWR, Carl Roth, Merck or Alfa Aesar and used without further purification.

#### Preparation

#### Flask Method

In a round-bottom flask equipped with a magnetic stirring bar, the DES used was heated until a clear, homogeneous liquid was formed. In this solvent a known amount of metal salt for a theoretical 10 w% loading was dissolved. As soon as the palladium salt was completely dissolved the mixture was heated under nitrogen atmosphere until 280 °C until a dry porous material was formed. This material was further pyrolysed in a muffle furnace at 440 °C under nitrogen atmosphere until a fine black powder rises.

#### Nozzle Method

In a round-bottom flask equipped with a magnetic stirring bar, the DES used was heated until a clear, homogeneous liquid was formed. In this solvent a known amount of metal salt for a theoretical 10 w% loading was dissolved. As soon as the metal salt was completely dissolved, the mixture was transferred to a heated nebulization apparatus. By the use of nitrogen pressure the mixture was sprayed on a heated surface and further pyrolysed in a muffle furnace under nitrogen atmosphere at different temperatures until a fine black powder rises.

#### Characterization

The turnover of the test reactions were determined by GC-MS using a BPX5 column (SGE, 30 m, I. D. 0.25 mm, film 0.25 µm) connected to a QP2010 Plus gas chromatograph with a Single Quad MS-detector (both Shimadzu, Japan) with helium as the carrier gas. 0.5 µL of the diluted sample was automatically injected via SSL-injector (290 °C) starting at 60 °C for 1 min, then heated to 170 °C at 11 °C min-1 and finally to 270 °C at 70 °C min<sup>-1</sup> and held for 3 min.

Scanning electron microscopy (SEM) was performed to determine the morphologies of the supporting material (SE detector), the distribution of the palladium on the support (BSE detector) and the composition of the support with the EDX detector. The samples were mounted on carbon tape and studied using a digital scanning electron microscope (Zeiss, DSM 940 A, Oberkochen, Germany) and operated in secondary imaging mode at 20 kV with a working distance of 33.0 mm.

Diffractogram measurements (XRD) were obtained by a general purpose X-ray diffractometer (Rigaku, MiniFlex 600, Tokyo, Japan) equipped with a high speed one-dimensional detector (Rigaku, D/teX Ultra, Tokyo, Japan) and a K $\beta$  foil filter. XRD patterns were recorded over the 2 $\theta$  range of 0°-90°, with a step width of 0.02°, a scanning speed of 2°/min and a  $CuK\alpha$  radiation generated at 40 kV and 15 mA. The measurements were analyzed by the Rigaku PDXL software (Integrated X-ray powder diffraction software).

The BET measurements were recorded on a Physisorption analyzer ASAP 2010 from Micromeritics.

#### **Activity Test Reactions**

In a round-bottom flask, 1 mmol of the 1-dodecene was dissolved in 5 mL methanol and 25 mg of the different Pd/CNO catalysts were added. The mixture was stirred at room temperature under hydrogen atmosphere and the conversion was checked and proved by GC-MS by frequent sampling for two hours.

To compare the activity of the catalysts, one sample was tested using a commercial Pd/C catalyst with the same conditions.

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Keywords: deep eutectic solvents · supported metal catalyst preparation • one step method • palladium

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**DESs as solvent and carbon source:** After dissolution of the palladium salt in the DES, the pyrolysis of the mixture under nitrogen atmosphere yields catalytically active palladium on supporting material composed of carbon, nitrogen and oxygen (CNO) by a simple single step preparation method without further activation (see picture). The activity of the catalysts prepared was evaluated in the hydrogenation of linear alkenes and compared with a commercial Pd/C catalyst. Melanie Iwanow, Jasmin Finkelmeyer, Anika Söldner, Manuela Kaiser, Tobias Gärtner, Volker Sieber, Burkhard König\*

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