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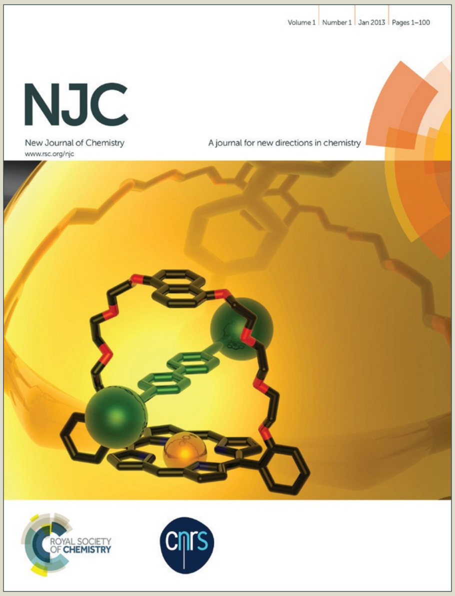

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Robustly supported rhodium nanoclusters: Synthesis and applications in selective hydrogenation of lignin derived phenolic compounds

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The stabilization of small rhodium nanoclusters (NCs) in polymer derived silicon carbonitride (SiCN) matrix is reported to generate highly robust and active solid catalysts for the selective hydrogenation of phenolic compounds. An aminopyridinato Rh complex was used to modify preceramic polymer (HTT1800) followed by its pyrolysis at 1100°C to afford small Rh NCs nicely dispersed over dense SiCN ceramic. For the synthesis of porous catalysts containing Rh NCs, microphase separation (followed by pyrolysis) of a diblock copolymer of HTT 1800 with hydroxy-polyethylene (PE-OH) was used. Both catalysts exhibit high activity for the hydrogenation of substituted phenols at room temperature and under low hydrogen pressure. The catalysts remained highly active and selective for consecutive six catalytic runs.

Introduction

Lignin constitutes 20-30% of the lignocellulose biomass and is considered as a potential source of phenolic compounds, for instance substituted guaicols which could be obtained from lignin via catalytic depolymerization.[1, 2] These substituted phenols are important raw materials for the production of important chemicals and materials (polymers).[3] Catalytic hydrogenation in this regard provides an efficient route towards the synthesis of these key chemicals. For instance, amination of cyclohexanol obtained by the selective hydrogenation of phenol could provide important organic compounds via C-N bond formation.[4] On the other, hydrogenation of phenol to cyclohexanone is important in the sense that the latter is an intermediate for the production of Nylon-6 polymer.[5] Industrial production of cyclohexanone from phenol is a two-step process where the second step, i.e., the dehydrogenation of cyclohexanol to cyclohexanone demands temperature above 400°C.[6] In the last few years many heterogeneous liquid phase catalysts have been developed for the selective hydrogenation of phenol under mild conditions.[7-14] One of the most outstanding examples is the dual-supported palladium catalyst of Han *et.al.;* showing high selectivity towards cyclohexanone within a high phenol conversion at 50°C.[15] However, the use of Lewis acids and non-green solvents narrows the applicability of the catalysts under experimental conditions. Worth mentioning is the work of Antonietti *et.al.;*[16] who achieved high selectivity with Pd@C_3N_4 using water as a green solvent. In polar solvents like water stability and reuse of the catalyst becomes an important consideration along with the possible leaching of catalytically active metal particles. Therefore, fabrication of highly active, selective and stable (reusable) catalysts for the hydrogenation of lignin derived phenolic compounds under mild and environmentally benign conditions are still demanding.

Rh seems to be an interesting metal for phenol hydrogenation since it provides high activity in arene hydrogenation[17, 18] and there are only few published examples for the selective hydrogenation of phenol to cyclohexanone with usable catalysts[19, 20] not requiring supercritical CO_2.[21, 22]

Polymer derived siliconcarbonitride (SiCN) ceramics offer high temperature stability, corrosion resistance, long-term durability and the low processing temperatures.[23-26] Via a molecular approach using amido-metal complexes[27-35] metal nanoparticles (NPs) had been generated in the SiCN matrix (M@SiCN) and used as robust catalysts for various reactions of industrial importance.[36-39] The unique feature of SiCN support is its ability to stabilize very small metal clusters and show an excellent reusability which may be attributed to the availability of nitrogen functions in the SiCN network.[40] Due to the fact that M@SiCN catalysts possess small surface areas and low metal dispersion, the catalytic activity of such catalysts is rather low. Until now different methods have been introduced to create a porous SiCN material utilizing both hard and soft templates.[41-48] Our group has previously reported the formation of SiCN nanofibers via the microphase separation and pyrolysis of the block polymer of commercial polycarbosilazane (HTT 1800) with

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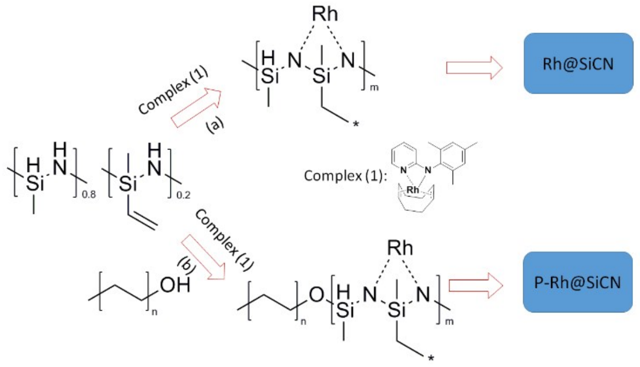

Scheme 1: Synthetic approaches for the fabrication of dense (route a) and porous (route b) Rh@SiCN catalysts. The first step in route (a) describes the chemical modification of polysilazane while route (b) involves the formation of a diblock copolymer and its modification with Rh ions. Second step in both routes corresponds to the pyrolysis under nitrogen leading to either dense (Rh@SiCN) or porous (P-Rh@SiCN) materials.

hydroxy-polyethylene (PEOH).[49] PEOH is cheap, can be eliminated under pyrolysis conditions and its block copolymer with HTT 1800 could provide different nanostructures upon microphase separation.[50] Here we report the fabrication of porous and non-porous rhodium NCs supported SiCN ceramics as active and selective catalysts for the hydrogenation of phenolic compounds.

Results and Discussion

The synthesis of the Rh@SiCN catalysts was carried out by the pyrolysis of chemically modified polycarbosilazane (HTT 1800). In the first step a rhodium complex (**1** in scheme 1) reacts with HTT 1800 by the elimination of the Ap^{TMA}H ligand and leads to the cross-linking of preceramic polymer. The "green body" upon pyrolysis at 1100°C provided the Rh@SiCN catalyst (Scheme 1, pathway-a) as confirmed by FT-IR studies (figure S1 in supporting information: SI) and solid state NMR (figure S2 in SI). The metal loading in the final materials is described in terms of Si/Rh ratio.

Transmission electron microscopy (TEM) provided the detailed microstructure of synthesized materials. In the case of Rh-10 (Si/Rh=10), as expected, agglomeration of NPs took place due the high metal content leading to broad distribution of particle size (figure S3, SI). The material with lower Rh metal content (Rh-20: Rh/Si ratio = 20) provided very small NPs with an average size of 1.6 nm (see figure 1a-c).

X-Ray powder diffraction (PXRD) measurement (figure 1d) showed the typical reflection pattern of the cubic phase of the rhodium at 2θ of 41.1°, 47.7° and 69.9° (reference code: 00-005-0685). The presence of elemental metal within the materials could be attributed to the reduction of Rh(II) ion under the reductive atmosphere of furnace due to the generation of hydrogen, ammonia and methane.

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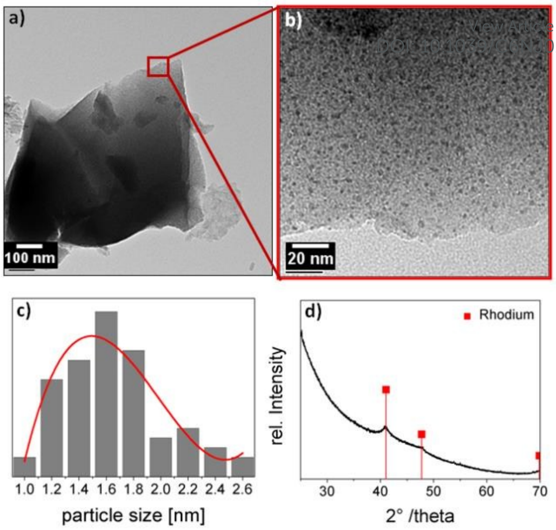

Fig. 1: (a), (b) TEM micrograph of a dense Rh@SiCN ceramic (Rh-20), (c) Particle size distribution with an average particle size of 1.6 nm, (d) PXRD pattern with rhodium reflexes and corresponding reference pattern (red).

So far we were successful in obtaining very small rhodium NPs nicely distributed in SiCN matrix. These materials possess very small surface area which could lead to severe mass transport constraints when used as catalysts. In order to introduce porosity within the materials a block copolymer of PE-OH with HTT 1800 was synthesized. PEOH was dissolved in toluene and mixed with the silazane precursor. Afterwards the rhodium complex, which catalyses the cross-linking reaction, was added. After 20 h reaction time the solvent was removed and a structured green body was obtained. During pyrolysis (at 1000°C under nitrogen) PEOH decomposes leaving behind the porous Rh@SiCN (p-Rh@SiCN) materials (Scheme 1, pathway 2). Again the very small particle size as was observed in dense ceramics previously prepared, was not compromised in this approach and homogeneously distributed rhodium NPs in a size range of 1.0 – 2.8 nm were obtained (figure 2a-b).

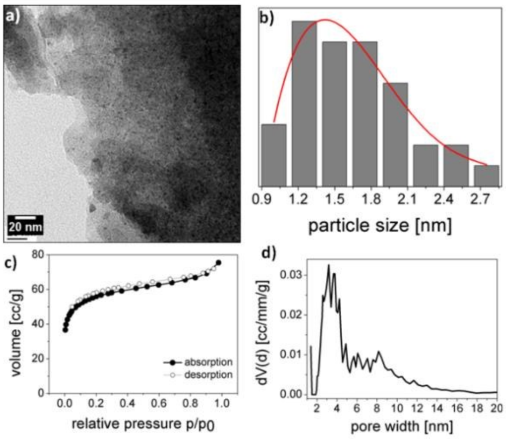

Fig. 2: (a) TEM micrograph of a porous Rh@SiCN ceramic, (b) Particle size distribution with an average particle size of 1.4 nm, (c) N_2 sorption isotherm showing a surface area of 205 m²/g, (d) Pore size distribution with a pore size in meso scale between 3 and 12 nm.

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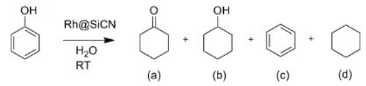
The existence of Rh(0) nanoparticles was confirmed by PXRD measurements which showed the reflection pattern of the cubic phase of the rhodium (see S4 in SI).

The success of the synthesis route and the generation of the porosity was established by N_2-adsorption. Adsorption-desorption isotherm of p-Rh@SiCN (figure 2c) is close to type-IV isotherm known to be shown by mesoporous materials, though high adsorption of nitrogen at P/P0 <0.1 also suggests the existence of micropores. The specific surface area of a p-Rh@SiCN material was found to be 205 m²/g. NLDFT was applied to adsorption branch of the isotherm which provided a pore size distribution (figure 2d) in the range 3 to 12 nm.

The porous Rh@SiCN (*p*-Rh-20) was investigated in the selective hydrogenation of phenol at room temperature. The results of the first screening with different solvents (entry 1-6) are shown in table 1.

Table 1. Hydrogenation of phenol over Rh@SiCN catalysts[a].



entry	p_{H2} (bar)	time (h)	solvent	additive	Conv. (%)	Sel. to (a) in %
1	6	1	EtOH	-	46	44
2	6	1	EtOAc	-	72	33
3	6	1	THF	-	38	38
4	6	1	toluene	-	38	68
5	6	1	H_2O	-	27	70
6	6	4	H_2O	-	100	0
7	6	2	H_2O	-	54	67
8	6	2	H_2O	chlorbenzene	26	77
9	6	2	H_2O	$ZnCl_2*4H_2O$	0	0
10	6	2	H_2O	acetone	37	82
11	6	2	H_2O	GVL	29	86
12	6	4	H_2O	GVL	67	72
13	10	3	H_2O	GVL	74	73
14 [b]	6	4	H_2O	GVL	23	80
15 [b]	6	6	H_2O	GVL	73	68
16	6	5	H_2O	GVL	99	73

[a] Reaction conditions: 2 mol% *p*-Rh-20 catalyst, 25°C, 3 ml solvent, 10 mmol additive; [b] 2 mol% Rh-20 catalyst. GVL=γ-valerolactone.

In ethanol (EtOH) and ethyl acetate (EtOAc) a high conversion of phenol but a low selectivity to cyclohexanone (CHN) was obtained (entries 1 and 2). In tetrahydrofuran (THF) and toluene (TOL) the catalyst showed almost the same activity but toluene was more selective towards CHN (entries 3 and 4). In solvent screening, water provided the highest selectivity to CHN (entry 5) and as it is an environment friendly solvent it was selected for further studies. In pure water almost quantitative conversion of phenol to cyclohexanol (CHL) was observed after four hours (entry 6). Notably, with the addition of chlorobenzene, $ZnCl_2*4H_2O$, acetone or γ-valerolactone (GVL) as co-solvents to water, the selectivity to CHN was greatly enhanced (entries 8 to 16). The consumption of acetone or GVL during the course of the reaction was not observed which shows their sole role as solvent or promoter, probably due to their binding with the CHN. As GVL is a renewable chemical accessible from biomass[51], was selected as a co-solvent for additional studies. The addition of a Lewis acid $ZnCl_2.4H_2O$ led to the deactivation of the catalyst (entry 9). Compared to dense material the porous catalysts has a higher activity (entry 14) since more metal is accessible due to increase in porosity of the materials.

The substrate scope was investigated in order to find out the effect of various substituents on phenol hydrogenation and results are presented in table 2. The dihydroxy arenes were selectively converted to hydroxyl-cyclohexanones with the highest selectivity observed in the case of catechol (entry 3) as compared to resorcinol (entry 2) and hydroquinone (entry 1) for which C-O bond cleavage was also observed providing CHN and CHL in low yield (< 20%). For lignin derived guaiacols almost similar selectivity to ketonic product was observed for ortho, para and meta-isomers (entry 4-6). However introduction of an electron donating alkyl group para to -OH resulted in an increased selectivity of 85-91% (entry 7-8). Recycling studies of the catalysts up to six consecutive runs are presented in Figure 3b.

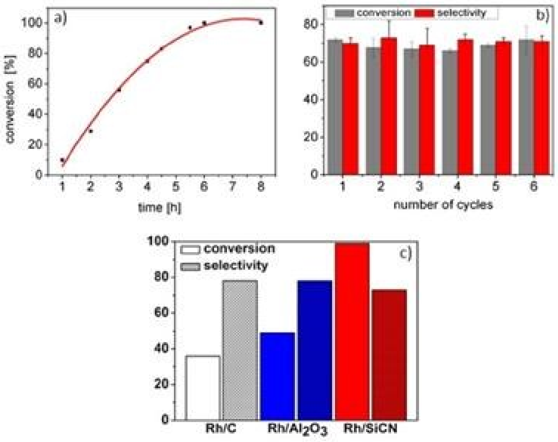


Fig. 3: Time conversion plot (a) and recycling studies (b) using p-Rh@SiCN catalysts. (c) Comparison of the *p*-Rh-20 with commercial available Rh/C and Rh/Al_2O_3 Conditions: Reaction conditions: 2 mol% catalyst, 6 bar, 25°C.

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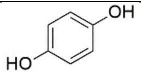
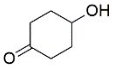
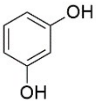
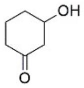
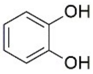
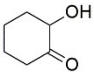
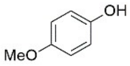
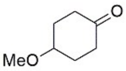
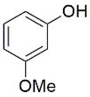
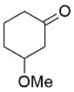
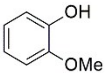
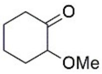
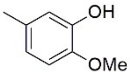
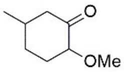
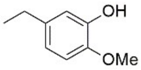
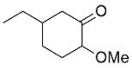
Table 2. Hydrogenation of hydroxylaromatic derivatives with porous Rh@SiCN. [a]

Ent.	substrate	time [h]	product	conv. [%]	sel.[1] [%]	sel.[2] [%]
1		7 h		95	67	0*
2		8h		94	66	0**
3		4 h		99	83	14
4		11 h		95	40	50
5		11 h		95	33	55
6		15 h		90	40	52
7		16 h		99	2	91
8		16 h		99	5	85

[a] Reaction conditions: 2 mol% Rh@SiCN-*b*-PE catalyst, 25°C, 3 ml H_2O, 10 mmol γ-valerolactone. [1] selectivity to alcohol; [2] selectivity to ketone; *10% cylclohexanone and 18% cyclohexanol was observed. **7% cyclohexanone, 19% cyclohexanol.

No loss in activity was observed so the NCs are firmly embedded in the SiCN matrix and no metal was found in the solution. Time conversion plot of phenol hydrogenation in water at 25°C is presented in Figure 3a. A full conversion was achieved in 5 hours. In contrast to the *p*-Rh-20 catalyst commercially available Rh catalysts showed similar a selectivity but were found less active (figure 3c). After 5 hours with the same catalyst loading of 2 mol% the *p*-Rh-20 catalyst achieved 99% conversion while Rh/Al_2O_3 and Rh/C showed 49% and 36% conversion respectively.

Conclusions

The generation and stabilization of small-sized rhodium nanoparticles in thermally robust silicon carbonitride matrix has been achieved by the pyrolysis (1100°C/nitrogen) of a chemically modified commercial polysilazane. An amido rhodium complex used for chemical modification also serves as a catalyst for the cross linking of polysilazane at room temperature via hydrosilylation reaction. The accessibility of rhodium nanoparticles was improved by the introduction of porosity and increasing surface area of the materials. This was achieved by synthesis of a block copolymer of a commercial polysilazane with hydroxyl- polyethylene and its subsequent pyrolysis that afforded porous Rh@SiCN catalysts. The size of the metal particles can be altered by adjusting the amount of added rhodium complex. These novel catalysts exhibit a high activity in the selective hydrogenation of phenol at room temperature and under low hydrogen pressure. Porous catalysts were found more reactive as compared to their dense counterparts. The catalysts offer reusability and offer broad substrate scope.

Experimental

Synthesis of the ligand: $Ap^{TMA}H$ (4-Methyl-pyridin-2-yl)-(2,4,6-tri-methyl-phenyl)-amin] was carried out using a reported method. Details of a typical synthesis are given in SI.

Synthesis of the $[Rh(Ap^{TMA})(cod)$ complex (1): A modified literature method was followed. 435 mg (1.92 mmol) $Ap^{TMA}H$ in 35 ml diethyl ether was cooled down to 0°C and 1.25 ml of butyl lithium (BuLi) were added. Afterwards a suspension of 473.5 mg (0.96 mmol) $[RhCl(cod)]_2$ and 20 ml diethyl ether were added at 0°C to the lithiated ligand and stirred overnight. Lithium chloride was filtered off from the complex solution and washed three times with 20 ml diethylether. The solution was concentrated and the complex crystalized at -20°C. Yield: 699 mg (83.5%).

1H NMR (500 MHz, CDCl3, 296 K): δ = 7.87 (d, 1H, NCH), 6.90 (d, 2H, arom. H), 6.79 (d, 1H, arom. H), 6.74 (s, 1H, arom. H), 5.27 (s, 4H, cod), 3.96 (bs, 6H, cod), 2.56 (s, 3H, ar-CH3), 2.20 (bs, 9H, ar. CH3), 1.57 (bs, 8H, cod) ppm.

13C NMR (125 MHz, CDCl3, 296 K): δ = 19.31, 21.38, 21.84, 31.67, 105.06, 107.99, 129.63, 133.29, 134.01, 141.90, 143.91, 151.03, 176.15 ppm.

Synthesis of a Rh@SiCN ceramic:

For the synthesis of Rh-10 (Si/Rh = 10) ceramic 338.84 mg and analogous for Rh-20 (Si/Rh = 20) ceramic 169.42 mg (0.389 mmol) $[Rh(Ap^{TMA})(cod)]$ was solved in 3 ml hexane. After addition of 0.5 ml (7.77 mmol) HTT 1800 the solution changed its colour from yellow to dark red. After 10 min at room temperature viscous material was generated. The greenbodies were put in a quartz boat and pyrolysed with the following program at 1100°C:

$$\mathrm{RT} \xrightarrow{1\ \mathrm{K/min}} 300\,^{\circ}\mathrm{C} \xrightarrow{0.5\ \mathrm{h}} 300\,^{\circ}\mathrm{C} \xrightarrow{5\ \mathrm{K/min}} 1100\,^{\circ}\mathrm{C} \xrightarrow{0.5\ \mathrm{h}} 1100\,^{\circ}\mathrm{C} \xrightarrow{4\ \mathrm{K/min}} \mathrm{RT}$$

The following ceramic yields were obtained: for Rh-10: 65.9% and 80.8% for Rh-20. The ceramics were pulverized using a ball miller for 20 minutes.

Synthesis of the porous Rh@SiCN ceramics:

The metal loading in the final material was adjusted in terms of silicon to Rh ratio (Si:Rh) and catalysts with a Si:Rh=10 (Rh-10) and Si/Rh=20 (Rh-20) were prepared. For a Rh-20, [PEOH:HTT 1800 weight ratio = 70:30], 233 mg of PEOH (Mn= 2110, Mw= 4053, PDI = 1.9) were solved in 5 ml toluene at 130°C. Afterwards 100 µl (1.554

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mmol) HTT 1800 were added without stirring the solution. After 1 hour 33.88 mg (for Rh-20) Rh-complex solved in 1 ml toluene were added. On the next day the solvent was removed and greenbodies were put in a quartz boat and pyrolyzed at 1000°C**.** The Rh-10 catalyst contains 13.0 wt% Rh and the Rh-20 contains 8.1 wt% Rh.

Catalytic studies:

The catalyst was pre-treated with 1.6 M NaOH solution and methanol for 16 hours at 80°C.

For the hydrogenation reactions a vial with 0.5 mmol substrate, 3 ml solvent and additive were placed in a steel autoclave. The autoclave was purged with hydrogen. After a certain reaction time EtOAc and 0.5 mmol n-dodecan as international standard were placed in the vial. After separation of the catalyst the solution was analyzed with GC.

For the recycle experiments the catalyst was separated by centrifugation at 2000 rpm and used again under the same conditions.

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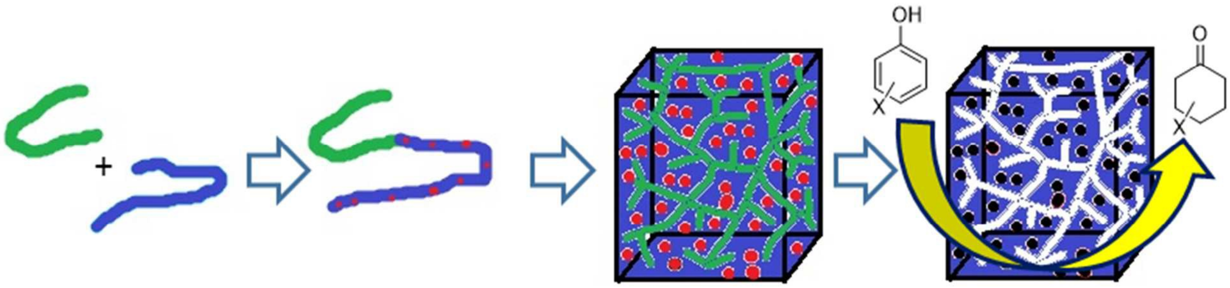

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