Development of Molecular and Solid Catalysts for the Direct Low-Temperature Oxidation of Methane to Methanol

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The direct low-temperature oxidation of methane to methanol is demonstrated on a highly active homogeneous molecular catalyst system and on heterogeneous molecular catalysts based on polymeric materials possessing ligand motifs within the material structure. The *N*-(2-methylpropyl)-4,5-diazacarbazolyl-dichloro-platinum(II) complex reaches significantly higher activity compared to the well-known Periana system and allows first conclusions on electronic and structural requirements for high catalytic activity in this reaction. Interestingly, comparable activities could be achieved utilizing a platinum modified poly(benzimidazole) material, which demonstrates for the first time a solid catalyst with superior activity compared to the Periana system. Although the material shows platinum leaching, improved activity and altered electronic properties, compared to the conventional Periana system, support the proposed conclusions on structure–activity relationships. In comparison, platinum modified triazine-based catalysts show lower catalytic activity, but rather stable platinum coordination even after several catalytic cycles. Based on these systems, further development of improved solid catalysts for the direct low-temperature oxidation of methane to methanol is feasible.
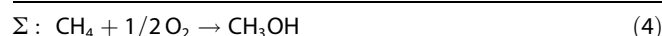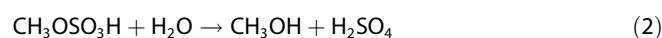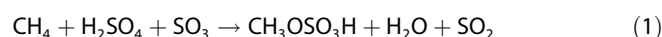
Introduction

The direct oxidation of methane to methanol has already challenged more than a generation of chemists. The high binding energy of the CH_3–H bond ($435 \ kJ \ mol^{-1}$) and the ease of overoxidation to form CO_2 place high demands on improving the activity and selectivity of potential catalytic systems. In scope of a changing raw material base, the efficient and sustainable utilization of remaining resources becomes imperative. Furthermore, development and optimization of technologies to eliminate greenhouse gas emissions are equally important.

The efficient use of the remaining natural gas reservoirs, which are estimated to hold for another 60 years, is a major challenge from a scientific and a technological point of view.[1] Due to its low density, transportation and storage of natural gas is complicated and often non-economical, resulting in "stranded gas", which is the burning of significant amounts in remote locations.

Consequently, efficient technology to convert natural gas onsite into liquid, such as methanol, would be highly desirable. Current technologies include synthesis gas formation in combination with Fischer–Tropsch technology. A local application is hampered by high energy demand and also by high capital costs of such plants due to the tremendous economy of scale. Therefore, a technology to convert methane onsite into liquid is attractive from both an ecological and an economical point of view.

The direct oxidation of methane to methanol is promising. In the past, numerous groups have investigated this process.[2–8] Key factors in the development of suitable catalyst systems are the selection of weakly coordinating solvent systems and protection of methanol against overoxidation. Therefore, research efforts have focused on systems in which methanol is not produced directly but in the form of methyl esters (i.e., methyl bisulfate) for a reaction in concentrated sulfuric acid [Equations (1)–(4)].[2–4] Indeed, such a process utilizing sulfuric acid and sulfur trioxide as oxidants would allow for a continuous process design combining (1) oxidation of methane to methyl bisulfate, (2) hydrolysis of methyl bisulfate to form methanol, and (3) reoxidation of SO_2.

$$CH_4 + H_2SO_4 + SO_3 \rightarrow CH_3OSO_3H + H_2O + SO_2 \qquad (1)$$

$$CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4 \qquad (2)$$

$$SO_2 + 1/2 \, O_2 \rightarrow SO_3 \qquad (3)$$

$$\Sigma: \quad CH_4 + 1/2 \, O_2 \rightarrow CH_3OH \qquad (4)$$

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Despite the potential of such a continuous sulfuric acid-based process for methane oxidation, some downsides should be mentioned: First of all, formation of one mole of methyl bisulfate requires not one, but two moles of SO_3, as the resulting water reacts further to form sulfuric acid with the second mole of SO_3. Additionally, oxidation of methane to CO_2 requires four moles of SO_3 per mole of methane. Consequently, when evaluating the economics of the process, reoxidation of SO_2 and reconcentration of the diluted sulfuric acid should be considered. In an earlier review, Conley et al. summarized the benchmark for this process to be a 1 mм catalyst concentration that generates ca. 2 м solution of methanol after about 1.5 h reaction time.[9]

For this process, the Shilov system, $[PtCl_2(H_2O)_2]$ appeared to be a very promising system showing catalytic activity, but suffered from instability due to the irreversible decomposition to Pt metal or insoluble polymeric Pt salts.[10] In contrast, Periana et al. reported on a homogeneous system for the selective, catalytic oxidation of methane to methanol via methyl bisulfate, catalyzed by mercuric ions, Hg^{II}, where the reduced metal can readily be reoxidized under the reaction conditions previously described.[5] The system reached a methane conversion of 50% and a selectivity to methyl bisulfate of 85%. Tl^{III}, Pd^{II}, and the cations of Pt and Au also oxidized methane to methyl bisulfate, but suffered from irreversible reduction or bulk metal formation.[5, 11] In further investigations, Au proved to be a stable catalyst system when combined with H_2SeO_4, which allowed reoxidation of the reduced species; however, turn over numbers (TONs) remained low (i.e., 32).[12]

Muelhofer et al. developed an alternative catalytic system in trifluoroacetic acid with trifluoroacetic acid methyl ester as the resulting species.[13] Under such reaction conditions, platinum complexes decomposed, producing platinum black. Palladium-based N-heterocyclic carbene (NHC) complexes proved to be stable under these reaction conditions, with sufficient activity to form up to 980% triflouroacetic acid methyl ester based on the amount of Pd in the system. Recently, Meyer et al. reported improved Pd complexes based on pyrimidine-functionalized NHC ligands, reaching TONs of 41 within 17 h reaction time.[14] Systematic complex and ligand design appear to open the way for further improvements. A superior system for methane oxidation in sulfuric acid has been reported by Periana et al.[15] They identified a platinum-bipyrimidine complex, [Pt(bpym)], reaching TONs of around 300 at 81% selectivity to methyl bisulfate as a highly promising system with the highest activity described thus far. Further investigations focused on exploration of alternative catalytic systems for the described process, including iridium–hydroxo complexes and rhenium complexes, and development of improved ligands for platinum complexes, such as cyclometalated systems.[16–18] The described efforts, however, did not result in any improved catalytic systems.[9, 19] Our investigation aimed to develop an improved catalyst system and to obtain insights regarding structure–activity relationships. We also demonstrated that the concept can be transferred to polymeric materials, which allows for the preparation of highly active solid catalysts for the direct oxidation of methane to methanol.

Results and Discussion

Homogeneous molecular catalyst for direct methane activation

We report the development of the platinum complex *N*-(2-methylpropyl)-4,5-diazacarbazolyl-dichloro-platinum(II), DACbz-Pt, which shows significantly improved activity in the direct low-temperature oxidation of methane to methanol, compared to the conventional Periana system dichloro(η-2-(2,2′-bipyrimidyl))platinum(II), [Pt(bpym)] (Figure 1).
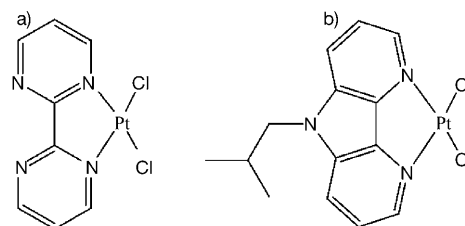

Figure 1. a) Dichloro(η-2-(2,2′-bipyrimidyl))platinum(II) and b) *N*-(2-methyl-propyl)-4,5-diazacarbazolyl-dichloro-platinum(II).

The complex has been synthesized based on a Buchwald–Hartwig cross coupling reaction of 2-chloro-3-iodopyridine and 3-amino-2-chloropyridine, followed by an alkylation with 2-methylpropylbromide, an intramolecular Yamamoto coupling, and complexation with $K_2[PtCl_4]$. This development is based on our search for π-acidic, chelating N-based ligands, with the expectation of having lower proton affinity and higher affinity for Pt^{II}, a π-donor metal.[15] The electronic properties of the ligand are different compared to those of 2,2′-bipyrimidine.

As a derivative of bipyridine, the electron density is higher than for the electron-deficient bipyrimidine. The tertiary nitrogen of pyrrole has an additional electron-donating effect on the aromatic system (Figure 1). Overall, the electron density on the platinum is higher and could be increased, for example by *para*-amino-substitution towards the chelating nitrogens (see the Supporting Information, Scheme S1).

The increased electron density on the platinum appeared to have a positive effect on the catalytic activity of the system. A significantly increased catalytic activity of DACbz-Pt was detected, with both superior TONs and turn over frequencies (TOFs) compared to the conventional Periana system. Consequently, these results gave insight into structure–activity relationships of this reaction and point towards the need for higher electron density on the platinum to further optimize the catalyst systems. Table 1 summarizes the catalytic activity of the molecular catalyst in comparison to the conventional Periana system. Both, [Pt(bpym)] and DACbz-Pt exhibited comparable methanol selectivities of >75% (after hydrolysis) and CO_2 as the main byproduct, determined by FTIR analysis of the gas phase. From a mechanistic point of view, additional investigations are necessary, but it is very likely that the catalytic cycle is similar to the one described by Periana for the original

Table 1. Catalytic activity of the molecular Periana catalyst and DACbz-Pt[a]

Catalyst[b]	Pt conc. [mmol L^{-1}]	TON[c]	TOF [s^{-1}][d]
[Pt(bpym)]	10	158	1.8×10^{-2}
[Pt(bpym)][e]	3.33	290	8.1×10^{-2}
[Pt(bpym)]	4	355	3.9×10^{-2}
[DACbz-Pt]	2.67	473	5.3×10^{-2}
[DACbz-Pt][e]	3.33	570	16×10^{-2}

[a] Methane conversions are summarized in the Supporting Information. [b] Reaction conditions: 15 mL H$_2$SO$_4$ (30% SO$_3$), 40 bar CH$_4$ pressure (25 °C), at 215 °C for 2.5 h. [c] TONs were calculated based on the ratio of produced methanol and Pt content of the catalyst (mol$_{MeOH}$mol$_{Pt}^{-1}$). [d] Calculated as average rate based on TON and reaction time. [e] Reaction time of 1 h.

system. A difference occurs upon protonation (Scheme 1). [Pt-(bpym)] has two accessible nitrogen atoms for protonation and DACbz-Pt has a pyrrole nitrogen. Deprotonation results for both systems but a ring-opening reaction degrades DACbz-Pt and causes a drop in catalytic activity. This degradation reaction would lead to bipyridyl-derivatives of the Pt catalyst. Nevertheless, investigations suggest the stability of the system do not point towards a significant fraction of decomposed catalyst, although this cannot fully be excluded.
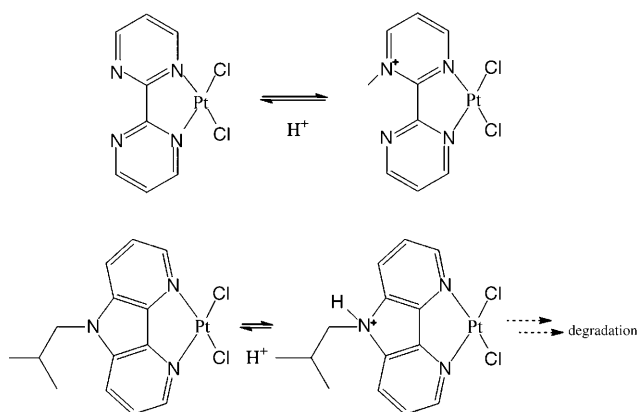
Scheme 1. Possible deactivation and degradation pathway.

Heterogeneous molecular catalysts for direct methane activation

Limited progress has been made concerning solid catalysts for the direct low-temperature oxidation of methane to methanol. Heterogeneously catalyzed reactions were almost exclusively studied at temperatures >250 °C. Basic oxides,[20,21] transition metal oxides,[7,22] or encapsulated Fe-phthalocyanine complexes[8] were reported, showing poor selectivity due to overoxidation, and maximum methanol yields of around 5%.[23] Consequently, the main challenges for this reaction appear to be increasing selectivity and minimizing overoxidation.

Knowledge gained from the investigation of homogeneous molecular catalysts for the direct low-temperature oxidation of methane to methanol and the low level of success concerning the development of selective solid catalysts for this reaction prompted us to combine the properties of both catalyst types. Such a combination is possible based on polymeric materials resembling potential ligand motifs within the structure, which allow platinum coordination at a molecular level. Additionally, such a material should withstand the harsh reaction conditions of the Periana system (i.e., oleum, 30% SO$_3$). However, not many polymeric materials fulfill these requirements. For example, melamine-based structures were investigated, but they simply decomposed under the reaction conditions.[24,25] Recently however, reports on two promising polymer types appeared, which could allow the envisaged platinum coordination and could prove to be stable under the required reaction conditions. Weber et al. described the synthesis of a mesoporous (poly)benzimidazole (PBI) network through polycondensation of 3,3′-diaminobenzidine, diphenyl isophthalate, and benzene-1,3,5-tricarboxylic acid triphenyl ester, together with silica spheres as a hard template to introduce porosity when removed.[26,28] Synthesis and structure of the PBI material and the potential platinum coordinations are shown in Scheme 2.

The second material reported by Kuhn et al. belongs to a new class of high-performance polymer frameworks which are thermally stable up to 400 °C and resist strong oxidizing conditions.[28,29] Recently, we introduced this material as a promising polymer for application in the direct oxidation of methane to methanol.[30] The material was formed by trimerization of aromatic nitriles in molten ZnCl$_2$.[28,29] For application in direct methane oxidation, 2,6-dicyanopyridine was used as a monomer resulting in a covalent triazine-based framework (CTF) with numerous bipyridyl motifs. Synthesis and structure of the material with possible platinum coordination sites resembling those of the molecular [Pt(bpym)] catalyst are described elsewhere.[30]

The materials were characterized by physicochemical techniques. Nitrogen sorption analysis of PBI reveals a type IV isotherm, corresponding to a mainly mesoporous material with a total pore volume of 0.19 cm^{3}g^{-1} and little porosity in the micropore region of about 0.01 cm^{3}g^{-1}. Brunauer–Emmett–Teller (BET) analysis reveals a specific surface area of around 112 m^{2}g^{-1} and Barrett–Joyner–Halenda (BJH) analysis of the adsorption branch shows an average pore size of 9 nm, both in agreement with the structural properties reported earlier.[26,28] The desorption branch, which is normally used, was not here since the isotherm shape suggested critical instability at p/p_0 close to 0.4. As reported previously,[30] CTF revealed a type I isotherm corresponding to a microporous material with a specific surface area of 1061 m^{2}g^{-1}, a pore volume of 0.93 cm^{3}g^{-1}, and an average micropore diameter of 1.4 nm. X-ray diffraction measurements (XRD) of both materials indicated an amorphous structure, although, in the case of CTF, short-range ordering cannot be excluded. X-ray photoelectron spectroscopy (XPS) measurements revealed a significantly lower nitrogen content of the PBI network compared to the CTF material, with C/N ratios of 6.1 and 3.2, respectively.

Platinum modification of the materials was carried out using two approaches: through precoordination of platinum in aque-
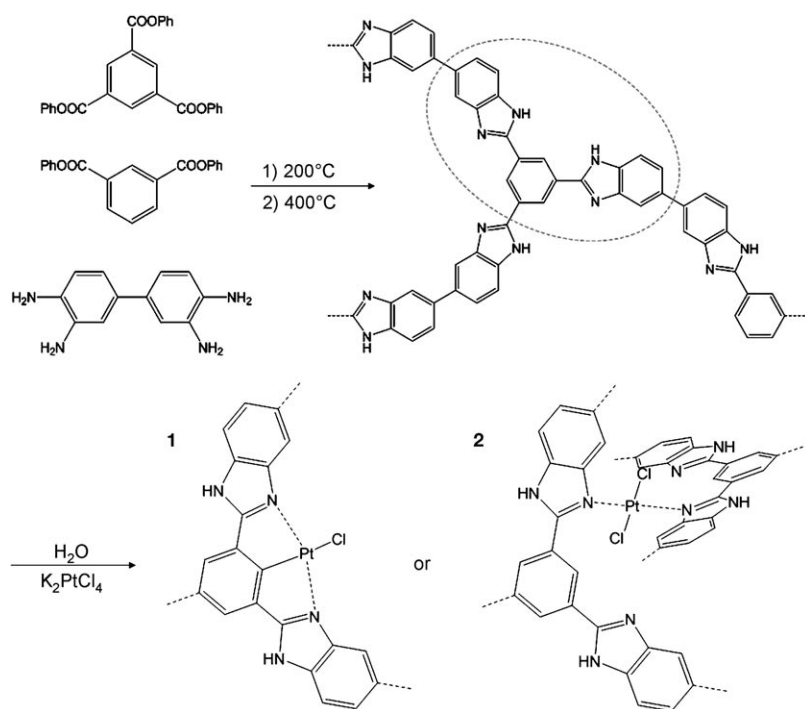
Scheme 2. Polycondensation of 3,3′-diaminobenzidine, diphenyl isophthalate, and benzene-1,3,5-tricarboxylic acid triphenyl ester to form a polybenzimidazole network (PBI) and possible platinum coordinations and in the material.

centrations obtained for the three consecutive cycles with Pt-PBI as the catalyst. Although Pt-PBI reached superior TONs, after the first run, methanol productivity decreased likely due to significant Pt leaching under the reaction conditions.

Energy dispersive X-ray spectroscopic analysis conducted by means of scanning electron microscopy (i.e., SEM/EDX), supports the notion of a homogeneous platinum distribution within the material (Figure 3). Before the application of Pt-PBI, the Pt content amounts to 8.3 wt.%; however, the material loses almost all of the Pt within three catalytic runs (i.e., < 0.4 wt.%). Accordingly, XPS measurements showed a N/Pt ratio of 3.4 prior to catalysis with binding energies of 72.12 and 72.7 eV for the Pt^{II} and Pt^{IV} species, respectively,

ous solution prior to catalysis; and through an in situ pathway, which involved mixing the material and the platinum precursor together in the reaction mixture. For both pathways, $K_2[PtCl_4]$ served as the platinum precursor. Precoordinated materials were denoted Pt-CTF and Pt-PBI, while in situ formed catalysts were termed $K_2[PtCl_4]$-CTF and $K_2[PtCl_4]$-PBI. The platinum-modified materials were tested as catalysts in the direct low-temperature oxidation of methane to methanol in concentrated sulfuric acid according to the conditions described earlier.

As reported recently,[30] we identified Pt-CTF and $K_2[PtCl_4]$-CTF as highly promising systems, showing on the one hand comparable activity to the molecular Periana catalyst, and on the other hand to each other, independent of the platinum coordination pathway (Table 2). Pt-CTF benefited from an activation effect, which results in low catalytic activity for the very first run, but significantly increased activity for all subsequent runs. Pt-PBI, however, appeared to be superior in terms of catalytic activity, reaching TONs of up to 340 for in situ coordinated $K_2[PtCl_4]$-PBI and even up to 550 for precoordinated Pt-PBI. Thus, comparable TONs for the newly developed molecular DACbz-Pt complex could be reached. Methanol (after hydrolysis) was found to be the main product, with selectivites > 75% for all the materials. CO_2 was identified as the major byproduct of the gas phase by FTIR analysis. Methane conversions are included in the Supporting Information. Table 2 summarizes the catalytic activity of the solid catalysts in comparison to the conventional Periana system.

High single-run activity is not the deciding factor concerning a solid catalyst; recyclability and stability over several cycles are more important. Figure 2 illustrates the final methanol con-

Table 2. Catalytic activity of Pt-modified PBI and CTF catalysts.[a]

Catalyst[a]	Pt conc. [mmol L^{-1}]	Final MeOH conc. [mol L^{-1}]	TON[b]
[Pt(bpym)]	4	1.49	355
[Pt(bpym)]	10	1.65	158
Pt-PBI[c]	1.7	0.95	559
$K_2[PtCl_4]$-PBI[d]	3.23	1.13	338
$K_2[PtCl_4]$-CTF[e]	7.25	1.54	201
Pt-CTF[f]	6.93	1.80	246

[a] Reaction conditions: 15 mL H_2SO_4 (30% SO_3), 40 bar CH_4 pressure (25 °C), at 215 °C for 2.5 h. [b] TONs based on the platinum content determined from SEM-EDX. [c] 60.5 mg Pt-PBI. [d] 20.1 mg $K_2[PtCl_4]$ and 40.2 mg PBI. [e] 92 mg CTF with 47.5 mg $K_2[PtCl_4]$. [f] Data from the 2nd run with 62 mg Pt-CTF.

which corresponds to atomically coordinated platinum. After three runs however, the platinum content went below the detection limit. Also, TEM/EDX measurements suggested a homogeneous distribution of atomically distributed platinum within the material. However, platinum nanoparticles appeared to be present within the material (Figure 4), although they can only account for a minor fraction of the total platinum content. Hardly any indications of Pt^0 species or platinum crystallites were found in the XPS or XRD measurements, respectively.

The origin of the strong leaching of this material is not fully clear, but may be related to an instable Pt coordination within the material under the reaction conditions. Possible explanations may be related to the relatively low nitrogen content of the PBI material. XPS measurements gave a C/N ratio of only
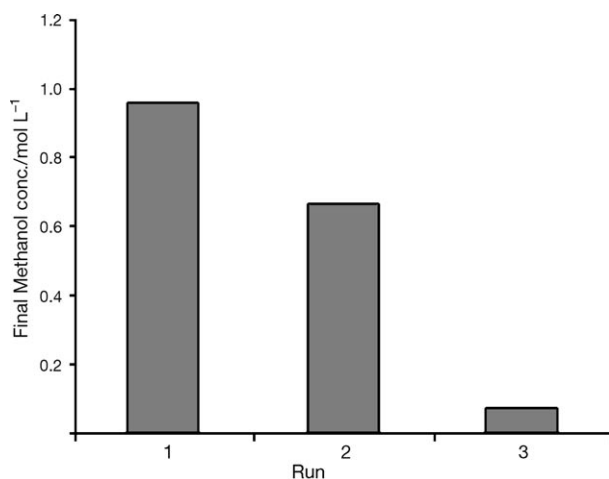
Figure 2. Methanol productivity of Pt-PBI in three consecutive catalytic runs (Reaction conditions: 15 mL H_2SO_4 (30 % SO_3), 60.5 mg Pt-PBI, 40 bar CH_4 pressure (25 °C), at 215 °C for 2.5 h).
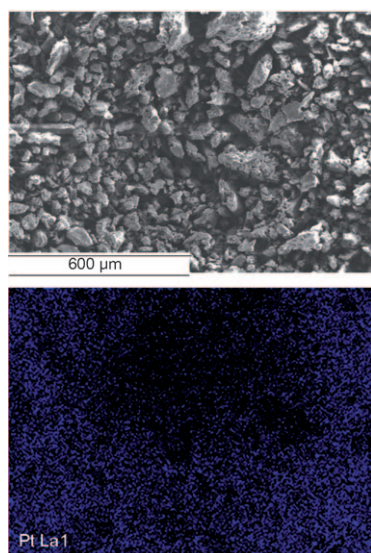

Figure 3. SEM image of Pt-PBI material and corresponding EDX Pt mapping.

Figure 4. TEM images of Pt-PBI prior to catalysis.

6.1, whereas CTF exhibited a value of 3.2. In contrast to the stable bidentate complex formed for [Pt(bpym)], a comparable platinum coordination within the PBI structure would most probably exhibit low stability due to the unfavorable bite angle between the two coordinating nitrogens. This could also be reflected by the observed platinum nanoparticle formation within the material structure which would be facilitated by a less stable Pt coordination. Besides, the formation of a pincer-type coordination as described by Fossey et al., **1** is likely to occur, resulting in a very stable platinum coordination (Scheme 2).[31] Under the reaction conditions, however, the coordinating carbon of the aromatic ring system is protonated, which leads to cleavage of the carbon–platinum bond, and thus causing an unstable bidentate ligand with an unfavorably wide bite angle. Alternatively, a platinum coordination between two different polymer branches may occur (Scheme 2,
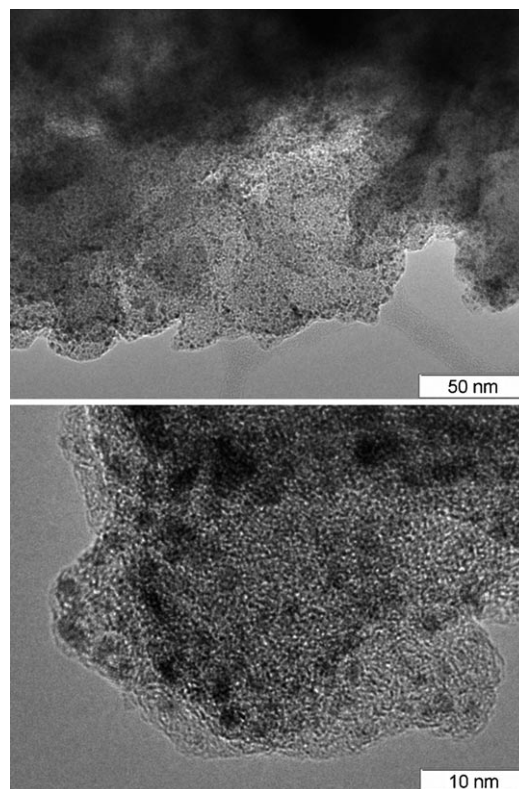
2). However, the lack of a chelating ligand may also result in low stability of the platinum coordination. In agreement with the latter assumption, in situ coordination to form $K_2[PtCl_4]$-PBI did not result in stable coordination of Pt. In contrast, both Pt-CTF and $K_2[PtCl_4]$-CTF exhibited stable catalytic activity over several runs, showing more than 250 turnovers even after six cycles, and only little decrease in platinum loading.[30] Concerning the relationship between electron density and catalytic activity, the platinum coordination in Pt-CTF is suggested to be comparable to that of [Pt(bpym)] resulting in similar activities. However Pt-PBI exhibits higher electron density compared to the electron deficient [Pt(bpym)] complex, and presumably even compared to DACbz-Pt; the carbon in the aromatic ring that replaced the chlorine ligand, leads to a higher electron density on the metal centre compared to a complex with two chlorine ligands. Nevertheless, DFT calculations should be carried out for further investigations.

Current investigations are aiming to develop and optimize the homogeneous and heterogeneous catalytic systems towards superior activity and stability, which may open up potential for industrial applications. Three main points are being addressed: 1) tuning of the electron density on the Pt through ligand modification of homogeneous catalysts to further substantiate conclusions on structure–activity relationship; 2) development of a wider range of solid catalysts on the basis of polymeric materials with sufficient stability and platinum coordination; 3) combination of both approaches by preparation of solid catalysts with optimized electron density and stability of the incorporated platinum.

Experimental Section

The synthesis of *N*-(2-methylpropyl)-4,5-diazacarbazolyl-dichloro-platinum(II) was based on a Buchwald–Hartwig cross coupling reaction of 2-chloro-3-iodpyridine and 3-amino-2-chlorpyridine, followed by an alkylation with 2-methylpropylbromide, an intramolecular Yamamoto coupling, and complexation with $K_2[PtCl_4]$. A detailed synthesis is described in the Supporting Information. The [Pt-(bpym)] complex, PBI, and CTF-based materials were synthesized as described elsewhere.[15,27–30] For platinum coordination, PBI (126 mg) and $K_2[PtCl_4]$ (64 mg), or CTF (170 mg) and $K_2[PtCl_4]$ (340 mg), respectively, were reacted in water for 4 h at 60 °C, filtered, washed with water, and dried overnight at 90 °C. Catalytic tests were carried out in a 50 mL stainless steel autoclave with a Teflon insert. The autoclave was filled with 15 mL (28.88 g; 295 mmol) oleum (30% SO_3) and catalyst (50–70 mg), closed, and flushed with argon. In the case of $K_2[PtCl_4]$-PBI, $K_2[PtCl_4]$ (20.1 mg) and PBI (40.2 mg), or in the case of $K_2[PtCl_4]$-CTF, CTF (92 mg) and $K_2[PtCl_4]$ (48 mg), were placed in the autoclave. The autoclave was pressurized with CH_4 (40 bar), heated to 215 °C, left for 2.5 h, and cooled to room temperature. The pressure was released slowly to prevent foam formation. The reaction solution was filtered through a glass frit to remove the solid catalyst, hydrolyzed by refluxing in 30 mL water for 4 h, and analyzed by HPLC. Methanol selectivity was estimated based on methanol formation and pressure drop during the reaction, while FTIR analysis of the released gas phase was used to determine the byproducts. In every recycling step, about 5–10 wt% of the catalyst material was lost in the frit during filtration, which was considered in the calculation of the catalytic activity. The TONs were calculated based on the ratio of produced methanol to the platinum content of the catalyst (mol_{MeOH}/mol_{Pt}). Platinum contents were determined by SEM-EDX (Pt-CTF and K_2-[PtCl_4]-CTF, runs 2–6) or was based on the used platinum amount ($K_2[PtCl_4]$-CTF, first run). The CTF material was characterized using nitrogen sorption measurements, XRD, TEM, and XPS. The platinum-containing catalysts were characterized using TEM, SEM/EDX, XPS, and XRD.

Acknowledgements

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