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Direct methane oxidation over Pt-modified nitrogen-doped carbons†

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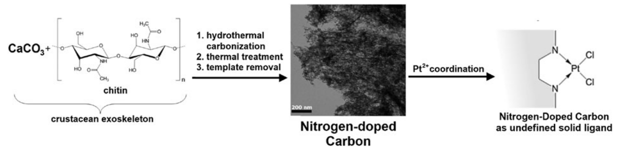
Nitrogen-doped carbons derived from biomass precursors were modified with Pt^{2+} and successfully tested as solid catalysts in the direct oxidation of methane in fuming sulfuric acid. Remarkably, the catalytic performance was found to be substantially better than the Pt-modified Covalent Triazine Framework (CTF) system previously reported, although deactivation is more pronounced for the biomass derived catalyst supports.

The direct utilization of methane *via* C–H activation remains a challenge as the development of efficient catalysts with sufficient activity and selectivity is hindered by the high binding energy of the methane C–H bond.[1–4] Thus, a viable methane-to-liquid process still suffers from ineffective catalytic systems. The C–H activation of hydrocarbons by transition metal complexes presents a promising pathway.[5–7] One of the most active catalytic systems is that reported by Periana and co-workers.[8–10] The dichlorobipyrimidyl platinum(II) complex (*i.e.* $Pt(bpym)Cl_2$) performs the catalytic oxidation in fuming or concentrated sulfuric acid, achieving high yields of methanol with selectivities $\geq 90\%$. Methylbisulfate is initially formed, which can then be hydrolyzed to methanol in high overall yields. In this process the solvent is used, simultaneously, as both a protecting and an oxidizing agent.[10,11] The limited catalytic activity as well as difficult product and catalyst separation pose challenges regarding industrial application of these approaches.[1,10] Alternative pathways for oxy-functionalization of C–H bonds were recently reviewed.[12] Nevertheless, currently neither homogeneous[10,12] nor heterogeneous[4,13–16] or enzymatic[17,18] catalysts allow a viable industrial application.

Recently, we reported the development of a solid catalyst, which mimicked the molecular Periana system by coordinatively binding a Pt^{2+} species to a nitrogen-rich Covalent Triazine Framework (CTF), acting as a solid ligand.[19] This material achieved turnover numbers comparable to the molecular Periana catalyst with stable catalytic performance over at least five recycling steps. Extending this approach to poly(benzimidazole) materials resulted in even higher TON, but significant Pt leaching was observed.[20] However, these results point towards strategies for further material development.

Herein, we report on the progress of catalyst development for methane oxidation in the Periana system. Specifically, we present a novel material that has higher activity than the recently published Pt@CTF system, although more pronounced deactivation is observed.

The novel solid catalysts reported here are based on nitrogen-doped carbons (NDC), which have gained significant interest in research due to their thermal/oxidation stability.[21] We have recently reported simple and low-cost routes to produce nitrogen-enriched carbonaceous scaffolds derived from biomass resources.[22–25] The hydrothermal carbonization and further thermal treatment of chitin-based precursors (*i.e.* the crustacean exoskeleton of lobster) generates highly porous nitrogen-doped carbons (*Ex*LOB) with a high surface area (>400 $m^2\ g^{-1}$) and tunable chemical properties (Scheme 1). In this study, such NDC materials were coordinatively



Scheme 1 Preparation of coordinatively modified Pt@NDC materials derived from crustacean exoskeleton of lobsters (*Ex*LOB).

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modified with Pt^{2+} species. Elemental analysis (EA) confirmed a stable Pt loading of ~6 wt% (Table S4, ESI†), while XPS investigations indicated metal coordination similar to Pt@CTF (Fig. S2 and S3, ESI†). Additionally, thermal stability and robustness towards acidic solvents make such materials very interesting as a possible solid catalyst in the Periana system.

Catalytic testing was initially performed in a simple batch autoclave set-up, using reaction conditions similar to those of Periana and co-workers (ESI†).[8] This set-up was suitable to investigate material stability and to screen catalytic materials in terms of methanol productivities. However, due to different ranges of achieved conversion and conversion before reaching the reaction temperature it could not be used for a true comparison of catalytic activities. Therefore, the most promising catalyst in terms of stability and activity, *i.e.* Pt-modified *Ex*LOB carbonized at 900 °C (Pt@*Ex*LOB-900), was tested in a modified set-up to investigate the catalytic behaviour in detail in order to determine the reaction rates, expressed as apparent turnover frequencies (TOFs). Pt-modified CTF as well as the molecular $Pt(bpym)Cl_2$ catalyst were tested under identical conditions as references. The set-up consisted of a Hastelloy autoclave that was filled partially with oleum and catalyst, and then flushed with argon. After heating the autoclave to reaction temperature, preheated methane from a second autoclave was added to start the reaction (ESI†). The pressure drop as a result of conversion of methane to methylbisulfate could be monitored *via* pressure indicators, and this pressure drop provides a measure of the reaction rate. Accordingly, pressure-time plots show autogenous pressure (~10 bar) of oleum and a sharp increase of pressure due to the addition of preheated methane (Fig. 1). Methane oxidation was carried out for 30 minutes before the reactor was quenched in a water bath. Subsequently, gas phase products were quantified by FT-IR, while the liquid phase was filtrated and hydrolysed to obtain methanol. Using this methodology, the carbon balance for the autoclave set-up could be closed within at least 95%, with carbon dioxide as the only by-product resulting from overoxidation of methylbisulfate or methane. Turnover frequencies could be calculated either from a pressure drop from 69 to 67.5 bar or as an integral value for the first 30 minutes from the amount of methanol produced (ESI†). The first method is preferred, since this allows comparison of performance in the same range of conversion. The latter method gives less accurate values, since for differently active catalysts, different pressure drops are reached over the 30 minutes studied, which influences the rate by, *e.g.* pressure dependency of reaction rates and different consumption of sulfur trioxide. Nevertheless, deviations between the two methods did not exceed 40% and typically were much smaller.

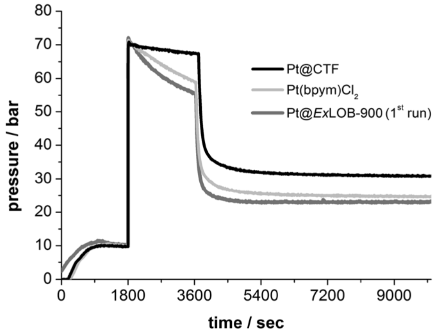

Fig. 1 Pressure–time plots for catalyst comparison (reaction conditions: 10 μmol Pt equivalents catalyst, 215 °C, 1000 rpm, 15 mL oleum (20 wt% SO_3), 30.4 mL Hastelloy autoclave).

Table 1 Conversions, yields, selectivities to methanol (methylbisulfate) and catalytic activities (TOFs) achieved under given reaction conditions

Entry	Catalyst	X (%)	Y (%)	S (%)	TOF[a] (h^{-1})	TOF[b] (h^{-1})
1	Pt@CTF	7.0	6.0	85.4	174	233
2	$Pt(bpym)Cl_2$	17.9	17.2	96.3	912	779
3	Pt@*Ex*LOB-900 (1st run)	33.8	31.7	94.0	2074	1227
4	Pt@*Ex*LOB-900 (2nd run)	18.5	17.6	95.2	1938	1516
5	Pt@*Ex*LOB-900 (3rd run)	6.0	5.6	91.6	1826	1802

[a] Determined from a pressure drop from 69 to 67.5 bar (ESI). [b] Determined from the amount of methanol produced within 30 minutes.

Fig. 1 shows the comparison of different catalysts containing the same amount of platinum. The achieved pressure curves indicate significant differences in activity between the catalytic materials. Calculated reaction rates from the pressure drop from 69 to 67.5 bar confirm this observation and show that the turnover frequency of Pt@*Ex*LOB-900 is substantially higher than that of the molecular $Pt(bpym)Cl_2$ catalyst (Table 1). Remarkably, the novel solid catalyst is significantly more active than previously developed Pt-modified CTF materials, indicating a strong influence of the carbon support. However, the structural difference at the active center is difficult to access especially for solid single-site catalysts since the acquisition of reliable information at the atomic level is challenging.

In addition, recycling experiments were performed to investigate the catalyst stability under the harsh reaction conditions. Pt@*Ex*LOB-900 was used in three subsequent runs under identical reaction conditions. However, catalyst amounts in subsequent runs were lower, due to losses by filtration and elemental analysis after each experiment, which led to decreasing conversions and thus decreasing pressure drops in subsequent runs (Fig. 2a). Pt@*Ex*LOB-900 achieved a high TOF of 2074 h^{-1} in the first run, which decreased to 1826 h^{-1} for the third run (Table 1 and ESI†). Thus, decreasing

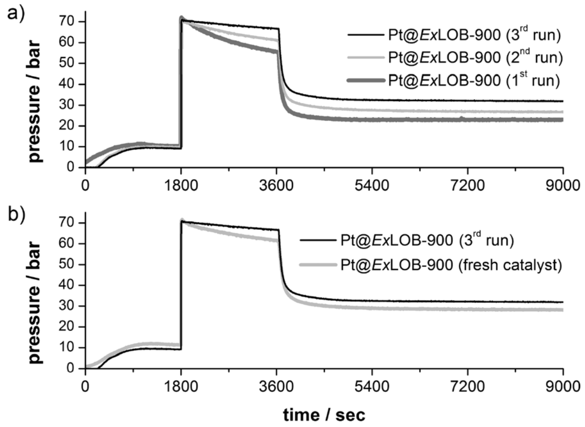

Fig. 2 (a) Pressure–time plots for Pt@*Ex*LOB-900 recycling experiments. (b) Pressure–time plots for fresh and recycled catalyst (Pt@*Ex*LOB-900 (3rd run)).

TOFs from recycling experiments indicate catalyst deactivation. This becomes more obvious when comparing pressure drops of Pt@*Ex*LOB-900 (3rd run) and the same amount of fresh catalyst (Fig. 2b). Since no leaching of Pt species and no significant changes in porosity could be observed the reason for deactivation remains as yet unclear (ESI†). Deactivation may result from the recycling procedure, *i.e.* from washing of the solid catalyst, or from changes of the catalyst during the reaction. It should also be mentioned that activity resulting from homogeneous species in solution under reaction conditions cannot fully be excluded, since hot filtration tests are so challenging under the applied reaction conditions that they could not as yet be performed. However, as Pt loading does not change during recycling experiments, irreversible leaching can be excluded.

Furthermore, it was observed that TOFs were dependent on catalyst concentration. Specifically, TOFs increased with a decreasing amount of Pt. Mass transfer limitation of methane into the solution could be excluded (Fig. S7, ESI†), and the reason for this behaviour remains unclear. Thus, the TOFs during recycling experiments are not fully comparable, since catalyst deactivation and rate dependency on the amount of platinum counteract each other. Since the TOF decreased although less platinum was present in subsequent runs, catalyst deactivation is probably even more pronounced than expressed by the TOFs presented in Table 1.

The very high selectivity to methylbisulfate or methanol, respectively, is unaffected by catalyst deactivation (Table 1). More precisely, a selectivity between 92 and 95% at high reaction rates and conversions was observed, which emphasizes the great advantage of the Periana system for methane activation in comparison to other approaches of heterogeneous catalytic systems.[13,14]

One might expect that the synthesis of the catalysts would not be reproducible due to the fact that natural raw materials are used for the preparation. The reproducibility of catalytic results was thus carefully examined for Pt@*Ex*LOB-900 and was found to be excellent (within a few percent deviation in produced methanol) for catalysts derived from the same batch of lobster shells. In addition, catalysts were prepared from a NDC support, which had been obtained from lobster shells from different regions, and also the produced amount of methanol of these samples deviates by less than ±5% from that of the other samples with no Pt leaching observed. The natural variability of the raw materials thus does not seem to be a major problem, although results for lobsters from two different regions certainly do not allow full generalization.

In conclusion, hydrothermal treatment and subsequent thermal carbonization of nitrogen containing biomass-derived precursors, followed by Pt coordination, gives access to novel highly active solid catalysts for direct methane oxidation *via* C–H activation. The initial catalytic activity of this material is superior to the molecular benchmark originally described by Periana and significantly better than that of the previously reported solid catalysts. Recycling experiments revealed that this novel solid looses activity to some extent. This deactivation, however, is not associated with loss of platinum, since the platinum leaching is negligible. The reason for the high initial activity in comparison to the molecular catalyst and the loss of activity are still under investigation. However, the remarkable catalytic performance may provide new insight for further targeted material development which in turn could bring catalytic methane utilization closer to technical feasibility.

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