Methane Oxidation

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Solid Catalysts for the Selective Low-Temperature Oxidation of Methane to Methanol**

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The development of catalyst systems for the direct low-temperature oxidation of methane to methanol has been one of the major challenges in catalysis over the last decades.[1–8] The high binding energy of the CH_3–H bond (435 kJ mol^{-1}) together with the ease of overoxidation to form CO_2 require not only a highly active but also a highly selective catalyst system to tackle this reaction.[9] In the past, various investigations addressed this challenge.[10–16] However, the catalysts mostly suffered from irreversible reduction and bulk metal formation, together with consequently poor selectivity.[5,6,13] Some palladium, gold, and mercury complexes with superior stability initially appeared to be promising but still suffer from turnover frequencies (TOFs) below 1 h^{-1}. In the field of heterogeneous catalysis, nearly all reported investigations involve temperatures far above 250 °C over basic oxides,[7,17] transition-metal oxides,[13] and iron complexes encapsulated in zeolites.[16] All these catalysts showed poor selectivity owing to overoxidation, and maximum methanol yields were around 5 %.[7,18]

Promising progress in molecular catalysis, however, has recently been made by Periana et al., who demonstrated the selective low-temperature oxidation of methane at temperatures around 200 °C over platinum bipyrimidine complexes in concentrated sulfuric acid.[19–22] Methane conversions above 90 % at 81 % selectivity to methylbisulfate were reached. However, despite these promising results, commercial application seems to be hampered by difficult separation and recycling of the molecular catalyst.

We report herein on the development of solid catalysts for the direct low-temperature oxidation of methane to methanol reaching high activity at high selectivity and stability over several recycling steps, which could provide a breakthrough for this reaction. The development is based on the recent discovery of a new class of high-performance polymer frameworks that are formed by the trimerization of aromatic nitriles in molten $ZnCl_2$.[23,24] The materials are thermally stable up to 400 °C and resist strongly oxidizing conditions, which made them appear promising as a solid matrix for methane oxidation along the lines of Periana's work for liquid-phase conditions. Utilizing 2,6-dicyanopyridine as monomer, a covalent triazine-based framework (CTF) with numerous bipyridyl structure units is accessible, which should allow coordination of platinum and resemble the coordination sites for platinum coordination in the molecular Periana catalyst (Scheme 1).

The CFT material was characterized with physicochemical techniques. Nitrogen sorption analysis of CTF reveals a type I isotherm corresponding to a microporous material with a specific surface area of 1061 m^2 g^{-1}, a pore volume of 0.934 cm^3 g^{-1}, and an average micropore diameter of 1.4 nm as determined by nonlocal DFT analysis. Pore volume and specific surface area are somewhat higher than reported in the initial publications on this material by Kuhn et al.[23,24] Although CTF materials based on 1,4-dicyanobenzene exhibit some regularity, X-ray diffraction measurements of the material based on 2,6-dicyanopyridine indicate a predominantly amorphous structure, and the material has at most short-range ordering. In line with this finding, TEM micrographs support the amorphous nature of the CTF, with pores in the micropore range and neither long-range nor short-range order.

For modification with platinum, two different routes were chosen, either an in situ pathway by simply combining CTF and the platinum precursor in the reaction mixture for the methane oxidation reaction ($K_2[PtCl_4]$-CTF), or by pre-coordination of platinum (Pt-CTF) in a separate step.

The platinum-modified material was tested in the direct methane oxidation in concentrated sulfuric acid according to the conditions described by Periana et al.[19] In principle, utilization of sulfuric acid and sulfur trioxide as oxidants, as schematically described in Equations (a)–(d), would allow design of a continuous process. All process steps, including methane oxidation to methyl bisulfate (a), hydrolysis to form free methanol (b), and reoxidation of SO_2 (c) could be integrated in such a system. A solid catalyst, with its advantages of easy separation and recyclability, would facilitate the implementation of such processes to allow efficient conversion of natural gas on-site.

$$CH_4 + H_2SO_4 + SO_3 \rightarrow CH_3OSO_3H + H_2O + SO_2 \quad (a)$$

$$CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4 \quad (b)$$

$$SO_2 + 1/2\,O_2 \rightarrow SO_3 \quad (c)$$

$$\Sigma CH_4 + 1/2\,O_2 \rightarrow CH_3OH \quad (d)$$

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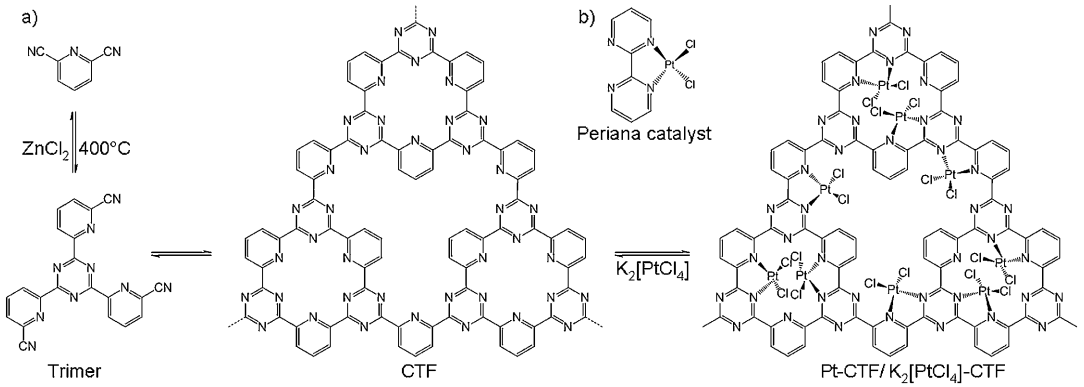

Scheme 1. a) Trimerization of 2,6-dicyanopyridine (DCP) in molten $ZnCl_2$, conversion to a covalent triazine-based framework (CTF), and subsequent platinum coordination (Pt-CTF); b) Periana's platinum bipyrimidine complex.

In a typical reaction, the catalyst is mixed with the oleum and the reactor is then sealed and pressurized with methane. The pressure in the vessel gradually decreases, suggesting consumption of methane. After workup of the reaction mixture, the formed methanol is analyzed to quantify the activity. Interestingly, the achieved methanol concentrations in the final reaction mixtures and the turnover numbers (TON) proved to be rather similar for all three systems (Pt-CTF, $K_2[PtCl_4]$-CTF, and the molecular Periana catalyst; Table 1). For all samples, selectivities for methanol formation above 75% could be reached. The major by-product, determined by FTIR analysis of the gas phase, is CO_2.

Table 1: Catalytic activity of the molecular Periana catalyst and the heterogeneous Pt-CFT and $K_2[PtCl_4]$-CFT catalysts in methane oxidation.

Catalyst[a]	Final methanol conc. [mol L^{-1}]	TON[b]
Periana catalyst[c]	1.65	158
Periana catalyst[d]	1.49	355
$K_2[PtCl_4]$-CTF[e]	1.54	201
Pt-CTF[f]	1.80	246

[a] Reaction conditions: 15 mL H_2SO_4 (30% SO_3), 40 bar CH_4 pressure (25 °C), 2.5 h at 215 °C. [b] TON based on the platinum content determined from SEM/EDX. [c] 65 mg Periana catalyst. [d] 26 mg Periana catalyst. [e] 48 mg CTF with 92 mg $K_2[PtCl_4]$. [f] Data from the second run with 62 mg Pt-CTF.

Although these results are promising, single-run activity is obviously not the decisive point for a heterogeneous catalytic system, but rather recyclability and stable catalytic activity of the material. Pre-coordination of platinum in the CTF material prior to catalysis leads to the Pt-CTF catalyst, which shows very stable activity over several runs with TONs above 250 (Figure 1 a). Surprisingly, the material exhibits very low activity in the first catalytic cycle, reaching a TON of only 26, which increases to stable values above 250 for subsequent cycles. The nature of the activation process is not yet fully clear but may be related to rearrangement of platinum species within the samples, resulting in formation of the active species under reaction conditions.

X-ray photoelectron spectroscopy (XPS) analysis of the CFT material reveals an average C/N ratio of 3.2:1 together with some intensity for Zn and Cl from material synthesis. After platinum coordination, XPS measurements of Pt-CTF reveal N/Pt ratios of 4.7:1 prior to catalysis, 4:1 after the first run, and 4.25:1 after the fifth run, indicating stable Pt coordination within the material even after several recycling steps.

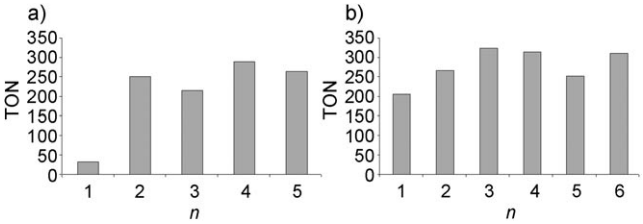

Figure 1. Catalytic activity of a) Pt-CTF and b) $K_2[PtCl_4]$-CFT in the direct oxidation of methane to methanol over several recycling steps *n*.

Combined TEM/EDX analysis (EDX = energy-dispersive X-ray spectroscopy) also supports a very homogenous platinum loading without detectable platinum clusters or nanoparticles within the Pt-CTF catalyst (Figure 2). Corresponding to atomically coordinated platinum, Pt^{II} is the

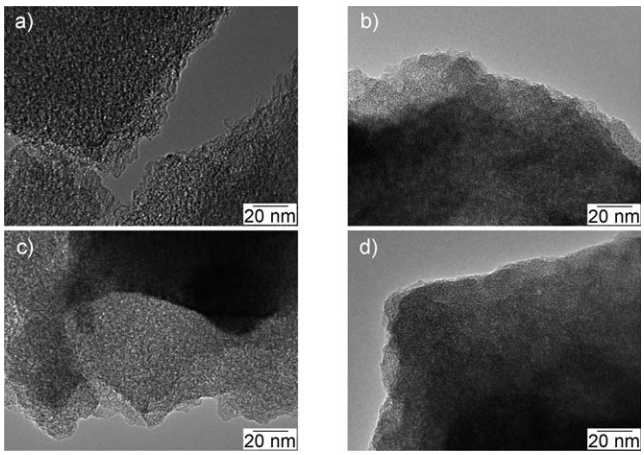

Figure 2. TEM micrographs of a) pure CTF, b) Pt-CTF from pre-coordination of platinum prior to catalysis, c) Pt-CTF after the first catalytic run, and d) Pt-CTF after utilization of the material in five catalytic runs.

predominant species detected by XPS with above 95% of the total intensity. XRD and TEM, however, additionally suggest the presence of a low concentration of extraframework Pt^0 in the form of agglomerated Pt nanoparticles outside the polymeric material. These particles have diameters of 2–3 nm and are already present in the sample after Pt coordination prior to catalysis.

Interestingly, simple addition of CTF and $K_2[PtCl_4]$ as platinum precursor in the catalytic reaction leads to formation of a very stable $K_2[PtCl_4]$-CTF catalyst as well. The material exhibits not only high activity from the very first catalytic run but also little deactivation, with TONs around 300 even after five recycling steps (Figure 1b). XPS analysis indicates that the material possesses a somewhat lower amount of incorporated platinum than Pt-CTF, reaching a N/Pt ratio of about 6.6:1 after six catalytic runs, which is due to the overall lower $K_2[PtCl_4]$ concentration utilized for the catalyst formed in situ. In this catalyst, exclusively Pt^{II} species were detected, corresponding to platinum coordinated in the fashion suggested in Scheme 1. TEM and SEM micrographs, together with EDX analysis, support the notion of homogeneously distributed platinum within the polymer matrix throughout the whole sample (Figure 3).

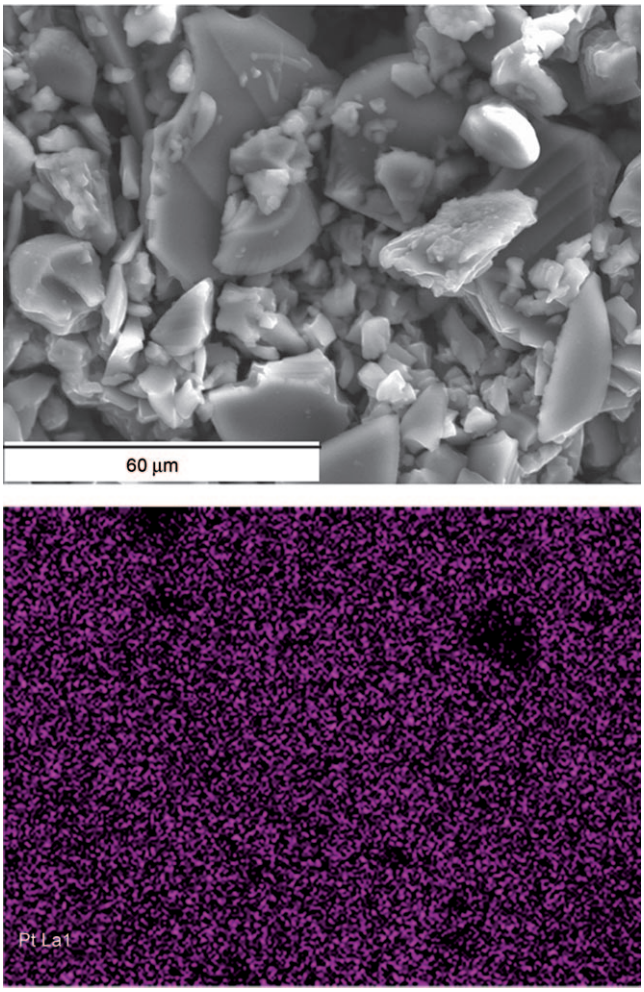

Figure 3. Top: SEM micrograph of the $K_2[PtCl_4]$-CFT material after five recycling steps; bottom: corresponding EDX Pt mapping.

Notably, for both types of catalyst, after several runs the chlorine concentration in the samples is reduced to below the detection limit of the EDX system, suggesting that chlorido ligands may not be necessary in the catalytic cycle.

In summary, we have shown that highly active solid catalysts for methane oxidation by SO_3 in concentrated sulfuric acid can be produced, and that these systems are stable over at least five recycling steps. This finding could reinvigorate research into such a process for commercial exploitation, which had already been scaled up to pilot scale for the molecular Pt bipyrimidine system, and thus make a small-scale methane activation process viable.

Experimental Section

Platinum bipyrimidine complexes and triazine-based materials were synthesized as described elsewhere.[4,7] For Pt coordination, CTF (170 mg) and $K_2[PtCl_4]$ (340 mg) 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 oleum (30% SO_3, 15 mL) and catalyst (50–70 mg), closed, and flushed with argon. In the case of $K_2[PtCl_4]$-CTF, the autoclave was charged with CTF (92 mg) and $K_2[PtCl_4]$ (48 mg). The reactor was pressurized with 40 bar CH_4 and heated to 215 °C, kept there for 2.5 h, and cooled down to room temperature. The pressure has to be released slowly to prevent foam formation. The reaction solution was filtered using a glass frit. The catalyst was rinsed with water to remove most of the remaining H_2SO_4 and dried at 90 °C prior to recycling. The reaction solution was hydrolyzed by heating at reflux in water for 4 h and analyzed by HPLC. Selectivity for methanol was estimated on the basis of methanol formation and pressure drop during the reaction, while FTIR analysis of the released gas phase was utilized to determine byproducts. In each recycling step, about 5–10 wt% of the catalytic material could not be recovered, which has been considered in calculation of the catalytic activity. Turn over numbers (TONs) were calculated on the basis of the ratio of produced methanol and the platinum content of the catalyst (mol_{MeOH}/mol_{Pt}). Platinum contents determined by SEM-EDX were used (Pt-CTF and $K_2[PtCl_4]$-CTF run 2–6), or the content was based on the amount of platinum utilized ($K_2[PtCl_4]$-CTF, first run). The CTF material has been characterized using nitrogen sorption measurements, XRD, TEM, and XPS analysis. The catalysts have been characterized using TEM, SEM/EDX, XPS, and XRD.

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