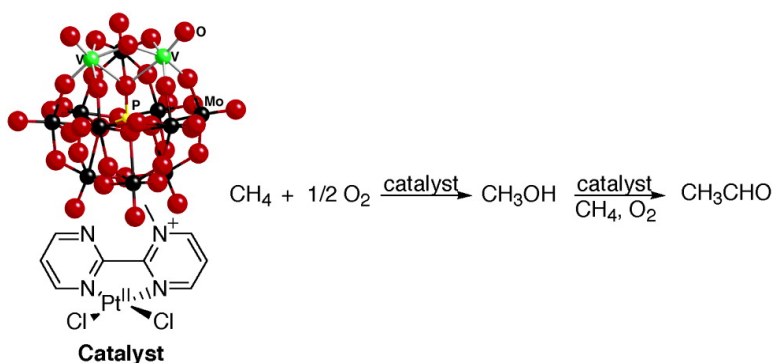Communication

Mild, Aqueous, Aerobic, Catalytic Oxidation of Methane to Methanol and Acetaldehyde Catalyzed by a Supported Bipyrimidinylplatinum–Polyoxometalate Hybrid Compound

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Catalyst

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Mild, Aqueous, Aerobic, Catalytic Oxidation of Methane to Methanol and Acetaldehyde Catalyzed by a Supported Bipyrimidinylplatinum−Polyoxometalate Hybrid Compound

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The selective transformation of alkanes leading to oxygenated petrochemicals such as alcohols, aldehydes, and carboxylic acids is important for improved utilization of petroleum and natural gas-based resources. In this context, controlled aerobic oxidation of methane is a key research objective. Although methane can be aerobically oxidized to methanol using methane monoxygenase enzymes, the oxidation requires the use of sacrificial reducing agents for oxygen activation.[1] Thus, there is significant interest in nonbiological systems for selective activation of saturated C−H bonds.[2] Particularly enticing is electrophilic alkane activation and oxidation by platinum(II) complexes originally reported by Shilov and co-workers using Pt(IV) salts as the stoichiometric oxidant.[3] In recent years, advances in these Pt(II)- and also Pd(II)-catalyzed reactions have been made from both synthetic (practical)[4] and mechanistic[5] points of view. The mechanistic work can be summarized by a probable catalytic cycle for aerobic oxidation of methane to methanol[2] (Scheme 1). The cycle has not, however, been definitively demonstrated, although some alkane[4c] and methane[4d] aerobic catalytic oxidation has been observed at high oxygen pressure, usually $P_{O_2} > 20-25$ bar.

We now report on the synthesis of a bipyrimidinylplatium−polyoxometalate ($H_5PV_2Mo_{10}O_{40}$) hybrid complex and its use as a supported (silica) catalyst for the mild, aerobic (50−60 °C, 1−2 bar O_2), aqueous oxidation of methane to methanol and then partially further to acetaldehyde (Scheme 2). Although methane has been oxidized directly to acetic acid with SO_3,[6] and acetic acid has also been formed from methane and CO and CO_2 (methanol over-oxidation products),[7] the significant formation of acetaldehyde without formation of acetic acid has not been previously reported.

The catalyst was prepared by the following synthetic sequence (details in Supporting Information): (a) reaction of 2,2′-bipyrimidine (bipym) with $PtCl_2(DMSO)_2$ to give $Pt(bipym)Cl_2$, (b) methylation of $Pt(bipym)Cl_2$ with Me_2SO_4 at one of the non-coordinated aromatic nitrogen atoms to yield the cationic methylated [Pt-(Mebipym)Cl_2]$^+HSO_4^-$, (c) an anion exchange reaction in aceto-nitrile between [Pt(Mebipym)Cl_2]$^+HSO_4^-$ and (POM) H_5PV_2-$Mo_{10}O_{40}$ to yield [Pt(Mebipym)Cl_2]$^+[H_4PV_2Mo_{10}O_{40}]^-$, which was then wet impregnated on a silica matrix. The $H_5PV_2Mo_{10}O_{40}$ polyoxometalate was chosen as counteranion to the cationic [Pt-(Mebipym)Cl_2]$^+$ species because of (a) its advantageous oxidation potential[8] needed to mediate the oxidation of a Pt(II) complex to a Pt(IV) complex (Scheme 1, step 2) and (b) its ability to very efficiently oxidize hydride species to protons and reduced poly-oxometalate that in the presence of dioxygen are easily reoxidized under mild conditions with formation of water.[8,9] See, for example, the oxidation of hydrogen (eq 1).

$$H_2 + H_5PV^V_2Mo_{10}O_{40} \xrightarrow{M} H_7PV^{IV}_2Mo_{10}O_{40} \xrightarrow{O_2} H_2O + H_5PV^V_2Mo_{10}O_{40} \quad (1)$$
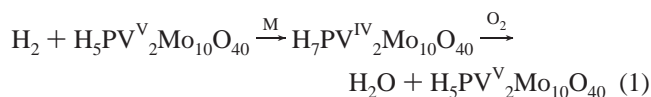
Scheme 1. Proposed Catalytic Cycle for Aerobic Methane Oxidation Consisting of Electrophilic Activation of Methane (1), Aerobic Oxidation of Pt(II) to Pt(IV) (2), Nucleophilic Cleavage of the Methyl−Pt(IV) Bond (3), and Ligand Exchange (4) Steps
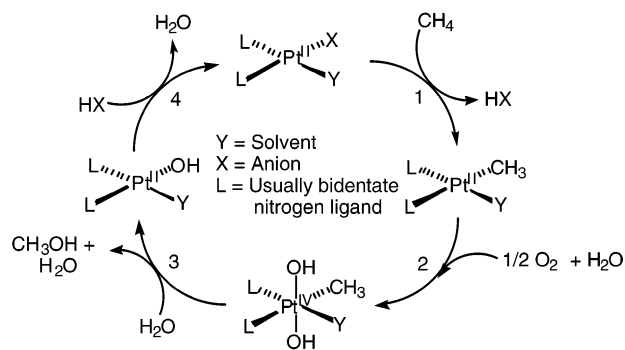
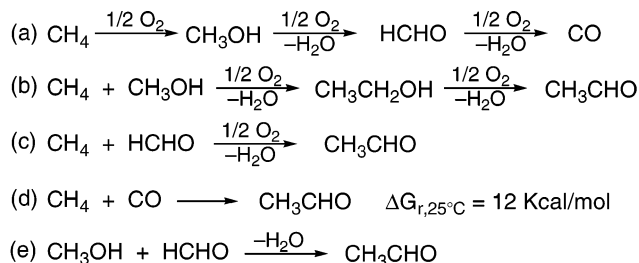**Scheme 2.** Bipyrimidinylplatinum−Polyoxometalate Catalyst and the Catalytic Transformation Observed

$$CH_4 + 1/2 O_2 \xrightarrow{catalyst} CH_3OH \xrightarrow[CH_4, O_2]{catalyst} CH_3CHO$$
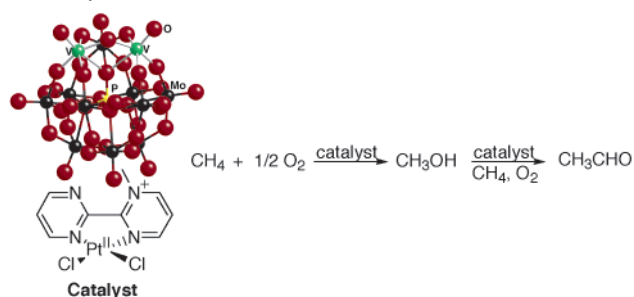
Catalyst

Table 1. Aerobic Oxidation of Methane Catalyzed by [Pt(Mebipym)Cl_2]$^+$[$H_4PV_2Mo_{10}O_{40}$]$^-$/SiO_2[a]

products, μmol				
CH_3OH	HCHO	CH_3CHO	acid (μmol)	TON
3	1	13	none	6
30	12	48	H_2SO_4 (150)	31
24	19	49	$H_5PV_2Mo_{10}O_{40}$ (60)	32
46	9	41	$H_5PV_2Mo_{10}O_{40}$ (30)	33

[a] Reactions conditions: 2.88 μmol of catalyst, 2 mL of H_2O, 0−150 μmol of acid, 30 bar CH_4, 2 bar O_2, 50 °C, 4 h in a 14 mL Parr autoclave. TON = moles of products per mole of catalyst.

Oxidation of methane was carried out as noted in Table 1. The results clearly show that there was significant turnover in the oxygen-mediated catalytic oxidation of methane (∼1% conversion) under mild conditions. As is known for these reactions,[3] excess acid was also needed. No significant formation of CO or CO_2 was monitored (GC−MS analysis of both the gas and liquid phases). No formation of acetic acid was measured. Probably, acetaldehyde is not further oxidized as a result of the mild reaction conditions coupled with the anti-autoxidation properties of the polyoxometa-late.[10] TEM analysis (1 nm resolution) of the supported catalyst

Scheme 3. Possible Reactions Involved in Acetaldehyde Formation

(a) $CH_4 \xrightarrow{1/2\ O_2} CH_3OH \xrightarrow[-H_2O]{1/2\ O_2} HCHO \xrightarrow[-H_2O]{1/2\ O_2} CO$

(b) $CH_4 + CH_3OH \xrightarrow[-H_2O]{1/2\ O_2} CH_3CH_2OH \xrightarrow[-H_2O]{1/2\ O_2} CH_3CHO$

(c) $CH_4 + HCHO \xrightarrow[-H_2O]{1/2\ O_2} CH_3CHO$

(d) $CH_4 + CO \longrightarrow CH_3CHO \qquad \Delta G_{r,25°C} = 12\ Kcal/mol$

(e) $CH_3OH + HCHO \xrightarrow{-H_2O} CH_3CHO$

after the reaction showed no formation of Pt aggregates due to reduction of the Pt complex. ICP-MS analysis also gave no indication of leaching of Pt into the solution. An active carbon support instead of a silica matrix was equally effective; hydrophobic silica was an inferior support. Simple Pt compounds such as *cis*-Pt(II)(NH$_3$)$_2$Cl$_2$ and K$_2$PtCl$_4$ showed no catalytic activity.

A key feature of a Shilov-type catalytic cycle is the formation of methanol via a nucleophilic cleavage of a Pt(IV)–methyl intermediate (Scheme 1, step 3), rather than a direct oxidation of an intermediate with O$_2$. Three experiments were carried out that support a nucleophilic cleavage pathway. (i) Oxidation of methane in the presence of HCl yielded 63 μmol of CH$_3$Cl, 11 μmol of CH$_3$OH, 2 μmol of HCHO, and 62 μmol of CH$_3$CHO (48 TON).[11] (ii) A reaction in the presence of ^{18}O-labeled water gave ^{18}O-labeled CH$_3$OH, HCHO, and CH$_3$CHO ($\sim$73 ± 3% enrichment).[12] Enrichment is reduced due to exchange of H$_2$^{18}O with the acid. (iii) Reaction in the presence of ^{18}O-labeled O$_2$ (96.3% enrichment) under standard reaction conditions (Table 1) yielded no ^{18}O-labeled products. Methyl chloride formation in the presence of HCl and the ^{18}O-labeling experiments support a nucleophilic cleavage pathway.[13]

The significant formation of acetaldehyde is a novel feature of this reaction. A time course profile (Figure 1S) of the reaction showed no induction period; methanol and acetaldehyde were accumulated immediately. The accumulation of formaldehyde was delayed and coincided with the inhibition of the reaction. Also, the oxidation of methane upon addition of 250 μmol of formaldehyde (conditions given in Table 1) was almost totally inhibited.

Conceivable reactions to consider for acetaldehyde formation are outlined in Scheme 3. To gain further insight into these possibilities, various additional experiments were carried out. (i) A reaction with CH$_4$/^{13}CH$_3$OH gave labeled CH$_3$^{13}CHO only at the carbonyl position,[14] but mostly unlabeled product was formed (CH$_3$CHO/ CH$_3$^{13}CHO $\sim$3/1). (ii) In the absence of methane, the oxidation of methanol to formaldehyde was very slow (Figure 2S); neither the polyoxometalate nor the [Pt(Mebipym)Cl$_2$]$^+$ ligand alone showed activity for alcohol oxidation. (iii) Similarly, the oxidation of ethanol was also slow (Figure 2S). (iv) Addition of a small amount of ^{13}CO to a methane oxidation reaction showed no formation of CH$_3$^{13}CHO, and only traces of CH$_3$OH ($\sim$1 TON), but no CH$_3$^{12}CHO was observed.[15]

From the results described above, one can draw the following conclusions. (i) Coupling of methanol and formaldehyde is not likely (Scheme 3e) because addition of ^{13}CH$_3$OH to a reaction yielded labeled acetaldehyde only at the carbonyl position. (ii) A pathway involving oxidative coupling of coordinated methanol and methane to yield ethanol that is then oxidized to acetaldehyde (Scheme 3b) is also unlikely since ethanol is only slowly oxidized under the reaction conditions and ethanol was not observed as an intermediate. (iii) Formation of acetaldehyde by reaction of methane with CO (Scheme 3d) is also improbable since CO strongly

inhibited the reaction and such a step has a $\Delta G_r = 12$ kcal/mol; other coupling reactions are driven by water formation. (iv) The most likely scenario for acetaldehyde formation is the oxidation of methane to formaldehyde via methanol, followed by its coupling with methane to yield the product, possibly occurring entirely in the coordination sphere of the catalyst (Scheme 3c). Accumulation of HCHO and then CO leads to deactivation (high concentrations of these inhibit the reaction).

The presence of the polyoxometalate in the [Pt(Mebipym)-Cl$_2$]$^+$[H$_4$PV$_2$Mo$_{10}$O$_{40}$]$^-$ hybrid catalyst is key in enabling mild aerobic oxidation of methane and possibly functions to facilitate both (a) oxidation of Pt(II) to Pt(IV) intermediates and (b) the addition of methane (also methanol) to a Pt(II) center by providing a conduit for improved oxidation of intermediate hydride species.

Supporting Information Available: Experimental details, NMR spectra of the [Pt(Mebipym)Cl$_2$]$^+$ ligand, and time course profiles for oxidations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) Authentic hydride species are immediately oxidized by H$_5$PV$_2$Mo$_{10}$O$_{40}$. See also: (a) Katamura, K.; Nakamura, T.; Sakata, K.; Misono, M.; Yoneda, Y. *Chem. Lett.* **1981**, 89−92. (b) Mizuno, N.; Katamura, K.; Yoneda, Y.; Misono, M. *J. Catal.* **1983**, *83*, 384−392.
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(11) Conditions: 2.9 μmol of catalyst, 300 μmol of HCl, 2 mL of H$_2$O, 30 bar CH$_4$, 2 bar O$_2$, 50 °C, 4 h. A control experiment showed no formation of CH$_3$Cl from CH$_3$OH.
(12) Conditions: 0.29 μmol of catalyst, 0.2 mL of H$_2$^{18}O (95.2% ^{18}O), 50 μmol of H$_2$SO$_4$, 30 bar CH$_4$, 2 bar O$_2$, 50 °C, 4 h. In a control experiment, <1.5% exchange between CH$_3$OH and CH$_3$^{18}OH was observed.
(13) It is possible that a H−Pt^{IV}−CH$_3$ intermediate is formed by oxidative addition of CH$_4$ to a Pt^{II} species. In such a scenario, the hydride may be oxidized by the polyoxometalate (ref 9) along with the nucleophilic cleavage step.
(14) Conditions: 2.88 μmol of catalyst, 1 mmol of ^{13}CH$_3$OH (99% ^{13}C), 2 mL of H$_2$O, 60 μmol of H$_5$PV$_2$Mo$_{10}$O$_{40}$, 30 bar CH$_4$, 2 bar O$_2$, 50 °C, 4 h. TON = 31.
(15) Conditions: 2.88 μmol of catalyst, 2 mL of H$_2$O, 60 μmol of H$_5$PV$_2$Mo$_{10}$O$_{40}$, 30 bar CH$_4$, 0.2 bar ^{13}CO (CH$_4$/CO = 150), 2 bar O$_2$, 50 °C, 4 h.

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