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Low temperature activation of methane over a zinc-exchanged heteropolyacid as an entry to its selective oxidation to methanol and acetic acid†

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A Zn-exchanged heteropolyacid supported onto silica (Zn-HPW/SiO₂) activates methane at 25 °C into Zn-methyl. At higher temperatures and with CH₄/O₂ or CH₄/CO₂, it gives methanol and acetic acid respectively.

Transformation of methane to oxygenates (*i.e.* methanol, formaldehyde or acetic acid) under economically attractive conditions remains an open challenge for the chemical industry.^{1–4} New catalytic processes must be developed to overcome all the constraints due to the chemical inertness of the substrates especially with respect to the high reactivity of the products and thermodynamic limitations. Despite the fact that many efforts have been made in the past decades, the commercial utilization of methane is still largely dependent on the multi-step syn-gas (CO + H₂) strategy, which is energy and cost intensive.² Although the homogenous catalysis system (such as Pd/H₂SO₄) is the most efficient system to date for the direct conversion of methane under mild conditions,^{5,6} the environmental concerns and the utilization of precious metals set drawbacks for its potential use. Some breakthroughs were achieved for the low temperature activation of methane^{7,8} to methanol or acetic acid using the environmentally benign heterogeneous catalysts in which transition metal modified zeolites catalyze the reaction.^{9,10}

Key to this development is the close examination of structure–reactivity relationships of already existing catalysts. In this context, metal oxides-based catalysts have been abundantly documented but suffer from the disadvantage of being structurally poorly understood.¹¹

In contrast, heteropolyacids (HPA) are structurally better understood but have shown lower performances, selective yet not very active, for light alkane oxidation.^{4,12–16} They also can be easily modified by the inclusion of metals (for instance in the addenda or as counter cations) with a significant effect on their reactivity.

Zinc-incorporated materials have been a subject of recent interest for the catalytic transformation of light alkanes.^{17–21} The dissociative adsorption of hydrogen and light alkanes has been addressed in the literature for bulk zinc oxide.^{17,22–26} Zinc is of particular interest as it has been proved recently that it accelerates the heterolytic dissociation of the C–H bond of CH₄ by a reaction between CH₄ and Zn²⁺ O^{2–} which is not the case for most other metal ions.²⁷

In the present study, we aimed to study the reactivity of Zn containing a heteropolyacid for methane activation. To our knowledge, we have been the first to report the formation of a Zn–CH₃ species at room temperature on the heteropolyacid surface with dual reactivity to transform into methanol (with oxygen) or acetic acid (with carbon dioxide) under milder reaction conditions.

A Zn exchanged heteropolyacid (Zn-HPW; **1**) was synthesized *via* ion exchange from the parent phosphotungstic acid (HPW) in water and using “filter paper” as a “template” (see ESI†). After calcination treatment this material is insoluble in water or in other common organic solvents. A suspension of **1** in water was mixed with silica (Aerosil 200) to form a slurry; removal of water *in vacuo* yielded silica supported Zn-HPW (Zn-HPW/SiO₂; **2**). **2** was then submitted to screening experiments using either pure CH₄ or mixtures such as CH₄–CO₂ or CH₄–O₂ under relatively mild conditions. A variety of techniques including elemental analysis, thermal gravimetric analysis, mass spectrometry, SSNMR, BET, and infrared spectroscopy were employed for characterization.

FTIR of **1** revealed a series of vibrations (1090 cm^{–1} for $\nu(\text{P}=\text{Oa})$, 980 cm^{–1} for $\nu(\text{W}=\text{Oa})$, 890 cm^{–1} for $\nu(\text{W}=\text{Ob}-\text{W})$, and 790 cm^{–1} for $\nu(\text{W}=\text{Oc}-\text{W})$.²⁸ These four IR peaks are characteristic of the main Keggin unit of HPW (see Fig. S1, ESI†). Interestingly, the structure is intact even after partial substitution (70%) of the protons of HPW with Zn²⁺. SSNMR experiments were recorded for **1**, **2** and HPW/SiO₂ (see Fig. S2, ESI†). The ³¹P spectrum of HPW is shifted from –11 to –4 ppm upon exchange of H⁺ with Zn²⁺. The nitrogen adsorption desorption isotherm (Fig. S3a and b, ESI†) is clear evidence of the formation of mesoporosity in Zn-HPW in contrast to the parent acid, HPW, which is non-porous.

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Partial substitution of protons of HPW by zinc results in a higher thermal stability as demonstrated by TGA-DSC analysis (Fig. S4a and b, ESI†). With isopropyl amine as the probe molecule in TPD, the acid strength of Zn-HPW revealed a profile, which was different than for its parents HPW (Fig. S5, ESI†): two types of acidity were observed, a moderate one (desorption peak centred around 330 °C) and a strong one (desorption peak centred around 473 °C). It is known that the incorporation of Zn introduces some Lewis acidity in heteropolyacid molecules.²⁹ The Zn exchanged heteropolyacids prepared in this work did not reveal a well-defined powder X-ray diffraction pattern (see Fig. S6, ESI†). The approximate elemental composition was determined using a combination of thermal and elemental analysis techniques (Table S1, ESI†), viz., $\text{Zn}_{1.4}\text{H}_{0.6}\text{PW}_{40}$.³⁰ It is assumed that since the Keggin structure remains intact, the zinc atoms are located outside this Keggin structure.

A few experiments were carried out to see if this new material could activate methane. To gain mechanistic insight, batch experiments were designed (A–C, *vide supra*) with a view to characterise the samples using SSNMR. Experiments were conducted for a combination of 0.5 mmol $^{13}\text{CH}_4$ (at 25 °C) (A), 0.5 mmol $^{13}\text{CH}_4$ + 0.5 mmol O_2 (heated to 250 °C) (B) and 0.5 mmol $^{13}\text{CH}_4$ + 0.5 mmol $^{13}\text{CO}_2$ (heated to 300 °C) (C). All samples (A, B and C) were characterized using ^{13}C SSNMR (see Fig. 1).

It should be noted that the Zn-HPW/SiO₂ precursor does not show any detectable carbon signal using ^{13}C SSNMR spectroscopy. For A, a new signal is observed at –23 ppm. It can be assigned to the zinc methyl species ($\text{Zn}-\text{CH}_3$),¹⁹ hence demonstrating that methane is being activated at room temperature on Zn-HPW/SiO₂. For B, a strong surface methanol (CH_3OH) signal is evident at 49 ppm. This resonance is quite intense and represents the condensation of gas phase methanol on the silica surface. This demonstrates that methane is oxidized to methanol starting at around 250 °C.

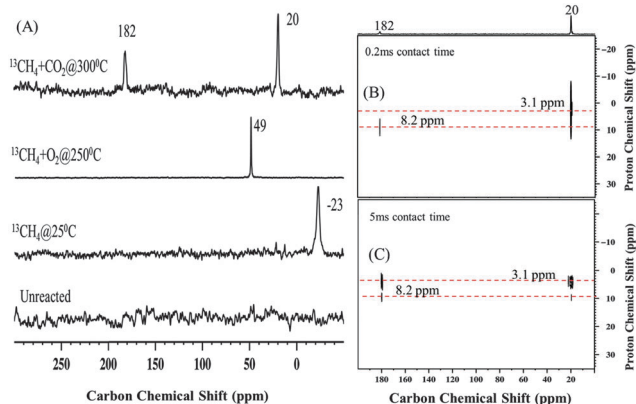


Fig. 1 (A) One-dimensional (1D) ^{13}C CP/MAS NMR spectrum of ^{13}C -enriched methane ($^{13}\text{CH}_4$) on Zn-HPW/SiO₂ catalyst at reaction temperatures of 25 °C (CH_4), 250 °C ($\text{CH}_4 + \text{O}_2$), 300 °C ($\text{CH}_4 + \text{CO}_2$) acquired at 400 MHz with 10 kHz MAS frequency with a repetition delay of 4 s, and 2 ms contact time. Exponential line broadening of 80 Hz was applied prior to Fourier transformation. (B) 2D ^1H – ^{13}C HETCOR spectrum with 0.2 ms contact time (B) and 5 ms (C) of Zn-HPW/SiO₂ catalyst 300 °C ($\text{CH}_4 + \text{CO}_2$) with 10 kHz MAS frequency, 5000 scans per t_1 increment, a 4 s repetition delay, 32 individual t_1 increments).

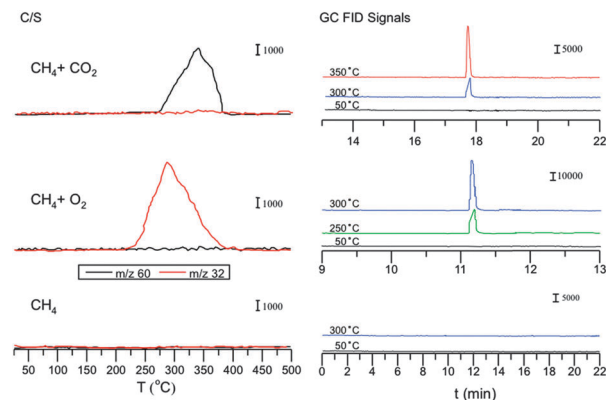


Fig. 2 Mass spectrometer signals (left hand side) and GC-FID peaks (right hand side) obtained during the reaction of Zn-HPW with different mixtures containing CH_4/He (bottom), CH_4/O_2 (middle), and CH_4/CO_2 (top) after heating from 25 up to 500 °C. The GC retention time for MeOH is about 11.2 min, whereas acetic acid is eluted at 17.8 min. The mass spectrometer signals in red are for $m/z = 32$ (MeOH) and the one in black is for $m/z = 60$ (acetic acid).

Upon heating methane in the presence of $^{13}\text{CO}_2$ at 300 °C, acetic acid ($^{13}\text{CH}_3^{13}\text{COOH}$) is formed on the surface that exhibits ^{13}C chemical shifts at 20 ppm ($-\text{CH}_3$) and 182 ppm ($-\text{COO}$). The two-dimensional (2D) CP/MAS ^1H – ^{13}C heteronuclear correlation (HETCOR) spectra (contact time 0.2 ms) (Fig. 2b) display a correlation between the carbon signal at 20 ppm ($-\text{CH}_3$) and a proton signal at 3.1 ppm ($-\text{CH}_3$) and a correlation between the carbon signal at 182 ppm ($-\text{COOH}$) and a proton signal at 8.2 ppm ($-\text{COOH}$). In the CP/MAS HETCOR spectra acquired with a longer contact time (5 ms) (Fig. 2c), the ^1H signals at 3.1 ppm ($-\text{CH}_3$) also correlate with the ^{13}C signals at approximately 180 ppm ($-\text{COO}$), consistent with the $-\text{CH}_3$ and $-\text{COO}$ functions belonging to the same molecule.

This material was also tested in a fixed bed reactor with 3 experimental gaseous conditions: (A') methane/helium (1 : 19), (B') methane/oxygen/helium (1 : 1 : 18) or (C') methane/carbon dioxide/helium (1 : 1 : 18). Flow through reactor control experiments in the absence of any sample were run to ensure that no products were formed by heating the A' or B' or C' gas mixtures in the reactor. In the pure methane flow experiment (A'), the only gases observed in addition to methane were hydrogen and carbon dioxide, both at a temperature of around 230 °C. It indicates that methane is oxidized non-selectively to CO_2 . The evolution of hydrogen strongly suggests that methane is activated by the proton of the heteropolyacid, in a similar fashion to alkane activation by acid catalysts.^{13,31}

Mixing methane with oxygen (B') resulted in the observation of methanol signals at temperatures between 250 and 400 °C with a maximum at 300 °C (see Fig. 2a). Carbon dioxide, the only by-product, is formed at the same temperature (230 °C) as for A'. Complementary experiments were conducted using $^{13}\text{CH}_4$ and O_2 as feeds. Labelled methanol $^{13}\text{CH}_3\text{OH}$ was formed (32 + 1 m/z) at the same temperature and with almost similar signal intensity; hence, confirming methane as the precursor of methanol. At this stage, any further proposal relating to the detailed

mechanism is speculative. We tentatively speculate that, similar to the classic carbanion reactions in organometallic chemistry,^{32,33} the zinc methyl species may be reacting with oxygen to form the methyl peroxy species (this species was not observed by ¹³C NMR spectroscopy) which can further decompose to form methanol. This mechanistic proposal is also supported by Han *et al.*,^{34,35} who observed the formation of methanol in the direct partial oxidation (DPO) of methane on Zn-modified ZSM-5 catalysts.

Under similar conditions to **B'** but using a mixture of methane and carbon dioxide (**C'**), the gas phase acetic acid signal was observed using a mass spectrometer. Acetic acid starts to form at 250 °C and the signal reaches its maximum intensity at around 350 °C. Separate experiments conducted with either ¹³CH₄ or ¹³CO₂ confirmed that the source of carbons in acetic acid *viz.* methyl carbon derived from methane while the carboxyl moiety was from carbon dioxide. No carbon monoxide or hydrogen is observed in the gaseous phase confirmed using both GC and mass analyzer. All points out to the synthesis of acetic acid directly from carbon dioxide and methane and not from syngas (although there are serious thermodynamic limitations for the reaction between methane and CO₂ into acetic acid). The zinc methyl species can effectively react with carbon dioxide through the insertion mechanism that has well been established in organometallic chemistry in homogeneous media for the reaction of organozinc compounds with carbon dioxide.³⁶ The surface carbonate species may serve as a reservoir for carbon dioxide to be inserted into the Zn–C bond of the zinc methyl species. Most likely the Brønsted proton either from Zn-HPW or the one formed from methane activation plays an important role in the final formation of acetic acid through proton transfer. Variable temperature NMR experiments will be helpful for the observation of possible intermediates related to the conversion of methane to methanol or acetic acid.

No acetic acid or methanol was formed with the parent HPW as a catalyst under identical conditions, indicating that the reaction requires active metal Zn for this transformation. We tried to regenerate the materials using a wide range of oxidants such as H₂O₂, air, water and N₂O, but the reaction become catalytic only for the formation of H₂ and CO₂.

To the best of our knowledge, this is the first report on the use of a Zn-substituted heteropolyacid. The superior performance of Zn exchanged HPW over its parent acid can be assigned to factors such as increased surface area and more importantly to the introduction of additional strong acidity.²⁹

The reaction mechanism begins with a Zn–CH₃ surface fragment from the activation of methane by the zinc counter cation (as shown by 2a). It can then undergo further transformation in the presence of O₂ or CO₂ at higher reaction temperatures. Remarkably the Zn–CH₃ species formed is stable and strongly bonded to the surface: it cannot be removed even after evacuation under high vacuum at room temperature. However, heating the zinc methyl species (300 °C for 1 h) formed in **A'** followed by gas phase analysis of by GC-MS revealed the evolution of methane. It indicates that the Zn–CH₃ species, even in the absence of an oxidizing or carbonating agent, could be protonated back

to methane. This implies that the conversion of methane to the zinc methyl species is a reversible process on Zn-HPW depending upon the temperature. It has been proposed that the zinc methyl species originates from activation of methane from Zn²⁺ cations possibly delocalized over oxygen atoms of a heteropolyacid similar to the observation with Zn exchanged zeolites.³⁷ Indeed, the dissociative adsorption of hydrogen, methane and ethane over acid–base Zn^{δ+}–O^{δ−} pairs was investigated by theoretical studies.¹⁷ Other calculation investigations on Zn doped La₂O₃ have favoured the existence of fragmented Zn–methyl adjacent to a hydroxyl group as generated by the reaction of methane with the metal oxide surface.³⁸

In conclusion, Zn-HPW/SiO₂ (2) was shown to activate methane for stoichiometric conversion to methanol (with O₂) and acetic acid (with CO₂). Remarkably, the activation of methane is achieved already at room temperature as evidenced by the first time detection of Zn–CH₃ on a Zn modified heteropolyacid.

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