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Methane Oxidation to Methanol in Water

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CONSPECTUS

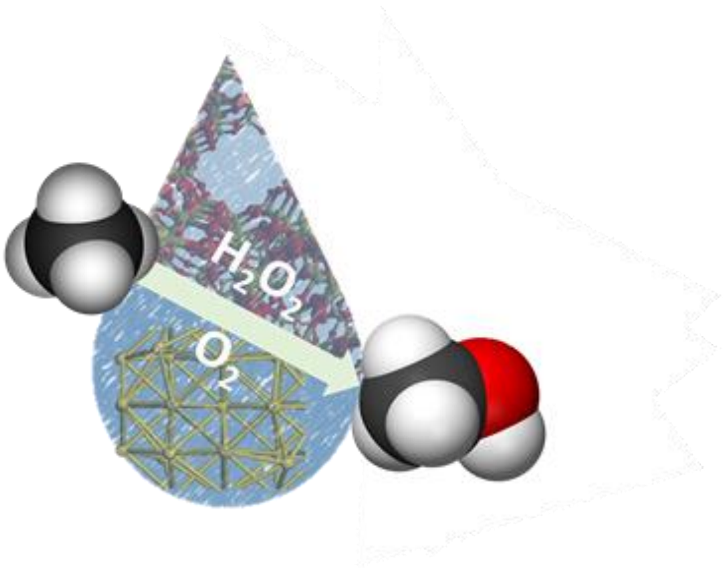
Methane represents one of the most abundant carbon sources for fuel or chemical production. However, remote geographical locations and high transportation costs result in a substantial proportion being flared at source. The selective oxidation of methane to methanol remains a grand challenge for catalytic chemistry, due to the large energy barrier for initial C-H activation and prevention of over oxidation to CO_2. Indirect methods such as steam reforming produce CO and H_2 chemical building blocks, however, they consume large amounts of energy over multi-stage processes. This makes the development of low temperature selective oxidation of methane to methanol highly desirable and explains why it has remained an active area of research over the last 50 years.

The thermodynamically favourable oxidation of methane to methanol would ideally use only molecular oxygen. Nature effects this transformation with the enzyme *methane monooxygenase (MMO)* in aqueous solution and ambient temperature with the addition of two equivalents of reducing cofactor. *MMO* active sites are Fe and Cu oxo-clusters and the incorporation of these metals into zeolitic frameworks can result in biomimetic activity. Most approaches to methane oxidation using metal doped zeolites use high temperature with oxygen or N_2O, however demonstrations of catalytic cycles without catalyst regeneration cycles are limited. Over the last 10 years we have developed Fe-Cu-ZSM-5 materials for the selective oxidation of methane to methanol in aqueous conditions at 50 °C using H_2O_2 as an oxidant (effectively O_2 + 2 reducing equivalents) which compete with *MMO* in terms of activity. To date these materials are among the most active and selective catalysts for methane oxidation at this mild condition but industrially H_2O_2 is an expensive oxidant to use in the production of methanol.

This observation of activity under mild conditions led to new approaches to utilise O_2 as the oxidant. Supported precious metal nanoparticles have been shown to be active for a range of C-H activation reactions using O_2 and H_2O_2, but the rapid decomposition of H_2O_2 over metal surfaces limits efficiency. We identified that this decomposition could be minimised by removing the support material and carrying out the reaction with colloidal AuPd nanoparticles. The efficiency of methanol production with H_2O_2 consumption was increased four orders of magnitude and crucially it was demonstrated for the first time that molecular O_2 could be incorporated into the methanol produced with 91% selectivity. The understanding gained from

these two approaches provides valuable insight into possible new routes to selective methane oxidation which will be presented here in the context of our own research in this area.

GRAPHICAL ABSTRACT



KEY REFERENCES

- Hammond, C.; Forde, M. M.; Ab Rahim, M. H.; Thetford, A.; He, Q.; Jenkins, R. L.; Dimitratos, N.; Lopez-Sanchez, J. A.; Dummer, N. F.; Murphy, D. M.; Carley, A. F.; Taylor, S. H.; Willock, D. J.; Stangland, E. E.; Kang, J.; Hagen, H.; Kiely, C. J.; Hutchings, G. J. **Direct Catalytic Conversion of Methane to Methanol in an Aqueous Medium by Using Copper-Promoted Fe-ZSM-5**. *Angew. Chemie. Int. Ed.* **2012**, 51 (21), 5129–5133. doi.org/10.1002/anie.201108706 *Demonstrates that methane can be selectively oxidised at relatively mild conditions with similar total turnover numbers to the enzymatic reaction using metal doped acidic zeolites.*[1]

- Hammond, C.; Dimitratos, N.; Jenkins, R. L.; Lopez-Sanchez, J. A.; Kondrat, S. A.; Ab Rahim, M. H.; Forde, M. M.; Thetford, A.; Taylor, S. H.; Hagen, H.; Stangland, E. E.; Kang, J. H.; Moulijn, J. M.; Willock D. J.; Hutchings G. J. **Elucidation and Evolution of the Active Component within Cu/Fe/ZSM-5 for Catalytic Methane Oxidation: From Synthesis to Catalysis** *ACS Catal.* **2013**, 3, 689-699. doi.org/10.1021/cs3007999 *A di-nuclear Fe-oxo site is described as a potential active site within the zeolite which interacts with H_2O_2 and methane and has similar structural features to the active site in the enzyme methane monooxygenase.*[2]

- Ab Rahim, M. H.; Forde, M. M.; Jenkins, R. L.; Hammond, C.; He, Q.; Dimitratos, N.; Lopez-Sanchez, J. A.; Carley, A. F.; Taylor, S. H.; Willock, D. J.; Murphy, D. M.; Kiely,

C. J.; Hutchings, G. J. **Oxidation of Methane to Methanol with Hydrogen Peroxide Using Supported Gold-Palladium Alloy Nanoparticles**. *Angew. Chemie. Int. Ed.* **2013**, 125 (4), 1318–1322.doi.org/10.1002/ange.201207717 *Catalysts that are active for H_2O_2 synthesis can initiate a radical chain reaction to produce methanol using preformed H_2O_2 and in situ formed H_2O_2 from the reaction of H_2 and O_2.*[3]

- Agarwal, N.; Freakley, S. J.; McVicker, R. U.; Althahban, S. M.; Dimitratos, N.; He, Q.; Morgan, D. J.; Jenkins, R. L.; Willock, D. J.; Taylor, S. H.; Kiely, C. J.; Hutchings, G. J. **Aqueous Au-Pd Colloids Catalyze Selective CH_4 Oxidation to CH_3OH with O_2 under Mild Conditions**. *Science,* **2017**, *358* (6360), 223–227. doi.org/10.1126/science.aan6515 *In the presence of H_2O_2 and O_2 colloidal AuPd nanoparticles can produce methanol with oxygen incorporation from molecular oxygen through a radical pathway at ambient temperature.*[4]

1. DIRECT METHANE CONVERSION – WHY IS IT IMPORTANT AND TOPICAL?

One of the greatest challenges in chemistry for academics and industrialists is the activation and selective oxidation of a C-H bond. The challenge is especially true for the selective oxidation of methane to methanol under mild reaction conditions, a reaction that has fascinated scientists for over a century. Our approach has focussed on the use of CuFe-ZSM-5[1,2] or AuPd colloidal nanoparticles[3,4] with H_2O_2 as the terminal oxidant. In this way we have opened a new catalytic approach that can pave the way to find a catalysed process for the selective oxidation of methane to methanol using O_2 as the terminal oxidant.

Methane is an abundant feedstock and is the major constituent of natural gas.[5-7] It can be extracted from shale gas and other sources, including emission from natural sources, such as natural wetlands, agriculture, and the generation of methane in landfills during waste decomposition. Although the life-time of methane in the atmosphere is much shorter than that of carbon dioxide, the emerging problem is that methane is more effective greenhouse gas than carbon dioxide being ca. 28-36 times more detrimental.[8] Moreover, the observed continuous rise in temperature of the planet can also contribute significantly to the rise of methane emission globally further exacerbating the climate problem. Therefore, the necessity to transform methane to a useful and more environmentally friendly chemical, as opposed to just flaring to form carbon dioxide is essential. At this moment, the majority of methane produced is combusted either for heating purposes or in the production of electricity. Unfortunately, especially in the case of oil fields, when methane is recovered it is directly flared, producing large amounts of carbon dioxide as a consequence. Indeed 4% of global natural gas production is flared annually as it is not considered economic for recovery and use. This represents a huge resource of 145×10^9 m^3/annum natural gas, but as it is flared it results in 2.75×10^8 tons of CO_2 be emitted to the environment.[9] Therefore, there exists a critical need to find an economic way to transform methane to useful and high value-added chemicals at the scale required for these geographic locations.

The chemical activation of methane is very challenging because its relative inertness ($\Delta H_{C-H} = 438.8$ kJ mol^{-1}) and low reactivity, which means that the current industrial utilization of methane tends to be based on indirect, energy intensive routes. For example, the conversion of methane to methanol, one of the most important products in moving towards a methanol economy, requires first the production of syngas (CO/H_2) using either steam reforming of methane or partial oxidation which require to be operated at a large scale to be economic. Syngas can subsequently be transformed to methanol using a copper catalyst. However, syngas can also be catalytically transformed to a range of important hydrocarbon products. Hence the direct conversion of methane to methanol has become a highly desirable prospect since it represents one of the most promising routes to direct utilisation of remote sources of natural gas. Early work on methane oxidation used high temperatures with oxide catalysts and this typically led to hydrocarbons rather than oxygenates as products[10] unless the reaction conditions were closely controlled.[11] Over many decades, the gas-phase oxidation of methane to methanol has been intensively investigated using a wide range of catalysts and different experimental conditions. It has been concluded that it is a major challenge to achieve a high selectivity to methanol while simultaneously maintaining high methane conversion since the methanol produced is more reactive than methane and overoxidation can predominate at high conversions and this facilitates the consecutive oxidation of methanol to other products such as formaldehyde, formic acid and carbon oxides. Considering all these observations, it is evident that an alternative approach for the selective oxidation of methane to methanol has to be discovered which avoids the use of high temperatures. This goal requires the development of novel catalysts that can oxidise methane selectively at lower reaction temperatures, *i.e.,* $\leq$200 °C and possibly considering the use of alternative oxidants. In this way, it may become possible to minimise the overoxidation of methanol and therefore improve the yield of methanol and other useful oxygenated products such as formaldehyde and formic acid.

2. BACKGROUND ON ALTERNATIVE APPROACHES

A range of low temperature approaches to this problem have to date been investigated with the majority of them having disadvantages that include incomplete catalytic cycles, low turnover frequency or space-time-yield or they pose unwanted environmental issues due to the choice of solvent, catalyst and oxidant involved. For example, several homogeneous catalysts have been proposed for methane oxidation using strong acidic conditions. Periana and co-workers reported the synthesis and utilisation of a bipyrimidyl -Pt complex in oleum for the conversion of methane to methyl bisulfate in the presence of concentrated sulphuric acid and using SO_3 as the desired oxidant.[12] The yield to methyl bisulfate achieved was above 70% with 81%

selectivity and to obtain the final desired methanol product, the methyl bisulfate is then reacted with water. The high selectivity achieved in this approach is due to the absence of free methanol during the oxidation step because the bisulfate acts as a protective group and therefore avoids the overoxidation issues observed when directly forming the methoxy species at higher temperatures which can be easily overoxidized. In a similar matter, Schüth and co-workers have proposed a heterogeneous bifunctional catalyst, based on the use of a platinum-modified covalent triazine framework (CTF-Pt) which gave results similar to that of the reaction proposed by Periana and showed high stability after recycling without a significant loss of activity or selectivity.[13] Although the results obtained from both these approaches were promising, from an industrial standpoint they are severely limited by the associated issues of toxicity, waste disposal, corrosion, difficulties with the recyclability of the acidic media, and the high capital cost for the construction of large scale plants.

Recently an alternative low temperature approach (at around 200 °C) has been proposed based on a stepwise conversion of methane to methanol as illustrated in Figure 1.

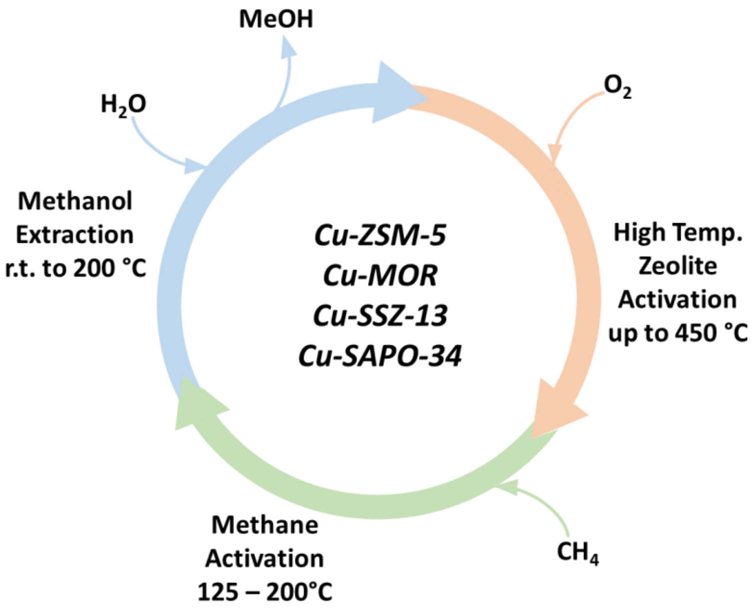


Figure 1. Illustration of the three-step conversion of methane to methanol including (i) typical activation of the material, (ii) oxidation of methane to form surface bound methanol precursors, and (iii) extraction of methanol, for example with water redrawn from ref 14.

In this new approach, the first step is the activation of catalyst material at high temperature, (~ 450 °C) using either O_2 or N_2O as the preferred oxidant. In the second step, the oxidant is removed from the reactor and methane is introduced and passed over the activated catalyst material at temperatures between 125 and 200 °C. In the final step, the surface methoxy formed at the active sites is extracted with water to form methanol. The active catalyst materials used in this stepwise approach were either Fe-ZSM-5 activated by N_2O or Cu-ZSM-5 activated by molecular oxygen. The proposed active sites in the case of the N_2O activated Fe-ZSM-5 catalysts were the bridging oxygen(μ_2) of the Fe-oxo species which facilitates hydrogen atom abstraction from methane.[14,15] In a similar way, the activation of Cu-ZSM-5 by molecular oxygen enabled the formation of bis(μ-oxo) di-copper clusters and these sites have been proposed to activate and convert methane to methanol. This stepwise approach has been extended to a range of additional zeolite frameworks which have shown an even higher methanol yield than those of the initial studies. Cu-mordenite catalysts when operated in a two stage non-closed catalytic cycle can form CH_3OH.[16-18] An oxidised Cu species is reacted with CH_4 to form a surface methoxyl which is subsequently extracted at a lower temperature with water. van Bokhoven and co-workers demonstrated[19] that Cu-mordenite can oxidise CH_4 with a continuous flow of H_2O to produce methanol; however, this reaction is stoichiometric rather than catalytic as the turnover is 0.21 mol CH_3OH/mol Cu. Despite the promising results yielded by this approach, Bokhoven and co-workers have reported[14] that significant improvements are still needed for the industrial utilisation of this stepwise process, particularly in the areas of (i) reactor design, (ii) development of materials that allow faster cycling, (iii) utilisation of lower amounts of water/acetonitrile during the extraction process to reach a higher concentration of methanol in the extraction solution, and (iv) improving the efficiency and economic viability of the stepwise process.

3. SELECTIVE METHANE OXIDATION USING AuPd ALLOYS WITH H_2O_2

An alternative low temperature approach as proposed by our group was the utilisation of H_2O_2 as the alternative oxidant under mild reaction conditions (50-70 °C) using water as the preferred solvent with all the initial experiments being conducted in batch autoclave reactors. It is known that methane monoxygenase can operate and activate methane selectively at similar temperatures (around 50 °C) with high selectivity to methanol and using water as the desired solvent using a di-iron cluster as the active site. In the methane monooxygenase the hydroperoxide oxidant is delivered by a cofactor that reduces molecular oxygen. Removal of the cofactor and using H_2O_2 only gives a very slow oxidation. We considered that there was considerable scope to design catalysts that can activate and convert methane to methanol under mild reaction conditions while avoiding overoxidation to CO_2. Sorokin and co-workers have also reported the activation of methane using H_2O_2 under mild conditions using a μ-nitrido iron phthalocyanine complex grafted onto a silica support as a possible bio-inspired heterogeneous catalyst.[20,21] However, this catalyst was unstable with significant leaching of iron occurring during the reaction and methanol was also formed by oxidation of the phthalocyanine complex.[22]

Our team was one of the winners of the 2007 Dow Methane Challenge[23] and the approach we initially adopted was based on catalysis by gold. We had previously shown that the combination of gold and palladium to form supported bimetallic nanoparticle catalysts were effective catalysts for the direct synthesis of H_2O_2[24] and the selective oxidation of benzyl alcohol to benzaldehyde.[25] We considered that alcohol oxidation and direct H_2O_2 synthesis can be linked through the formation of a hydroperoxy species in solution and that these hydroperoxy species could be useful oxidants as is the case for methane monooxygenase. Based on this observation, our initial work on low temperature selective methane oxidation investigated the performance of Au-Pd nanoparticles supported on TiO_2 in an aqueous solvent using H_2O_2 at 50°C.[26] Catalysts were prepared by impregnation and the most active contained a 5 wt.% metal loading (1:1 Au:Pd). The catalyst was highly selective towards methyl-hydroperoxide and methanol (>90%), although the productivity was relatively low ($0.28\ mol_{(products)}kg_{(cat)}^{-1}h^{-1}$). Changing the support material from TiO_2 to CeO_2, SiO_2, Al_2O_3 or carbon did not result in an improved performance. The primary reaction product was methyl-hydroperoxide which was subsequently converted to methanol. Once generated methanol was further oxidised to formic acid, which was a major route to the formation of carbon dioxide. In addition, carbon oxides could be formed by direct conversion of methyl-hydroperoxide and methanol, allowing us to propose the reaction scheme presented in Figure 2.

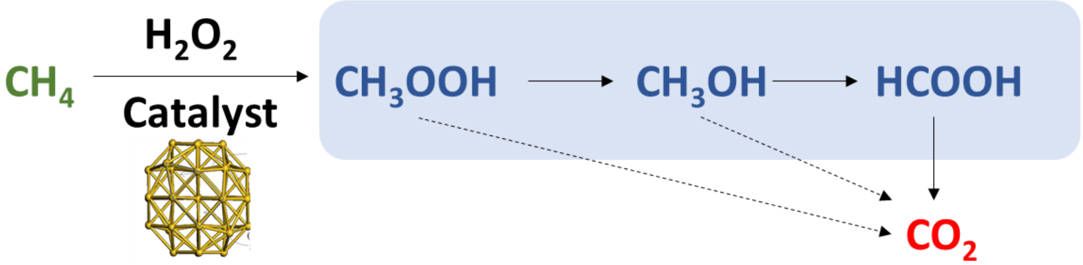


Figure 2. Methane oxidation using H_2O_2 over Au-Pd/TiO_2 supported catalysts.

Since gold-palladium bimetallic nanoparticle catalysts are effective for the direct synthesis of H_2O_2 from H_2/O_2,[27-29] and because they are also selective for methane oxidation with H_2O_2, we postulated that it should be conceptually possible to generate hydroperoxy radicals *in-situ* from hydrogen and oxygen and subsequently use them to selectively oxidise methane. Hence, the Au-Pd/TiO_2 catalyst prepared by an impregnation route was investigated using a mixture of methane, hydrogen and oxygen, diluted with nitrogen to ensure our experiments were conducted outside of the flammable limits.[26] The *in-situ* hydroperoxy approach demonstrated a clear advantage as methanol selectivity was increased to 68% from 49% when using preformed H_2O_2, whilst the productivity remained constant. When the reaction was carried out with molecular oxygen (i.e. without co-fed hydrogen, and without H_2O_2), there was no selectivity towards oxygenated products. In these initial studies the decomposition of H_2O_2 or the non-selective utilisation of hydrogen in the in situ peroxy experiments remained the major problem.

In more recent work, we have investigated varying the preparation procedure for the Au-Pd/TiO_2 catalyst, to attempt to improve the productivity of methane oxidation using H_2O_2. Gold-palladium bimetallic nanoparticles were deposited onto TiO_2 using a stabiliser-free colloidal preparation immobilisation route.[30] In particular, thermal treatment of the TiO_2 support prior to deposition of the metal nanoparticles, and thermal treatment of the supported catalyst, were used as strategies to control the mean metal particle size and the ratio of rutile/anatase and the metal particle size respectively. High temperature thermal treatments were found to be the most beneficial, with TiO_2 calcination at 800°C for 3 h prior to metal deposition, followed by the same treatment after metal deposition producing the best catalyst. A productivity of 0.677 $mol_{(products)}kg_{(cat)}^{-1}h^{-1}$ was achieved, whilst the H_2O_2 consumption remained high.

Although our bimetallic gold-palladium supported catalysts showed promising activity for methane selective oxidation, they still exhibited relatively low rates of product formation. In an attempt to improve on the methane oxidation activity of bimetallic Au-Pd catalysts, trimetallic Au-Pd-Cu catalysts supported on TiO_2 were investigated for low temperature selective oxidation of methane with H_2O_2 at 50 °C. Encouragingly, the rate of methane oxidation using the Au-Pd-Cu/TiO_2 catalysts was increased by a factor of 5, when compared to Au-Pd/TiO_2. Furthermore, the selectivity to oxygenated products remained very high (>95%), demonstrating that considerable scope still exists for design of multi-component metal nanoparticles for selective methane oxidation at low temperatures. However, as the catalyst productivity increases using such nanoparticle-alloy catalysts, there is also a general increase of the amount of H_2O_2 consumed with an associated decrease in the efficiency of H_2O_2 utilisation.

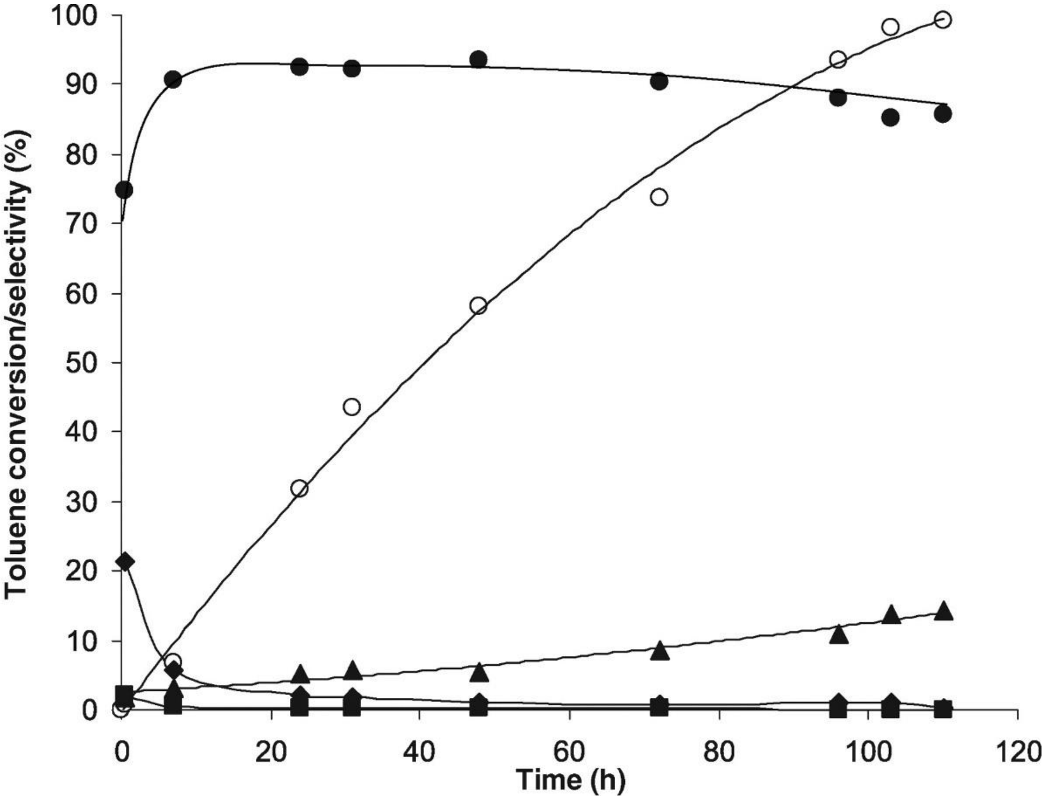


Figure 3. Toluene conversion using 1 wt% AuPd/C,160°C; P_{O2}0.1 MPa; toluene (20 ml); catalyst (0.8 g,) ○ conversion, ■ benzyl alcohol selectivity, ◆ benzaldehyde selectivity, ▲ benzoic acid selectivity, ● benzyl benzoate. Reproduced with permission from ref 31. Copyright 2011 AAAS.

As part of our studies on C-H bond activation with AuPd alloys we decided to investigate the oxidation of the methyl group in toluene as a more reactive model for such oxidation reactions.

For this we used molecular oxygen as the terminal oxidant.[31] By elevating the temperature we found that toluene could be oxidised in a solvent-free reaction to form benzyl benzoate in very high yields (Figure 3). The high selectivity to benzyl benzoate rather than forming benzoic acid is considered to be due the reaction of two of the initial products namely benzyl alcohol and benzaldehyde to form a hemiacetyl that is subsequently oxidised to the ester. We reasoned that if similar chemistry could be carried out with methane in place of toluene this could form the basis of a new reaction. Unfortunately, this has not been found to be possible to date but this is still an area of active research.

4. METHANE OXIDATION USING ZSM-5 CATALYSTS WITH H_2O_2

As metal-support interactions can be a key factor in heterogeneous catalysis, we decided the nature of the support required more careful investigation. Our work based around bimetallic gold-palladium nanoparticles for methane selective oxidation largely focused on using TiO_2 as a support, and we developed an understanding that the metal support interface was largely responsible for the excessive decomposition of H_2O_2, resulting in the low efficiency of its use to effectively oxidise methane. Consequently, our strategy of catalyst design started to focus on identification of more effective catalyst support and in particular an acidic support could be beneficial in stabilising H_2O_2 as acid is often utilised as a stabiliser during H_2O_2 synthesis. At the same time, by drawing on the analogy with methane monooxygenase, we also postulated that confinement of the reactants would be a beneficial factor in bringing together important small molecular reacting species with the active sites in the catalyst. This led us to investigate microporous zeolites as supports for selective methane oxidation catalysts.

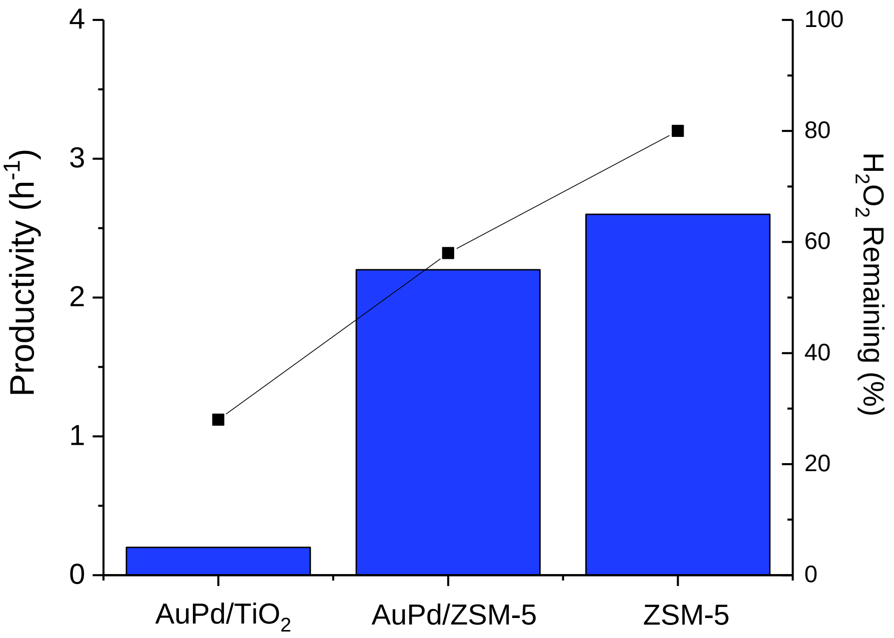


Figure 4. Methane oxidation with AuPd and ZSM-5 catalysts showing that ZSM-5 by itself is a superior catalyst. *Reaction conditions:* Catalyst (27mg, calcined 400^{o}C, 3 h); $P_{(CH4)}$:30.5 bar; [H_2O_2]:0.5M; 50^{o}C; 30 min; 1500 rpm.

Although we initially investigated ZSM-5 as a support for the Au-Pd nanoparticles, to our surprise it quickly became evident that ZSM-5 was more active *without* being decorated with Au-Pd nanoparticles (Figure 4). Indeed, H-ZSM-5 (SiO_2/Al_2O_3 = 30) calcined at 550°C was identified as the most active Si:Al ratio from a range of ZSM-5 materials we investigated. Under standard reaction conditions (Figure 4), ZSM-5 gave a conversion of 0.3% with 95% selectivity towards oxygenated products of methyl-hydroperoxide, methanol and formic acid.[32] The reason for the enhanced activity was due to some extent to the decrease in decomposition of H_2O_2.

To further elucidate the identity of the catalytically active species, elemental analysis was employed, showing that the ZSM-5 contained a small, but nevertheless significant amount, of iron in the zeolite framework. When additional iron was added in the form of extra-framework species, there was a further increase in the methane conversion to 0.7% and the high selectivity towards methanol maintained, with only low quantities of carbon oxides formed. Spectroscopic investigations using EXAFS revealed that iron was present as a di-iron complex containing antiferromagnetically coupled high-spin octahedral Fe^{3+} centres. Combining data from characterisation experiments with DFT molecular modelling studies we proposed a closed catalytic cycle for methane selective oxidation as shown in Figure 5.

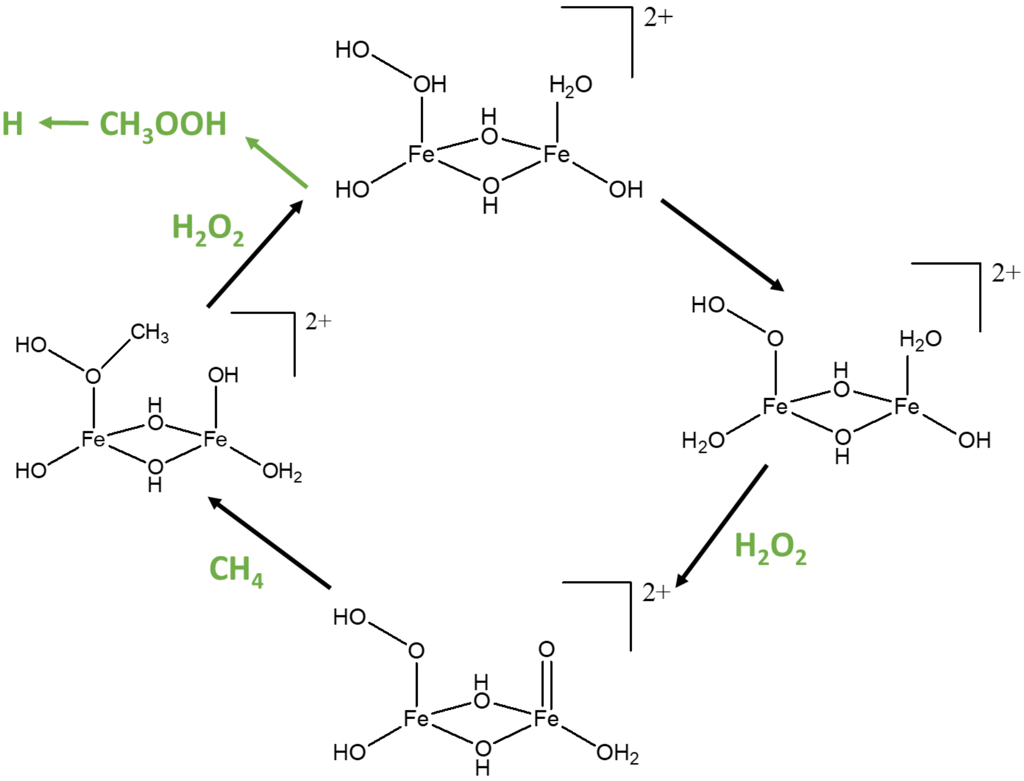


Figure 5 Proposed cycle for the catalytic selective oxidation of methane by a binuclear iron species in ZSM-5.

In common with our previous observations on methane oxidation with H_2O_2 using Au-Pd/TiO_2 catalysts, methyl-hydroperoxide was also the primary reaction product over the Fe-ZSM-5 catalyst. Subsequently, the methyl-hydroperoxide formed can then undergo selective conversion to methanol, or a non-selective conversion to formic acid. Formic acid is also produced by consecutive oxidation of methanol, and once formed formic acid is the precursor to form undesirable carbon oxides. The catalytic cycle requires two equivalents of H_2O_2 to produce a single equivalent of methanol, providing an upper limit on the efficiency of H_2O_2 use.

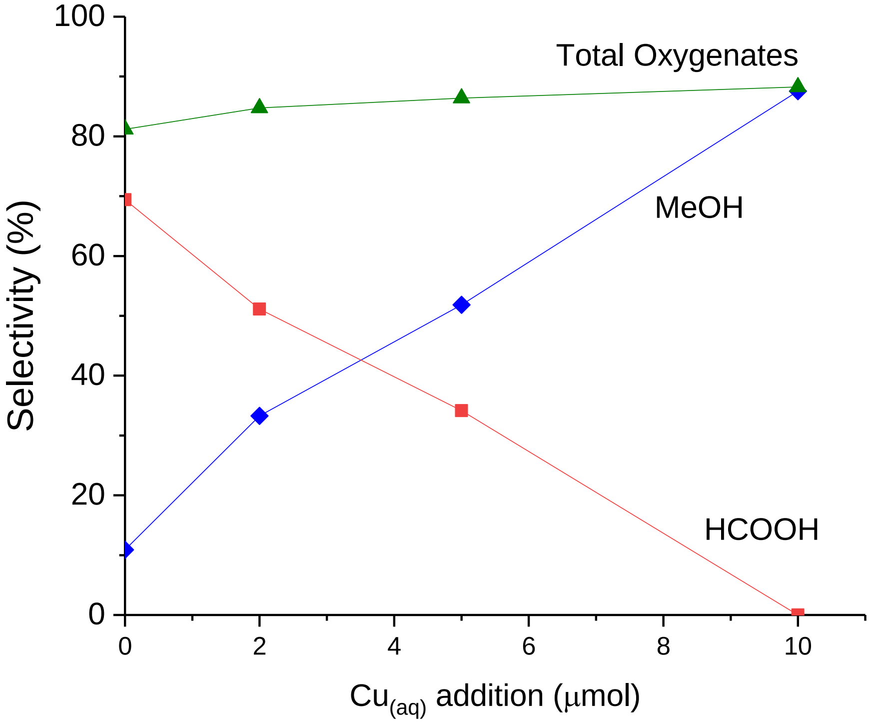


Figure 6. Effect of adding Cu^{2+} to a reaction catalysed by Fe-ZSM-5. *Reaction conditions:* $P(CH_4)$:30.5 bar; $[H_2O_2]$:0.5M; 50°C; 30 min; 1500 rpm.

Increasing the iron concentration further increased the catalyst activity, however, it had a deleterious effect on methanol selectivity.[32] For a 2.5 wt.% Fe-ZSM-5 (30) catalyst a typical product distribution was 1% methyl-hydroperoxide, 10% methanol, 72% formic acid and 17% carbon oxides, hence impeding over-oxidation of methanol was an important factor to increase its yield. A key discovery was the importance of adding copper to the Fe-ZSM-5 catalyst. Incorporating copper, either as an extra-framework species or as homogeneous Cu^{2+} ions in solution (Figure 6), markedly increased the selectivity to methanol whilst maintaining methane conversion.[32] We found that the acidity of ZSM-5 was leading to a higher level of H_2O_2 decomposition and that by using the non-acidic silicalite-1 framework improved results could be achieved. Adding Cu in an additional solid to the heterogeneously catalysed reaction had a marked effect (Figure 7). With a Fe-silicalite catalyst without Cu added it is possible to achieve a 10% methane conversion with a total oxygenate selectivity of 96% but this was mainly formic acid and only 8% methanol was observed. Addition of Cu-slilicate, and inactive material in this reaction. Enables 93% selectivity to methanol to be achieved at 9.5% conversion. The addition of Cu^{2+} clearly hindered the oxidation of methanol to formic acid. EPR studies demonstrated that the Cu^{2+} species were acting as scavengers for hydroxyl radicals, which were responsible for the over-oxidation of methanol to formic acid.[23] The proposed reaction scheme operating with iron and copper added to the ZSM-5 framework is shown in Figure 8. We demonstrated that these bimetallic catalysts could be used in a continuous flow reactor without deactivation but with 93% methanol selectivity at 0.5% conversion.[33] The mechanism using this catalyst does not involve the formation of surface bound methoxyl species which has proved problematic to desorb as methanol in other approaches.

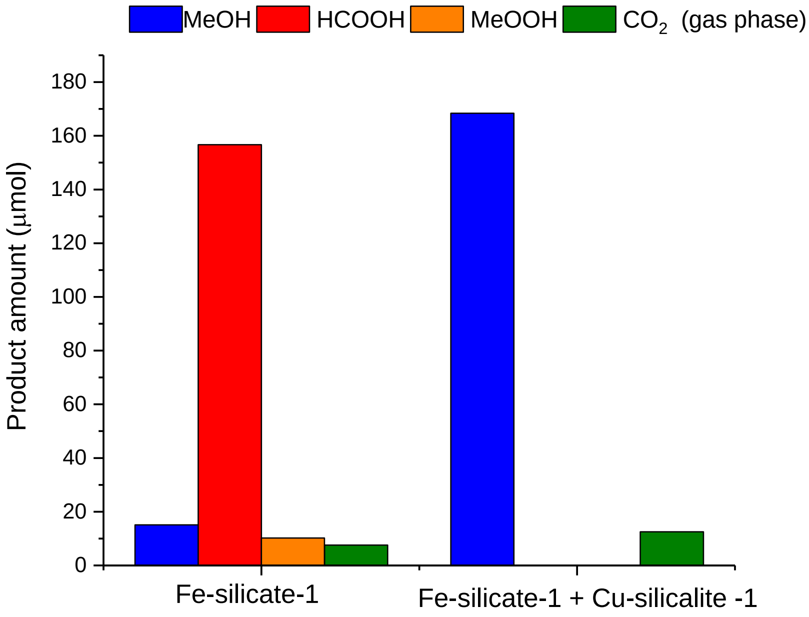


Figure 7. Addition of Cu-slicalite-1 to Fe-silicalite-1 switches the reaction selectivity from formic acid to methanol. Reaction conditions: P(CH_4)3 bar; [H_2O_2]1.0M; 70°C, 30 min; 1500 rpm.

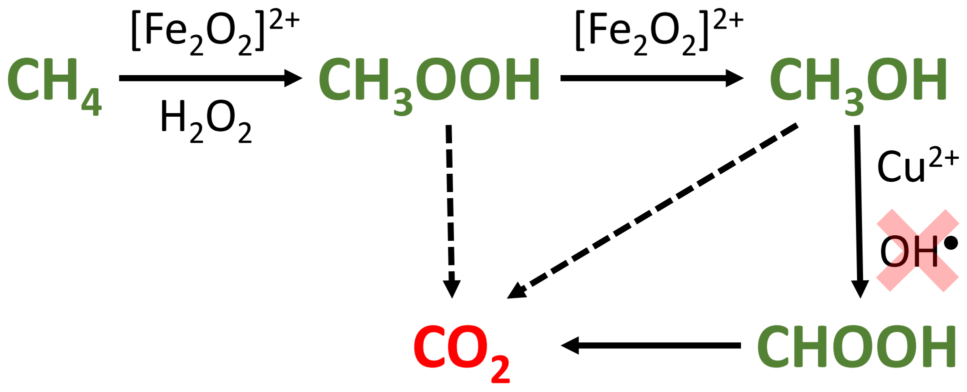


Figure 8. Proposed reaction scheme for copper-iron-ZSM-5 catalyst.

5. A RETURN TO AuPd CATALYSTS

In the earlier part of this account, we demonstrated that we could achieve closed catalytic cycles for low temperature selective oxidation of methane using either supported Au-Pd catalysts, Cu/Fe/ZSM-5 or Cu-slicalite-1 + Fe-silicalite-1 catalysts. These oxidations were carried out using H_2O_2 as oxidant. Unfortunately, the use of H_2O_2 is economically unfavourable, as its cost can be greater than methanol. Hence, the goal is to selectively oxidise methane to methanol using molecular oxygen. As noted earlier we could successfully oxidise the methyl group of toluene using Au-Pd/TiO_2 and AuPd/C catalysts using molecular oxygen in in a solvent-free reaction.[31] A direct analogy can be drawn between the selective oxidation of the primary C-H bond in toluene and the primary C-H bond in methane, and our study demonstrated the fundamental fact that selective oxidation of a primary C-H bond could be achieved under relatively mild conditions using molecular oxygen. However before switching all of our attention to using molecular oxygen, we needed to understand why the efficiency of H_2O_2 usage was often very poor, especially when using TiO_2 supported Au-Pd catalysts, as they have been so effective in direct H_2O_2 synthesis.

Against this background, we investigated H_2O_2 decomposition and methane selective oxidation using H_2O_2 over a range of sol immobilised gold-palladium nanoparticle catalysts on a range of different supports. To differentiate the relative contributions to H_2O_2 decomposition by the support and the colloidal nanoparticles, decomposition over the support only and unsupported colloidal nanoparticles were studied in addition to the regular sol-immobilised catalysts. Interestingly, H_2O_2 decomposition was very low over the unsupported AuPd colloid as well as a range of, and it was only when the colloid was immobilised on the support surface that the peroxide decomposition rate was enhanced significantly (Figure 9). This led us to intensively investigate the polyvinylpyrrolidone (PVP) stabilised Au-Pd colloidal suspension for methane oxidation by H_2O_2, and it was found to be extremely active and selective towards methanol and oxygenates at 50°C.[34] The choice of using PVP was crucial as the PVP does not decompose during the oxidation reaction to produce methyl-hydroperoxide, methanol or formic acid. In contrast, use of polyvinyl alcohol as the colloid stabiliser does give rise to methanol in a blank reaction. Comparing the colloidal suspension with the same colloidal nanoparticles supported on TiO_2, the unsupported colloidal catalyst was an order of magnitude more active and produced methyl-hydroperoxide and methanol with over 90% selectivity. The unsupported colloidal catalyst was also very stable, displaying no evidence of metal leaching or nanoparticle agglomeration, and the methane oxidation performance was consistently repeatable when fresh aliquots of H_2O_2 were added (Figure 10). Although there was some sintering of the AuPd nanoparticles on use (Figure 11) the catalyst retained activity. The initial experiments were conducted with methane and H_2O_2 alone but we realised the H_2O_2 was also decomposing during reaction giving rise to some O_2 and so we decided to add O_2 to the reaction and we observed that the amount of oxygenated products increased (Figure 10). Use of $^{18}O_2$ showed that the oxygen in the methanol product originated from molecular oxygen (Figure 10) and this represented the first example of low temperature selective oxidation of methane to methanol where molecular oxygen is incorporated. We showed that by decreasing the amount of H_2O_2 added we could produce more mol oxygenates as products when compared to the mol of H_2O_2 added. We referred to this as the gain factor (Figure 10) which with appropriate reaction conditions we could reach ca. 1.6.

We investigated the mechanism for this reaction with the Au-Pd nanoparticles using EPR spectroscopy and we identified using spin trapping experiments that H_2O_2 forms hydroxyl radicals in solution by interaction with the nanoparticle. We concluded that the interaction of H_2O_2 with the AuPd colloidal nanoparticle leads to a hydroxyl radical flux that reacts with CH_4 in solution as this will be in excess. This will lead to the generation of methyl radicals which can react with O_2 to form methyl-hydroperoxide as the primary product which then reacts further to form methanol with the oxygen in the C-OH bond originating from O_2. We observed that at least 70% of oxygen in the methanol product originated from molecular oxygen as some O_2 is produced from H_2O_2 decomposition in a parallel pathway. Based on our experimental observations and identification of radical species in the reaction media we were able to propose a reaction scheme to rationalise our observations (Figure 12). In this reaction the H_2O_2 acts as an initiator to produce very reactive hydroxyl radicals that activate methane. Once all of the H_2O_2 is consumed the reaction ceases, but addition of further H_2O_2 starts the reaction again (Figure 10). Although it was possible to dramatically increase the efficiency of H_2O_2 use, it was still an essential ingredient, as removing it completely and carrying out the reaction with molecular oxygen alone resulted in no methane oxidation. Hence, we propose that the H_2O_2 plays a crucial role in the formation of hydroxyl radicals for molecular methane activation and that the unsupported bimetallic colloidal nanoparticle is efficient at producing these radicals.

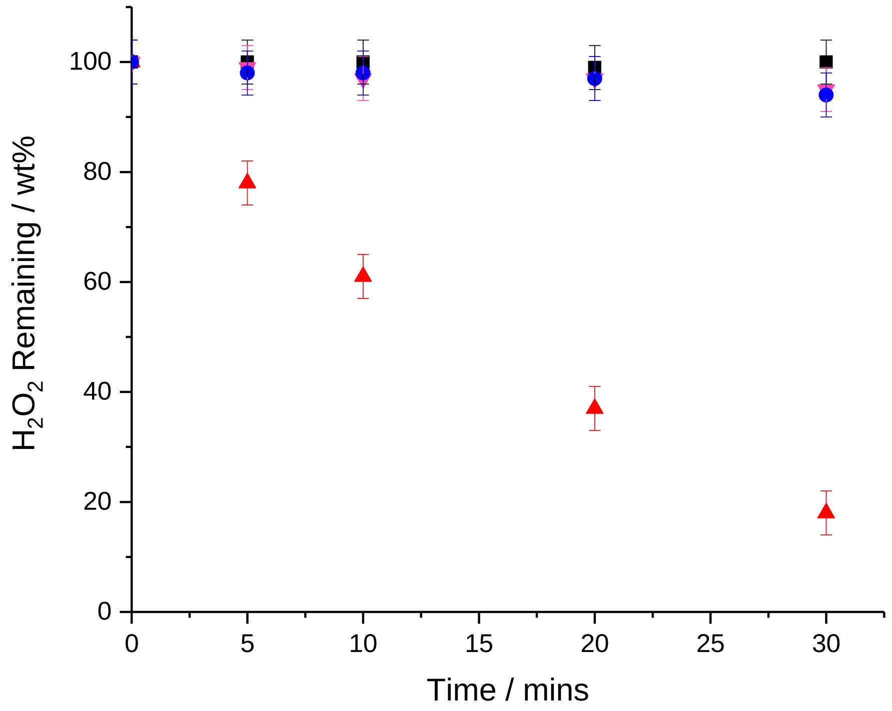


Figure 9. Decomposition of 4 wt% H_2O_2 in H_2O (10 mL) with stirring at ambient temperature and pressure. Key: ■ water; ▼ AuPd colloid (0.66 μmol metal); ● TiO_2 (9mg); ▲ AuPd/TiO_2 (0.66 μmol metal, 9mg).

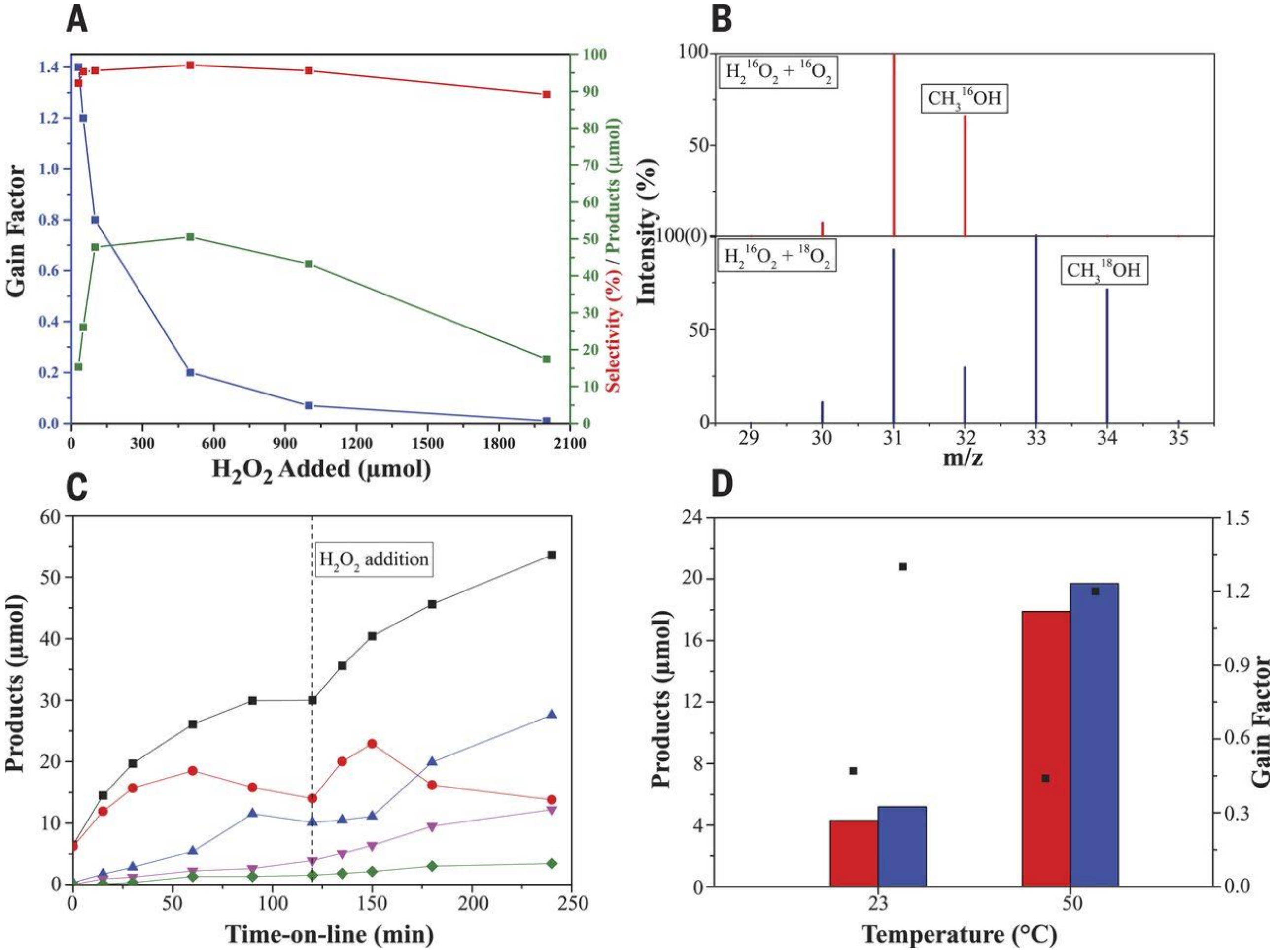


Figure 10. Methane oxidation using unsupported AuPd colloids. (A) Gain factor (blue line), selectivity (red line) and total amount of products (green line) as a function of the different amounts of H_2O_2 used. (B) GC-MS spectra of CH_3OH formed (m = 32 and 34 for $CH_3{}^{16}OH$ and $CH_3{}^{18}OH$ respectively) during methane oxidation via $H_2{}^{16}O_2$ + $^{16}O_2$ (*upper spectrum)* or $H_2{}^{16}O_2$ + $^{18}O_2$ (*lower spectrum*). (C) Time-on-line and AuPd colloid re-use study for the methane oxidation reaction employing 50 μmol H_2O_2 and 5 bar O_2 showing no induction period. Total products (black line), and individual products (CH_3OOH (red line), CH_3OH (blue line), HCOOH (pink line) and CO_2 (green line)), subsequent second addition of H_2O_2 is made at 20 min (D) Oxidation of CH_4 performed at 23° and 50°C with 50 μmol H_2O_2. The blue and red bars represent reactions performed with and without 5 bar O_2, respectively. The black squares (■) indicate their respective gain factors. Reproduced with permission from ref 34. Copyright 2017 AAAS.

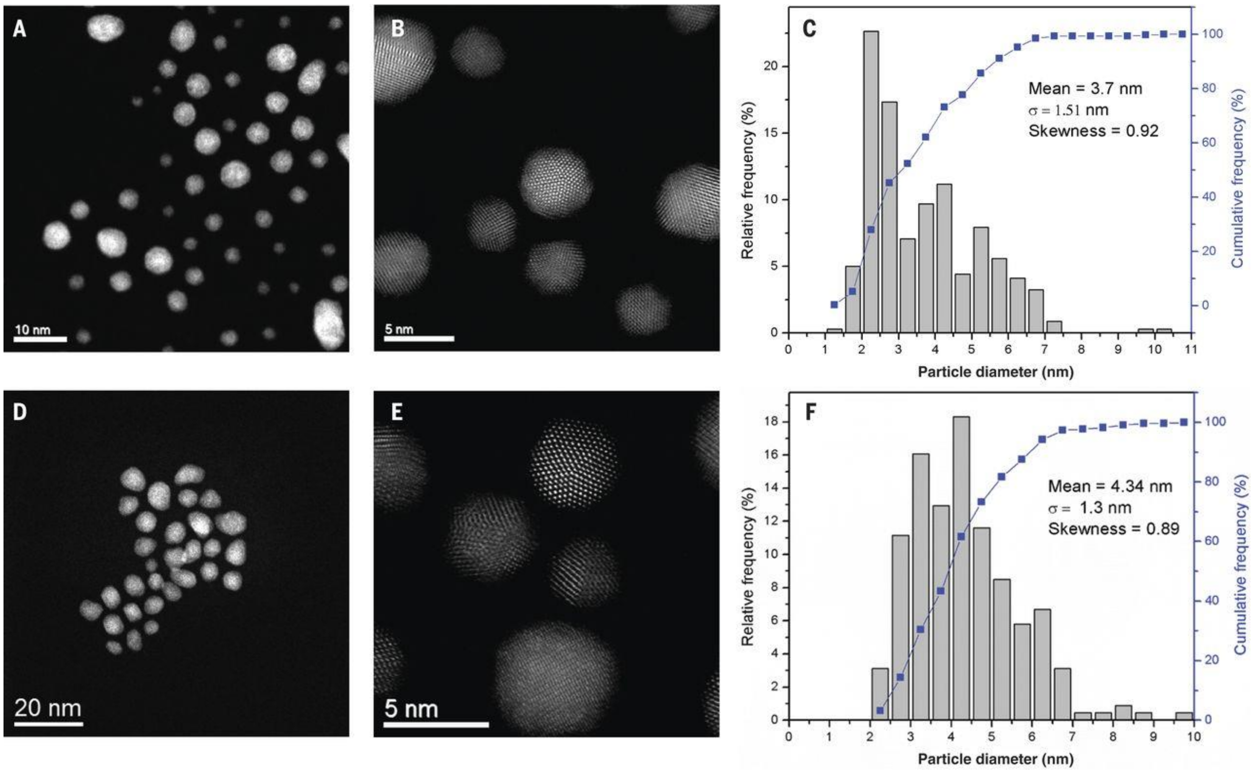


Figure 11. Representative HAADF images and particle size distributions for the unsupported AuPd-PVP sol in the fresh (A to C) and after a CH_4 oxidation reaction (D to F). Reproduced with permission from ref 34. Copyright 2017 AAAS.

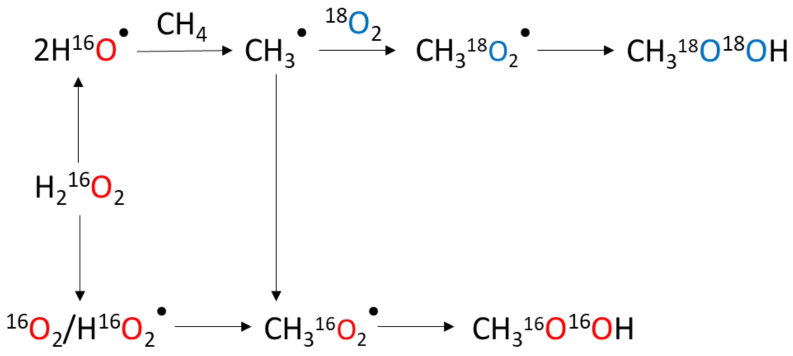


Figure 12. Proposed reaction scheme for methane oxidation using colloids in the presence of H_2O_2 and O_2.

6. CONCLUSIONS AND PERSPECTIVES

Using AuPd colloids and Cu promoted Fe-zeolites as catalysts we have shown that using H_2O_2 as an oxidant in water as the preferred solvent it is possible to oxidise methane to methanol in a closed catalytic cycle. At the time of these studies this advance was a step change but as methanol formation required excess H_2O_2 the advance was not of commercial interest. However, it is important that oxygen is used as the oxidant rather than H_2O_2. In our investigations we also showed that reacting methane with H_2 and O_2 to form H_2O_2 in situ also was effective. In this case the H_2 is being used as a co-reductant and this is very similar to a recent study by Stephanopolous and co-workers[35] where methane was oxidized with O_2 with CO as the co-reductant. A related study by Ma and co-workers also shows the importance of CO as a co-reductant for ethane oxidation. In the future we need to identify catalysts and reaction conditions where methane can be oxidized with O_2 without the requirement for a co-reductant. Recent studies by Roman-Leshkov[37,38] have shown that Cu-mordenite can be used for a continuous flow gas phase oxidation of methane using O_2 and water. The turn-over numbers are only just catalytic, but it shows that a continuous catalytic cycle can be achieved; however, this requires immense improvement. Very recently it has been found that water is the source of the oxygen in the methanol and O_2 is required to close the catalytic cycle by oxidizing Cu.[39]

Considering using H_2O_2 as an initiator for generating $^{\bullet}CH_3$ we consider that other routes to generate $^{\bullet}CH_3$ could be used. Rather than using H_2O_2, it would be highly desirable to devise a method of coupling the AuPd colloidal catalyst with a photochemical[40] or electrochemical fuel cell[41] to generate $^{\bullet}OH$ for H abstraction to facilitate $^{\bullet}CH_3$ radical formation. If a flux of $^{\bullet}CH_3$ radicals can be established at 150-200 ^{o}C and quenched with O_2 this could provide the basis for a viable new route to methanol. Hence, the overarching remaining research is to identify catalysts that can activate methane with O_2 in a continuous flow reactor enabling this flux of $^{\bullet}CH_3$ radicals to be continuously produced enabling a concentrated product stream of methanol to be produced; the approach we describe presents a starting point for this quest.

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Notes

The authors declare no competing financial interest.

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