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Aqueous Au-Pd colloids catalyze selective CH₄ oxidation to CH₃OH with O₂ under mild conditions

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Abstract

The selective oxidation of methane, the primary component of natural gas, remains an important challenge in catalysis. Using colloidal gold-palladium nanoparticles rather than the same nanoparticles supported on titanium oxide, we oxidized methane to methanol with high selectivity (92%) in aqueous solution at mild temperatures. Using isotopically labeled O_2 as an oxidant in the presence of H_2O_2 , we demonstrate that the methanol produced incorporated a substantial fraction (70%) of gas-phase O_2 . More oxygenated products were formed than H_2O_2 consumed, suggesting that the controlled breakdown of H_2O_2 activates methane which subsequently incorporates molecular oxygen through a radical process. If a source of methyl radicals can be established, then the selective oxidation of methane to methanol using molecular oxygen is possible.

In industry, CH₄ is used as a feedstock by first indirectly converting it to methanol (CH₃OH) via the production of synthesis gas (CO + H₂) at high temperatures and pressures, an expensive and energy intensive process (1). The direct oxidation of CH₄ to CH₃OH, which is challenging as overoxidation must be avoided, has been the subject of intensive study for many decades (2,3). Cyclic gas phase oxidation of CH₄ with metal-exchanged zeolite catalysts with O₂, N₂O or H₂O require high temperatures (200° to 500°C) to activate the oxidant and desorb product CH₃OH (4-8). Liquid-phase reactions typically use milder reaction conditions; however, a closed catalytic cycle is often not achieved. Periana and co-workers reported that electrophilic metals such as Hg and Pt-complexes are active for methane oxidation (9,10). These systems require high temperatures (180°C) and strongly acidic media such as oleum to facilitate the reaction. Oxidation products are trapped as methyl-bisulphate to protect against overoxidation, which are then hydrolyzed to release methanol and SO₂. This catalyst was later heterogenized using a solid carbon framework to anchor the Pt catalyst (11). Similarly, cationic Au in solution can oxidize CH₄ in the presence of even stronger oxidizing agents such as selenic acid which prevents the formation of metallic gold (12).

More benign oxidants such as hydrogen peroxide (H₂O₂) with Fe-complexes have also been demonstrated to oxidize C-H bonds (13). Yuan *et al.* previously showed activation of CH₄ with dissolved gold chloride and H₂O₂ at 90°C, but observed agglomeration and precipitation of the catalyst from the solution (14). Pd²⁺ was also reported to catalyze CH₄ oxidation to methyltrifluoroacetate using peroxytrifluoroacetic acid generated by H₂O₂ and trifluoroacetic anhydride (15). Similarly, heterogeneous catalysts based on Fe-ZSM-5 and Cu modified ZSM-5 have been used for methane activation to methylhydroperoxide (CH₃OOH), CH₃OH, and formic acid (HCOOH) in aqueous media at 50 °C (16). H₂O₂ is considered a desirable benign oxidant, second only to molecular O₂ for this reaction, as the side decomposition product is water.

We have also reported CH₄ oxidation using supported gold-palladium nanoparticles (NPs) under mild aqueous conditions using H₂O₂ as oxidant at 50 °C. The reaction proceeded through a radical mechanism as both methyl (•CH₃) and hydroxyl (•OH) radicals were observed by electron paramagnetic resonance (EPR) spectroscopy (17). However, the relatively high cost of H₂O₂ for even stoichiometric oxidation of CH₄ makes it difficult to envisage a chemical process based on this chemistry that would be economically viable.

Incorporation of O₂ into the primary oxidation products would represent substantial progress toward a feasible CH₄ to CH₃OH process. Here we report this reaction under mild conditions using colloidal AuPd NPs in the presence of both H₂O₂ and O₂. We show that by removing the support material from the catalyst, a substantial improvement in activity is achieved and O₂ is incorporated into the primary products, with the selectivity to primary products reaching >90% with minimal CO₂ produced.

We prepared polyvinylpyrrolidone (PVP) stabilized AuPd (1:1 molar ratio) colloids and supported catalysts by immobilizing the colloid on TiO₂ (see Supplementary Material for all experimental details) (18, 19). We investigated CH₄ oxidation was investigated in water with H₂O₂ as oxidant at 50 °C and 30 bar CH₄ for 30 min (19). With the supported colloid material, 1% AuPd/TiO₂ catalyst (Table 1, Entry 1), minimal reaction products were observed (primary oxygenate selectivity 26%) as determined by quantitative nuclear magnetic resonance (NMR) analysis (16,19). In this experiment, most of the H₂O₂ was decomposed (73%). A gain factor, defined as the mol oxygenate produced /mol H₂O₂ consumed, was calculated to be 2×10^{-3} .

This high rate of H₂O₂ degradation was considered detrimental to the reaction either by (i) the termination of reactive radical chains caused by radical concentrations being too high or (ii) by consumption of H₂O₂ at such a high rate that it does not allow sufficient interaction with the low amount of solubilized CH₄. We investigated which component of the catalyst was responsible for the high H₂O₂ degradation rates. We observed (Fig. S1) that the degradation of H₂O₂ at room temperature under atmospheric pressure was low in the presence of bare TiO₂ and unsupported AuPd colloidal NPs. Only when the AuPd NPs were supported on TiO₂ did the catalyst exhibit a high rate of H₂O₂ degradation, suggesting that either the interfacial sites at the support/metal interface (20) or a change in the morphology of the NP (21) upon immobilization led to the high H₂O₂ degradation rates (22).

This finding, coupled with the known ability of high surface area TiO₂ to quench radical reactions (23), led us to evaluate the ability of unsupported PVP-stabilized AuPd colloids to catalyze CH₄ oxidation. We utilized 1000 μmol H₂O₂, and using the same amount of metal as in the supported catalyst, observed substantially more product (15.7 μmol) compared to the supported catalysts (Table 1, entry 2), while much less H₂O₂ (38%) was consumed. Furthermore, the primary products, CH₃OOH and CH₃OH, were produced with 90% selectivity. The colloidal catalyst was an order of magnitude more efficient than the solid

AuPd/TiO₂ catalyst with respect to products generated per unit amount of H₂O₂ consumed, with a gain factor of 3×10^{-2} compared to 2×10^{-3} .

The presence of CH₃OOH, CH₃OH, HCOOH and CO₂ in the product stream suggests a consecutive oxidation pathway, as previously observed (16, 17). Experiments with isotopically labeled ¹³CH₄ confirmed that the carbon source was CH₄ and not the organic stabilizer, PVP, present in the colloidal solution (Fig. S2). Carbon-based products containing the label were present in quantities corresponding to the amount of labeled ¹³CH₄ present; in addition, no carbon-based products were observed when CH₄ was not present (Table S1).

STEM-HAADF (Scanning transmission electron microscopy- high angle annular dark field) imaging of the fresh AuPd-PVP colloids showed them primarily to have multiply-twinned icosahedral structures, although some cuboctahedral NPs were also detected (Fig. 1, A and B). The AuPd-PVP colloids ranged in size between ~2 and 12 nm and had a mean diameter of 3.7 nm (Fig. 1C). STEM-XEDS (X-ray energy dispersive spectroscopy) compositional analysis showed the AuPd-PVP NPs to have a similar Au:Pd ratio irrespective of their size (Fig. S3). Transmission electron microscopy (TEM) analysis of the sol-immobilized AuPd/TiO₂ samples (Fig. S4) showed the AuPd NPs to have a similar size, morphology, and composition to their colloidal counterparts. X-ray photoelectron spectroscopy (XPS) analysis of both the supported and colloidal samples showed that both Au and Pd were metallic in nature with minor PdCl₂ components detected in the colloidal samples (Figs. S5 & S6).

Previous EPR spin-trapping studies revealed the presence of both •OH and •CH₃ radicals during reactions with a sol-immobilized AuPd catalyst suggesting that the reaction mechanism is radical based (17,24). The observation that the primary product was CH₃OOH implies that the primary termination step is either between •CH₃ and •OOH radicals or from recombination of •CH₃ with dissolved O₂ in the solution originating from the decomposition of H₂O₂ (25). In the case of the unsupported colloidal catalyst, which decomposes H₂O₂ at a much slower rate but makes substantially more products, we rationalized that •CH₃ was being produced over a longer time-scale and that adding O₂ to the reaction mixture would promote oxygen incorporation through the generation of •CH₃OO radicals. The reaction of •CH₃ with O₂ has been reported to occur at high rates in gas-phase reactions (26). The addition of 5 bar of O₂ (Table 1, Entry 3) to the reaction resulted in an increased product yield (26.8 μmol) compared to the H₂O₂ only reaction (Table 1, Entry 2) while maintaining a high selectivity to primary oxygenates (95%). The gain factor also remained an order of magnitude higher

than that of the supported catalyst and was more than doubled that of the colloidal catalyst with H₂O₂-only. These results suggest that the presence of additional O₂ (beyond that originating from H₂O₂ decomposition) promoted the termination steps that generate primary products.

To demonstrate the incorporation of O₂ into the primary products using the colloidal catalyst at 5 bar, ¹⁸O₂ was added to the reaction mixture. Solutions from isotopic labeling reactions were analyzed by gas chromatography-mass spectrometry (GC-MS) which resulted in the degradation of the CH₃OOH primary oxidation product to CH₃OH **due to the high injection temperature**; however, good agreement was observed between the combined amount of CH₃OOH and CH₃OH determined by NMR and the amount of CH₃OH determined by GC-MS (Fig. S7). Mass spectrometry analysis of the reactions using H₂¹⁶O₂ and ¹⁸O₂, revealed that CH₃OH mass fragments containing the ¹⁸O label were responsible for 51% of the observed signal. (Fig. S8). Reactions in the absence of H₂O₂ at 50 °C (Table 1, Entry 4) showed no generation of oxygenated products confirming that H₂O₂ was a necessary ingredient for the reaction to take place. These results show that under mild aqueous reaction conditions, colloidal AuPd NPs can catalyze the reaction of H₂O₂ + CH₄ + O₂ with incorporation of O₂ into the primary reaction products.

We investigated decreasing the amount of H₂O₂ used in order to increase efficiency with the aim of generating more than one primary oxygenate species per molecule of H₂O₂ consumed. Figure 2A shows that by decreasing the amount of H₂O₂ from 2000 to 1000 μmol over 60 mins while maintaining 5 bar O₂ in the gas phase, the quantity of products formed initially increased from 18 to 43 μmol. This increase coincided with a reduction in the amount of H₂O₂ consumed (from 81% to 64%) indicating that a much greater efficiency was achieved with less H₂O₂ (a full breakdown of products is given in Table S2).

For a radical mechanism, an excess of H₂O₂ could likely cause termination of radical reactions and limiting product formation. A further reduction in the amount of H₂O₂ from 1000 to 500 μmol resulted in a slight increase in reaction products from 43 to 50 μmol suggesting the reaction had become limited by the availability of a reactant other than the radical species generated by H₂O₂, *i.e.*, either O₂ or CH₄ as determined by their solubility in the aqueous reaction media. Decreasing the amount of H₂O₂ further resulted in lower consumption of H₂O₂, but also led to a decrease in product formation, probably because of a reduction in the concentration of radicals generated. For the optimized amount of H₂O₂ (50

μmol) (Table 1, entry 5) the gain factor, reached 1.2, and represents an increase by three orders of magnitude over the corresponding 1% AuPd/TiO₂ sol-immobilized catalyst together with a higher selectivity to primary oxygenates. Furthermore, ¹⁸O₂ isotopic labeling experiments carried out under these optimized conditions again revealed substantial incorporation of ¹⁸O₂ (*ca.* 50%) into the primary products (Fig. S9).

In all the isotopically labelled reactions, CH₃OOH was decomposed to CH₃OH during the analysis. To ensure that thermal decomposition did not result in loss of the isotopic label, we quantitatively (confirmed by NMR analysis) reduced CH₃OOH to CH₃OH with NaBH₄ before performing GC-MS analysis. Using this procedure to prevent thermal decomposition of CH₃OOH in the presence of atmospheric oxygen, more than 70% of the CH₃OH detected showed incorporation of the ¹⁸O label (Fig. 2B). In the previous isotope labeling experiments, radical decomposition of labelled CH₃OOH in the presence of air and any remaining H₂O₂ resulted in an underestimate of the degree of ¹⁸O incorporation (27).

We conducted control experiments with unsupported monometallic Au and Pd colloids, along with the corresponding precursor metal chlorides using the same metal concentration of 6.6 μmol under identical reaction conditions (Table 1, entries 6-9). The monometallic Au and Pd colloids as well as the metal chloride precursors showed no activity for CH₄ oxidation. In fact, the HAuCl₄ and Pd colloid precipitated during the reaction. Hence, alloyed AuPd NPs show a synergistic effect in terms of activity and stability for this reaction. Recently, leaching of precious metals into reaction solutions to generate clusters containing 3 to 5 atoms has been implicated in catalytic reactions and characteristically show an induction period at the start of the reaction as the clusters form (28). HAADF-STEM analysis of the used colloid, showed some limited particle growth, but no evidence of subnanometer clusters or isolated Au-atoms was found either before or after 30 min of reaction under optimized reaction conditions (Fig. 1, D to F).

Furthermore, no substantial differences in the concentrations of cationic Au or Pd content were observed by XPS measurements on pre- or post-reaction AuPd-PVP colloids (Fig. S5). Time-on-line analysis indicates that there is no induction period associated with this reaction system and that products were generated even before the 50°C reaction temperature was reached. The catalyst being colloidal rather than a solid powder likely removed some mass transfer limits that create an induction period (Fig. 2C). This observation, coupled with inactivity of the monometallic Au- and Pd- sols and metal chloride precursors, indicates that

the bimetallic colloidal NPs are the active catalyst. The presence of reaction products at the start of the reaction (*i.e.*, just after completion of the heating ramp at 2.25°C/min) suggests that there is some activity at even lower temperatures. As the reaction proceeded, the total amount of product generated plateaus at ~120 min (Fig. 2C, Table S3) which coincided with the depletion of H₂O₂ from the reaction mixture. After adding more H₂O₂, more products were generated and a similar oxidation rate was achieved, indicating that the AuPd colloid was stable during this time (Fig. 2C, Table S4).

As the reaction time was increased further, some overoxidation of the primary products was observed, but the level of CO₂ production remained at < 4% of the total products formed over the entire 240 min duration (Table S4, Entry 4). We also conducted reactions at room temperature both with and without the addition of 5 bar O₂ as part of the reaction mixture and observed activity with similar levels of primary oxygenate selectivity (96%). A gain factor 1.35 is observed at room temperature in presence of O₂ (Fig. 2d) similar to the reaction performed at 50°C in the presence of O₂ (Table S5) producing 5.4 μmol of products with only 4 μmol H₂O₂ consumption, corresponding to a productivity of 10.4 mol_{oxygenates} kg_{cat}⁻¹ h⁻¹. This productivity compares favorably with that reported for methane monooxygenase (pMMO) from *M. capsulatus* (Bath) (5.05 mol_{methanol} kg⁻¹ h⁻¹) (29), a biological system that selective oxidizes CH₄.

Preliminary kinetic analysis shows a first order dependence on colloid, CH₄ and H₂O₂ concentration (Figure S10) indicating a rate determining step including CH₄ and H₂O₂ with an observed activation energy of 39 kJ mol⁻¹. Because the reaction only proceeds when H₂O₂ is present in the reaction mixture, the initial activation of CH₄, to •CH₃ is likely to occur through a radical mechanism (Scheme 1), a process that is suppressed by the presence of a catalyst support such as TiO₂ (see Table S6 for this comparison). These •CH₃ radicals can react quickly with dissolved O₂, which results in incorporation of >70 % O₂ into the primary reaction products under optimized conditions. Some products containing ¹⁶O were formed through radical reactions between •CH₃ with either •¹⁶O¹⁶OH or ¹⁶O₂ generated from the decomposition of H₂¹⁶O₂. The •CH₃ radicals were generated via hydrogen abstraction by •OH from H₂O₂ and this initiation step activates CH₄ (Scheme 1). In the optimized reaction, 10 μmol H₂O₂ and 5 bar ¹⁸O₂ were required to generate 20 μmol, where the primary products contained 70% ¹⁸O (14 μmol) and 30% ¹⁶O (6 μmol). These isotopic ratios and the reaction scheme proposed are broadly in-line with the total amount of H₂O₂ consumed (16 μmol), where 10 μmol was used to generate •CH₃ radicals and 6 μmol was used in ¹⁶O products via

decomposition. Greater efficiency was achieved in terms of O₂ incorporation, by utilizing H₂O₂ to activate CH₄ rather than using it to supply oxygen into the primary products. Although CH₄ activation via •OH was required for formation of •CH₃ radicals, once formed, they readily reacted with O₂ to form CH₃OH

With this mechanism in mind, we tested an iron-based Fenton's type catalyst with H₂O₂ to investigate if •OH in the absence of the AuPd colloid could activate methane, but negligible product formation was observed (Table S7). Therefore, the presence of the AuPd colloidal nanoparticles are also essential for CH₄ activation. We propose that in principle, other routes for the generation of •CH₃ radicals could be used to facilitate this chemistry. For example, rather than using H₂O₂, it would be highly desirable to devise a method of coupling the AuPd colloidal catalyst with a photochemical (30, 31) or electrochemical fuel cell (32, 33) to generate •OH for H abstraction in order to facilitate •CH₃ radical formation.

Table 1. Catalytic activity. Comparison of catalytic activity of supported and unsupported colloidal Au-only, Pd-only and AuPd catalysts for the liquid phase oxidation of CH₄ using H₂O₂. *Test conditions:* Reaction time = 0.5 h; Stirring speed = 1500 rpm; Pressure CH₄= 30 bar; Reaction temperature =50 °C with stirred heating ramp rate of 2.25 °C/min.

Entry	Catalyst	H ₂ O ₂ μmol	O ₂ bar	Amount of Product (μmol)				Primary Oxygenate Selectivity / %	Oxygenate Productivity /mol kg _{cat} ⁻¹ h ⁻¹	H ₂ O ₂ Consumed / %	Gain Factor
				CH ₃ OOH	CH ₃ OH	HCOOH	CO ₂				
1	1% AuPd/TiO ₂	1000	0	0.0	0.4	0.00	1.2	26	0.03	73	2 × 10 ⁻³
2	AuPd colloid	1000	0	11.8	3.3	0.6	1.1	90	29.4	38	3 × 10 ⁻²
3	AuPd colloid	1000	5	17.4	7.6	1.8	1.5	88	53.6	27	9 × 10 ⁻²
4	AuPd colloid	0	5	0	0	0	0.2	0	0	0	-
5	AuPd colloid	50	5	15.7	2.8	1.2	0.3	92	39.4	44	1.2
6	Pd colloid	50	5	0	0	0	0.7	0	0	22	0
7	Au colloid	50	5	0	0	0	0.1	0	0	12	0
8	PdCl ₂	50	5	0	0	0	0.3	0	0	5	0
9	HAuCl ₄	50	5	0	0	0	0.2	0	0	10	0

Entry 1: Sol-immobilized solid catalyst, 100 mg (6.6 μmol metal in 10 mL water)

Entries 2-7: Colloidal catalysts (10 mL, 6.6 μmol of metal)

Entries 8, 9: Homogeneous metal precursor solutions (6.6 μmol metal in 10 mL water)

Figure 1. Catalyst characterization. Representative HAADF images and particle size distributions for the unsupported AuPd-PVP sol in the fresh (**A to C**) and after a CH₄ oxidation reaction (**D to F**).

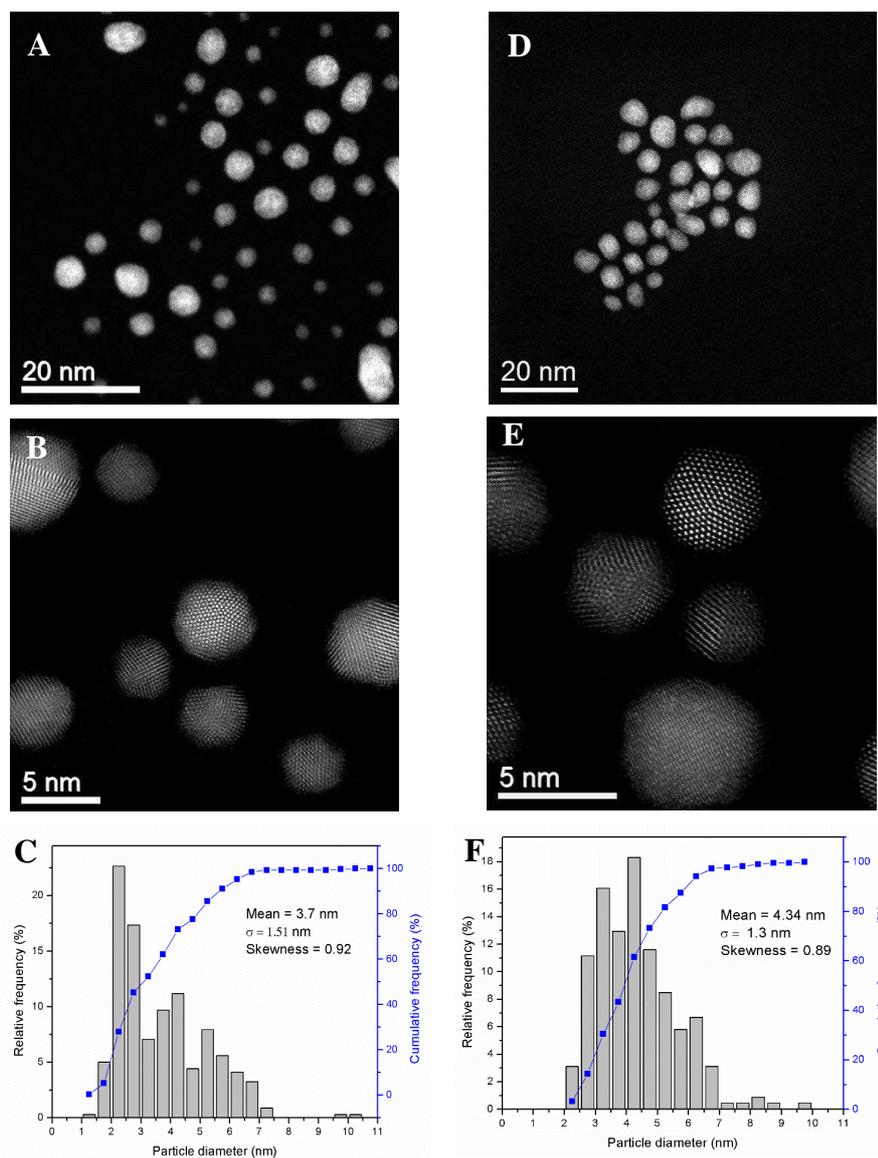
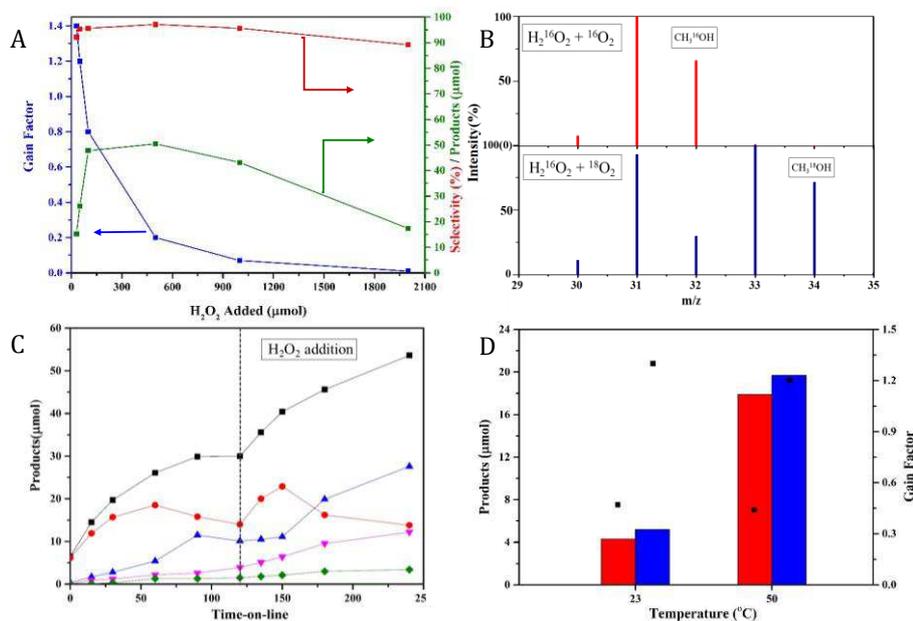


Figure 2. Methane oxidation reactions carried out over unsupported AuPd colloids.



(A) Gain factor (blue line), selectivity (red line) and total amount of products (green line) as a function of the different amounts of H₂O₂ used.

(B) GC-MS spectra of CH₃OH formed ($m = 32$ and 34 for CH₃¹⁶OH and CH₃¹⁸OH respectively) during methane oxidation with a AuPd colloid via H₂¹⁶O₂ + ¹⁶O₂ (*upper spectrum*) or H₂¹⁶O₂ + ¹⁸O₂ (*lower spectrum*). For CH₄ oxidation with ¹⁸O₂, > 70% of ¹⁸O₂ molecules were incorporated in the CH₃OH product.

(C) Time-on-line and AuPd colloid re-use study for the methane oxidation reaction employing 50 µmol H₂O₂ and 5 bar O₂ showing no induction period. Total products (black line), and individual products (CH₃OOH (red line), CH₃OH (blue line), HCOOH (pink line) and CO₂ (green line)) generated as a function of time-on-line. The black dotted vertical line at 120 min indicates a subsequent second addition of H₂O₂.

(D) Oxidation of CH₄ performed at 23° and 50°C with 50 µmol H₂O₂. The blue and red bars represent reactions performed with and without 5 bar O₂, respectively. The black squares (■) indicate their respective gain factors.

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