Direct oxidation of methane to acetic acid catalyzed by Pd²⁺ and Cu²⁺ in the presence of molecular oxygen

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Methane is catalytically converted primarily to acetic acid in concentrated sulfuric acid using a combination of Pd²⁺ and Cu²⁺ in the presence of oxygen.

The conversion of methane to acetic acid has attracted recent interest as a pathway for the synthesis of this important commodity. Previous efforts have focused primarily on either the carbonylation or carboxylation of methane in acid solutions.[1,2] Periana *et al.* have recently reported that acetic acid can be made directly from methane without the addition of CO_x.[3] The reaction is carried out in concentrated sulfuric acid and is catalyzed by Pd(II). After 7 h of reaction at 180 °C, 82 mM acetic acid and 38 mM methanol are formed.[4] The reaction is 90% selective to these products with the only byproduct being CO_2. The carbonylation of methane is posited to occur *via* a "CO" species formed by the oxidation of methanol derivatives. The overall stoichiometry of the reaction is $2CH_4 + 4H_2SO_4 \rightarrow CH_3COOH + 4SO_2 + 6H_2O$. During the reaction particles of Pd black are formed due to the reduction of Pd(II) to Pd(0). It is hypothesized that Pd(II) may be regenerated by sulfuric acid oxidation of Pd(0); however, this process is slow.

We recently showed that methanesulfonic acid (MSA) can be synthesized by the reaction of methane with a mixture of SO_2 and O_2.[5] This reaction is catalyzed in either CF_3SO_3H or H_2SO_4 by a mixture of Pd(II) and Cu(II) salts. The presence of O_2 together with a Cu(II) salt prevents the loss of Pd(II) species as Pd black. Here we demonstrate that the addition of a Cu(II) salt and O_2 to a Pd(II) salt dramatically increases the production of acetic acid from methane and inhibits Pd black precipitation.

In a typical reaction, CH_4 and O_2 were reacted at 180 °C in a high pressure, glass-lined autoclave containing catalytic amounts of $PdSO_4$ and $CuCl_2$ dissolved in concentrated sulfuric acid (96% w/w).[6] After a 4 h reaction time, an equal volume of water was added to the product solution in order to hydrolyze any anhydrides. Reaction products were analyzed by ¹H NMR.[7]

In our autoclave and under reaction conditions identical to those used by Periana *et al.* (*i.e.* no $CuCl_2$ or O_2), the products were 9 mM CH_3COOH and 7 mM CH_3OH. This is about a factor of five lower than that reported by Periana *et al.*[3] We measured the carbon selectivity to acetic acid and methanol to be 65%. SO_2 was not detected in the gas phase possibly due to relatively low amounts produced and its high solubility in sulfuric acid. At the end of the 4-h reaction period, Pd particles were found at the bottom of the reaction vessel. When Cu(II) and molecular oxygen were added to the reaction mixture, acetic acid production increased to 49 mM but the methanol concentration remained low at 4 mM. MSA was also observed as one of the products (5 mM). However, in contrast to what was found in the absence of Cu(II) and O_2, the reaction solution retained its light red color. The autoclave head space contained both CO and CO_2. The carbon selectivity to acetic acid and methanol was determined to be 47%.

Reactions were also carried out with Hg(II) and Pt(II) – two other electrophilic metal cations active for the oxidation of hydrocarbons. As shown in Table 1, entries 1–2, neither metal is as effective as palladium (entries 3–5). In agreement with earlier work,[8] both Hg(II) and Pt(II) catalyze the formation of methanol derivatives, mainly methyl bisulfate, but do not contribute to the formation of acetic acid. Table 1 also demonstrates that the anion of the Pd(II)

salt appears to have virtually no effect on the yields of acetic acid and methanol.

Using the Pd/Cu/O_2 mixture, we evaluated the effect of reaction conditions with the aim of maximizing the acetic acid yield. Table 2 presents the results of varying Cu to Pd ratio, time, temperature, oxygen pressure, and methane pressure. Entries 1 and 2 demonstrate that Pd is required for the formation of products, whereas a comparison of entries 1, 3, and 4 shows that the yield of acetic acid decreases and the yield of methanol increases with increasing Cu to Pd ratio. Entries 5–9 indicate that longer reaction times and higher reaction temperatures increase the yield of acetic acid production but do not strongly influence the yield of methanol. Comparison of entries 1, 10, and 11 shows that the yield of acetic acid increases strongly with increasing O_2 partial pressure, as does the yield of acetic acid relative to methanol, suggesting that methanol derivatives are an intermediate in the formation of acetic acid. The effect of methane partial pressure can be seen by examining entries 1, 12, and 13. As one would expect, the production of both acetic acid and methanol increases with increasing methane pressure. In fact, the best acetic acid production, 132 mM, was achieved using 600 psig of methane.

The effects of Cu(II) and O_2 on the suppression of Pd black formation can be explained in terms of reactions 1 and 2 below, which are similar to those occurring in the Wacker process.[9]
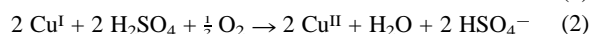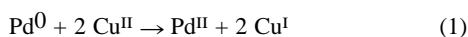
Table 1 Effect of catalyst composition

Catalyst	Co-catalyst	AcOH (mM)	MeOH (mM)
HgCl₂	—	0	18
PtCl₂	—	0	8
PdCl₂	—	10	8
PdSO₄	—	9	7
PdSO₄	CuCl₂	49	4

Reaction conditions: 3 mL 96% H_2SO_4; 20 mM catalyst and co-catalyst; 400 psi CH_4; 30 psi O_2 (only when co-catalyst is present); 180 °C; 4 h.

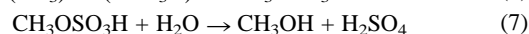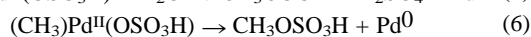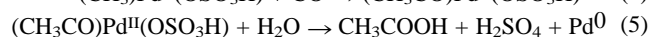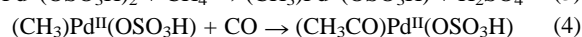**Table 2** Effect of varied reaction conditions on the product distributions

Entry	PdSO₄ (mM)	CuCl₂ (mM)	t (h)	T (°C)	O₂ (psig)	CH₄ (psig)	AcOH (mM)	MeOH (mM)
1	20	20	4	180	30	400	49	3.7
2	0	20	4	180	30	400	0	0
3	20	6.7	4	180	30	400	66	2.1
4	20	60	4	180	30	400	11	6.9
5	20	20	2	180	30	400	44	4.7
6	20	20	6	180	30	400	106	4.5
7	20	20	4	160	30	400	45	5.7
8	20	20	4	140	30	400	18	63
9	20	20	4	120	30	400	4.4	37
10	20	20	4	180	0	400	2.5	3.6
11	20	20	4	180	150	400	73	2.3
12	20	20	4	180	30	200	27	1.7
13	20	20	4	180	30	600	132	7.2

Reaction conditions (unless otherwise noted): 3 mL 96% H_2SO_4; 20 mM $PdSO_4$; 20 mM $CuCl_2$; 400 psig CH_4; 30 psig O_2; 180 °C; 4 h.

$$Pd^0 + 2\,Cu^{II} \rightarrow Pd^{II} + 2\,Cu^I \qquad (1)$$

$$2\,Cu^I + 2\,H_2SO_4 + \tfrac{1}{2}\,O_2 \rightarrow 2\,Cu^{II} + H_2O + 2\,HSO_4^- \qquad (2)$$

Since oxidation of Pd(0) by Cu(II) and O_2 is faster than oxidation by H_2SO_4, the formation of Pd black is suppressed relative to what is observed in the absence of Cu(II) and O_2. Preliminary analysis using UV-vis spectroscopy shows that approximately an order of magnitude more Pd(II) remains in solution when Cu(II) and O_2 are present ($\sim$ 3 mM) than when they are absent ($<$ 0.2 mM). These results also indicate that Cu(II) and O_2 slow Pd black formation but do not eliminate it.

Although the reaction pathway to acetic acid is not clear, it is reasonable to suppose that the reaction of Pd(II) with methane results in the formation of a CH_3–Pd(II) complex, as shown in reaction 3. Periana *et al.*[3] have proposed that a "CO" species derived from methanol may then carbonylate this complex to produce CH_3CO–Pd(II) (reaction 4). Reaction of the acetyl group with water (reaction 5) leads to the formation of CH_3COOH and Pd(0), which can then be reoxidized, as described above. The proposed pathway is similar to that for the synthesis of MSA from CH_4, SO_2, and O_2 catalyzed by Pd^{2+}.[5] In that work it was proposed that SO_2 inserts into the CH_3–Pd bond. Methyl bisulfate is formed by the decomposition of $(CH_3)Pd^{II}(OSO_3H)$, reaction 6. At the water levels present in concentrated sulfuric acid this product does not hydrolyze, and thus methanol is formed *via* reaction 7 only upon addition of water at the end of the reaction.

$$Pd^{II}(OSO_3H)_2 + CH_4 \rightarrow (CH_3)Pd^{II}(OSO_3H) + H_2SO_4 \qquad (3)$$

$$(CH_3)Pd^{II}(OSO_3H) + CO \rightarrow (CH_3CO)Pd^{II}(OSO_3H) \qquad (4)$$

$$(CH_3CO)Pd^{II}(OSO_3H) + H_2O \rightarrow CH_3COOH + H_2SO_4 + Pd^0 \qquad (5)$$

$$(CH_3)Pd^{II}(OSO_3H) \rightarrow CH_3OSO_3H + Pd^0 \qquad (6)$$

$$CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4 \qquad (7)$$
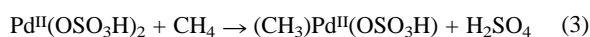
In summary, methane can be catalytically converted to acetic acid in concentrated sulfuric acid using a combination of $PdSO_4$, $CuCl_2$, and O_2. Acetic acid yield is increased dramatically compared to that obtained using $PdSO_4$ alone. $CuCl_2$ and O_2 appear to promote the rate of Pd(0) oxidation to Pd(II) during the catalytic cycle and, thereby, inhibit the deposition of Pd black. The presence of O_2 also increases the selectivity to acetic acid relative to methanol. Further work is in progress to understand the sources of CO and CO_2, and the factors controlling product selectivity.

Notes and references

1 (*a*) A. Bagno, J. Bukala and G. Olah, *J. Org. Chem.*, 1990, **55**, 4284; (*b*) M. Lin and A. Sen, *Nature*, 1994, **368**, 613; (*c*) T. Nishiguchi, K. Nakata, K. Takaki and Y. Fujiwara, *J. Organomet. Chem.*, 1992, **7**, 1141; (*d*) G. Nizova, G. Suss-Fink, S. Stanislas and G. Shul'pin, *Chem. Commun.*, 1998, 1885; (*e*) M. Asadullah, T. Kitamura and Y. Fujiwara, *Angew. Chem., Int. Ed.*, 2000, **39**(14), 2475; (*f*) G. Chaepaikin, A. Bezruchenko, A. Leshcheva, G. Boyko, I. Kuzmenkov, E. Grigoryan and A. Shilov, *J. Mol. Catal. A: Chem.*, 2001, **169**, 89.
2 (*a*) Y. Taniguchi, T. Hayashida, T. Kitamura and Y. Fujiwara, *Std. Surf. Sci. Catal.*, 1998, **114**, 439; (*b*) E. Wilcox, G. Roberts and J. Spivey, *Appl. Catal. A: Gen.*, 2002, **226**, 317; (*c*) M. Zerella, S. Mukhopadhyay and A. Bell, *Org. Lett.*, 2003, **5**(18), 3193; (*d*) M. Golombok and W. Teunissen, *Ind. Eng. Chem. Res.*, 2003, **42**, 5003.
3 R. Periana, O. Mironov, D. Taube, F. Bhalla and C. Jones, *Science*, 2003, **301**, 814.
4 The reaction products are acetic acid and methyl bisulfate. Hydrolysis yields acetic acid and an equilibrium mixture of methyl bisulfate and methanol.
5 S. Mukhopadhyay and A. Bell, *Chem. Commun.*, 2003, 1590.
6 In a 50 mL glass autoclave liner, 0.0121 g (20 mM) of $PdSO_4$, and 0.0081 g (20 mM) of $CuCl_2$ were dissolved in 3 mL (5.52 g) of 96% sulfuric acid. A small Teflon-coated stir bar was added prior to sealing the autoclave. The reactor was purged with Ar and then pressurized with 400 psig of CH_4 and 30 psig of O_2. The reactor was heated to 180 °C and maintained for 4 h. Upon completion of the reaction, the reactor was quenched in ice water to $<$ 35 °C and then vented. Upon opening the reactor, 3 mL of water were added to the product mixture.
7 For ^1H NMR analysis, D_2O was used in a capillary as the lock reference. Depending on the concentrations of the products, the acetic acid (2.0–2.1 ppm), methanol (3.3–3.4 ppm), and methyl bisulfate (3.6–3.7 ppm) shifted slightly. Two unidentified by-products, which are smaller than that for methanol, appear in the ^1H NMR spectrum at 4.0–4.1 ppm and 4.4–4.5 ppm.
8 (*a*) R. Periana, D. Taube, E. Evitt, D. Loffler and P. Wentrcek, *Science*, 1993, **259**, 340; (*b*) R. Periana, D. Taube, S. Gamble, H. Taube, T. Satoh and H. Fujii, *Science*, 1998, **280**, 560.
9 G. Parshall, *Homogeneous Catalysis*, 1980, John Wiley & Sons, Inc, New York.