Pt-catalyzed oxidative carbonylation of methane to acetic acid in sulfuric acid

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Abstract

The oxidative carbonylation of methane to acetic acid was investigated using Pt(II) cations as the catalyst and sulfuric acid as the solvent. The reactions were carried out at $180\,^\circ C$ in a sealed batch reactor containing either fuming or concentrated (96 wt%) sulfuric acid (3 ml) and $PtCl_2$ (20 mM) in the liquid-phase, and pressurized with CH_4 (400 psi) and CO (400 psi). In the absence of CO, the only product is methyl bisulfate, but in the presence of CO, this product undergoes carbonylation to acetic acid. CO also serves as a reducing agent and can reduce the catalytically active Pt(II) to Pt(0), which is inactive. The catalyst activity can be increased by promoting the re-oxidation using co-catalyst, such as $CuCl_2$ and O_2. Thus, a balance must be maintained between oxidizing and reducing conditions in order to minimize or avoid the loss of Pt(II).
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1. Introduction

The direct conversion of methane to acetic acid has been the subject of a number of recent studies focused on finding strategies for converting methane to higher valued liquid products [1]. One of the approaches explored is the oxidative carbonylation of methane: $CH_4 + CO + \text{``O''} \rightarrow CH_3COOH$. The source of the "O" can be molecular O_2 or a liquid-phase oxidant, such as H_2SO_4. Fujiwara and co-workers have used Pd and Cu cations together with CF_3COOH in the presence of O_2. The apparent turnover frequency (TOF), defined as the moles of CH_3COOH formed per unit time per mole of catalyst time, was only $\sim 10^{-5}\,s^{-1}$ at $80\,^\circ C$ [2]. Sen and co-workers examined the use of Rh cations dissolved in water. Even though the methane pressure was higher than in the previous system (54 atm versus 20 atm), the catalyst activity was similar [3]. The apparent TOF at $80\,^\circ C$ could be increased to $6 \times 10^{-4}\,s^{-1}$ by replacing some of the water with an organic acid, but this decreased the selectivity to acetic acid [4]. Grigoryan and co-workers [5] and Shilov and co-workers [6] have also used Rh in aqueous and/or acidic solutions at $95\,^\circ C$. Good selectivity was achieved and the apparent TOF increased to 1×10^{-4} and $2.5 \times 10^{-3}\,s^{-1}$, but at the expense of a high ratio of halides to catalyst (10:1) and high methane pressure (~ 60 atm). Related research has shown that Pt(II) in anhydrous sulfuric acid catalyzes methane conversion to methyl bisulfate [7], and that Pt(II) also can catalyze the carbonylation of alcohols to carboxylic acids [8]. In the present work, we show that Pt(II) can catalyze the carbonylation of methyl bisulfate to acetic acid, as well as the oxidative carbonylation of methane to acetic acid at $180\,^\circ C$. The apparent TOF of the methane oxidative carbonylation reaction is $1.5 \times 10^{-4}\,s^{-1}$ when using a moderate pressure of methane (27 atm). Although this apparent TOF is lower than that for the current process for making acetic acid from methanol, the oxidative carbonylation of methane is appealing because it enables the synthesis of acetic acid from methane in a single step, rather than the three steps now required using methanol as the intermediate.

2. Experimental

All reactions were carried out in a 50 ml Parr autoclave made of Hastelloy C. To minimize problems with reproducibility due to trace amounts of water retained in crevices of the autoclave head, all parts of the reactor were cleaned and dried thoroughly before each experiment. The temperature of the reacting mixture

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was measured with a thermocouple located in a well made of Hastelloy C, which was wrapped with Teflon tape to minimize exposure of the metal to the reaction mixture. The reaction mixture was contained in a glass liner. In a typical methane oxidative carbonylation reaction, 0.0160 g (20 mM) $PtCl_2$ (Aldrich) and 3 ml of 127 wt% H_2SO_4 or 96 wt% H_2SO_4 (Aldrich) were added to the liner. For methyl bisulfate carbonylation reactions, approximately 0.0115 g (120 mM) methanol was added to 3 ml of 127 or 96 wt% H_2SO_4. For all reactions, after placing the glass liner in the autoclave, it was sealed and purged with N_2. The autoclave was then pressurized at room temperature typically with 400 psi of CO (99.5%, Praxair) and then an additional 400 psi of CH_4 (99.97%, Praxair) (except for methyl bisulfate carbonylation reactions). The reactor was brought to 180 °C in ∼15 min and then held at this temperature for 4 h. On completion of the reaction, the autoclave was quenched in ice water to <35 °C, and then vented. On opening the autoclave, the solution was further chilled before adding 3 ml of water.

Liquid-phase reaction products were analyzed using ^{1}H NMR. D_2O was used in a capillary as the lock reference. A known amount of t-butanol was added to each sample and used as an internal standard for quantification. The liquid-phase products typically observed were acetic acid (CH_3COOH), methanesulfonic acid (CH_3SO_3H), methanol (CH_3OH), methyl bisulfate (CH_3OSO_3H), sulfoacetic acid (HO_3SCH_2COOH), and methane disulfonic acid ($CH_2(SO_3H)_2$). The chemical shifts for these products were as follows: acetic acid, 2.0–2.1 ppm; methanesulfonic acid, 2.8–2.9 ppm; methanol, 3.3–3.4 ppm; methyl bisulfate, 3.6–3.7 ppm; sulfoacetic acid, 4.0–4.1 ppm; and methane disulfonic acid, 4.4–4.5 ppm.

The yield of each liquid-phase product is reported in terms of the concentration of that product observed after a fixed period of reaction. Even though water is added to the reaction mixture prior to ^{1}H NMR analysis, the reported concentrations are calculated on the basis of the volume of liquid present in the autoclave liner prior to the addition of water. Testing with standards showed that product concentrations could be determined to within 5% of the actual values using this method. No methanol is observed prior to the addition of water to the reaction products, and only after the addition of water is some of the methyl bisulfate hydrolyzed to methanol. Since methanol derives from

methyl bisulfate, any methanol measured is reported as methyl bisulfate.

3. Results and discussion

Prior work has shown that Pt(II) in sulfuric acid catalyzes the conversion of methane to methyl bisulfate, CH_3OSO_3H [7]. As seen in Table 1, a much higher yield of methyl bisulfate is obtained in fuming H_2SO_4 (127 wt%) than in concentrated H_2SO_4 (96 wt%). The higher yield obtained in fuming H_2SO_4 is due to the presence of free SO_3, which is a stronger oxidant than H_2SO_4. However, starting with the same concentration of methyl bisulfate, the carbonylation of this compound to acetic acid is more effective in 96 wt% H_2SO_4 than in 127 wt% H_2SO_4. It is also seen that not only is more acetic acid produced in 96 wt% H_2SO_4, but the reaction is also more selective to acetic acid in this medium, since much less $CH_2(SO_3H)_2$ is produced. If CH_4 and CO are introduced into the reactor together, the total yield of acetic acid decreases significantly in 127 wt% H_2SO_4, but increased in 96 wt% H_2SO_4. Since the sum of all liquid-phase products using each solvent is larger than the concentration of Pt, the reaction is clearly catalytic. However, the overall production of liquid-phase products is greater in 127 wt% H_2SO_4, but the selectivity to acetic acid is larger in 96 wt% H_2SO_4. Additionally, since 127 wt% H_2SO_4 is anhydrous, the desired acetic acid product in this solvent is present as acetyl sulfate (the mixed anhydride of acetic acid and sulfuric acid), $CH_3C(O)OSO_3H$. By contrast, in 96 wt% H_2SO_4 there is sufficient water to hydrolyze any $CH_3C(O)OSO_3H$ to CH_3COOH.

As noted above, in 96 wt% H_2SO_4, 17.5 mM acetic acid is produced in the presence of 400 psi CO. Table 2 shows the effects of varying the CO pressure. The yield of all liquid-phase products remains relatively constant with increasing CO partial pressure; however, the concentration of acetic acid increases and the concentration of methyl bisulfate decreases. In the absence of CO, no acetic acid is produced, indicating clearly that CO is the source of the carboxylate carbon in acetic acid.

Table 3 shows that the yields of all products decrease when the methane pressure is decreased. In the absence of methane, no liquid-phase products are formed, although carbon dioxide is detected in the reactor headspace. These results indicate that

Table 1
Methane oxidation, methyl bisulfate carbonylation, and methane oxidative carbonylation

H_2SO_4 concentration	CH_3COOH (mM)	CH_3OSO_3H (mM)	CH_3SO_3H (mM)	HO_3SCH_2COOH (mM)	$CH_2(SO_3H)_2$ (mM)
$CH_4 + H_2SO_4$[a]					
127 wt%	0.4	1147	1.5	18.0	13.7
96 wt%	0	18.0	0.2	0.7	1.4
$CH_3OSO_3H + CO + H_2SO_4$[b]					
127 wt%	29.8	13.3	0.7	2.8	22.7
96 wt%	53.1	14.0	1.0	1.9	3.4
$CH_4 + CO + H_2SO_4$					
127 wt%	56.5	35.0	1.0	3.0	12.7
96 wt%	17.5	7.3	0	0.8	1.3

Reaction conditions: 3 ml H_2SO_4 solvent, 20 mM $PtCl_2$, 400 psi CH_4, 400 psi CO, 180 °C, 4 h.

[a] No CO present.

[b] No CH_4 present and 0.0115 g (120 mM) CH_3OH added.

Table 2
Effect of CO pressure

CO (psi)	CH_3COOH (mM)	CH_3OSO_3H (mM)	CH_3SO_3H (mM)	HO_3SCH_2COOH (mM)	$CH_2(SO_3H)_2$ (mM)
0	0	18	0.2	0.7	1.4
100	8.9	16.9	0.0	0.8	1.2
200	16.4	10.7	0.2	1.2	0.9
400	17.5	7.3	0	0.8	1.3

Reaction conditions: 3 ml 96 wt% H_2SO_4, 20 mM $PtCl_2$, 400 psi CH_4, 180 °C, 4 h.

Table 3
Effect of CH_4 pressure

CH_4 (psi)	CH_3COOH (mM)	CH_3OSO_3H (mM)	CH_3SO_3H (mM)	HO_3SCH_2COOH (mM)	$CH_2(SO_3H)_2$ (mM)
0	0	0	0	0	0
200	5.2	3.5	0	0	0.8
400	17.5	7.3	0	0.8	1.3

Reaction conditions: 3 ml 96 wt% H_2SO_4, 20 mM $PtCl_2$, 400 psi CO, 180 °C, 4 h.

Table 4
Effect of O_2 pressure

O_2 (psi)	CH_3COOH (mM)	CH_3OSO_3H (mM)	CH_3SO_3H (mM)	HO_3SCH_2COOH (mM)	$CH_2(SO_3H)_2$ (mM)
0	17.5	7.3	0	0.8	1.3
30	15.5	4.6	5.8	1.8	3.3
100	15	9.2	16.9	0.0	0
150	19	12.9	34.2	1.0	0.9

Reaction conditions: 3 ml 96 wt% H_2SO_4, 20 mM $PtCl_2$, 400 psi CH_4, 400 psi CO, 180 °C, 4 h.

methane is the source of the methyl group of acetic acid as well as the source of all other liquid-phase products.

Interestingly, increasing the partial pressure of oxygen has no effect on the yield of acetic acid, as shown in Table 4. (Gas pressures were chosen such that the mixture did not enter the explosive regime during a reaction [9].) However, with increasing O_2 partial pressure the selectivity to acetic acid decreases. The product that is impacted the most by oxygen partial pressure is methanesulfonic acid; the yield of this product increases linearly from 0 mM in the absence of oxygen to 34 mM in the presence of 150 psi O_2. The effect of oxygen pressure on methanesulfonic acid production is likely due to the increasing rate of CH_4 reacting with SO_2, a process that has been reported previously and found to be aided by the presence of oxygen [10].

As the temperature of the reaction is lowered from 180 to 160 °C, the acetic acid yield drops significantly, but the methyl bisulfate yield increases (Table 5). The loss of acetic acid at lower temperatures may be due to the higher activation energy for carbonylation versus sulfonation of methyl groups associated with Pt centers, which are formed by activation of CH_4 (see below). Thus, methyl bisulfate is still formed, but at the lower temperature its reaction with CO is slowed, resulting in a reduced acetic acid production and a higher final concentration of methyl bisulfate.

As seen in Table 6, the yield of acetic acid increases at the expense of methyl bisulfate with increasing reaction time. However, the other sulfur-containing products increase almost linearly with time. These results suggest that methyl bisulfate may

Table 5
Effect of temperature O_2 pressure

T (°C)	CH_3COOH (mM)	CH_3OSO_3H (mM)	CH_3SO_3H (mM)	HO_3SCH_2COOH (mM)	$CH_2(SO_3H)_2$ (mM)
160	10.7	20.9	0.5	0.0	0
180	17.5	7.3	0	0.8	1.3

Reaction conditions: 3 ml 96 wt% H_2SO_4, 20 mM $PtCl_2$, 400 psi CH_4, 400 psi CO, 180 °C, 4 h.

Table 6
Effect of time

Time (h)	CH_3COOH (mM)	CH_3OSO_3H (mM)	CH_3SO_3H (mM)	HO_3SCH_2COOH (mM)	$CH_2(SO_3H)_2$ (mM)
1	4.9	28.1	0	0.3	0
2	10.8	12.3	0	0.4	0.5
4	17.5	7.3	0	0.8	1.3

Reaction conditions: 3 ml 96 wt% H_2SO_4, 20 mM $PtCl_2$, 400 psi CH_4, 400 psi CO, 180 °C.

Table 7
Effect of Pt salt

Pt salt	CH_3COOH (mM)	CH_3OSO_3H (mM)	CH_3SO_3H (mM)	HO_3SCH_2COOH (mM)	$CH_2(SO_3H)_2$ (mM)
$PtCl_2$	17.5	7.3	0	0.8	1.3
$(NH_3)_4PtCl_2$	18.1	6.2	0	1.2	0.9
$(bpy)PtCl_2$	10.1	1.9	0	1.3	0.9
$(bpym)PtCl_2$	1.2	5.9	0	0	0
$Pt(acac)_2$	31.6	0	0	4.3	13.2

Reaction conditions: 3 ml 96 wt% H_2SO_4, 20 mM $PtCl_2$, 400 psi CH_4, 400 psi CO, 180 °C, 4 h.

be produced rapidly at the start of the reaction and then undergo subsequent carbonylation. However, not all of the methyl bisulfate is converted to acetic acid. The combined concentration of CH_3COOH and CH_3OSO_3H is less after 4 h than after 1 h. The sum of all of the liquid-phase products decreases with time from 1 to 4 h, suggesting that methyl bisulfate is slowly oxidized to CO_x ($x = 1, 2$). This interpretation agrees with what was seen in Table 1: CO can carbonylate methyl bisulfate, but the conversion is not complete, and some of the CH_3OSO_3H is oxidized to CO_x ($x = 1, 2$).

Pt(0) is known to be active for catalyzing the oxidation of compounds such as CH_3OSO_3H to CO_x [7]. Although Pt(II) is added to the reactor, Pt(0) is formed under reactions conditions, as evidenced by the presence of a black precipitate at the end of reactions. Additionally, the color of a solution after a reaction depends on the reaction conditions, ranging from golden brown to colorless. In the absence of CO, the solution has a strong golden brown color, presumably due to Pt(II). However, this color fades as the CO pressure is increased, until the solution becomes colorless after reaction in the presence of 400 psi of CO. When only CO was in the reactor headspace initially, then all the Pt(II) was reduced to Pt(0), resulting in the formation of CO_2 and leaving the solution colorless. In the presence of 400 psi CO, the golden brown color characteristic of Pt(II) was observed to come back only when the temperature was reduced from 180 to 160 °C.

Attempts to quantify the concentration of Pt(II) in 96 wt% H_2SO_4 after the reactions were not successful. Depending on the method of preparation and H_2SO_4 concentration, Pt cations can form different complexes in solution. The oxidation state of these complexes can vary (II or IV) and the complexes can be in the form of monomeric or polymeric species [11]. In addition, the structures in which Pt(II) occurs may change under reaction conditions. For this reason, UV–visible spectroscopy could not be used in a quantitative manner to establish the concentration of Pt(II) remaining in solution after reaction.

The reduction of Pt(II) cations to Pt(0) has been observed previously, and several attempts have been made to either stabilize Pt(II) or to re-oxidize Pt(0) back to Pt(II) [7,12]. Work by Periana et al. has shown that Pt(II) can be stabilized against reduction by coordination with neutral N-containing ligands, such as bypyridine and bipyrimidine [7]. We observed that in concentrated sulfuric acid at 180 °C, $PtCl_2$ is insoluble, as is $(bpym)PtCl_2$ ($bpym = 2,2'$-bipyrimidine). $(NH_3)_4PtCl_2$, bubbles upon addition to concentrated H_2SO_4 at room temperature (presumably releasing ammonia) and dissolves quickly, but the solution is colorless. Interestingly, $(bpy)PtCl_2$ ($bpy = 2,2'$-bipyridine) dissolves at room temperature forming a yellow solution, but at 180 °C, an orange precipitate forms, and the solution remains yellow. $Pt(acac)_2$ dissolves at room temperature to give the golden brown color that was observed previously, and it maintains this color at 180 °C. The activity of each of these salts is shown in Table 7. Adding NH_3, (bpy), or (bpym) ligands to $PtCl_2$ does nothing or hinders activity towards making acetic acid. It is believed that the NH_3 ligands dissociate from Pt(II) upon addition to solution, leaving $PtCl_2$. This explains why the results for $PtCl_2$ and $(NH_3)_4PtCl_2$ are almost identical. The ligands (bpy) and (bpym) are the worst, probably because they bind tightly to Pt(II) and do not leave enough sites for CH_4 and CO to react with Pt(II). Relative to $PtCl_2$, $Pt(acac)_2$ is more efficient likely because it takes an active form more readily, as indicated by the immediate change in the solution color to golden brown [13]. Quite possibly, this is due to the higher solubility of $Pt(acac)_2$ relative to $PtCl_2$ in concentrated H_2SO_4.

Attempts were made to add a co-catalyst in order to facilitate the re-oxidation of Pt(0) back to Pt(II) in a manner analogous to that used the Wacker Process for the re-oxidation of Pd(0) back to Pd(II) [14]. Table 8 presents the results obtained using this approach. It is evident that using $CuCl_2$ or $VO(acac)_2$ together

Table 8
Effect of co-catalyst

Co-catalyst	CH_3COOH (mM)	CH_3OSO_3H (mM)	CH_3SO_3H (mM)	HO_3SCH_2COOH (mM)	$CH_2(SO_3H)_2$ (mM)
None[a]	17.5	7.3	0	0.8	1.3
$VO(acac)_2$	22.3	21.5	11.8	0	0
$CuCl_2$	24.4	37.2	1.0	3.0	12.7
$AgCl_2$	9.7	4.2	1.1	0.6	1.3
$CuCl_2$[b]	42.0	12.4	24.7	2.9	5.7

Reaction conditions: 3 ml 96 wt% H_2SO_4, 20 mM Pt salt, 400 psi CH_4, 400 psi CO, 100 psi O_2, 180 °C, 4 h.

[a] No O_2 added.

[b] $Pt(acac)_2$ was added instead of $PtCl_2$.

with O_2 increases the yields of acetic acid and, more dramatically, the yield of methyl bisulfate. (Controlled studies confirm that the "acac" ligands do not react to become acetic acid [13], and neither $CuCl_2$ nor $VO(acac)_2$ by itself is active under reaction conditions [15].) The solution color after reaction is darker when these co-catalysts are present, but it is not clear how much of this increase in color is due to an increase in Pt(II) concentration versus the presence of the co-catalyst itself.

Finally, an attempt was made to see whether the yield of acetic acid could be increased by using the most soluble Pt salt, $Pt(acac)_2$, together with $CuCl_2$ and O_2 to re-oxidize Pt(0). The acetic acid yield in this case increased to 42.0 mM, corresponding to an apparent TOF of $1.5 \times 10^{-4}\,s^{-1}$. Unfortunately, the formation of byproducts also increased, and again, due to the presence of $CuCl_2$, it was not possible to use the solution color as a qualitatively gauge of how much Pt(II) was retained in solution after reaction.

The exact identity of the Pt(II) complexes under reaction conditions is not known; however, it was observed that no reaction products were formed in the absence of Pt(II), indicating that Pt(II) is an essential component. Theoretical studies of Pt(II)-catalyzed conversion of CH_4 conversion to CH_3OSO_3H in anhydrous H_2SO_4 [16] have shown that Pt(II) may be present as PtX_2 (where $X = Cl^-$ or OSO_3H^-) or $(PtCl_2)_n$ oligomers. These calculations indicate that only monomeric PtX_2 is active, and that methane reacts with PtX_2 to form a CH_3–Pt(II) species. The solvent can then oxidize the Pt in these species to CH_3–Pt(IV). The product CH_3OSO_3H is formed via reductive elimination and the catalyst, PtX_2, is regenerated. A reaction mechanism developed on the basis of these findings is depicted by steps 1–3 in Fig. 1. In this scheme, X is taken to be HSO_4^-, since the concentration of bisulfate anions far exceeds the concentration of the anion in the parent Pt salt (e.g., Cl^- or $acac^-$). Thus, the anion in the parent Pt salt is assumed to affect only the solubility of the salt in concentrated sulfuric acid.

If CO is present in the reactor, the above mechanism is altered, as shown by steps 1, 2, 5, and 6 of Fig. 1. A $(CH_3)PtX_3$ species is still formed, but now the methyl group can originate from CH_3OSO_3H (via step 4) as well as CH_4. CO can insert into the CH_3–Pt bond, creating an acyl, CH_3CO–Pt(IV), complex. This step competes with the elimination of CH_3OSO_3H from $(CH_3)PtX_3$. Once CH_3CO–Pt(IV) is formed, reaction with water produces CH_3COOH and restores the active catalyst. Thus, introducing CO drives the mechanism towards acetic acid formation. However, high CO partial pressures also contribute to the reduction of Pt(II) to Pt(0), and hence, to the loss of Pt from solution. Therefore, a balance between oxidizing and reducing conditions must be maintained in the reactor in order to minimize or avoid the loss of active Pt(II).

4. Conclusions

Pt(II) in concentrated sulfuric acid catalyzes the oxidative carbonylation of methane to acetic acid. The reaction rate increases with increasing methane and carbon monoxide partial pressures; however, excessively high CO partial pressures are to be avoided, since they contribute to the reduction of active Pt(II) to inactive Pt(0). The Pt(II) cannot be stabilized by neutral ligands such as bpy or bpym without sacrificing catalytic activity. The rate of Pt(0) oxidation to Pt(II) can be increased, though, by the addition of $CuCl_2$ and O_2, or $VO(acac)_2$ and O_2. This approach is appealing, but work must continue to improve the selectivity to acetic acid.

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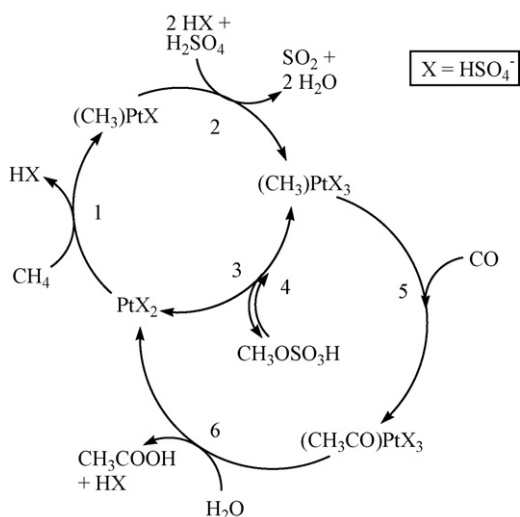

Fig. 1. Proposed reaction pathway.

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