

## Direct catalytic sulfonation of methane with SO<sub>2</sub> to methanesulfonic acid (MSA) in the presence of molecular O<sub>2</sub>

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**Methane is transformed selectively to methanesulfonic acid at low temperature by liquid-phase sulfonation of methane with SO<sub>2</sub> and O<sub>2</sub> in the presence of Pd- and Cu-salts as the catalysts.**

The selective catalytic functionalization of methane to value added products is a subject of considerable contemporary interest. Because of favorable thermodynamics, many authors have investigated the oxidation and oxidative carbonylation of methane.<sup>1</sup> By contrast, the sulfonation of methane has not received as much attention despite its commercial importance.<sup>2</sup> It has been shown<sup>3a-f</sup> that in the presence of a free radical initiator methane can be sulfonated with SO<sub>3</sub> in fuming sulfuric acid to methanesulfonic acid (MSA) under very high methane pressure. Most recently we have shown that methane can be sulfonated to MSA by SO<sub>2</sub> in the presence of an excess amount of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.<sup>3g</sup> The same approach, however, does not work if O<sub>2</sub> is used instead of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> as the oxidant. Thus, there is incentive to identify a catalytic system that would enable the use of molecular O<sub>2</sub>. While Ishii and coworkers have reported success in the vanadium-catalyzed sulfonation of adamantane to the corresponding sulfonic acids using SO<sub>2</sub> and O<sub>2</sub>, methane did not undergo sulfonation to methanesulfonic acid.<sup>3h</sup> The question therefore arises whether SO<sub>2</sub> and O<sub>2</sub> can be used for methane sulfonation. In this communication, we show that methane will undergo liquid-phase sulfonation to MSA with SO<sub>2</sub> and O<sub>2</sub> in acid solvents, with catalytic amounts of Pd- and Cu-salts (Scheme 1).

In a typical reaction<sup>4</sup> (Scheme 1) methane was reacted with SO<sub>2</sub> in CF<sub>3</sub>SO<sub>3</sub>H to form MSA in presence of Pd- and Cu-salts in a high-pressure, glass-lined, Parr autoclave. Reactions were carried out for 12 h at 85 °C and the MSA thus formed was identified and quantified by <sup>1</sup>H NMR.<sup>3b,c</sup> Use of <sup>13</sup>C enriched methane and <sup>1</sup>H, <sup>13</sup>C NMR of the reaction mixture confirmed that MSA is the only liquid-phase product generated from methane in presence of SO<sub>2</sub>. The conversions are reported on the basis of the limiting reagent, SO<sub>2</sub>, and defined as the ratio of the moles of SO<sub>2</sub> converted to MSA to the moles of SO<sub>2</sub> fed initially to the reactor.

Table 1 shows the effect of different catalyst combinations on the rate of methane sulfonation. In the absence of any catalyst or co-catalyst, no conversion of SO<sub>2</sub> to MSA was achieved (Table 1, entry 1). The use of PdCl<sub>2</sub> in the absence of CuCl<sub>2</sub> gives only 6% conversion of SO<sub>2</sub> to MSA, whereas use of CuCl<sub>2</sub> in the absence of PdCl<sub>2</sub> gives only 1% conversion of SO<sub>2</sub> to MSA (Table 1, entries 2, 3). SO<sub>2</sub> conversions of 12–20% to MSA were obtained when PdCl<sub>2</sub> and CuCl<sub>2</sub> were used together (Table 1, entries 4, 5). A nearly identical conversion was obtained after 12 h of reaction when CuCl<sub>2</sub> was replaced by Cu<sub>2</sub>Cl<sub>2</sub> (Table 1, entry 6). Similar levels of SO<sub>2</sub> conversion to MSA were achieved with acetate, trifluoroacetate, or triflate salts of Pd(II)

and CuCl<sub>2</sub> or with PdCl<sub>2</sub> and acetate, trifluoroacetate, or triflate salts of Cu(II) (Table 1, entries 7–12). Chloride salts of Rh(III), Hg(II), Co(II), Pt(II), Ru(III), Al(III), Ag(I), Ca(II), Fe(III), together with CuCl<sub>2</sub> showed very little or no activity, as did VOCl<sub>3</sub> and VO(acac)<sub>2</sub> with CuCl<sub>2</sub> (Table 1, entries 13–23). Pd(acac)<sub>2</sub> and Cu(acac)<sub>2</sub> also gave very little product (Table 1, entry 24).

Table 2 shows the effect of different process parameters on the rate of methane sulfonation using PdCl<sub>2</sub> salts as the catalyst and CuCl<sub>2</sub> as the co-catalyst. Reactions were performed to study the effect of methane pressure on the rate of MSA formation. Increasing the CH<sub>4</sub> pressure from 200 to 1200 psig increased the conversion of SO<sub>2</sub> to MSA from a barely detectable level to 12% (Table 2, entries 1–5).

The rate of sulfonation reaction depends on the SO<sub>2</sub> pressure. No MSA was detected in the absence of SO<sub>2</sub>; however, approximately 0.1 mmol of CF<sub>3</sub>SO<sub>3</sub>CH<sub>3</sub> was formed. With an increase in SO<sub>2</sub> pressure from 0 to 30 psig, the conversion of SO<sub>2</sub> to MSA increased from 0 to 12% (Table 2, entries 5–8).

No MSA was formed in the absence of O<sub>2</sub>. With an increase in O<sub>2</sub> pressure from 0 to 30 psig, the conversion of SO<sub>2</sub> to MSA increased from 0 to 12%. However, a further increase had no effect on MSA production (Table 2, entries 9–12).

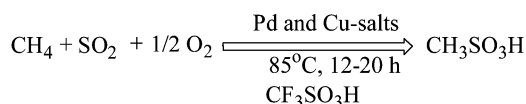
Increasing the amount of PdCl<sub>2</sub> from 0.05 to 0.2 mmol, the conversion of SO<sub>2</sub> to MSA increased from 3 to 12%. A further

**Table 1** Effect of different metal chlorides on the sulfonation<sup>a</sup>

Entry	Catalyst	Co-catalyst	t/h	MSA/ mmol	% SO <sub>2</sub> to MSA <sup>b</sup>
1	None	None	16	0	0
2	PdCl <sub>2</sub>	None	12	0.71	6
3	None	CuCl <sub>2</sub>	14	0.12	1
4	PdCl <sub>2</sub>	CuCl <sub>2</sub>	12	1.42	12
5	PdCl <sub>2</sub>	CuCl <sub>2</sub>	40	2.36	20
6	PdCl <sub>2</sub>	Cu <sub>2</sub> Cl <sub>2</sub>	12	1.18	10
7	Pd(CH <sub>3</sub> COO) <sub>2</sub>	CuCl <sub>2</sub>	12	1.42	12
8	Pd(CF <sub>3</sub> COO) <sub>2</sub>	CuCl <sub>2</sub>	12	1.18	10
9	Pd(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	CuCl <sub>2</sub>	12	1.3	11
10	PdCl <sub>2</sub>	Cu(CH <sub>3</sub> COO) <sub>2</sub>	18	1.18	10
11	PdCl <sub>2</sub>	Cu(CF <sub>3</sub> COO) <sub>2</sub>	17	1.3	11
12	PdCl <sub>2</sub>	Cu(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	16	1.42	12
13	RhCl <sub>3</sub>	CuCl <sub>2</sub>	12	0.35	3
14	HgCl <sub>2</sub>	CuCl <sub>2</sub>	12	0.24	2
15	CoCl <sub>2</sub>	CuCl <sub>2</sub>	12	0.12	1
16	PtCl <sub>2</sub>	CuCl <sub>2</sub>	12	0	0
17	RuCl <sub>3</sub>	CuCl <sub>2</sub>	12	0	0
18	AlCl <sub>3</sub>	CuCl <sub>2</sub>	12	0	0
19	AgCl	CuCl <sub>2</sub>	16	0	0
20	CaCl <sub>2</sub>	CuCl <sub>2</sub>	12	0	0
21	FeCl <sub>3</sub>	CuCl <sub>2</sub>	14	0	0
22	VOCl <sub>3</sub>	CuCl <sub>2</sub>	12	0	0
23	VO(acac) <sub>2</sub>	CuCl <sub>2</sub>	12	0	0
24	Pd(acac) <sub>2</sub>	Cu(acac) <sub>2</sub>	12	0.35	3

<sup>a</sup> Reaction conditions: methane, 1200 psig (321 mmol); SO<sub>2</sub>, 30 psig (11.82 mmol); molar ratio of methane to SO<sub>2</sub>, 27; O<sub>2</sub>, 30 psig (11.82 mmol); PdCl<sub>2</sub>, 0.2 mmol; CuCl<sub>2</sub>, 0.3 mmol; solvent, CF<sub>3</sub>SO<sub>3</sub>H, 5 ml; temperature, 85 °C.

<sup>b</sup> This is the ratio of the moles of SO<sub>2</sub> converted to MSA to total moles of SO<sub>2</sub> taken initially in this reaction.



**Scheme 1** Direct sulfonation of methane to methanesulfonic acid.

**Table 2** Effect of process parameters on the sulfonation reaction<sup>a</sup>

Entry	CH <sub>4</sub> /psig	SO <sub>2</sub> /psig	O <sub>2</sub> /psig	PdCl <sub>2</sub> / mmol	CuCl <sub>2</sub> / mmol	T/°C	% SO <sub>2</sub> to MSA
1	200	30	30	0.2	0.3	85	tr
2	400	30	30	0.2	0.3	85	1
3	650	30	30	0.2	0.3	85	2
4	1000	30	30	0.2	0.3	85	8
5	1200	30	30	0.2	0.3	85	12
6	1200	0	30	0.2	0.3	85	0
7	1200	10	30	0.2	0.3	85	3
8	1200	20	30	0.2	0.3	85	7
9	1200	30	0	0.2	0.3	85	0
10	1200	30	10	0.2	0.3	85	6
11	1200	30	20	0.2	0.3	85	9
12	1200	30	40	0.2	0.3	85	10
13	1200	30	30	0.05	0.3	85	3
14	1200	30	30	0.1	0.3	85	7
15	1200	30	30	0.3	0.3	85	12
16	1200	30	30	0.2	0.05	85	7
17	1200	30	30	0.2	0.1	85	8
18	1200	30	30	0.2	0.2	85	10
19	1200	30	30	0.2	0.3	65	2
20	1200	30	30	0.2	0.3	75	8
21	1200	30	30	0.2	0.3	100	13

<sup>a</sup> Reaction conditions: time, 12 h; solvent, CF<sub>3</sub>SO<sub>3</sub>H, 5 ml.

increase in the amount of PdCl<sub>2</sub> had no effect on the MSA conversion (Table 2, entries 13–15).

When the amount of CuCl<sub>2</sub> was increased from 0.05 to 0.3 mmol, the SO<sub>2</sub> conversion to MSA increased from 7 to 12% (Table 2, entries 16–18). In the absence of CuCl<sub>2</sub>, Pd-black particles were observed in the reaction mixture after 4 h of reaction, whereas in presence of CuCl<sub>2</sub> the appearance of Pd-black particles was not so prominent. This suggests that CuCl<sub>2</sub> enhances the rate of oxidation of Pd(0) to Pd(II) species.

The conversion of SO<sub>2</sub> to MSA increased from 2 to 12% when the temperature was raised from 65 to 85 °C. At 100 °C, a 13% conversion of SO<sub>2</sub> to MSA was achieved and a trace amount of CF<sub>3</sub>SO<sub>3</sub>CH<sub>3</sub> was also detected (Table 2, entries 19–21).

The reaction requires a highly acidic solvent. When performed in H<sub>2</sub>SO<sub>4</sub>, 5% conversion of SO<sub>2</sub> to MSA was observed; however, no reaction was observed using acetic acid as the solvent. A 12% conversion of SO<sub>2</sub> to MSA was achieved using CF<sub>3</sub>SO<sub>3</sub>H as the solvent. To verify that the solvent CF<sub>3</sub>SO<sub>3</sub>H does not react with CH<sub>4</sub> to give CH<sub>3</sub>SO<sub>3</sub>H and CHF<sub>3</sub> (CH<sub>4</sub> + CF<sub>3</sub>SO<sub>3</sub>H → CH<sub>3</sub>SO<sub>3</sub>H + CHF<sub>3</sub>), a controlled reaction was performed in presence of O<sub>2</sub> and catalysts in CF<sub>3</sub>SO<sub>3</sub>H. No SO<sub>2</sub> was added. Under these conditions, MSA was not detected after 12 h of reaction. Likewise, no CHF<sub>3</sub> was detected by <sup>19</sup>F NMR. A small amount of CF<sub>3</sub>SO<sub>3</sub>CH<sub>3</sub> was observed as the sole product.

The mechanism by which Pd(II) and Cu(II) promote the sulfonation of CH<sub>4</sub> to MSA is not understood. It seems plausible to suggest, though, that the reaction proceeds *via* an electrophilic substitution of high valent Pd-species with CH<sub>4</sub><sup>1h–j,5,6</sup> and subsequent SO<sub>2</sub> insertion and oxidation<sup>3h</sup> to form MSA and Pd(0). Cu(II) then promotes the reoxidation of Pd(0) to Pd(II) in presence of O<sub>2</sub>.<sup>7</sup>

In conclusion, we have developed a highly selective low-temperature reaction protocol to sulfonate methane to methane-

sulfonic acid using SO<sub>2</sub> as the sulfonating agent and O<sub>2</sub> as the oxidant in the presence of a redox catalyst system comprising Pd(II) and Cu(II) salts. The reaction is highly selective, and as much as 20% of the SO<sub>2</sub> charged is converted to MSA with only 30 psig SO<sub>2</sub>, the maximum available pressure. The product MSA can be isolated from the reaction mixture by distillation under reduced pressure.

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## Notes and references

- (a) C. L. Hill, *Activation and functionalization of Alkanes*, Wiley, New York, 1989; (b) M. G. Axelrod, A. M. Gaffney, R. Pitchai and J. A. Sofranko, *Natural Gas Conversion II*, Elsevier, Amsterdam, 1994, p. 93; (c) G. A. Olah and A. Molnar, *Hydrocarbon Chemistry*, Wiley, New York, 1995; (d) G. J. Hutchings, M. S. Scurrell and J. R. Woodhouse, *Chem. Soc. Rev.*, 1989, **18**, 251; (e) R. M. Ormerod, *Chem. Soc. Rev.*, 2003, **32**, 17; (f) K. Otsuka and Y. Wang, *Appl. Catal.*, 2001, **222**, 145; (g) A. Ueno, *Catalysis*, 2000, **15**, 185; (h) G. Dyker, *Angew. Chem., Int. Ed.*, 1999, **38**, 1698; R. A. Periana, D. J. Taube, E. R. Evitt, D. G. Loffer, P. R. Wentreck, G. Voss and T. Masuda, *Science*, 1993, **259**, 340; (i) R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh and H. Fujii, *Science*, 1998, **280**, 560; (j) R. A. Periana, O. Mirinov, D. J. Taube and S. Gamble, *Chem. Commun.*, 2002, 2376.
- (a) *Ullmann's Encyclopedia of Industrial Chemistry*, VCH, Weinheim, 1994, **Vol. A25**, pp. 503–506; (b) F. M. Beringer and R. A. Falk, *J. Am. Chem. Soc.*, 1959, **81**, 2997; (c) H. A. Young, *J. Am. Chem. Soc.*, 1937, **59**, 811; (d) R. C. Murray, *J. Chem. Soc.*, 1933, 739.
- (a) N. Basicckes, T. E. Hogan and A. Sen, *J. Am. Chem. Soc.*, 1996, **118**, 13111; (b) L. J. Lobree and A. T. Bell, *Ind. Eng. Chem. Res.*, 2001, **40**, 736; (c) S. Mukhopadhyay and A. T. Bell, *Ind. Eng. Chem. Res.*, 2002, **41**, 5901; (d) S. Mukhopadhyay and A. T. Bell, *Org. Process. Res. Dev.*, 2003, **7**, 161; (e) S. Mukhopadhyay and A. T. Bell, *Angew. Chem., Int. Ed.*, 2003, **42**, 1019; (f) S. Mukhopadhyay and A. T. Bell, *Angew. Chem., Int. Ed.*, 2003, in press; (g) S. Mukhopadhyay and A. T. Bell, *J. Am. Chem. Soc.*, 2003, **125**, 4406; (h) Y. Ishii, K. Matsunaka and S. Sakaguchi, *J. Am. Chem. Soc.*, 2000, **122**, 7390.
- In a 100-ml glass lined high pressure Parr autoclave reactor, 0.2 mmol PdCl<sub>2</sub>, 0.3 mmol CuCl<sub>2</sub>, and 5 ml of trifluoromethanesulfonic acid were charged together with a small Teflon coated magnetic stir bar. The reactor was then pressurized with 30 psig SO<sub>2</sub>, 30 psig O<sub>2</sub>, and then ultimately with 1200-psig methane from the adjacent connecting cylinders. The reactor was then heated to 85 °C under stirring and kept at that temperature for 12 h. After the stipulated period of time, the reactor was cooled to room temperature and opened to collect the reaction mixture. The mixture was then added slowly to 1.0 g of water and then taken for <sup>1</sup>H NMR analysis. D<sub>2</sub>O and methanol were used in a capillary as the lock references. The corresponding chemical shift for MSA was 2.78 to 2.98 ppm, depending on the concentration of MSA in the mixture.
- Pd and Cu catalyst combination is used for the carbonylation of methane to acetic acid in CF<sub>3</sub>COOH as the solvent, see (a) T. Nishiguchi, K. Nakata, K. Takaki and Y. Fujiwara, *Chem. Lett.*, 1992, 1141; (b) A. Sen, *Platinum Met. Rev.*, 1991, **35**, 126; (c) L.-C. Kao, A. C. Hutson and A. Sen, *J. Am. Chem. Soc.*, 1991, **113**, 700; (d) Carbene based Pd-catalyst has been used recently for methane oxidation, see M. Muehlhofer, T. Strassner and W. A. Herrmann, *Angew. Chem., Int. Ed.*, 2002, **41**, 1745.
- Pt-salt based methane activation by Shilov chemistry, see (a) A. E. Shilov and G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer Academic Publishers: Dordrecht, 2000; (b) For a nice mechanistic recent review see J. A. Labinger and J. E. Bercaw, *Nature*, 2002, **417**, 507.
- For the role of co-catalysts in PdCl<sub>2</sub> catalyzed C–H bond activation in benzene, see S. Mukhopadhyay, G. Rothenberg, G. Lando, K. Agbaria, M. Kazanci and Y. Sasson, *Adv. Synth. Catal.*, 2001, **343**, 455.