A High-Yield, Liquid-Phase Approach for the Partial Oxidation of Methane to Methanol using SO₃ as the Oxidant

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Abstract: A direct approach for producing methanol from methane in a three-step, liquid phase process is reported. In the first step, methane is reacted with SO₃ to form methanesulfonic acid (MSA) at 75 °C using a free-radical initiator and MSA as the solvent. Urea-H₂O₂ in combination with RhCl₃ is found to be the most effective initiator (57% conversion of SO₃; 7.2% conversion of CH₄). MSA is then oxidized by SO₃ at 160 °C in a second step to produce a mixture containing methyl bisulfate and some methyl methanesulfonate (87% conversion of MSA). In the third step, the mixture of methyl bisulfate and methyl methanesulfonate is hydrolyzed in the presence of an organic solvent, to produce an organic phase containing methanol and an aqueous phase containing sulfuric acid and some MSA (63% conversion of methyl bisulfate; 72% conversion of methyl methanesulfonate). Overall, 58% of the MSA (of which 23% is derived from methane) is converted to methanol.

Keywords: catalytic oxidation; C–H activation; methane; methanol; rhodium; sulfur trioxide

Attempts to carry out the partial oxidation of methane^[1–12] to methanol in the gas phase have met with limited success because of difficulties in controlling the free radical processes that are involved. Since methanol is more reactive than methane, the formation of CO and CO₂ via secondary combustion is unavoidable. While a variety of catalysts, mostly metal oxides, have been reported for the partial oxidation of methane to methanol, all require high temperatures and the reported methanol yields based on methane have generally been less than 10%.

An indirect approach for the conversion of methane to methanol has been reported by Periana et al.^[13–16] These authors have demonstrated that methane can be converted to methyl bisulfate in a single-step using Hg²⁺, Pt-complexes, or I₂⁺ as catalysts. The reaction is

carried out in fuming sulfuric acid at temperatures of 180–220 °C, and bisulfate yields of up to 43% based on methane can be achieved. Since methyl bisulfate cannot be readily separated from sulfuric acid, it is hydrolyzed to methanol by addition of water to the methyl bisulfate-sulfuric acid solution. Separation of methanol from the resulting solution is difficult, and the dilute sulfuric acid solution remaining must be concentrated before it can be recycled. Here, we show that pure methanol can be produced from methane and SO₃ in a three-step process that avoids the use of sulfuric acid as a solvent and enables the facile separation of methanol. Concentrated sulfuric acid is produced as a by-product, which can either be sold or reprocessed to elemental sulfur.

In a typical reaction, methanesulfonic acid (MSA) is formed in a high-pressure, glass-lined autoclave by reacting ¹³CH₄ with SO₃ dissolved in CH₃SO₃H containing a free radical initiator.^[17–22] Reactions are carried out for 6 h at 75 °C. CH₃SO₃H is then oxidized in the presence of a catalyst to CH₃OSO₃H and CH₃SO₃CH₃ by reaction with SO₃ at temperatures of 130–185 °C. Products are identified and quantified by ¹H and ¹³C NMR spectroscopy. In the last step, CH₃OSO₃H is hydrolyzed in the presence of an organic solvent. The methanol is then distilled from the organic phase and identified by NMR, GC-MS, and Raman spectroscopy.

Table 1 shows the effects of initiator composition on the sulfonation of methane to MSA with SO₃ at 75 °C. Conversions are expressed in terms of SO₃ since it is the limiting reagent and CH₄ is present in excess. K₄P₂O₈ is the least effective initiator, whereas K₂S₂O₈, urea-H₂O₂, and CaO₂ are moderately effective. However, urea-H₂O₂ in combination with RhCl₃ is the most effective initiator, enabling 57% of the SO₃ to be converted to MSA using MSA as the solvent. Previous studies

Table 1. Effect of initiator composition on the yield of methanesulfonic acid (MSA).^[a]

#	Initiator [mmol]	MSA produced, [mmol]	% Conversion of SO ₃ to MSA	Volumetric productivities to MSA [mol cm ⁻³ s ⁻¹]
1	K ₂ S ₂ O ₈ , 0.07	5	24	7.71×10^{-8}
2	K ₄ P ₂ O ₈ , 0.07	3	14	4.62×10^{-8}
3	CaO ₂ , 0.09	9	43	1.38×10^{-7}
4	Urea-H ₂ O ₂ , 0.4	7	33	1.05×10^{-7}
5	Urea-H ₂ O ₂ , 0.4/RhCl ₃ , 0.1	12	57	1.85×10^{-7}

^[a] Reaction conditions: ¹³CH₄, 600 psig (166 mmol); SO₃, 21 mmol; MSA, 3.96 g; time, 6 h; temperature, 75 °C.

Table 2. RhCl₃-catalyzed oxidation of MSA by SO₃ to methyl bisulfate.^[a]

#	T [°C]	Oxidant [mmol]	% Conversion of MSA [mmol]	% Conversion of MSA to CH ₃ OSO ₃ H [mmol]	% Conversion of MSA to CH ₃ SO ₃ CH ₃ [mmol]	% Selectivity to CH ₃ X ^[b]	Mol of CH ₃ X ^[b] cm ⁻³ s ⁻¹
1	130	SO ₃ , 15	8 (4.2)	8 (4.2)	0 (0)	100	2.92×10^{-8}
2	150	SO ₃ , 15	12 (6.3)	9 (5)	3 (0.7)	100	3.96×10^{-8}
3	160	SO ₃ , 15	15 (8)	10 (5.5)	4 (1.0)	94	4.51×10^{-8}
4 ^c	185	SO ₃ , 15	18 (9.5)	4 (2)	11 (3.0)	84	2.31×10^{-8}
4	160	SO ₃ , 21	33 (17.5)	26 (14)	5 (1.2)	93	1.05×10^{-7}
5	160	SO ₃ , 30	48 (25.4)	30 (16)	15 (4.0)	94	1.38×10^{-7}
6	160	SO ₃ , 55	88 (47)	55 (29)	28 (7.5)	93	2.53×10^{-7}
7	160	SO ₃ , 64	100 (53)	49 (26)	38 (10)	87	2.50×10^{-7}
8 ^d	120	H ₂ O ₂ , 30	0 (0)	0 (0)	0 (0)	0	0
9	160	O ₂ , 33	2 (1)	2 (1)	–	50	6.94×10^{-9}
10 ^e	160	SO ₃ , 65	100 (53)	96 (51)	0 (0)	96	5.9×10^{-7}

^[a] Reaction conditions: MSA, 5.11 g, (53 mmol); T, 160 °C; time, 10 h. RhCl₃, 0.1 mmol.

^[b] CH₃X is methanol equivalent (CH₃OSO₃H and CH₃SO₃CH₃).

^[c] 15 h.

^[d] 6 h.

^[e] H₂SO₄ is the solvent.

utilizing the initiators listed in Table 1 have shown that 75 °C is an optimal temperature, since at higher temperatures the initiator rapidly decomposes, producing O₂.^[22] Since the reaction is thought to occur *via* a free radical mechanism,^[17–22] the presence of O₂ inhibits the sulfonation of methane to MSA. Thus, for example, sulfonation at 160 °C in fuming sulfuric acid results in a 4% conversion of SO₃ to CH₃OSO₃H after 6 h of reaction, but no formation of MSA.

Table 2 shows the effects of different reaction conditions on the oxidation of MSA to CH₃X (CH₃OSO₃H or CH₃SO₃CH₃) by SO₃. When a mixture containing 15 mmol of SO₃ and 53 mmol MSA was heated at 130 °C for 10 h, 8% of the MSA charged into the reactor was transformed to CH₃OSO₃H with 100% selectivity (Figure 1a). Increasing the temperature to 150 °C raised the conversion of MSA to CH₃X to 12%, of which 75% was CH₃OSO₃H and 25% was CH₃SO₃CH₃. At 160 °C, 15% of the MSA was converted to products, of these products 94% appeared as CH₃X and the balance as a mixture of CH₃OSO₂OCH₃, CH₂(SO₃H)₂, and CH₃(SO₃)_nH. While CH₃OSO₃H remained as the major

Figure 1. (a) ¹³C NMR of the mixture after 10 h of reaction between MSA and SO₃, T = 130 °C; SO₃, 15 mmol. (b) ¹³C NMR of the mixture after 10 h of reaction between MSA and SO₃, T = 160 °C; SO₃, 55 mmol.

product at 160 °C (Figure 1b), CH₃SO₃CH₃ became the major product when the reaction temperature was raised to 185 °C.

The effect of the amount of SO₃ on the oxidation of MSA to CH₃X was also studied. Raising the amount of

Table 3. Single-pass extractive hydrolysis of CH₃OSO₃H to CH₃OH in a solvent.

#	Mol ratio of H ₂ O/CH ₃ OSO ₃ H	Solvent	T [°C]	Percent of MeOH extracted into the solvent phase [mol %]	H ₂ SO ₄ in the aqueous phase [wt %]
1	1	CH ₂ Cl ₂	25	6	87
2	3	CH ₂ Cl ₂	25	17	65
3	5	CH ₂ Cl ₂	25	29	54
4	7	CH ₂ Cl ₂	25	32	44
5	10	CH ₂ Cl ₂	25	39	36
6	5	CH ₂ Cl ₂	40	46	54
7	5	CHCl ₃	61	62	54
8 ^b	5	CHCl ₃	61	58	49
9 ^c	5	CHCl ₃	61	53	45
10 ^d	5	CHCl ₃	61	61	54
11 ^e	5	CHCl ₃	61	53	54
12	5	C ₂ H ₄ Cl ₂	83	63	54
13 ^f	5	C ₂ H ₄ Cl ₂	83	72	—

[a] Reaction conditions: CH₃OSO₃H, 0.375 g; solvent, 7 g; time, 2 h; N₂, 300 psig. The reaction progress is monitored by ¹H NMR.

[b] 10 wt %; MSA was added in the feed.

[c] 20 wt %; MSA was added in the feed.

[d] 5 g CHCl₃ were used.

[e] 3 g CHCl₃ were used.

[f] 0.375 g of CH₃SO₃CH₃ were used instead of CH₃OSO₃H.

SO₃ added to the reaction mixture from 15 to 64 mmol increased the conversion of MSA from 15% to 100%. While the selectivity to CH₃X was independent of the amount of SO₃, the distribution between CH₃OSO₃H and CH₃SO₃CH₃ shifted from 85% CH₃OSO₃H to 72%.

MSA oxidation by H₂O₂, O₂, and H₂SO₄ was also considered. H₂O₂ was inactive at 130 °C and only a small amount of CH₃OSO₃H was observed when O₂ was used as the oxidant. A 12% conversion of MSA to CH₃OSO₃H was achieved at 160 °C after 10 h of reaction in 100% H₂SO₄ and no CH₃SO₃CH₃ was observed. When H₂SO₄ was used as the solvent and SO₃ as the oxidant, 96% of the initial MSA charged into the reactor was converted to CH₃OSO₃H and, again, no CH₃SO₃CH₃ was observed.

Table 3 shows the effectiveness of the single-pass extractive hydrolysis of CH₃OSO₃H in the presence of a water immiscible organic solvent. Low boiling halogenated solvents such as CH₂Cl₂, CHCl₃, and C₂H₄Cl₂ were used. For a fixed set of hydrolysis and extraction conditions, CHCl₃ and C₂H₄Cl₂ showed comparable effectiveness, and both solvents were superior to CH₂Cl₂. Since the extent of CH₃OSO₃H hydrolysis depends on the molar ratio of H₂O/CH₃OSO₃H, the value of this ratio was varied. Table 3 shows that as the ratio increases from 1 to 10, the percent extraction of CH₃OH increases rapidly at first but then more slowly. At the same time, the weight percent of H₂SO₄ in the aqueous phase decreases monotonically. A molar ratio of 5 to 1 H₂O to CH₃OSO₃H resulted in a 29% extraction of methanol in one step and an aqueous phase containing 54 wt % H₂SO₄. To determine the effect of MSA on the extraction of metha-

nol, experiments were performed in which 10 and 20% MSA was present in the feed. The extraction efficiency decreased by a small amount as the amount of MSA increased. Reducing the ratio of organic solvent to CH₃OSO₃H from 20 to 13 had little effect on the methanol extraction efficiency; however, decreasing this ratio to 10 had a noticeable detrimental effect. The hydrolysis of CH₃SO₃CH₃ to CH₃OH was carried out under conditions identical to those used for CH₃OSO₃H (entry 12 in Table 3). A methanol extraction of 72% could be achieved starting from CH₃SO₃CH₃, as apposed to 63% in the case of CH₃OSO₃H.

As seen in Table 3, the final sulfuric acid concentration in the aqueous phase remained close to 60 wt %. This level is sufficiently high for direct use in the dyes, paint, and pharmaceutical industries. 100% H₂SO₄ could be produced by solar concentration or by addition of SO₃.

To confirm the formation of methanol as the final product, the extract obtained using ClCH₂CH₂Cl was fractionated. The product that was condensed was identified as pure methanol on the basis of ¹³C NMR (49 ppm) and Raman spectroscopy (1039, 1459, 2840, 2949, and 3341 cm⁻¹).

In conclusion, we have demonstrated a high-yield approach for the selective conversion of methane to methanol. The proposed scheme could readily be incorporated into a refinery, since the SO₃ required for the process could be produced by oxidation of H₂S, the product of petroleum hydrosulfurization.^[23–26] The SO₂ formed during the oxidation of MSA can be recovered readily and reoxidized to SO₃. The concentrated sulfuric acid

produced as a by-product of $\text{CH}_3\text{OSO}_3\text{H}$ hydrolysis could be sent to the Claus process where it would react with H_2S to produce elemental sulfur which would finally be transformed to SO_3 by catalytic oxidation with air.

Experimental Section

Typical Procedure

In a typical reaction, a 100-mL, glass-lined, high-pressure Parr autoclave reactor was charged with 0.4 mmol of urea- H_2O_2 , 0.1 mmol of RhCl_3 , 3.76 g of MSA, and 21 mmol of SO_3 . A small Teflon-coated magnetic stir bar was used to stir the reaction mixture. The reactor was purged with N_2 to expel the air and pressurized with 600 psig of $^{13}\text{CH}_4$. The reactor was then heated to 75°C under stirring and kept at that temperature for 6 h. After the stipulated period of time, the reactor was cooled, purged with N_2 , and opened to add extra SO_3 to the reaction mixture. The autoclave was then closed, purged with N_2 and then pressurized with 300 psig of N_2 gas and heated slowly to 160°C . The reaction mixture was stirred at 160°C for 10 h. After this period, the reactor was cooled, the pressure was released, and the reactor was purged with N_2 gas. The reaction mixture was analyzed ^1H and ^{13}C NMR. D_2O was used in a capillary as the lock reference. The ^1H NMR chemical shift was 2.87 ppm to 3.04 ppm for MSA, 3.76 ppm to 3.98 ppm for $\text{CH}_3\text{OSO}_3\text{H}$, 3.13 ppm and 3.83 ppm for $\text{CH}_3\text{SO}_3\text{CH}_3$, the range of chemical shifts in each case depending on the product concentration. A ^1H NMR chemical shift of 3.27 ppm was observed for CH_3OH . The corresponding ^{13}C NMR chemical shifts are: 39.5–40.5 ppm for MSA, 60–60.5 ppm for $\text{CH}_3\text{OSO}_3\text{H}$, and 35.5–36.0 ppm and 58.0–58.5 ppm for $\text{CH}_3\text{SO}_3\text{CH}_3$.

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References

- [1] C. L. Hill, *Activation and Functionalization of Alkanes*, Wiley, New York, **1989**.
- [2] M. G. Axelrod, A. M. Gaffney, R. Pitchai, J. A. Sofranko, *Natural Gas Conversion II*, Elsevier, Amsterdam, **1994**.
- [3] A. E. Shilov, G. B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer Academic Publishers, Dordrecht, **2000**.
- [4] a) G. A. Olah, A. Molnar, *Hydrocarbon Chemistry*, Wiley, New York, **1995**; b) M. Lin, A. Sen, *Nature* **1994**, 368, 613–615.
- [5] H. D. Gesser, N. R. Hunter, *Catal. Today* **1998**, 42, 183–189.
- [6] J. H. Lunsford, *Catal. Today* **2000**, 63, 165–174.
- [7] K. Otsuka, Y. Wang, *Appl. Catal. A: Gen.* **2001**, 222, 145–161.
- [8] S. Mukhopadhyay, A. T. Bell, *Chem. Commun.* **2003**, 1590–1591.
- [9] M. Zerella, S. Mukhopadhyay, A. T. Bell, *Org. Lett.* **2003**, 5, 3193–3196.
- [10] G. A. Foulds, B. F. Gray, *Fuel Proc. Tech.* **1995**, 42, 129–50.
- [11] J. A. Labinger, J. E. Bercaw, *Nature* **2002**, 417, 507.
- [12] S. Mukhopadhyay, A. T. Bell, *J. Mol. Catal. A: Chem.* **2004**, 211, 59–65.
- [13] R. A. Periana, D. J. Taube, E. R. Evitt, D. G. Loffer, P. R. Wentreck, G. Voss, T. A. Masuda, *Science* **1993**, 259, 340–343.
- [14] R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, *Science* **1998**, 280, 560–564.
- [15] R. A. Periana, O. Mironov, D. J. Taube, S. Gamble, *Chem. Commun.* **2002**, 2376–2377.
- [16] R. A. Periana, G. Bhalla, W. J. Tenn, III, K. J. H. Young, X. Y. Liu, O. Mironov, C. J. Jones, V. R. Ziatdinov, *J. Mol. Catal. A: Chem.* **2004**, 220, 7–25.
- [17] N. Basicckes, T. E. Hogan, A. Sen, *J. Am. Chem. Soc.* **1996**, 118, 13111–13112.
- [18] M. Asadullah, T. Kitamura, Y. Fujiwara, *Angew. Chem. Int. Ed.* **2000**, 39, 2475–2478.
- [19] S. Mukhopadhyay, A. T. Bell, *Ind. Eng. Chem. Res.* **2002**, 41, 5901–5905.
- [20] S. Mukhopadhyay, A. T. Bell, *Angew. Chem. Int. Ed.* **2003**, 42, 1019–1021.
- [21] S. Mukhopadhyay, A. T. Bell, *J. Am. Chem. Soc.* **2003**, 125, 4406–4407.
- [22] S. Mukhopadhyay, A. T. Bell, *Angew. Chem. Int. Ed.* **2003**, 42, 2990–2993.
- [23] R. H. Hass, J. W. Ward, *US Patent* 4,444,742, **1982**.
- [24] J. Z. Zhang, F. J. Millero, *Geochimica Acta* **1993**, 57, 1708–1718.
- [25] P. Schoubye, *European Patent* 852,159, **1998**.
- [26] Y. V. Filatov, V. V. Igin, L. M. Varshavskaya, A. A. Ryzhkova, *Zh. Prikl. Khimii* **1988**, 61, 1226–1231.