A High-Yield, Liquid-Phase Approach for the Partial Oxidation of Methane to Methanol using SO_3 as the Oxidant

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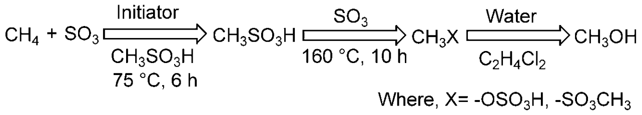
Received: December 27, 2004; Accepted: April 4, 2005

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 SO_3 to form methanesulfonic acid (MSA) at 75 °C using a free-radical initiator and MSA as the solvent. Urea-H_2O_2 in combination with $RhCl_3$ is found to be the most effective initiator (57% conversion of SO_3; 7.2% conversion of CH_4). MSA is then oxidized by SO_3 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 CO_2 *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 Hg^{2+}, Pt-complexes, or I_2^+ 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 SO_3 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 $^{13}CH_4$ with SO_3 dissolved in CH_3SO_3H containing a free radical initiator.[17–22] Reactions are carried out for 6 h at 75 °C. CH_3SO_3H is then oxidized in the presence of a catalyst to CH_3OSO_3H and $CH_3SO_3CH_3$ by reaction with SO_3 at temperatures of 130–185 °C. Products are identified and quantified by ^1H and ^{13}C NMR spectroscopy. In the last step, CH_3OSO_3H 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 SO_3 at 75 °C. Conversions are expressed in terms of SO_3 since it is the limiting reagent and CH_4 is present in excess. $K_4P_2O_8$ is the least effective initiator, whereas $K_2S_2O_8$, urea-H_2O_2, and CaO_2 are moderately effective. However, urea-H_2O_2 in combination with $RhCl_3$ is the most effective initiator, enabling 57% of the SO_3 to be converted to MSA using MSA as the solvent. Previous studies

DOI: 10.1002/adsc.200404394

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	$K_2S_2O_8$, 0.07	5	24	7.71×10^{-8}
2	$K_4P_2O_8$, 0.07	3	14	4.62×10^{-8}
3	CaO_2, 0.09	9	43	1.38×10^{-7}
4	Urea-H_2O_2, 0.4	7	33	1.05×10^{-7}
5	Urea-H_2O_2, 0.4/$RhCl_3$, 0.1	12	57	1.85×10^{-7}

[a] Reaction conditions: $^{13}CH_4$, 600 psig (166 mmol); SO_3, 21 mmol; MSA, 3.96 g; time, 6 h; temperature, 75 °C.

Table 2. $RhCl_3$-catalyzed oxidation of MSA by SO_3 to methyl bisulfate.[a]

#	T [°C]	Oxidant [mmol]	% Conversion of MSA [mmol]	% Conversion of MSA to CH_3OSO_3H [mmol]	% Conversion of MSA to $CH_3SO_3CH_3$ [mmol]	% Selectivity to CH_3X[b]	Mol of CH_3X[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_2O_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. $RhCl_3$, 0.1 mmol.
[b] CH_3X is methanol equivalent (CH_3OSO_3H and $CH_3SO_3CH_3$).
[c] 15 h.
[d] 6 h.
[e] H_2SO_4 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 O_2.[22] Since the reaction is thought to occur *via* a free radical mechanism,[17–22] the presence of O_2 inhibits the sulfonation of methane to MSA. Thus, for example, sulfonation at 160 °C in fuming sulfuric acid results in a 4% conversion of SO_3 to CH_3OSO_3H 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 CH_3X (CH_3OSO_3H or $CH_3SO_3CH_3$) by SO_3. When a mixture containing 15 mmol of SO_3 and 53 mmol MSA was heated at 130 °C for 10 h, 8% of the MSA charged into the reactor was transformed to CH_3OSO_3H with 100% selectivity (Figure 1a). Increasing the temperature to 150 °C raised the conversion of MSA to CH_3X to 12%, of which 75% was CH_3OSO_3H and 25% was $CH_3SO_3CH_3$. At 160 °C, 15% of the MSA was converted to products, of these products 94% appeared as CH_3X and the balance as a mixture of $CH_3OSO_2OCH_3$, $CH_2(SO_3H)_2$, and $CH_3(SO_3)_nH$. While CH_3OSO_3H remained as the major product at 160 °C (Figure 1b), $CH_3SO_3CH_3$ became the major product when the reaction temperature was raised to 185 °C.

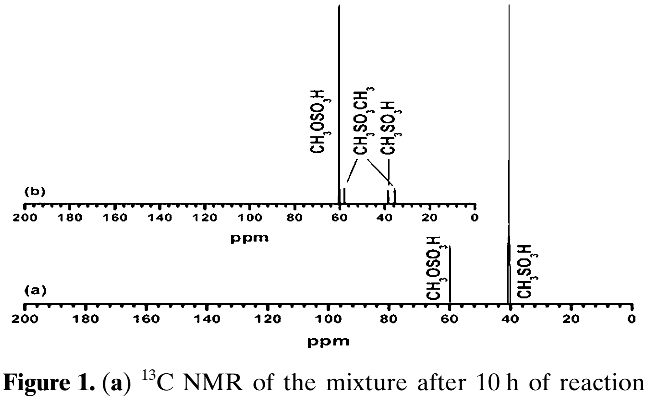


Figure 1. (**a**) ^{13}C NMR of the mixture after 10 h of reaction between MSA and SO_3, $T = 130$ °C; SO_3, 15 mmol. (**b**) ^{13}C NMR of the mixture after 10 h of reaction between MSA with SO_3, $T = 160$ °C; SO_3, 55 mmol.

The effect of the amount of SO_3 on the oxidation of MSA to CH_3X was also studied. Raising the amount of

Table 3. Single-pass extractive hydrolysis of CH_3OSO_3H to CH_3OH in a solvent.

#	Mol ratio of H_2O/CH_3OSO_3H	Solvent	T [°C]	Percent of MeOH extracted into the solvent phase [mol %]	H_2SO_4 in the aqueous phase [wt %]
1	1	CH_2Cl_2	25	6	87
2	3	CH_2Cl_2	25	17	65
3	5	CH_2Cl_2	25	29	54
4	7	CH_2Cl_2	25	32	44
5	10	CH_2Cl_2	25	39	36
6	5	CH_2Cl_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	$C_2H_4Cl_2$	83	63	54
13[f]	5	$C_2H_4Cl_2$	83	72	–

[a] Reaction conditions: CH_3OSO_3H, 0.375 g; solvent, 7 g; time, 2 h; N_2, 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 $CHCl_3$ were used.

[e] 3 g $CHCl_3$ were used.

[f] 0.375 g of $CH_3SO_3CH_3$ were used instead of CH_3OSO_3H.

SO_3 added to the reaction mixture from 15 to 64 mmol increased the conversion of MSA from 15% to 100%. While the selectivity to CH_3X was independent of the amount of SO_3, the distribution between CH_3OSO_3H and $CH_3SO_3CH_3$ shifted from 85% CH_3OSO_3H to 72%.

MSA oxidation by H_2O_2, O_2, and H_2SO_4 was also considered. H_2O_2 was inactive at 130 °C and only a small amount of CH_3OSO_3H was observed when O_2 was used as the oxidant. A 12% conversion of MSA to CH_3OSO_3H was achieved at 160 °C after 10 h of reaction in 100% H_2SO_4 and no $CH_3SO_3CH_3$ was observed. When H_2SO_4 was used as the solvent and SO_3 as the oxidant, 96% of the initial MSA charged into the reactor was converted to CH_3OSO_3H and, again, no $CH_3SO_3CH_3$ was observed.

Table 3 shows the effectiveness of the single-pass extractive hydrolysis of CH_3OSO_3H in the presence of a water immiscible organic solvent. Low boiling halogenated solvents such as CH_2Cl_2, $CHCl_3$, and $C_2H_4Cl_2$ were used. For a fixed set of hydrolysis and extraction conditions, $CHCl_3$ and $C_2H_4Cl_2$ showed comparable effectiveness, and both solvents were superior to CH_2Cl_2. Since the extent of CH_3OSO_3H hydrolysis depends on the molar ratio of H_2O/CH_3OSO_3H, the value of this ratio was varied. Table 3 shows that as the ratio increases from 1 to 10, the percent extraction of CH_3OH increases rapidly at first but then more slowly. At the same time, the weight percent of H_2SO_4 in the aqueous phase decreases monotonically. A molar ratio of 5 to 1 H_2O to CH_3OSO_3H resulted in a 29% extraction of methanol in one step and an aqueous phase containing 54 wt % H_2SO_4. To determine the effect of MSA on the extraction of methanol, 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 CH_3OSO_3H 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 $CH_3SO_3CH_3$ to CH_3OH was carried out under conditions identical to those used for CH_3OSO_3H (entry 12 in Table 3). A methanol extraction of 72% could be achieved starting from $CH_3SO_3CH_3$, as apposed to 63% in the case of CH_3OSO_3H.

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% H_2SO_4 could be produced by solar concentration or by addition of SO_3.

To confirm the formation of methanol as the final product, the extract obtained using $ClCH_2CH_2Cl$ was fractionated. The product that was condensed was identified as pure methanol on the basis of ^{13}C 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 SO_3 required for the process could be produced by oxidation of H_2S, the product of petroleum hydrodesulfurization.[23–26] The SO_2 formed during the oxidation of MSA can be recovered readily and reoxidized to SO_3. The concentrated sulfuric acid produced as a by-product of CH_3OSO_3H 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 $^{13}CH_4$. 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 160ºC. 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 CH_3OSO_3H, 3.13 ppm and 3.83 ppm for $CH_3SO_3CH_3$, 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 CH_3OSO_3H, and 35.5–36.0 ppm and 58.0–58.5 ppm for $CH_3SO_3CH_3$.

Acknowledgements

This work was supported by a grant from BP as a part of the Methane Conversion Cooperative.

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. Wentrcek, 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. Basickes, 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. Prik. Khimii* **1988**, *61*, 1226–1231.