

Contents lists available at ScienceDirect

Applied Catalysis A: General



journal homepage: www.elsevier.com/locate/apcata

Methane oxidation to methyl bisulfate in oleum at ambient pressure in the presence of iodine as a catalyst

Beata Michalkiewicz

The West Pomeranian University of Technology in Szczecin, ul. Pułaskiego 10, 70-322 Szczecin, Poland

ARTICLE INFO

ABSTRACT

Article history: Received 23 November 2010 Received in revised form 4 January 2011 Accepted 6 January 2011 Available online 13 January 2011

Keywords: Methane Oleum Methyl bisulfate Iodine

1. Introduction

The selective oxidation of methane to liquid products such as methyl ester, methanol acetic acid has been of great interest as it is an alternative route for conversion of natural gas to high-addedvalue products. A great deal of research effort has been made to develop homogenous catalytic systems for the low temperature selective oxidation in acids, mainly sulfuric acid or oleum. Usually various metals from B group of periodic table of elements were applied as catalyst. Methane was oxidized to products such as methanol [1-3], esters [3-8], sulfonic acid [9-11], and acetic acid [13–15]. The examples of such catalytic systems are: 20 wt.% SO₃ in oleum + dichloro(γ -2-{2,20-dipirymidyn})platinum(II) [4], Pd(CF₃COO)₂+CF₃COOH [5], HgSO₄+H₂SO₄ [6], Pd+oleum [7]. Bjerrum applied a new series of iodine containing compounds such as I₂, KI, NaI, CH₃I, I₂O₅, KIO₃ and KIO₄ in oleum contained 65 wt.% SO₃. [16,17]. Methyl bisulfate yield equal to 73% was obtained at 180 °C and 5.1 MPa. Iodine was used as a catalyst by the other authors in lower concentrated oleum: 25% [18], 2% [19].

Three different reactions of methane oxidations were proposed:

 $CH_4 + 2SO_3 \rightarrow CH_3OSO_3H + SO_2[17]$

 $CH_4 + 2H_2SO_4 \rightarrow CH_3OSO_3H + 2H_2O + SO_2[6]$

Methane oxidation to methyl bisulfate at ambient pressure in absorption reactor packed with glass balls in presence of iodine as a catalyst was investigated. The process was performed at temperature 120-130 °C, sulfur trioxide concentration in oleum 16-25 wt.%, catalyst concentration 0.008-0.024 mol dm⁻³, methane flow: $8.69 \text{ cm}^3 \text{ min}^{-1}$. The optimal conditions for high ester concentration were defined. © 2011 Elsevier B.V. All rights reserved.

 $CH_4 + SO_3 + H_2SO_4 \rightarrow \ CH_3OSO_3H + \ SO_2 + H_2O\left[18\right]$

It is commonly believed that methyl bisulfate can be hydrolyzed to methanol in a separate step according to the reaction:

 $CH_3OSO_3H + H_2O \rightarrow CH_3OH + H_2SO_4$

All authors performed the methane oxidation in acids at high pressure (at least 1 MPa). The best results were obtained under 3.45–5.5 MPa.

The aim of our investigation was to demonstrate that it is possible to carry out a methane esterification at ambient pressure with iodine as a catalyst. Lowering of the pressure is very desirable. In order to ensure good gas absorption in oleum the packed column as reactor was applied. To our best knowledge, there is only one publication concerned with methane oxidation at ambient pressure [20] and there is no report in the literature, referring to the application of iodine as a catalyst in methane oxidation to methyl bisulphate at ambient pressure.

2. Experimental

Methane oxidation was performed in tubular reactor packed with glass balls. Such reactor design allowed to increase methane dissolving in oleum. At the top of the reactor oleum contained iodine was slowly drooped. Methane was supplied at the bottom. The apparatus is described in detail in the previous paper [20]. The liquid mixture was collected after pass through the reactor and recycled back to the reactor. One pass lasted for 6 h.

E-mail address: beata.michalkiewicz@zut.edu.pl

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2011.01.014



Fig. 1. The methyl bisulfate concentration in the reaction mixture vs. time of the reaction. Methane flow: $8.69 \text{ cm}^3 \text{ min}^{-1}$, temperature: $130 \,^{\circ}\text{C}$, sulfur trioxide concentration: 25 wt.%, catalyst concentration: $0.016 \text{ mol dm}^{-3}$.

The qualitative analysis of the reaction mixture after pass through the reactor was performed by ¹³C NMR. The methyl ester was hydrolyzed to methanol by means of water and quantitatively analyzed by gas chromatography.

3. Result and discussion

On the basics of ¹³C NMR measurements (spectra not presented here) one can conclude that hydrogen bisulfate was the only liquid product of the methane oxidation. After hydrolysis only methanol was observed by means of ¹³C NMR spectroscopy (no methyl ester was present) so concentration of ester in oleum can be determine by the GC analysis of methanol.

The number of passes through the reactor influence on methyl bisulfate concentration was investigated. The methane flow was equal to 8.69 cm³ min⁻¹. Oleum contained 25 wt.% of SO₃ was used. The temperature of the reaction mixture was maintained at 130 °C. Concentration of I₂ was equal to 0.016 mol dm⁻³. Plot of the dependence of the methyl bisulfate concentration in the reaction mixture vs. time is presented in Fig. 1. The best number of liquid reaction mixture pass was found to be equal to 5, this means 30 h of the time of the reaction. The lengthening of the reaction time over 30 h did not lead to increase the concentration of the ester. The slight drop



Fig. 2. The methyl bisulfate concentration vs. initial sulfur trioxide concentration. Time of the reaction: 30 h, methane flow: $8.69 \text{ cm}^3 \text{ min}^{-1}$, temperature: $130 \degree \text{C}$, catalyst concentration: $0.016 \text{ mol } \text{dm}^{-3}$.



Fig. 3. The methyl bisulfate concentration vs. temperature. Time of the reaction: 30 h, methane flow: 8.69 cm³ min⁻¹, sulfur trioxide concentration: 25 wt.%, catalyst concentration: 0.016 mol dm⁻³.

was observed. The reason of the ester concentration decreasing can be complex and requires further investigations. This fact explains that during dropping of the reaction mixture into the reactor sulfur trioxide and methyl bisulfate partially escaped.

The initial sulfur trioxide concentration in oleum influence on the ester concentration in reaction mixture after 30 h of the reaction time is presented in Fig. 2. The methane flow and temperature were equal to 8.69 cm³ min⁻¹, 130 °C, respectively. The exponential growth of the concentration of the methyl bisulfate versus initial SO₃ concentration was observed. The significant influence of the sulfur trioxide on the methane oxidation was observed.

The investigation on the significance of the temperature of the methane oxidation to methyl bisulfate after 30 h was performed. The methane flow was maintained at $8.69 \text{ cm}^3 \text{ min}^{-1}$, and initial sulfur trioxide concentration was equal to 25 wt. The highest ester concentration was obtained at $130 \,^{\circ}\text{C}$ (Fig. 3). The rapid increase was observed between 120 and $130 \,^{\circ}\text{C}$. After $130 \,^{\circ}\text{C}$ slow decrease of methyl bisulfate concentration was obtained. This course can be explained by growing the reaction rate with the temperature and fast evaporation of sulfur tri-

18

16 14 12 C_{E} [mmol dm⁻³] 10 8 6 4 2 0 8 10 12 14 16 18 20 22 24 26 28 F_{CH_4} [cm³ min⁻¹]

Fig. 4. The methyl bisulfate concentration in the reaction mixture vs. methane flow. Time of the reaction: 30 h, temperature: $130 \,^{\circ}$ C, sulfur trioxide concentration: 25 wt.%, catalyst concentration: 0.016 mol dm⁻³.



Fig. 5. The methyl bisulfate concentration in the reaction mixture vs. catalyst concentration. Time of the reaction: 30 h, temperature: $130 \,^{\circ}$ C, sulfur trioxide concentration: 25 wt.%, catalyst concentration: 0.016 mol dm⁻³.

oxide and ester at highest temperatures. The first one is more important at low temperature. The others are essential at high temperature.

Very strong influence of the methane flow on its oxidation in oleum was found. The observations were performed after 30 h of the reaction, at temperature $130 \,^{\circ}$ C, and sulfur trioxide concentration 25 wt.% (Fig. 4). The highest methyl bisulfate concentration was achieved at $8.69 \, \mathrm{cm}^3 \, \mathrm{min}^{-1}$ methane flow. Low flow of methane is recommended for good gas dissolving and preventing of sulfur trioxide and ester escape.

The catalyst concentration in oleum influence on the ester concentration in reaction mixture after 30 h of the reaction time is presented in Fig. 5. The methane flow and temperature were equal to 8.69 cm³ min⁻¹, 130 °C, respectively. Methyl bisulfate concentration increased when the iodine concentration was increased. At low catalyst concentration, increase of the iodine content resulted in rapid growing of the ester concentration. Above 0.016 mol dm⁻³ I₂ concentration change in methyl bisulfate concentration was low.

4. Conclusions

Methane oxidations to methyl bisulfate in oleum in presence of iodine as a catalyst can be performed at ambient pressure. The concentration of ester depends on the time of the reaction (number of passes of the liquid through the reactor), methane flow, temperature, sulfur trioxide and catalyst concentration. In order to obtain high methyl bisulfate yield high sulfur trioxide concentration and low methane flow is recommended. The optimum of temperature is equal to 130 °C and the time of the reaction is equal to 30 h. Contrary to the reactors applied usually to this process [1–19], reactor described by us can work in continuous system. Further detailed investigation is needed.

Acknowledgement

The financial support of the Polish Ministry of Education and Science under the contract no. N N205 3705 33 is gratefully acknowledged

References

- [1] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2897-2932.
- [2] A. Sen, Acc. Chem. Res. 31 (1998) 550–557.
- [3] J. Cheng, Z. Li, M. Haught, Y. Tang, Chem. Commun. (2006) 4617-4619.
- [4] R.A. Periana, D.J. Taube, E.R. Evitt, D.G. Loffler, P.R. Wentrcek, G. Voss, T. Masuda, Science 259 (1993) 340-343.
- [5] A. Sen, M.A. Benvenuto, M. Lin, A.C. Hutson, N. Basickes, J. Am. Chem. Soc. 116 (1994) 998-1003.
- [6] R.A. Périana, D.J. Taube, S. Gamble, H. Taube, T. Satoh, H. Fujii, Science 280 (1998) 560-564.
- [7] B. Michalkiewicz, K. Kałucki, J. Sośnicki, J. Catal. 215 (2003) 14-19.
- [8] X. Gang, H. Birch, Y. Zhu, H.A. Hjuler, N.J. Bjerrum, J. Catal. 196 (2000) 287–292.
- [9] S. Mukhopadhyay, A.T. Bell, Angew. Chem. Int. Ed. 42 (2003) 1019–1021.
- [10] S. Mukhopadhyay, A.T. Bell, J. Am. Chem. Soc. 125 (2003) 4406-4407.
- [11] S. Mukhopadhyay, A.T. Bell, Chem. Commun. (2003) 1590-1591.
- [12] M. Lin, A. Sen, Nature 368 (1994) 613-615.
- [13] G.V. Nizova, G. Suss-Fink, S. Stanislas, G.B. Shul'pin, Chem. Commun. (1998) 1885–1886.
- [14] C. Jia, T. Kitamura, Y. Fujiwara, Acc. Chem. Res. 34 (2001) 633-639.
- [15] R.A. Periana, O. Mironov, D. Taube, G. Bhalla, C.J. Jones, Science 301 (2003) 814-818.
- [16] N.J. Bjerrum, G. Xiao, H.A. Hjuler, US Patent 6,380,444.
- [17] X. Gang, Y. Zhu, H. Birch, H.A. Hjuler, N.J. Bjerrum, Appl. Catal. A 261 (2004) 91–98.
- [18] B. Michalkiewicz, M. Jarosinska, I. Łukasiewicz, Chem. Eng. J 154 (2009) 156-161.
- [19] R.A. Periana, O. Mirinov, D.J. Taube, S. Gamble, Chem. Commun. (2002) 2376–2377.
- [20] B. Michalkiewicz, P. Kosowski, Catal. Commun. 8 (2007) 1939–1942.