



Alkali Earth Metal Molybdates - Selectivity and Stability as Catalysts for the Selective Oxidation of Methanol to Formaldehyde

Thrane, Joachim; Høj, Martin; Thorhauge, Max; Mentzel, Uffe Vie; Jensen, Anker Degn

Publication date:
2019

Document Version
Peer reviewed version

[Link back to DTU Orbit](#)

Citation (APA):

Thrane, J., Høj, M., Thorhauge, M., Mentzel, U. V., & Jensen, A. D. (2019). *Alkali Earth Metal Molybdates - Selectivity and Stability as Catalysts for the Selective Oxidation of Methanol to Formaldehyde*. Abstract from 26th North American Catalysis Society Meeting, Chicago, Illinois, United States.

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Alkali Earth Metal Molybdates - Selectivity and Stability as Catalysts for the Selective Oxidation of Methanol to Formaldehyde

Joachim Thrane^{1*}, Martin Høj¹, Max Thorhauge², Uffe Vie Mentzel² and Anker Degn Jensen^{1*}

¹Technical University of Denmark, Kongens Lyngby, Denmark

²Haldor Topsøe A/S, Kongens Lyngby, Denmark

*joathr@kt.dtu.dk or aj@kt.dtu.dk

Introduction

Formaldehyde is the most important aldehyde commercially available as it is an irreplaceable C₁ building block for higher-valued products [1]. The annual global production of formaldehyde is expected to increase with 4.8-5.8% per year and reach 36.6 million tons by 2026 [2, 3]. Formaldehyde is mainly produced through either the silver process or the Formox process [1].

In the Formox process, methanol is selectively oxidized over an iron molybdate catalyst (MoO₃/Fe₂(MoO₄)₃), which achieve high selectivities (92-95%) at high conversions (>99%) [1]. The catalyst is however not stable under the reaction conditions due to formation of volatile molybdenum compounds [4]. The alkali earth metal molybdates have been reported to have high thermal stability [5], with expected lower volatility of Mo in MeOH atmosphere, and their properties as catalysts for selective oxidation of methanol are scarcely investigated in the literature.

Materials and Methods

The catalysts (MMoO₄, M:Mo = 1.0 and 1.1, M = Mg, Ca, Sr and Ba) were synthesized by a citric acid, sol-gel method from C₆H₈O₇·H₂O (Sigma Aldrich, ≥ 99.0%), (NH₄)₆Mo₇O₂₄·4H₂O (Merck, 99.3-101.3%), Sr(NO₃)₂ (Sigma-Aldrich, ≥ 99.0%), Ba(NO₃)₂ (VWR, ≥ 99.0%), Ca(NO₃)₂·4H₂O (Sigma-Aldrich, 99-103%), Mg(NO₃)₂·6H₂O (VWR, ≥ 98.0%). The samples were calcined at 500 °C. The catalysts were investigated in a lab scale fixed bed reactor setup described elsewhere [6]. Samples were characterized by BET and XRD.

Results and Discussion

MMoO₄ (M = Mg, Ca, Sr, Ba) catalyst samples with stoichiometric amounts and 10 mole% Mo in excess were prepared by sol-gel synthesis. It was found by XRD, that phase pure samples were synthesized for the Mg and Ca (including a molybdenum oxide phase in case of Mo excess), but carbonate phases as well as other M:Mo oxide phases formed for Sr and Ba. The surface area of the samples decreased when going down the group II elements, and was higher for the stoichiometric samples than when Mo was in excess, see Table 1.

The samples with excess molybdenum had superior selectivity compared to the samples which were stoichiometric (Figure 1a, the Sr and Ba catalysts were far less active and are not shown here). Furthermore, it can be seen that the Mo:Ca = 1.1 and Mo:Mg = 1.1 samples have the same selectivity as function of conversion. The activity of the catalysts with excess Mo was also superior to stoichiometric catalysts, even though the surface areas were much lower, as seen in Table 1. This shows that the excess Mo also have a significant role w.r.t. the activity and selectivity for the oxidation of methanol to formaldehyde. This has also been found for the

Table 1. Catalyst system and its characterizations. M = Mg, Ca, Sr or Ba.

Cation	Mo:M	MMoO ₄ wt%	SSA [m ² /g]	Cation	Mo:M	MMoO ₄ wt%	SSA [m ² /g]
Mg	1.1	95.5	33.0	Sr	1.1	81.1	3.7
	1.0	100	45.3		1.0	90.5	6.0
Ca	1.1	94.9	13.1	Ba	1.1	69.6	3.5
	1.0	100	34.3		1.0	35.1	2.8

industrial iron molybdate type catalyst [7]. When the stability was tested for 100 h on stream (Figure 1b) it was found that the first order rate constant for methanol oxidation decreased faster for the M:Mo = 1.1 samples, than the M:Mo = 1.0 samples. This is probably due to the initial vaporization of the excess Mo. Furthermore, it was found that the CaMoO₄ catalysts were significantly more stable than the MgMoO₄ catalysts, which might be related to the thermal stability, which is reported higher for CaMoO₄ than for MgMoO₄ [5].

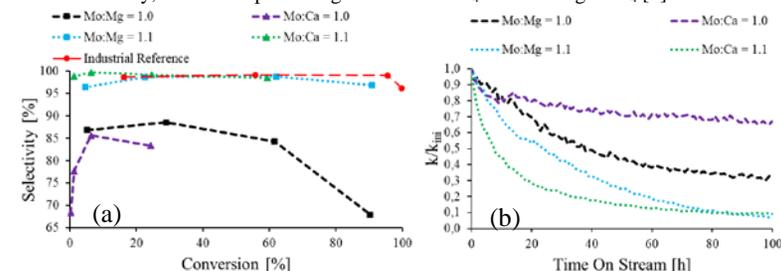


Figure 1. (a): Reversible product corrected selectivity (DME = 2 MeOH, DMM = 2 MeOH + CH₂O, MF = CO + MeOH) towards formaldehyde vs. the conversion of methanol achieved at 250 °C, 300 °C, 350 °C and 400 °C. (b): Stability as time on stream at 400 °C for 100 h. Testing Conditions: Catalyst loading: 25 mg (except for Mo:Mg = 1.1, where it was 8 mg) 150-250 μm particles, SiC for dilution 150 mg. Feed: ~5 % MeOH in 127.5 NmL/min of N₂ and 15 NmL/min of O₂.

Significance

This investigation contributes to the knowledge necessary to mitigate the problem of low catalyst stability in the Formox process by investigation new materials.

References

1. A. W. Franz et al., Formaldehyde, Ullmann's enc. of ind. chem., 2016.
2. [prnewswire.com/news-releases/global-formaldehyde-market-2018-2022-300633054.html](https://www.prnewswire.com/news-releases/global-formaldehyde-market-2018-2022-300633054.html), Accessed: 10.11.2018
3. [transparencymarketresearch.com/formaldehyde-market.html](https://www.transparencymarketresearch.com/formaldehyde-market.html), Accessed: 10.11.2018
4. B. I. Popov, V. N. Bibin, B. K. Boreskov, Kin. i Kat. 17 (1976), p. 371
5. Gmelin Handbook of Inorganic and Organometallic Chemistry, Molybdän, 1935.
6. M. Høj, A. D. Jensen, J.-D. Grunwaldt, Appl. Cat. A: Gen. 451 (2013), p.207
7. C. Brookes, M. Bowker, P. Wells, Catalysts 6 (2016), p. 92