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

Joachim Thrane1, Martin Høj1, Max Thorhauge2, Uffe Vie Mentzel3 and Anker Degr Jensen1*
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 alkaline 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%), 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 ºC. 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. Samples were characterized by BET and XRD.

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 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].

Significance

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

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

<table>
<thead>
<tr>
<th>Cation</th>
<th>Mo:M</th>
<th>MMoO4 wt%</th>
<th>SSA [m2/g]</th>
<th>Cation</th>
<th>Mo:M</th>
<th>MMoO4 wt%</th>
<th>SSA [m2/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>1.1</td>
<td>95.5</td>
<td>33.0</td>
<td>Sr</td>
<td>1.1</td>
<td>81.1</td>
<td>3.7</td>
</tr>
<tr>
<td>1.0</td>
<td>100</td>
<td>45.3</td>
<td></td>
<td>1.0</td>
<td>90.5</td>
<td>6.0</td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>1.1</td>
<td>94.9</td>
<td>13.1</td>
<td>Ba</td>
<td>1.1</td>
<td>69.6</td>
<td>3.5</td>
</tr>
<tr>
<td>1.0</td>
<td>100</td>
<td>34.3</td>
<td></td>
<td>1.0</td>
<td>35.1</td>
<td>2.8</td>
<td></td>
</tr>
</tbody>
</table>

References

4. B. I. Popov, V. N. Bibin, B. K. Boreskov, Kin. i Kat. 17 (1976), p. 371