Spinel-type catalysts with low molybdenum content for methanol oxidation

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Abstract

Formaldehyde is an important chemical which is produced through selective oxidation of methanol. In the Formox process an iron and molybdenum oxide catalyst is currently used. A problem with this catalyst is loss of molybdenum, which causes decrease in selectivity, activity and increase in pressure drop. Catalysts with spinel-type structure have previously showed good potential in selective oxidation of methanol. In this study, three different catalysts containing iron and molybdenum and having a spinel-type structure have been investigated. The catalysts have the chemical formula Fe$_{3-x}$Mo$_x$O$_{4+\delta}$ and catalysts with x=0.2 and 0.5 have been tested. The study suggest that spinel-type catalyst with a low content of molybdenum have equally good selectivity and better stability than the currently used iron and molybdenum oxide catalyst. Also, the study shows that increasing the amount of molybdenum in the spinel-type catalyst does not affect the catalytic properties much. Instead increasing the amount of molybdenum appears to increase the rate of molybdenum loss.

Keywords: spinel-type catalysts, methanol oxidation, formaldehyde, molybdenum, iron, x-ray diffraction, deactivation, volatilization

Introduction

Formaldehyde is an important industrial chemical, which is used to produce many industrial- and consumer articles. Today, formaldehyde is produced through partial oxidation of methanol, and two competing processes are commercially available [1]. One of these processes is called the Formox process. It utilizes a catalyst made from iron molybdate and molybdenum oxide in multiple tube reactors [1], [2]. The process operates with approximately 10 vol% methanol, 10 vol% oxygen and mainly nitrogen as balance [2]. A well known problem associated with the Formox process is the deactivation of the catalyst caused by volatilization of molybdenum from the hot-spot zone of the reactor, which result in lower activity and selectivity to formaldehyde. The molybdenum then condensates as needle shaped crystals near the outlet of the reactor, thereby causing an increased pressure drop over the reactor. The sublimation is increased when the methanol partial pressure in the reaction gas is increased [2], [3].
The spinel-type structure consists of oxygen ions forming a face centered cubic lattice with cations occupying some of the interstices [4]. The spinel-type structure allows for the cations to change oxidation state by taking up extra oxygen and introducing cation vacancies [5], [6]. The ability to take up and give off oxygen without risking structural collapse makes the spinel-type structure a promising candidate, which potentially could replace the current catalyst.

In previous studies, catalysts with a spinel-type structure exhibited good selectivity towards formaldehyde at high conversion of methanol and also good stability during oxidation [5]. One study showed that a spinel-type structure was actually formed during methanol oxidation, which also suggests that the spinel-type structure would be stable during methanol oxidation [6].

Since the spinel-type structure appeared to have good stability during methanol oxidation [5] and iron- and molybdenum oxides are well proven as formaldehyde catalysts [1], [2], [3] catalysts with spinel-type structure containing iron and molybdenum will be investigated.

**Experimental**

**Catalyst preparation**

The catalysts have been produced with different molybdenum contents using two different methods, which are described below.

In the first method, a 0.5 M iron solution was prepared from iron(III) nitrate and a 0.5 M molybdenum solution was prepared from ammonium heptamolybdate. These solutions were then mixed in appropriate ratios to create catalysts with the desired metal composition and homogenized by addition of nitric acid. A precipitation was obtained by rapidly raising the pH to 4 through addition of 3 M ammonia solution. The suspension was then left at 50 °C for two hours to allow for particle coarsening. The precipitates were then filtered and washed first with water, then acetone and finally water again. The precipitate was calcined for 16 hours in a gas mixture consisting of water, hydrogen and argon. The logarithmic ratio between water and hydrogen was ln(H₂O/H₂) = 0.5 and the temperature was 475 °C [5], [6].

In the second method, a 3.2 M solution of potassium hydroxide was prepared and nitrogen was bubbled through the solution to remove oxygen. Then a 0.8 M molybdenum solution prepared from ammonium heptamolybdate was added and the mixture was heated to 80 °C. A 0.8 M iron(II) solution, prepared from iron(II) sulphate was added drop wise in appropriate ratio to the molybdenum solution. This instantly caused a black precipitate to form. A 0.8 M sodium nitrate solution was added to oxidize the suspension. The amount of sodium nitrate was determined from the reaction formula in Eq. 1.

\[
(4-4x)H^+(3-x)Fe^{2+}+xMo^{6+}+(2-2x)NO_3^− \rightarrow Fe^{2+}+(2-x)Fe^{3+}+xMo^{5+}+(2-2x)NO_2+(2-2x)H_2O
\]

Eq. 1

The suspension was left at 80 °C with nitrogen still bubbled through for five hours. Then it was filtered and washed with water, acetone and water again. Finally it was dried at 100 °C over night [8].

**Catalyst characterization**

The catalysts were characterized using different methods both before and after the stability tests.

The specific surface areas of the catalysts were measured using a Micrometrics Tristar 3000 instrument. A five point BET isotherm (p/p⁰ between 0.05 and 0.2) was recorded for nitrogen adsorption at liquid nitrogen temperature. All the samples were degassed at 250 °C for at least four hours before the measurements.
The catalysts were also characterized using x-ray powder diffraction (XRD) to determine the crystal structure. The XRD was performed on a Seifert XRD 3000 TT diffractometer using Ni-filtered Cu Kα radiation. Rotating sample holders were used, and data was collected between 5° and 80° 20 in steps of 0.1°.

The content of the different metals in the catalysts was measured at “Växtekologens lab” at Lund University using inductively coupled plasma atomic emission spectroscopy (ICP-AES). The metal content was also measured using atomic absorption spectroscopy (AAS).

**Catalytic performance measurements**

The catalysts were tested for selective oxidation of methanol to formaldehyde. The prepared catalyst materials were first ground, then pressed into tablets which were crushed and finally sieved to particles with diameters between 250 and 425 µm. The catalysts particles were placed in stainless steel reactor tubes with an outer diameter of 6 mm and kept in position by a small amount of glass wool. For improved temperature control the reactor tubes were placed inside an aluminium block, which was kept at 300 °C. The catalysts were heated under a flow of nitrogen before applying the reaction gas, consisting of 160 Nml Ar/min, 20 Nml O2/min and 20 Nml methanol/min.

The products were analysed on a Hiden HPR20 mass spectrometer (MS) and a Varian CP-3800 gas chromatograph (GC), which was equipped with a HayeSep C column, a TCD detector and FID detector preceded by a methanizer. The substances analysed were carbon monoxide and carbon dioxide (COx), formaldehyde (FA), dimethyl ether (DME), methanol (MeOH), methyl formate (MF) and dimethoxymethane (DMM).

The equipment was also used to test the stability of the catalysts over a period of 75 hours. Here the catalysts were subjected to reaction gas during the days and during the night the catalysts were kept under flow of nitrogen at 300 °C.

![Figure 1. Diffraction patterns of the investigated catalysts before (left) and after (right) 75 hours in methanol oxidation.](image-url)
Results

Three different catalysts were produced and tested. Also, a commercially available catalyst containing iron molybdate and molybdenum trioxide was tested for comparison. The tested catalysts are listed in Table 1.

Table 1. The different catalysts tested in this study.

<table>
<thead>
<tr>
<th>Name</th>
<th>Chemical formula</th>
<th>Method of manufacturing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo02-R</td>
<td>Mo_{0.2}Fe_{2.8}O_{4+\delta}</td>
<td>Reduction by hydrogen</td>
</tr>
<tr>
<td>Mo02-O</td>
<td>Mo_{0.2}Fe_{2.8}O_{4+\delta}</td>
<td>Oxidation by sodium nitrate</td>
</tr>
<tr>
<td>Mo05-O</td>
<td>Mo_{0.3}Fe_{2.5}O_{4+\delta}</td>
<td>Oxidation by sodium nitrate</td>
</tr>
<tr>
<td>Ref</td>
<td>MoO_3 and Fe_2(MoO_4)_3</td>
<td>-</td>
</tr>
</tbody>
</table>

XRD measurements

The samples were examined with XRD both before and after the stability tests. In Figure 1 it can be seen that Mo02-R, Mo02-O and Mo05-O all consist of pure spinel-type phases before the stability test. After the stability test, however, all three samples show the presence of α-Fe_2O_3, which forms when molybdenum is lost from the catalysts. The commercial catalyst, Ref, shows no sign of α-Fe_2O_3, but Fe_2(MoO_4)_3 and MoO_3 have been reduced to FeMoO_4 and MoO_2, respectively.

BET measurements

The specific surface areas of the catalysts were also measured both before and after the stability test. The surface areas of Mo02-O and Mo05-O had decreased by approximately 70%, probably due to the fact that they had not been calcined prior to testing. Freshly prepared Mo02-O and Mo05-O had the specific surface area 39 and 30 m^2/g, respectively, whereas Mo02-R had a specific surface area of 16 m^2/g. That for the commercial catalyst was only 6 m^2/g. Neither the commercial catalyst, nor Mo02-R lost any surface area during the stability test.

ICP-AES and AAS

The ICP-AES and the AAS results were in good agreement as can be seen in Table 2 and Table 3. They both showed that more
molybdenum was lost from the commercial catalyst than from the spinel-type catalysts. Also, increasing the amount of molybdenum in the spinel-type catalyst seemed to increase the rate of molybdenum loss, as can be seen in Table 2 and Table 3.

Table 2. Results from ICP-AES before and after the stability test. Molybdenum loss in µmol Mo per mol MeOH converted.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mo/Fe before</th>
<th>Mo/Fe after</th>
<th>Mo loss (µmol Mo/mol MeOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo02-R</td>
<td>0.079</td>
<td>0.079</td>
<td>0.06</td>
</tr>
<tr>
<td>Mo02-O</td>
<td>0.088</td>
<td>0.087</td>
<td>0.06</td>
</tr>
<tr>
<td>Mo05-O</td>
<td>0.14</td>
<td>0.14</td>
<td>0.66</td>
</tr>
<tr>
<td>Ref</td>
<td>2.31</td>
<td>1.94</td>
<td>7.7</td>
</tr>
</tbody>
</table>

Table 3. Results from AAS before and after the stability test. Molybdenum loss in µmol Mo per mol MeOH converted.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Mo/Fe before</th>
<th>Mo/Fe after</th>
<th>Mo loss (µmol Mo/mol MeOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo02-R</td>
<td>0.080</td>
<td>0.068</td>
<td>3.2</td>
</tr>
<tr>
<td>Mo02-O</td>
<td>0.084</td>
<td>0.079</td>
<td>0.78</td>
</tr>
<tr>
<td>Mo05-O</td>
<td>0.13</td>
<td>0.11</td>
<td>4.4</td>
</tr>
<tr>
<td>Ref</td>
<td>2.11</td>
<td>1.84</td>
<td>5.8</td>
</tr>
</tbody>
</table>

Catalytic performance

The measurements revealed that all four catalysts tested were equally selective towards formaldehyde, all showing over 95% selectivity at 60-90% conversion of methanol. The tests also revealed that the commercial catalyst, Ref, was more than six times as active as the spinel-type catalyst, which all showed similar activities.

The spinel-type catalysts, however, retained their activity and selectivity longer than the commercial catalyst. The conversion, activity and selectivity of all the catalysts can be seen in Figure 2. Of the spinel-type catalysts, Mo02-O exhibited the best stability.

Discussion

The investigations showed that catalysts with spinel-type structure incorporating iron and molybdenum are of interest in selective oxidation of methanol. In fresh form all spinel-type catalysts showed similar activity and selectivity, indicating that the active surface of all three catalysts are very similar. Previous studies showed that iron and molybdenum oxide catalysts have a thin, amorphous layer with a high concentration of molybdenum [9]. Possibly, such an amorphous layer with a higher concentration of molybdenum exists also in the catalysts with spinel-type structure.

In Figure 2 it appears as though the spinel-type catalyst with the highest molybdenum concentration, Mo05-O, has lost most of its selectivity towards formaldehyde during the 75 hours in methanol oxidation. However, the main byproduct is dimethoxymethane which is only formed when methanol conversion is low. If the catalyst had not lost 70 % of the surface area, then conversion of methanol would have been higher and probably, formaldehyde would be formed instead of dimethoxymethane. The selectivity towards formaldehyde and dimethoxymethane together for Mo05-O at the end of the stability test is 97 %.

The molybdenum losses from the spinel-type catalysts were smaller compared to the commercial catalyst. In previous studies the spinel-type structure has also proven to be very stable during methanol oxidation [5]. Mo02-O exhibited the smallest molybdenum loss, followed by Mo02-R. They both had approximately the same amount of molybdenum and Mo05-O, which had twice the amount of molybdenum, exhibited a greater loss of molybdenum. Also the spinel-type catalyst with higher molybdenum content, Mo05-O, exhibited no boost in selectivity or activity compared to the other spinel-type catalysts, Mo02-O and Mo02-R. In other studies, addition of excess
molybdenum has been reported to increase both activity and selectivity in methanol oxidation [10]. Excess molybdenum also helps to retain activity and selectivity in the commercial catalysts, where it can replace the molybdenum that is lost from the active regions [9]. In the spinel-type catalysts these positive effects are not encountered as there is no excess molybdenum.

In Figure 1 it can be seen that Mo05-O seems to have the same amount of α-Fe2O3 as Mo02-O, which contain less than half the amount of molybdenum, but otherwise is very similar. This is in good agreement with the ICP-AES and AAS measurements which showed that Mo05-O lost more molybdenum during the testing.

The catalysts Mo02-O and Mo02-R have the same crystal structure and the same chemical composition, but still they differ in deactivation behavior. According to the XRD, Mo02-R have less α-Fe2O3, but according to the ICP-AES and AAS Mo02-R also had lost more molybdenum when compared to Mo02-O. One possible explanation is that the crystal structure can be retained even when molybdenum is lost and that Fe3O4+δ catalysts the total oxidation of methanol, yielding mainly COx instead of formaldehyde [5]. This proves that the method of manufacturing the spinel-type catalysts is important for their catalytic properties.

**Conclusion**

Different catalysts with spinel-type structure have been tested for the selective oxidation of methanol to formaldehyde. The spinel-type catalysts showed similar selectivity to formaldehyde as a commercial catalyst and furthermore retained their activity and selectivity better than the commercial catalyst.

**Acknowledgements**

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**References**