Formaldehyde production from methanol and methyl mercaptan over titania and vanadia based catalysts

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1 Introduction

The commercial formaldehyde production process uses methanol and air as a feed mixture, and either silver or metal oxides (V_2O_5, FeMo) as catalysts to intensify the reaction (Gerberich & Seaman 1994). Formaldehyde can be produced also by using mercaptans as reactants. This is attractive, since the process will, at the same time, reduce the emissions of these very malodorous compounds (Burgess et al. 2002, Wachs 1999). For example, wood pulping process emits significant amounts of methanol and mercaptans. In kraft pulp mills 70 to 80% of total VOC (Volatile Organic Compound) emissions are methanol emissions (Ojala et al. 2005). Nowadays the treatment process of these streams includes enrichment by steam stripping and then incineration or in some cases treatment in bio-treatment bonds (Burgess et al. 2002). The main reactions that take place during methanol (MeOH) and methyl mercaptan (MM) selective partial oxidation to formaldehyde (FO) are the following (Burgess et al. 2002):

$$CH_3OH + {}^1/_2O_2 \rightarrow CH_2O + H_2O \quad (1)$$
$$CH_3SH + 2O_2 \rightarrow CH_2O + SO_2 + H_2O \quad (2)$$

One can observe that, in addition to formaldehyde, also H_2O and SO_2 are formed. Also the by-products, H_2O and dimethyl disulfide (DMDS), are formed during the complete oxidation of methanol and partial oxidation of methyl mercaptan. The produced formaldehyde may also react further with oxygen to form either complete or partial oxidation products, i.e. CO, CO_2 and H_2O. (Burgess et al. 2002; Reuss et al. 1988)

2 Objectives of the research

Bulk metal oxides or metallic silver catalysts currently used in the commercial methanol process are deactivating in the presence of sulphur (Burgess et al. 2002). Different catalysts for oxidizing both methanol and mercaptans have been under investigation (Wachs 1999), however, new catalysts for this process are still needed. This paper focuses on the activity studies of three different catalysts which were used to test the oxidation of methanol and methyl mercaptan as a mixture. The effects of different process variables on the formation of formaldehyde are also evaluated.

3 Results

3.1 Experimental methods

The laboratory tests were performed with three different catalysts; pure titanium dioxide TiO_2 (surface area ~1 m^2/g) (Ti), 3 % vanadium pentoxide on silicon dioxide V_2O_5/SiO_2 (VSi) (~230 m^2/g) and 3 % vanadium pentoxide on silicon dioxide + 10 % titanium dioxide $V_2O_5/(SiO_2 + 10\%TiO_2)$ (VSiTi). The selective catalytic oxidation tests were performed in a laboratory scale, in a tubular quartz reactor operating at atmospheric pressure (see Figure 1).

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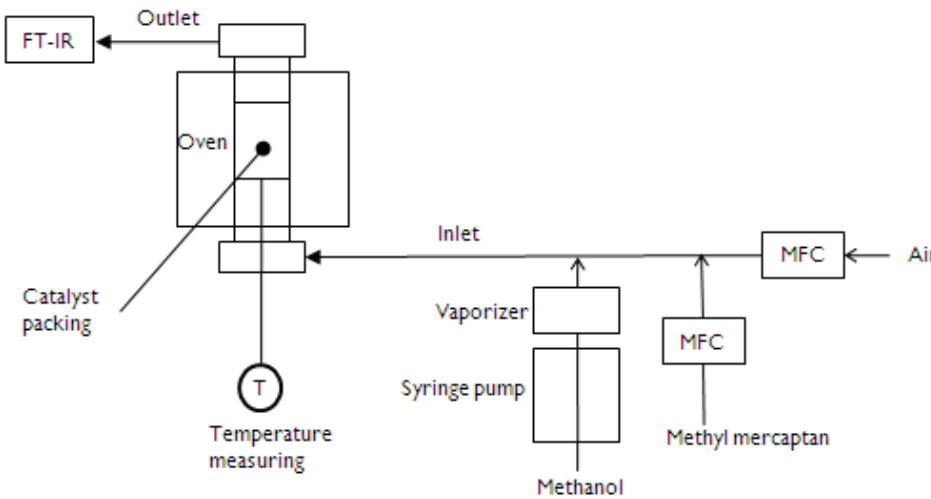

Figure 1 *Schematic of the experimental set-up.*

The total concentration of reactants was 1000 ppm (MeOH 500 ppm + MM 500 ppm). Methanol was fed by a syringe pump to a vaporizer and mixed with controlled amount of air. Methyl mercaptan gas was fed through a mass flow controller (MFC) and similarly mixed with air. The total gas flow through the reactor was maintained at 1 dm^3 min^{-1} giving GHSV of ~85 000 h^{-1}. The catalyst bed was fixed in the middle of the reactor tube between glass wool plugs and the temperature was measured prior to the catalyst bed. The outlet gas flow was analyzed by using the Gasmet FTIR gas analyzer Dx–4000 with peltier-cooled mercury-cadmium-telluride (MCT) detector and resolution of 8 cm-1 with 50 scans co-added.

The experimental variables used in the catalyst testing were the catalyst type and catalyst loading in the reactor (10 mg and 100 mg). All the catalysts were mixed in the reactor with quartz sand so that the total mass (catalyst and quartz sand) was 1 g. At the beginning of the experiments, the formation of formaldehyde was tested also with quartz sand packing (1 g). The "light-off" activity tests were carried out with a heating rate of 10°C/min starting from room temperature to the desired temperature level (500°C). The stability of each catalyst was also tested by raising the temperature to the previously determined optimal temperature level, and keeping it there for 6 hours. The tests were repeated and they showed good repeatability. The catalysts maintained well their activity and selectivity in all the test cases.

3.2 Result of the experiments

The results of the oxidation of methanol and methyl mercaptan mixture are presented in Figure 2. Both of the feed compounds are reacting completely with the VSiTi catalyst and the other two catalysts give good results as well.

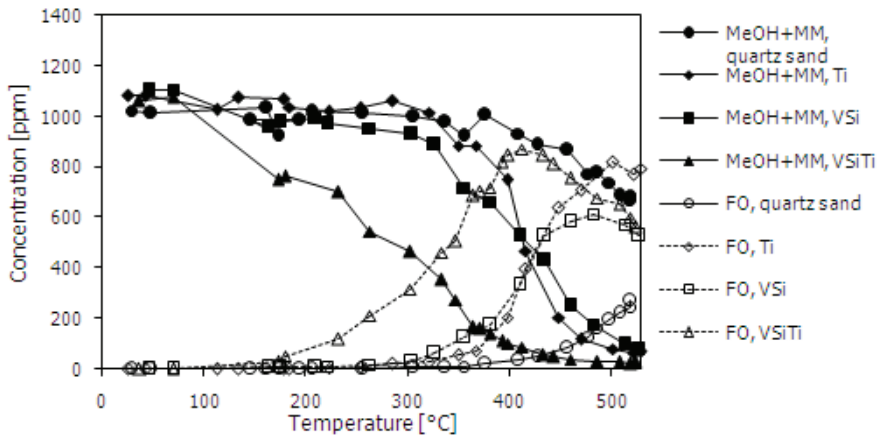

Figure 2 *Oxidation of methanol-methyl mercaptan mixture (500 ppm + 500 ppm) to formaldehyde.*

The maximum formaldehyde formation, conversion and selectivity at optimal temperature of the oxidation of methanol-methyl mercaptan mixture are presented in Tables 1 and 2. The results show that the activity of the catalysts can be presented as follows: VSiTi>Ti>VSi. For the VSiTi catalyst, the optimal temperature for the formation of formaldehyde was significantly (about 70-90°C) lower than that with Ti and VSi catalysts. Catalyst loading (10 mg or 100 mg) had also a great impact on the formation of formaldehyde. With the VSi and Ti catalysts the 10 mg catalyst loading was not adequate and the formation of formaldehyde was not significant.

Table 1 *The effect of the catalyst loading and quartz sand on the maximum formaldehyde formation.*

Catalyst	Max. formaldehyde concentration [ppm]		
	1 g Quartz sand	10 mg cat. loading	100 mg cat. loading
Quartz sand (1 g)	270		
Ti		440	820
VSi		540	610
VSiTi		*	870

* not determined

Table 2 *Conversions and selectivities over the tested catalysts (100 mg catalyst loading).*

Catalyst	Optimal temperature	Conversion	Selectivity
Quartz sand (1 g)	520	42	85
Ti	500	91	93
VSi	480	82	75
VSiTi	410	91	96

The VSiTi catalyst forms formaldehyde selectively. Other detected reaction products, as expected, were SO_2, DMDS, CO_2 and CO. The formations of by-products upon testing of 100 mg of the VSiTi catalyst are presented in Figure 3. SO_2 is formed as a by-product when oxidizing methyl mercaptan to formaldehyde. The long-term stability test was carried out with all the three catalysts and the methanol-methyl mercaptan mixture as the reactant. During the period of 6 hours at optimal reaction temperature no signs of activity decline were observed.

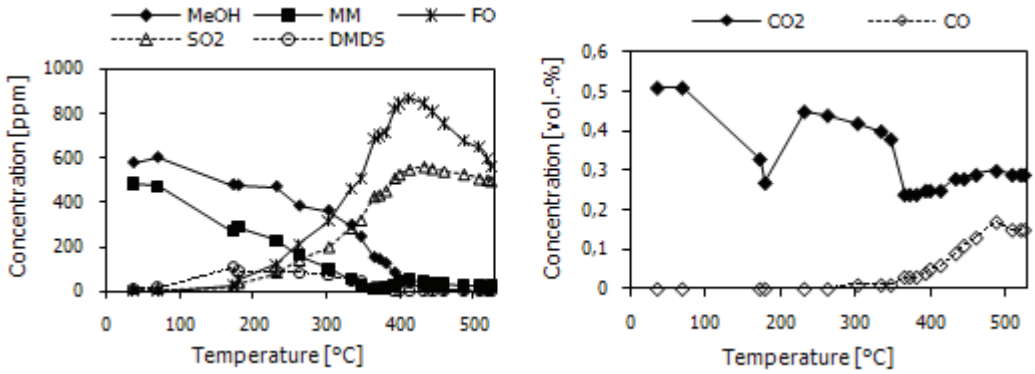

Figure 3 *Formation of by-products in oxidation of the methanol and methyl mercaptan mixture over 100 mg of the VSiTi catalyst.*

4 Relevance of the research

Converting methanol and TRS emissions (Total Reduced Sulphur) to formaldehyde has a positive environmental impact. The selective oxidation of methanol and methyl mercaptan to formaldehyde will reduce the emissions of malodorous compounds. Compared to incineration the formation of carbon dioxide may be avoided when this process is used. In addition, formaldehyde is a valuable chemical, and thus it would have economically positive impacts on the pulp mills as well.

References

Burgess, T.L., Gibson, A.G., Furstein, S.J. and Wachs I.E. (2002) Converting waste gases from pulp mills into value-added chemicals, **Environmental Progress** Vol.(21): 137–141.

Gerberich, H.R. and Seaman, G.C. (1994) Formaldehyde. In: J. Kroschwitz(eds.) **Kirk-Othmer Encyclopedia of Chemical Technology**, New York, Vol.(11): 929–950.

Ojala, S., Lassi, U., Ylönen, R., Keiski, R., Laakso, I., Maunula, T.and Silvonen, R. (2005) Abatement of malodorous pulp mill emissions by catalytic oxidation – pilot experiments in Stora Enso Pulp Mill, Oulu, Finland, **Tappi journal** Vol.(4): 1–6.

Reuss, G., Disteldorf, W., Grundler, O. and Hilt, A. (1988) Formaldehyde. In: W. Gerthartz (eds.), **Ullmann's Encyclopedia of Industrial Chemistry**, Vol.(A11): 619–651.

Wachs, I.E. (1999) Treating methanol-containing waste gas streams, United States patent 5907066 May 25

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