

## ***Interactive comment on “Atmospheric methanol measurement using selective catalytic methanol to formaldehyde conversion” by S. J. Solomon et al.***

**S. J. Solomon et al.**

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### **General comments**

We thank the anonymous referees for their efforts in reading the manuscript and offering useful comments that have helped us to improve it. Our specific responses follow each referee comment below.

### **Specific comments**

#### **1) Response to the comments of Reviewer-1**

*1) Some CIMS instruments, such as the Ionicon PTRMS are certainly expensive but*

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are as field transportable as some of the other instruments listed.

We do agree that the instruments listed are all advantageous for one reason or the other. But comparatively, the newly developed method is more easily portable, sensitive, accurate and less expensive which is ideal for field campaigns. The PTR-MS and other CIMS instruments may indeed be classified as field transportable. On the other hand, such instruments generally weigh around 150 kg. As such, these instruments are not casually moved to a field site with limited vehicle access (e.g., remote forest location) or installed at the top of a 30 meter sampling tower. Similar arguments hold for standard GC instruments as well. While the instrument we describe may only be slightly less cumbersome in size, it can easily be lifted by a single individual of average build and could therefore be installed in locations accessible only with great difficulty to CIMS and PTR-MS instruments

2) *It is noted that at flow rates lower than 1.6 L min<sup>-1</sup>, the optimum conversion efficiency decreased slightly. The authors note a partial explanation in the following sentence (lines 17-20). The authors of this paper (Solomon et al.) may want to cite a reference (T. H. Kim et al., Catalysis Letters, 2004, vol. 98, pp.161-165) in which Kim et al. address the specific issue of longer residence times decreasing the formaldehyde yield. These authors attribute this observation to the subsequent oxidation of formaldehyde to carbon monoxide.*

Decreasing the total flow rate (F) of the feed mixture (L min<sup>-1</sup>) and keeping the catalyst weight constant (W) increases the catalyst contact time of the reactant mixture (W/F). Increasing the time intermediate species remain in contact with the active sites on the catalyst surface can lead to secondary reactions including the re-adsorption of the formaldehyde formed. The proposed reaction mechanism and its products are described in *Pernicone et al., 1969 and Santacesaria et al., 1981*. A recent review by *Soares et al [2005]* shows that the catalyst selectivity towards formaldehyde decreases due to the formation of by-products such as dimethyl ether (CH<sub>3</sub>OCH<sub>3</sub>), methyl formate (HCOOCH<sub>3</sub>), dimethoxy methane ((CH<sub>2</sub>O)<sub>2</sub>CH<sub>2</sub>), carbon monoxide (CO) and carbon

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dioxide (CO<sub>2</sub>). Nevertheless, the main byproduct depends on the reaction conditions, nature of the catalyst, composition of reaction mixture, and on the conversion level. The recent work by *Kim et al [2004]* points out subsequent oxidation of formaldehyde to CO. However, depending on experimental conditions, other products may also form.

As suggested by the reviewer, a couple of sentences and references have been added in the relevant section to make the point clear.

## II) Response to the comments of Reviewer-2

1) *Catalyst: Since the goal of the research is not the development of a catalyst, the authors may consider to use a commercial oxidation catalyst instead of manufacturing their own. Commercial catalysts are available in reproducible batches, while good reproducibility is difficult to achieve among different research laboratories.*

The reviewers point is well taken. Before the onset of this study we tried to obtain a commercial catalyst sample, however, no supplier we asked was willing to provide one. Industrial catalysts are usually protected by patents and it is very hard to obtain them for laboratory experiments. Additionally, the exact formulation of an industrial catalyst usually remains unknown. The catalyst used in the present work can be reproducibly produced in the laboratory and the catalytic behavior (activity and selectivity) is similar to that of an industrial catalyst [*Soares et al., 2001*].

2,3) *Section 3.1.1., conversion efficiency. This quantity should be defined as the reverse of the definition in the text at lines 6-8, i.e. moles of HCHO/moles MeOH. Otherwise conversion efficiencies > 1 are obtained.*

In our experiments we measure the number of moles of formaldehyde per number of moles of methanol entering the catalytic converter, which is given by,

$$Y_{HCHO} = S_{HCHO}/100 * X = (n_{HCHO})_{out}/(n_{MeOH})_{in} * 100$$

where Y is yield, S is selectivity for formaldehyde, X is the methanol conversion efficiency, and n is the number of moles.

We appreciate very much the comment and have made the necessary changes to the text.

4) *The explanation is not clear why there is any methanol conversion at all when no oxygen is present. Methanol may decompose thermally to HCHO and H<sub>2</sub>, or oxygen could stem from the oxide catalyst itself. Were these possibilities examined?*

There is experimental evidence that oxygen from the lattice structure can participate in the methanol to formaldehyde oxidation reaction [Pernicone et al., 1969; Liberti et al, 1972]. The reaction mechanism is believed to be a Mars van Krevelen redox type mechanism. Thus, in the absence of oxygen in the reaction mixture, the catalyst surface becomes reduced, which decreases catalyst activity and selectivity. The reduced phase, FeMoO<sub>4</sub>, is less active and selective than Fe<sub>2</sub>(MoO<sub>4</sub>)<sub>3</sub> which is generally referred to as the active phase.

We appreciate very much the suggestion by the reviewer, a couple of sentences and references have been added in the relevant section to make the point clear

5) *I recommend testing H<sub>2</sub>S, SO<sub>2</sub> and NH<sub>3</sub> as potential poisons present in air.*

We are performing a wide range of studies in the laboratory to elucidate possible interference from different gases in the atmosphere under various conditions. As part of this, the interference of H<sub>2</sub>O, NH<sub>3</sub>, H<sub>2</sub>S, SO<sub>2</sub> and CO<sub>2</sub> was or will be tested, and will be presented in a future publication.

From the previous experimental results [Rozanov et al., 2001] it is evident that NH<sub>3</sub> in particular can be adsorbed by the acidic active sites thus could be a strong inhibitor of the main reaction.

## References

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