

## Methanol decomposition as a first stage for methanol only routes to acetic acid.

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### Introduction

Large-scale industrial routes such as the Monsanto and BP Chemicals Cativa<sup>TM</sup> processes are homogeneous and require the presence of halide promoters [1]. Whilst these processes are highly selective, they suffer the obvious disadvantages of homogeneous routes, and furthermore the requirement for halide promoters has a number of negative implications, including those upon the materials of construction for large-scale reactors. Within the literature, a number of heterogeneous catalysts have been reported to be active for the promoter-free carbonylation reaction. These have included carbon supported cobalt molybdenum formulations [2], carbon supported nickel chloride – copper chloride compositions [3], silica supported ion exchanged heteropolyacids [4], and copper mordenite [5]. Other routes to acetyls investigated include ethane oxidation [6], direct syn gas conversion [7] and a variety of different routes from methane [8]. One attractive route to acetic acid, which does not seem to have been widely explored, is the application of methanol only containing feeds in which the CO required for the carbonylation step is generated by the incomplete decomposition of the methanol feed. This area has been of recent interest and the approach we have taken is the combination of two catalysts in the same reactor – one exhibiting moderate activity for methanol decomposition and the other a promoter free carbonylation catalyst. In terms of the latter catalyst, one consideration is its tolerance to comparatively large levels of hydrogen. The primary focus of this presentation is the methanol decomposition catalyst component and this will be described in most detail, although some initial results of the direct carbonylation reaction will be presented.

On surveying the methanol decomposition literature, it is apparent that there have been a wide-range of different materials investigated under a wide-range of different conditions [9]. Generally, studies have concentrated upon single catalyst types and few, if any, have compared different general types of catalyst. Accordingly, we have investigated this aspect and these results will form the primary focus of this presentation.

### Materials and Methods

Methanol decomposition has been studied at atmospheric pressure in a fixed bed microreactor with on-line gc analysis. Typically a feed of 40% CH<sub>3</sub>OH in Ar and a catalyst bed weight of 0.3g has been employed. As governed by the envisaged application, attention has been restricted to reaction temperatures of 250 and 300 °C.

### Results and Discussion

In this study, we have investigated the activities of a wide-range of different methanol decomposition catalysts which allows direct comparisons, not available from the literature, to be drawn. Indeed, to our knowledge the highest activity material, NiB, has not

been previously reported as a catalyst for this reaction. The results of activity testing at 300°C for some of materials tested are presented in Table 1.

**Table 1. Carbon monoxide space time yields over various catalysts at 300°C (40% CH<sub>3</sub>OH in Ar).**

Catalyst	STY CO (g/kg/h)
NiB	3445
17wt% Pd/CeO <sub>2</sub> -ZrO <sub>2</sub>	3291
3wt% Pd/CeO <sub>2</sub>	3228
9wt% Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	1911
1.5wt% Pd/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	1443
NiAl	1340
Cu/ZnO	495

These results will be discussed in further detail, along with their application for methanol only routes to acetyls. Examples of the latter process will be given, employing atmospheric pressure studies and using copper mordenite as the carbonylation catalyst component. Whilst the overall yields of this process are low, primarily as a consequence of the low reaction pressure employed, they are fairly significant in terms of the atmospheric methanol carbonylation activity of the copper mordenite catalyst.

### Significance

Whilst a wide range of literature describing catalytic activity for methanol decomposition is available, very few studies can be used to compile an activity index between the various different classes of catalyst. This study addresses this aspect and furthermore demonstrates the possibility of the development of methanol only route to acetic acid.

### References

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