Titania–silica supported vanadia catalyst for formaldehyde production from sulphur contaminated methanol

–Industrial emissions to valuable products

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BACKGROUND OF THE RESEARCH

- Methanol which is contaminated with reduced sulphur compounds is formed in the pulp mills → incineration
- Methanol is the main single source of volatile organic compounds (VOC) emissions from the Kraft pulp mill
- Catalytic conversion of this waste gas stream to valuable chemical

FORMALDEHYDE

→ environmentally and economically positive impacts to the mills

- Catalysts that are used in a commercial formaldehyde production can not be used because those are poisoned by sulphur. Silver or metal oxide catalysts are used in the commercial process.

Methanol conversion to formaldehyde

Reactions:

$$CH_3OH + \tfrac{1}{2}O_2 \longrightarrow CH_2O + H_2O$$

$$CH_3CH_3OH \longrightarrow CH_2O + H_2$$

$$H_2 + \tfrac{1}{2}O_2 \longrightarrow H_2O$$

By-products:

$$CH_3OH + \tfrac{3}{2}O_2 \longrightarrow CO_2 + 2H_2O$$

$$CH_2O + O_2 \longrightarrow CO_2 + H_2O$$

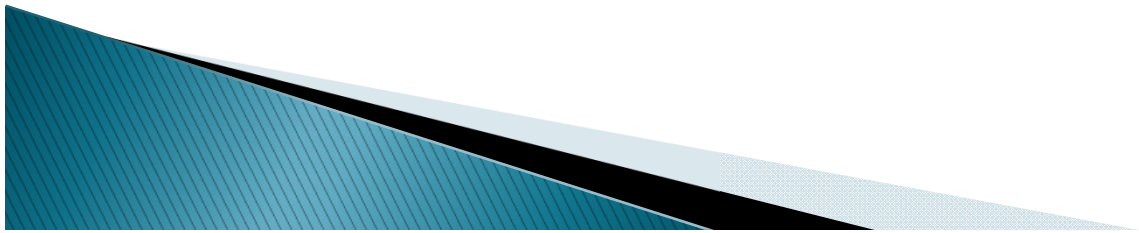
$$CH_2O \longrightarrow CO + H_2$$

Methyl mercaptan conversion to formaldehyde

Reactions:

$$CH_3SH + 2O_2 \longrightarrow CH_2O + SO_2 + H_2O$$

$$2CH_3SH + \tfrac{1}{2}O_2 \longrightarrow CH_3SSCH_3 + H_2O$$



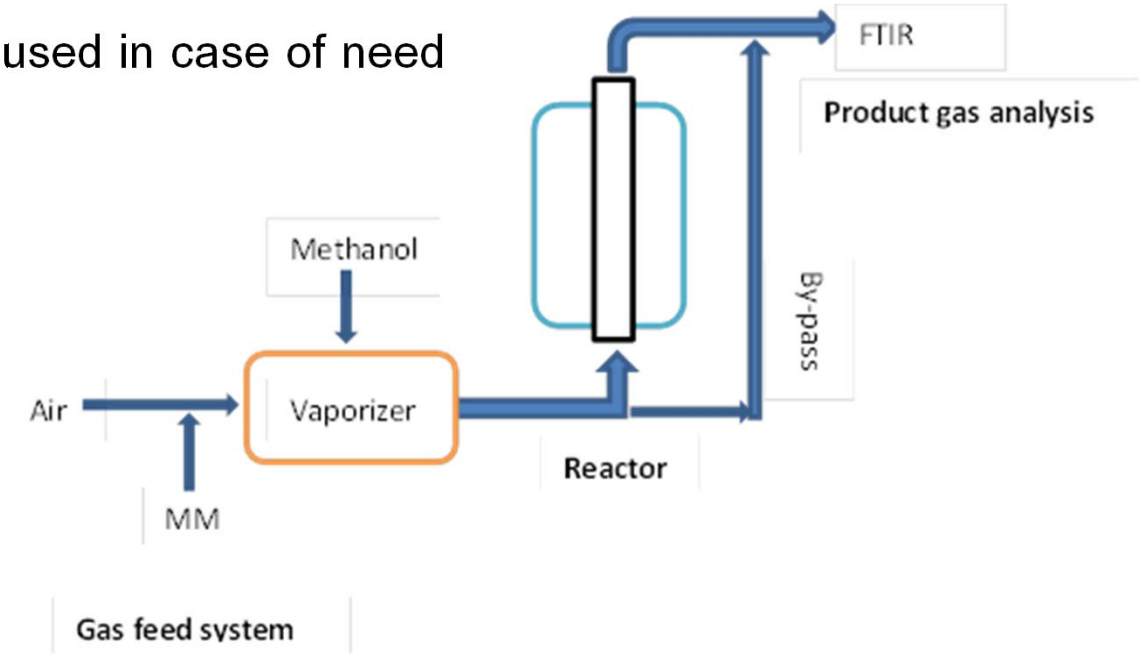
OBJECTIVES FOR THE WORK

- Different vanadia and titania based catalysts for formaldehyde production from methanol and methyl mercaptan mixture will be investigated and composition of the catalyst will be optimized
- The reaction mechanism over vanadia/titania-silica catalyst is studied in detail
- Study of the catalyst deactivation

- Taking part in the development of FTIR-PAS measurement device for hot gases.

RESEARCH METHODS

- Catalyst preparation with sol-gel method
- Selected catalyst characterization techniques (BET, XRD,..)
- Catalyst activity test with laboratory scale reactor set-up
- Surface reaction mechanism studies with DRIFT
- Other selected methods used in case of need



TASKS

TASK 1

Literature survey on methanol and mercaptans and their formation and handling in the pulp industry, commercial formaldehyde manufacturing methods and different catalysts for oxidizing methanol and methyl mercaptan.

- Master's Thesis Work (2008) Formaldehyde production from methanol and methyl mercaptan.

TASK 2

Oxidation of methanol and methyl mercaptan over vanadia and titania based catalysts. Activity of three different catalysts, TiO_2, V_2O_5/SiO_2 and V_2O_5/SiO_2+TiO_2 are tested to compare the activities and selectivities.

- Koivikko N., Laitinen T., Ojala S., Pitkäaho S., Kucherov A., Keiski R. L. (2011) Formaldehyde production from methanol and methyl mercaptan over titania and vanadia based catalysts. Applied catalysis B: Environmental, 103 (2011) 72-78.

TASK 3

Development of FTIR-PAS measurement technology for hot gases. Laboratory scale measurements.

- Hirschmann C., Koivikko N., Raittila J., Tenhunen J., Ojala S., Rahkamaa-Tolonen K., Marbach R., Hirschmann S., Keiski R. L. (2011) FT-IR-cPAS – New photoacoustic measurement technique for analysis of hot gases: a case study on VOCs, Sensors 11 (2011) 5270-2589.

TASK 4

Catalyst preparation and optimization of the catalyst composition of V_2O_5/SiO_2+TiO_2 catalyst for formaldehyde production.

IN PROGRESS

Based on the first catalytic tests, new catalyst have been prepared and tested for the reaction. Goal is to find the best composition for the catalyst and to deepen the catalyst characterization.

TASK 5

Surface reaction mechanism over vanadia/titania-silica catalyst and deactivation study of the catalyst.

2013-2014

Goal is to reveal the reaction mechanism over the catalyst for the reaction and understand the specified characteristics of the catalyst which affect the activity of the catalyst in the reaction in specified reaction conditions

Writing the thesis and dissertation

2015

RESEARCH GROUP

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Closely related research works in the laboratory of Mass and Heat Transfer process laboratory in the University of Oulu

- M.Sc.(Eng.) Tiina Laitinen (CO_2 utilisation and formaldehyde production in pulp and paper industry (calculation and modeling)
- M.Sc. (Chem.) Anass Mouammine (catalyst materials for formaldehyde production)

Other related research works in the field of Catalysis:

- Satu Pitkäaho, Darif Bouchra, Sanna Päivärinta, Tuomas Nevanperä, Marja Kärkkäinen, Zouhair El Assal

THANK YOU!