

## Ethylene oxychlorination over $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst in micro- and milli-structured reactors

Z. Vajglová<sup>1,2</sup>, A. Moro<sup>1</sup>, N. Kumar<sup>1</sup>, K. Eränen<sup>1</sup>, M. Peurla<sup>3</sup>, J. Peltonen<sup>3</sup>, D. Yu. Murzin<sup>1</sup>, T. Salmi<sup>1</sup>

<sup>1</sup>Åbo Akademi University, Johan Gadolin Process Chemistry Centre (PCC), Laboratory of Industrial Chemistry and Reaction Engineering, Biskopsgatan 8, Turku/Åbo, Finland, email: zvajglov@abo.fi, <sup>2</sup>Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Prague, Czech Republic, <sup>3</sup>University of Turku, Turku/Åbo, Finland

Heterogeneously catalyzed gas-phase ethylene oxychlorination by oxygen and hydrogen chloride to 1,2-dichloroethane is one of the principal steps in the industrial production of the important vinyl chloride monomer, needed for the synthesis of polyvinyl chloride (PVC). The main by-products of ethylene oxychlorination are chloroethane, 1,1,2-trichloroethane, trichloroacetaldehyde, tetrachloromethane, trichloromethane, carbon monoxide, and carbon dioxide [1, 2].

Ethylene oxychlorination was performed over  $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$  catalyst in a micro-channel reactor and in a milli-tubular reactor. The microreactor used was a stainless steel equipment designed for gas-phase reactions (GPMR mix) produced and purchased from the Institut für Mikrotechnik Mainz (IMM). The channels of reactor were 90 – 100  $\mu\text{m}$  deep, 460  $\mu\text{m}$  in diameter and 9.5 mm long. The fixed bed millireactor used for comparative experiments was a quartz tube with a length of 30 cm and an inner diameter of 1 cm.

A coppermodified catalyst was prepared by a conventional evaporation-impregnation method without any promoters (e.g. K, Na, La). Copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , p.a., Honeywell) was used as a cupric chloride precursor. The laboratory-prepared catalyst was characterized by nitrogen physisorption, Fourier transform infrared spectroscopy using pyridine, temperature programme desorption of  $\text{CO}_2$ , scanning electron microscopy, energy dispersive X-ray microanalysis and transmission electron microscopy.

The reaction was conducted at 200 – 250 °C and under atmospheric pressure, with a weight space velocity (WHSV) of 0.7 – 30  $\text{g}(\text{C}_2\text{H}_4)/\text{g}(\text{cat})/\text{h}$  and residence time 0.04 – 7.2 s (Figure 1). The gaseous products were analyzed on-line applying Agilent GC 6890N equipped with FI and TC detectors and HP-Plot/U Column (30 m  $\times$  530  $\mu\text{m}$   $\times$  20  $\mu\text{m}$ ), molsieve/Column (60 m  $\times$  50  $\mu\text{m}$   $\times$  20  $\mu\text{m}$ ). Injection was performed a six-way valve. Continuous GC analysis was applied with a sampling frequency of 65 min.

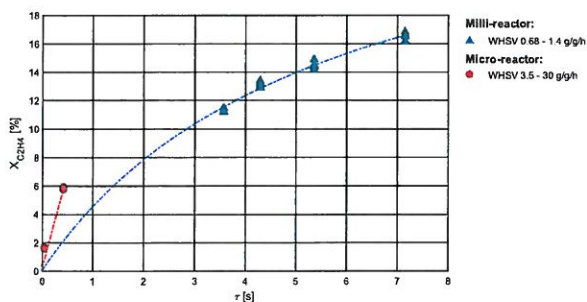




Figure 1 Ethylene oxychlorination over  $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ : influence of residence time on ethene conversion at 200 °C

The time-on-stream behaviour of ethene conversion and selectivity to 1,2-dichloroethane demonstrated a stable catalyst performance in the millireactor. These measured data were steady and reproducible within the entire temperature range (200 – 250 °C). On the other hand, in the microreactor, continuous deactivation of the same type of catalyst was observed, accompanied by an decreasing selectivity to 1,2-dichloroethane. The results of the study also revealed that the selectivity of the desired product, 1,2-dichloroethane varied with the ethene conversion. In the microreactor, the 1,2-dichloroethane selectivities of 4.7% and 53.6% were achieved with the ethene conversions of 1.6% and 6.4%, respectively. The other important product was chloroethane. The formation of vinyl chloride by-product of 1.6% was observed only at the highest temperature 250 °C with highest ethene conversion achieved (6.4%). No other by-products were observed. In the millireactor, the 1,2-dichloroethane selectivities exceeding 96% were achieved at ethene conversions higher than 11% within the entire experimental range. Chloroethane, vinyl chloride, 1,2-dichloroethylene (trans) were formed, but only in minor amounts.

#### Acknowledgments

The work is a part of the activities of Johan Gadolin Process Chemistry Centre (PCC), a centre of excellence financed by Åbo Akademi University. Financial support to Zuzana Vajglová from the Johan Gadolin Scholarship Programme is gratefully acknowledged.

#### References

1. Rout, K.R., E. Fenes, M.F. Baidoo, R. Abdollahi, T. Fuglerud, and D. Chen, *Highly Active and Stable  $\text{CeO}_2$ -Promoted  $\text{CuCl}_2/\text{Al}_2\text{O}_3$  Oxychlorination Catalysts Developed by Rational Design Using a Rate Diagram of the Catalytic Cycle*. ACS Catalysis, 2016. 6(10): 7030-7039.
2. Montebelli, A., E. Tronconi, C. Orsenigo, and N. Ballarini, *Kinetic and Modeling Study of the Ethylene Oxychlorination to 1,2-Dichloroethane in Fluidized-Bed Reactors*. Industrial & Engineering Chemistry Research, 2015. 54(39): 9513-9524.

## Ethylene oxychlorination over $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ catalyst in micro- and milli-structured reactors

Z. Vajglová<sup>1,2</sup>, A. Moro<sup>1</sup>, N. Kumar<sup>1</sup>, K. Eränen<sup>1</sup>, M. Peurla<sup>3</sup>, J. Peltonen<sup>3</sup>, D. Yu. Murzin<sup>1</sup>, T. Salmi<sup>1</sup>

<sup>1</sup>Åbo Akademi University, Johan Gadolin Process Chemistry Centre (PCC), Laboratory of Industrial Chemistry and Reaction Engineering, Biskopsgatan 8, Turku/Åbo, Finland, email: zvajglov@abo.fi, <sup>2</sup>Institute of Chemical Process Fundamentals of the ASCR, v. v. i., Prague, Czech Republic, <sup>3</sup>University of Turku, Turku/Åbo, Finland

Heterogeneously catalyzed gas-phase ethylene oxychlorination by oxygen and hydrogen chloride to 1,2-dichloroethane is one of the principal steps in the industrial production of the important vinyl chloride monomer, needed for the synthesis of polyvinyl chloride (PVC). The main by-products of ethylene oxychlorination are chloroethane, 1,1,2-trichloroethane, trichloroacetaldehyde, tetrachloromethane, trichloromethane, carbon monoxide, and carbon dioxide [1, 2].

Ethylene oxychlorination was performed over  $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$  catalyst in a micro-channel reactor and in a milli-tubular reactor. The microreactor used was a stainless steel equipment designed for gas-phase reactions (GPMR mix) produced and purchased from the Institut für Mikrotechnik Mainz (IMM). The channels of reactor were 90 – 100  $\mu\text{m}$  deep, 460  $\mu\text{m}$  in diameter and 9.5 mm long. The fixed bed millireactor used for comparative experiments was a quartz tube with a length of 30 cm and an inner diameter of 1 cm.

A coppermodified catalyst was prepared by a conventional evaporation-impregnation method without any promoters (e.g. K, Na, La). Copper(II) chloride dihydrate ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ , p.a., Honeywell) was used as a cupric chloride precursor. The laboratory-prepared catalyst was characterized by nitrogen physisorption, Fourier transform infrared spectroscopy using pyridine, temperature programme desorption of  $\text{CO}_2$ , scanning electron microscopy, energy dispersive X-ray microanalysis and transmission electron microscopy.

The reaction was conducted at 200 – 250 °C and under atmospheric pressure, with a weight space velocity (WHSV) of 0.7 – 30  $\text{g}(\text{C}_2\text{H}_4)/\text{g}(\text{cat})/\text{h}$  and residence time 0.04 – 7.2 s (Figure 1). The gaseous products were analyzed on-line applying Agilent GC 6890N equipped with FI and TC detectors and HP-Plot/U Column (30 m  $\times$  530  $\mu\text{m}$   $\times$  20  $\mu\text{m}$ ), molsieve/Column (60 m  $\times$  50  $\mu\text{m}$   $\times$  20  $\mu\text{m}$ ). Injection was performed a six-way valve. Continuous GC analysis was applied with a sampling frequency of 65 min.

