A new way of probing reaction networks: analyzing multidimensional parameter space

Raoul Naumann d'Alnoncourt, Yury V. Kolen'ko, Robert Schlögl, Annette Trunschke

Department of Inorganic Chemistry, Fritz Haber Institute, Berlin, Germany

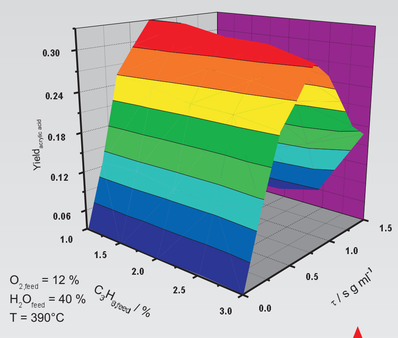
Introduction

- partial oxidation of propane to acrylic acid in one step:
  very complex reaction network,
  no microkinetic model in literature
- no industrial process, only academic research
- best catalyst: MoVTeNb mixed oxide, M1
- present study:
  screening reaction conditions in wide range,
  using well characterized sample of phase pure M1
- goals:
  optimizing reaction conditions
  understanding catalytic properties of M1
- experimental:
  sample prepared by coprecipitation, spray-drying, and phase purification using H_2O_2, details in [1]
  catalytict measurements in 10 fold parallel set-up (ILS, Berlin), details in [2]

[1] Y. V. Kolen'ko, W. Zhang, R. Naumann d'Alnoncourt, F. Girgsdies, T. W. Hansen, T. Wolfram, R. Schlögl, A. Trunschke, ChemCatChem, submitted
[2] R. Naumann d'Alnoncourt, Y. V. Kolen'ko, R. Schlögl, A. Trunschke, CCHTS, submitted

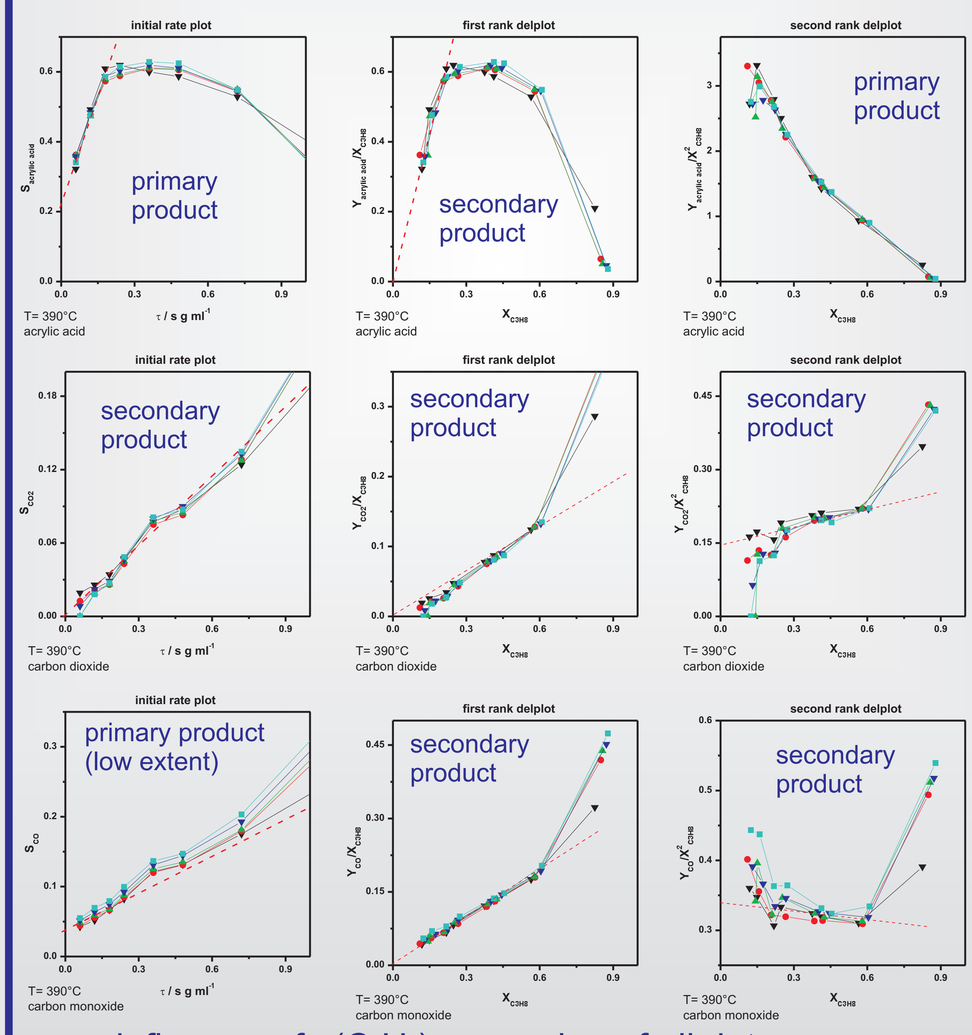
Results of propan variation

- **test conditions:**
  T: 350°C - 390 °C;
  $x(C_3H_8)_{feed}$: 1.0 - 3.0%;
  $x(O_2)_{feed}$: const. at 12.0%;
  $x(H_2O)_{feed}$: const. at 40%;
  ghsv: 2500 - 60000 ml/(gh);
  τ: 0.06 - 1.44 gs/ml.



- in agreement with oxygen variation results:
  $Y_{acrylic\ acid}$ max. at 0.72 gs/ml, low $x(C_3H_8)_{feed}$ beneficial
- determination of reaction rank of products from initial rate plots and delplots [3]

[3] N. A. Bhore, M. T. Klein, K. B. Bischoff, Ind. Eng. Chem. Res. 1990, 29, 313-316

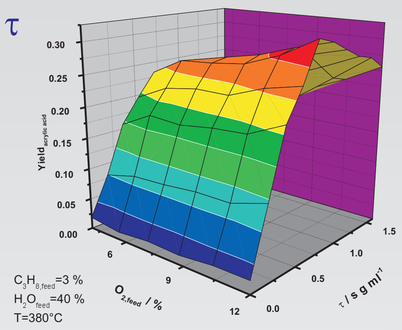


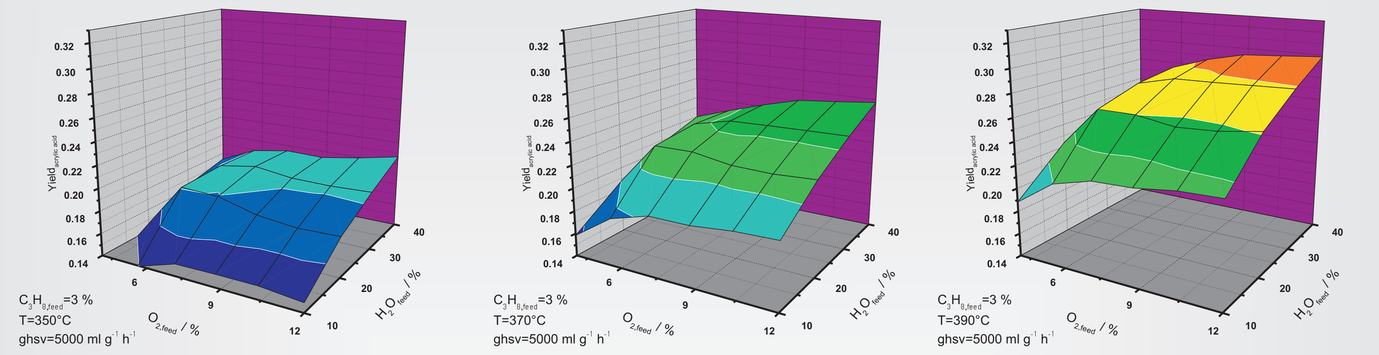
- no influence of $x(C_3H_8)_{feed}$, overlap of all data
- acrylic acid is primary and secondary product
  at least two different pathways,
  eventually two different active sites

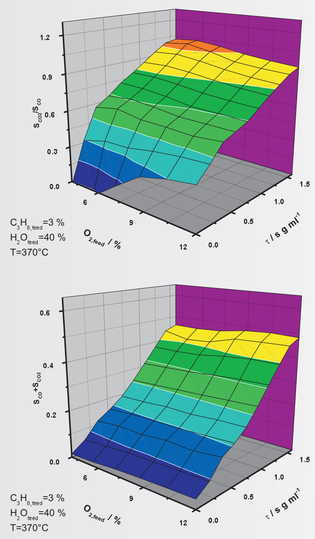
Results of oxygen and steam variation

- **test conditions:**
  T: 350°C - 390 °C;
  $x(C_3H_8)_{feed}$: const. at 3.0%;
  $x(O_2)_{feed}$: 4.5% -12.0%;
  $x(H_2O)_{feed}$: 10% - 40%;
  ghsv: 2500 - 60000 ml/(gh);
  τ: 0.06 - 1.44 gs/ml.

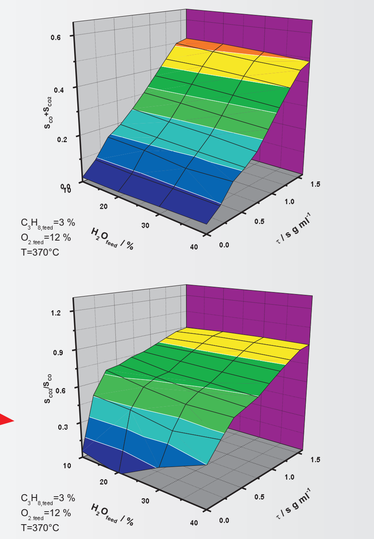
- First, $Y_{acrylic\ acid}$ increase with τ
- $Y_{acrylic\ acid}$ max. at 0.72 gs/ml (ghsv=5000 ml/(gh))
- then $Y_{acrylic\ acid}$ decrease.



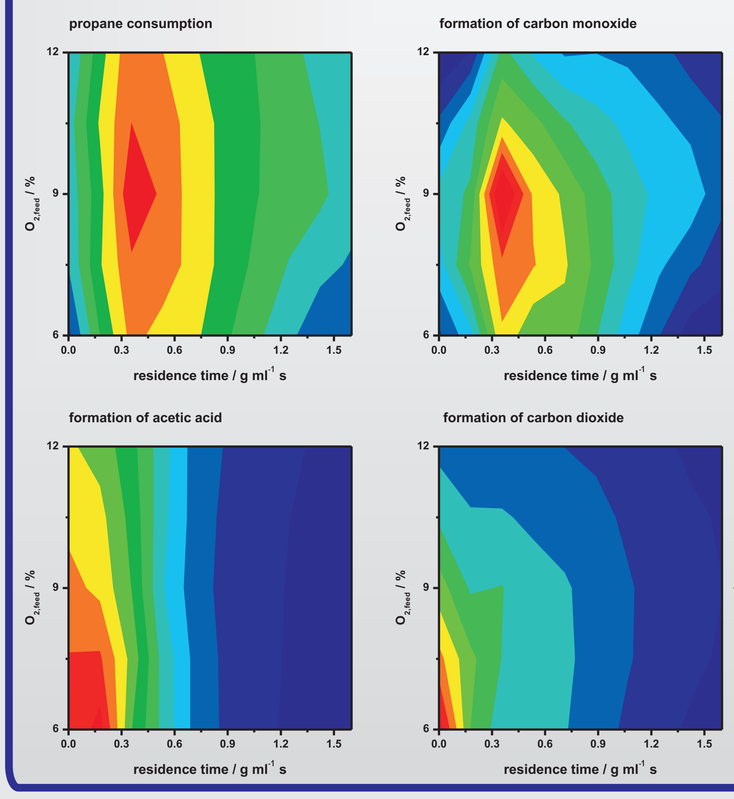




- high oxygen and steam content beneficial for acrylic acid synthesis (high yield)
- total oxidation (S to CO and CO_2) hardly influenced by
  oxygen content
  or steam content



higher yield of acrylic acid due to higher conversion of propane



Values from Arrhenius plots in arbitrary units as function of oxygen content and contact time

mechanistic information from comparison of patterns:

- CO formation is coupled to propane consumption, but not coupled to acetic acid formation
- acetic acid formation and CO_2 formation are coupled

Conclusions

optimization of reaction conditions:

- high steam content beneficial
- net oxidizing conditions beneficial:
  high oxygen content beneficial
  low propane content beneficial
- optimum contact time at ca. 0.72 gs/ml (5000 ml/(gh))
- total oxidation of products at longer contact times

insight into reaction network:

- no influence of $x(O_2)_{feed}$ on selectivities to CO and CO_2
- acrylic acid is sec. and prim. product
- maybe two different catalytic sites
- low total combustion of propane: CO and CO_2 mainly sec. products
- acetic acid formation coupled to CO_2 formation