Stage I and Stage II High Throughput Techniques for the development of mixed oxides DeNOx catalysts

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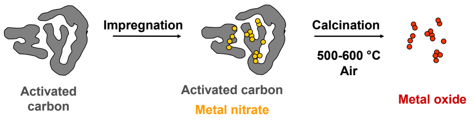
Motivation

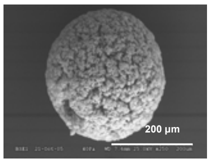
- Need to focus on inventing new catalyst composition that allow to break away from current limits. Need to shift to more complex catalyst compositions.[1]
- High-throughput approach allows to explore a vast combination of new catalytic materials.
- Stage I : very high throughputs and qualitative assessment of candidate materials.
- Stage II: further evaluation with comparable results to conventional reactor.
- Activated carbon route provides a synthesis method easily parallelized to produce new mixed oxides compositions.
- Combinations of Al, Mg, Mn, Co, Ni, Cu, Fe, Zr and La are used to prepared the new catalyst compositions.

Library Synthesis: Activated Carbon Route[2,3]

- Activated carbon is an ideal exotemplate: highly porous material with a large internal surface area (500-2100 m^2/g).
- The activated carbon synthesis involve:
  - 1st step: Impregnation with concentrated metal salt precursor solutions.
  - 2nd step: Calcination and removal of activated carbon.
- Mixtures of oxides nanoparticles are formed with surface areas between 50 and 300 m^2/g.
- High calcination temperatures and catalyst compositions with high Al content produce spinel phases with high thermal stability, and potential catalytic activity (d_p≈5-20nm).



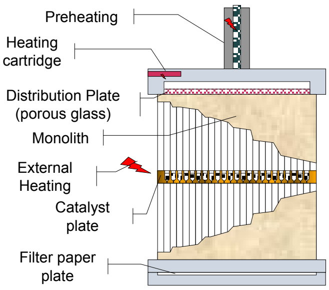
Library synthesis done with the help of a robot.



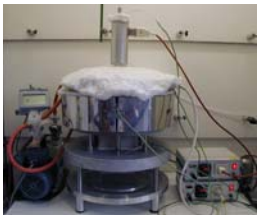
SEM picture of a mixed oxide prepared with a spherical activated carbon.

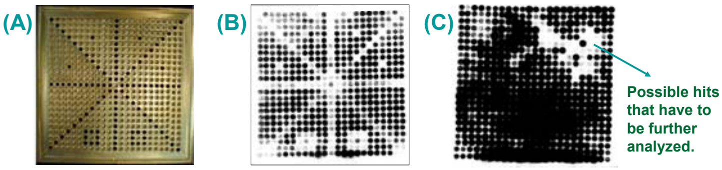
Stage I

- Stage I reactors need to be highly integrated. Parallelizing multi-channel reactors is not any longer a valid approach. Reactors for primary screening need a format highly integrated with the solid synthesis, or the analytical technique for optimum performance.[4]
- Development of a 529 (23x23) independent channels reactor with the help of monolith blocks, which distribute the flow and act as independent channels.[4] Catalysts are placed in brass plate with 3.5 mm inner diameter and 20 mm high bores.
- The reactor is designed to operate in connection with the color detection system introduced by Busch et al.[5] The presence of NO is detected by the color change of a filter paper impregnated with an organic dye. After the catalyst bed the gas flow through the filter paper changes the color in case of NO or NO_2.
- Mixtures of high content Al with combinations of 3 or 4 other elements (with 10% content) are used for the prescreening.

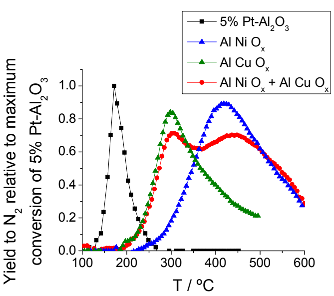


~50 mg catalyst/position
Space velocity 4.000 h^{-1}
1000 ppm NO
1000 ppm C_3H_6
5% O_2, rest N_2





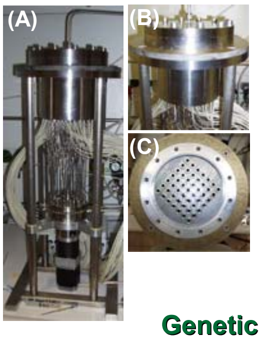
(A) Brass plate with 23x23 positions, filled with the geometric distribution of 5 wt% Pt on γ- Al_2O_3, SiO_2 and γ- Al_2O_3. (B) Filter paper result when reaction temperature is 215ºC; 1000 ppm NO, 1000 ppm C_3H_6, no O_2, rest N_2. In positions with 5 wt% Pt on γ- Al_2O_3, NO reacts with C_3H_6 to yield N_2, and no color change is seen. The black and white scan amplifies the differences. (C) Filter paper resulting from reaction at 210ºC with different mixed oxides with high content of Al and combinations of 3 or 4 other elements, each at 10%.



- When a hit is discovered in the 529 reactor, it is confirmed and further analyzed in detail in a single tube reactor.
- Reaction conditions: 1500 ppm NO, C_3H_6, 5% O_2, rest N_2. GSHV ≈ 60.000 h^{-1}.
- $Al_{0.9}Cu_{0.1}O_x$ shows 40% yield to N_2 at 300ºC.
- $Al_{0.9}Ni_{0.1}O_x$ shows 42% yield to N_2 at 420ºC.
- Two consecutive catalyst beds of $AlNiO_x$ and $AlCuO_x$ in the correct order achieve high yields over a wide temperature range.

Stage II

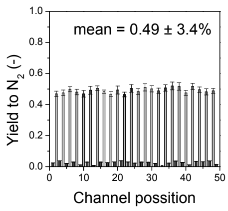
- 49 parallel pass flow Stage II reactor for an accurate and fast screening.
- The analysis is done by FTIR where concentrations of NO, NO_2, N_2O, C_3H_6, CO and CO_2 can be monitored.
- This reactor concept allows to measure 10 data points at different temperatures for all 49 catalysts in 26 hours (at 20.000 h^{-1} GSHV) with a maximal error of 5 %.



Images of the 49 parallel channel reactor setup: (A) side view on the complete setup, (B) top view on the open reactor (C) closed reactor.

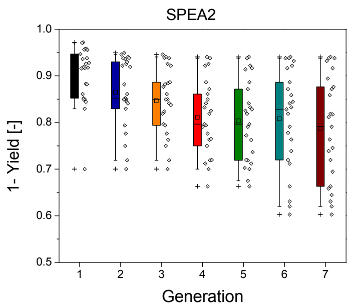
~50 mg catalyst
1500 ppm NO
2000 ppm C_3H_6
5% O_2, rest N_2
GSHV 20.000 h^{-1}

NO to N_2 conversion distribution measured with Pt/Al_2O_3.

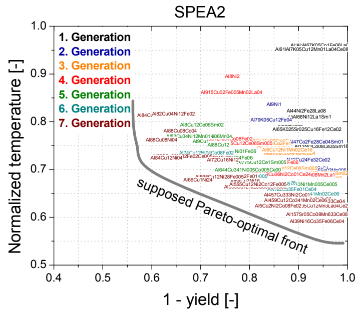


Genetic algorithm optimization

- Genetic algorithms are highly flexible heuristic global optimization methods.
- The heuristics include techniques, which are inspired by evolutionary biology: The maintaining of a population of potential solutions and incorporation of recombination, mutation and selection steps during each generation.
- Pareto optimization or multi-objective optimization includes the search for multiple solutions of a problem with respect to several goals.
- Genetic algorithm were applied to optimize a system, consisting of metal oxides consisting of combinations of 10 elements, selected from the transition metals (Cu, Ni, Co, Fe, Mn), the lanthanides (La, Ce, Sm) and the alkali metal (K, Sr) group.
- The catalyst are optimized with respect to the conversion to N_2 and the temperature at which the yield is maximal (the so called peak temperature).



Evolution of the objective function (1 – conversion of NO to N_2).



Visualisation of the solutions in the objective space for each generation.

Conclusions

- "Simple" catalyst compositions (ternary oxides) show better performance than more complex compositions.
- Most of the oxides oxidize NO to NO_2, which reacts with C_3H_6 and yields N_2.
- The N_2O yield is less than 5% for all mixed oxides.
- Stage II screening approach in combination with genetic algorithms is a valuable tool for high throughput investigations of new catalysts.
- Mixtures of Al-Ni-Cu and combinations thereof show best performance.

Literature

[1] J.N. Armor. *Catalysis Today 1995*, 26, 99-105.
[2] M. Schwickardi; T. Johann; W. Schmidt; F. Schüth. *Chem. Mat.* 2002, 14 (9), 3913-3919.
[3] F. Schüth. *Angew. Chem. Int. Ed.* 2003, 42, 3604-3622.
[4] F. Schüth et al. *Catalysis Today* 2006, 117 (1-3), 284-290.
[5] O. M. Busch; C. Hoffmann; T. R. F. Johann; H. Schmidt; W. Strehlau; F. Schüth. *J. Am. Chem .Soc.* 2002, 124 (45), 13527-13532.

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