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SELECTIVE CATALYTIC REDUCTION OF NO_X USING CERIA-ZIRCONIA BASED CATALYSTS

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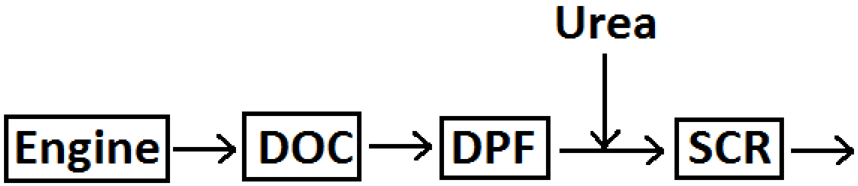
NO_X EMISSIONS

- Sources:
  - Stationary sources
  - Motor vehicles
  - Agriculture
- Problems:
  - Respiratory health effects
  - Smog
  - Acid rain
  - Ozone depletion
- NO_x emission standards
  - Euro 6 in Europe
  - Tier 2 and 3 in USA
  - MARPOL Annex VI in USA (sea areas)

NH_3-SCR

- Applied commercially since 1973 (Japan)
- Main technology to reduce NO_x emissions
  - In SCR NO_x is reduced by NH_3 to N_2 and H_2O
- Urea ($CO(NH_2)_2$) has been used as a source for NH_3.
- Applications:
  - Stationary engines
  - Diesel vehicles
  - Ships



CATALYST DEACTIVATION

- Chemical deactivation: Poisons adsorb on catalysts' active sites
  - Catalysts' ability to reduce NO_x emissions decreases
- Potassium (K), sodium (Na), phosphorous (P)
  - Originates from biofuels
  - Use of biofuels increases

- Sulphur dioxide (SO_2) in exhaust gas
  - Coal combustion
  - Petroleum combustion
  - Shipping
  - Metal smelting

www.aertc.org/research.asp

www.freewidewallpapers.com/ship/ship-best-desktop-hd-wallpape

BACKGROUND

- Vanadium-based SCR catalysts (V_2O_5/TiO_2-WO_3)
  - Efficient in NO_x reduction by NH_3 or urea
  - Main commercial solution
  - Drawbacks:
    - Use limits in certain fields due to vanadium pentoxide (V_2O_5)
    - Active in oxidizing SO_2 to SO_3 (→ increased particulate emissions)
    - Low thermal durability (max. 600ºC)
    - Sensitivity to certain poisons like P, K, Na, Ca and Mg

→New alternative V-free catalysts are needed for SCR of NO_x

W-CeZr oxide?

OBJECTIVE

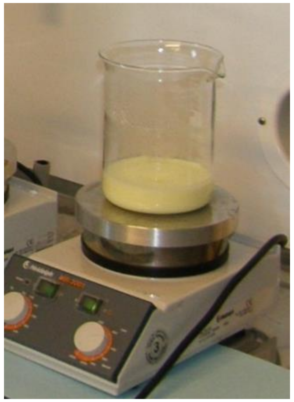
1. To develop *novel materials for NH_3-SCR* with high NO_x reduction activity for high temperature conditions

2. To provide *new information on poisoning*
(as literature data related to the effect of poisons on studied catalysts is not much available).

CATALYST PREPARATION

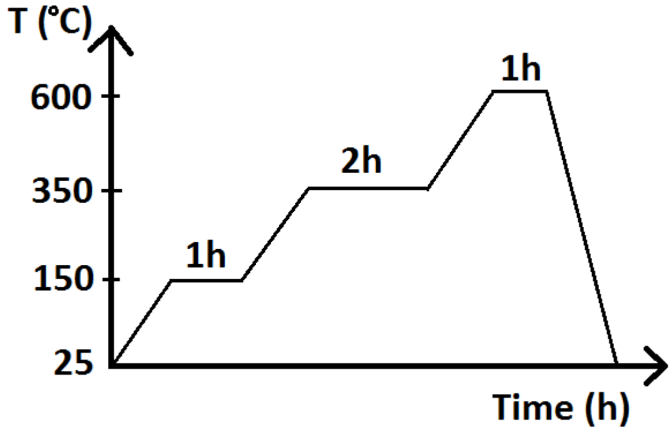
- Used materials
  - Tungsten (W), AMW ($(NH_4)_6H_2W_{12}O_{40}$) was used as an active material
  - CeZr oxide used as support material

- Preparation by a wet impregnation method



Mixing

Drying

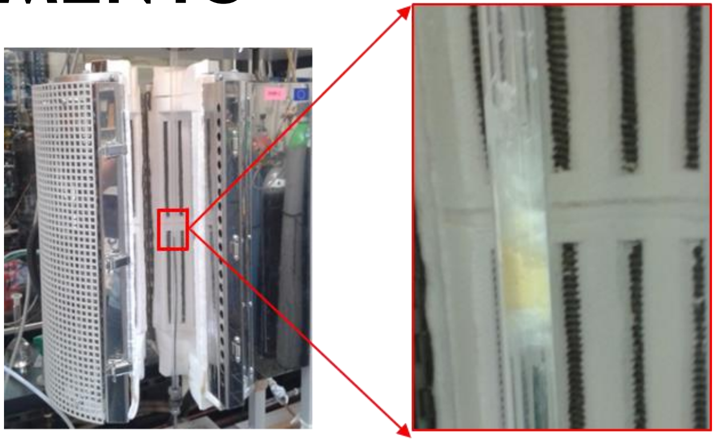


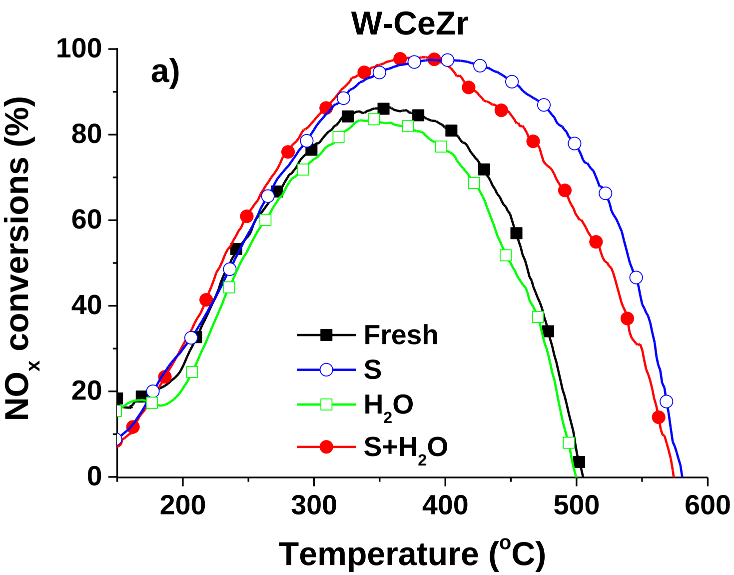
Calcination

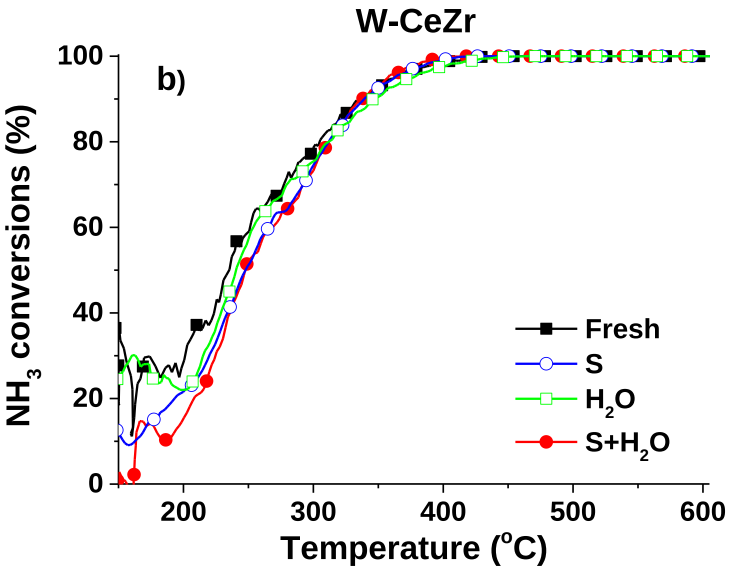
→ **Target: 3.0 wt.% of W on CeZr oxide**

S- AND H_2O-TREATMENTS

- Treatments were done in gas phase for 5h at 400°C.
- Sulphur content on catalysts: 1.6-1.9 wt% (XRF)



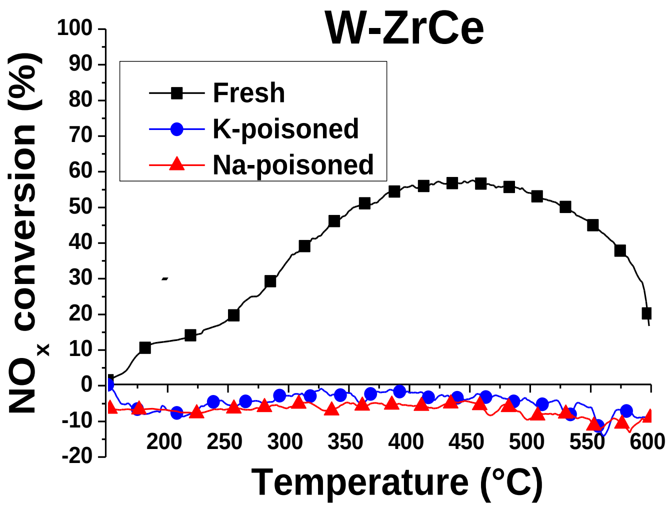


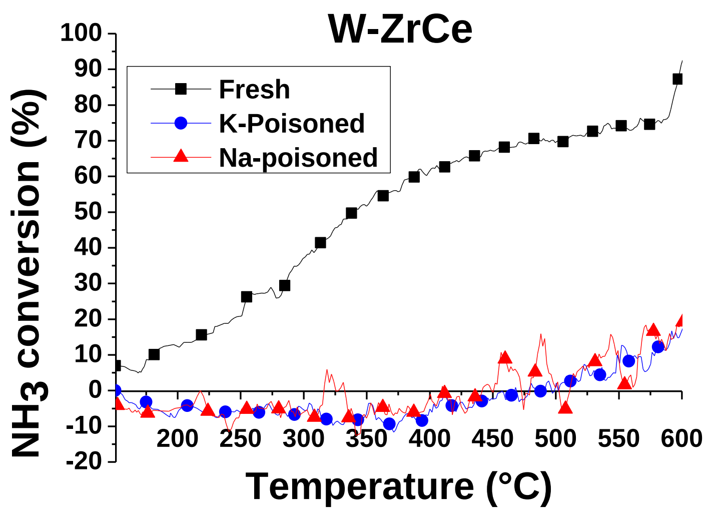


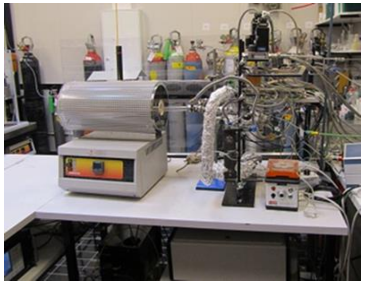
<u>Gas concentrations</u>
900 ppm NO
100 ppm NO_2
1000 ppm NH_3
10 vol.% H_2O
10 vol.% O_2
Balance N_2

K- AND NA-TREATMENTS

- Treatments were done using wet impregnation method
- K and Na contents on catalysts was 0.9-1.0 wt% (AAS)







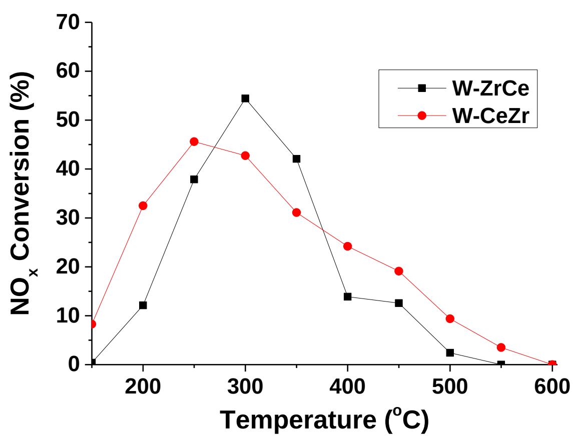
Gas concentrations
900 ppm NO
100 ppm NO_2
1000 ppm NH_3
10 vol.% H_2O
10 vol.% O_2
Balance N_2

H_2-SCR

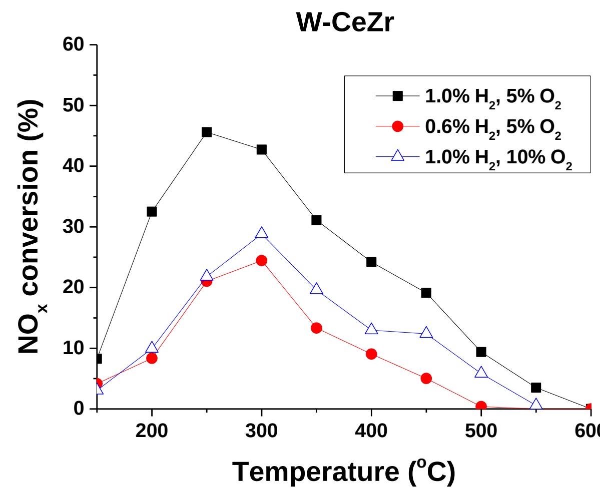
- H_2 is more environmentally-friendly reductant than NH_3.
    - No N_2O and NH_3 emissions.

- Gas mixture in activity tests:
    - 520 ppm NO_x, 0.6-1.0 vol% H_2, 5-10 vol% O_2, 10 vol% CO_2, Balance N_2

- Two different CeZr supports
    - W-ZrCe (Zr-rich)
    - W-CeZr (Ce-rich)



- Three different gas mixtures
    - H_2 and O_2 content was adjusted



This study was done in co-operation with the University of Cyprus.

CONCLUSIONS

- SO_2 enhanced the SCR activity of W-CeZr catalyst.
- H_2O-treatment decreased the NH_3-SCR activity of W-CeZr catalyst slightly.
- K and Na deactivated the W-CeZr catalysts.
  - The effect of K and Na needs to verified in gas phase.
- NH_3 is more active reductant than H_2 in case of W-CeZr catalyst.
- Based on these results, W-CeZr catalyst showed a great potential to be used in NH_3-SCR applications in the presence of SO_x.

PUBLICATIONS

- Reviewed articles in international journals
  - Väliheikki A, Kolli T, Huuhtanen M, Maunula T, Kinnunen T, Keiski RL (2013) “The effect of biofuel originated potassium and sodium on the NH_3-SCR activity of Fe-ZSM-5 and W-ZSM-5 catalysts” Topics in Catalysis 56, p.602-610.
  - Väliheikki A, Petallidou KC, Kalamaras CM, Kolli T, Huuhtanen M, Maunula T, Keiski RL, Efstathiou AM (2014) “Selective Catalytic Reduction of NO_x by Hydrogen (H_2-SCR) on WO_x-promoted $Ce_zZr_{1-z}O_2$” Applied Catalysis B: Environmental 156–157, p.72–83
  - Väliheikki A, Kolli T, Huuhtanen M, Maunula T, Keiski RL “Activity enhancement of W-CeZr oxide catalysts by SO_2 treatment in NH_3-SCR” submitted to Topics in Catalysis in 2014.

- The Conference papers
  - Väliheikki A, Kolli T, Huuhtanen M, Maunula T, Kinnunen T, Keiski RL (2012) ”The influence of potassium and sodium on W-ZrCe oxide NH_3-SCR catalysts” East Meets West 2012 Conference proceedings.
  - Keiski RL, Kolli T, Väliheikki A, Kärkkäinen M, Valtanen A, Pietikäinen M, Oravisjärvi K, Huuhtanen M (2012) ”Recent research in the field of NO_x reduction”. East Meets West 2012 Conference proceedings.

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Thank you for your attention!