Modeling SCR on zeolite catalysts

A summary of observations on SCR kinetics based on the open literature

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Outline

- **Zeolite SCR catalysts : introduction**
- **Zeolites vs V_2O_5 based catalysts**
- **Experimental observation relevant to modeling**
- **SCR mechanisms**
- **Proposed models**
- **Unresolved issues**

Zeolite catalysts for SCR of lean NOx

- **Molecular sieves (ZSM-5, mordenite, Y-zeolite) used to promote specific reactions & achieve desired selectivity**
- **Alternatives to Vanadia based SCR catalysts but not as extensively studied (at least in open literature)**
- **useful for both hydrocarbon SCR or NH_3 SCR**
- **Few commercial formulations (Engelhard, Johnson Matthey) available, more under development**
  - **based mostly on metal-ion-exchanged ZSM-5**

Zeolites vs. V_2O_5 based catalysts (1)

- **Zeolites catalysts are less understood but seem to offer certain advantages (especially Fe-ZSM-5)**
  - Useful for both HC & NH_3 SCR **(Hwang, 1997; Ogura, 2000; Park, 2000; Rebrov, 2000; Wang, 2000; Poignant, 2001; Neylon, 2004)**
  - Higher NOx reduction efficiency of NH_3 SCR
    - Fe-ZSM-5 is 5-7 times more active (resulting in near 100% conversion even at 4.6×10^5/hr SV) than V_2O_5 catalyst in 400^oC-450^oC range based on first order global rates **(Long*, 1999)**
    - Conversion is about twice on Cu-ZSM-5 compared to V_2O_5 in 150^oC-250^oC range **(Sullivan, 1995)**
    - NH_3 oxidation on zeolites slightly higher but the product is N_2 and not NOx **(Sullivan, 1995; Qi, 2004)**
  - Low hydrothermal stability and vulnerability to SO_2 poisoning of Cu/Co-ZSM-5 **(Amiridis, 1996; Traa, 1999)**, Fe-ZSM-5 reported to be highly stable to $550°C$-600^oC **(Feng,1997;Long,1999)**

Zeolites vs. V_2O_5 based catalysts (2)

- May have a broader temperature window (~250°C-600°C) for selectivity of NO SCR towards N_2 (Sullivan, 1995; Long, 1999)
  - even if N_2O forms, it may decompose (Rauscher, 1999; Coq, 2000) (kinetics available for Cu-ZSM-5) or undergo SCR with both NH3 (Mauvezin, 1999, Coq, 2000) and hydrocarbons (Pophal, 1997; Perez-Ramirez, 2004)
  - NO promotes N_2O decomposition (above 350°C), but inhibits N_2O SCR with hydrocarbons on Fe-zeolites (Perez-Ramirez, 2004)
  - synergy between NO SCR and N_2O SCR (Coq, 2000) with NH_3 (has not been observed on V_2O_5 catalysts so far)
- $NO_2/NO = 1$ is optimal for conversion in V_2O_5 catalysts
- SCR stoichiometry : $\alpha = NH_3/NOx$
  - $\alpha = 1$ when $NO > NO_2$
  - $\alpha > 1$ when $NO_2 > NO$
  - NO_2 SCR produces N_2O which requires additional NH_3 for reduction
  - Additional NH_3 consumed by direct oxidation

Zeolites vs. V_2O_5 based catalysts (3)

- **Effect of H_2O and SO_2**
  - **substantially lower oxidation of SO_2 to SO_3 (Long, 1999)**
  - **Fuel S content had no effect on Fe-ZSM-5 (Xu, 2002)**
  - **SO_2 reduces the Fe-ZSM-5 SCR activity slightly at low temperatures but enhances it at high temperatures (> 350ºC) in the presence of H_2O (Li, 1999; Long*,1999; Long, 2000; Neylon, 2004).**
  - **Adverse effect of H_2O was observed on metal-ZSM-5 in one study with protocol conditions for stationary power (Ramachandran, 2000)**
- **Hypothesis : SO_2 forms sulfate ions and increases surface acidity**
  - **increased SCR activity at high temperatures (Long*, 1999)**
  - **these ions reduce NO oxidation which is rate limiting at low temperaratures**
- **Toxicity is a concern with V_2O_5 catalysts**

Observations relevant to modeling (1)

- **Mechanisms may be generic but calibration is needed for each catalyst sample**
  - NH_3 **oxidation depends on Si/Al ratio (10 is optimal(Long, 2001) for N_2 selectivity), Fe/Al range of 0.19-0.43 optimal for NO SCR on Fe-ZSM-5 (Long, 2000)**
  - **Activity depends on precursors used in ion-exchange ($FeCl_3$ is considered the best) (Delahay,2005; Yang, 2005)**
  - **Sublimation/solid-state ion) & hydrocarbons (Cant,2000) (though the reactions following exchange better than aqueous exchange for low temperature performance (Delahay,2005; Yang, 2005)**
- **NO oxidation rate limiting for NO SCR at T < 350°C with both NH_3 (Long, 2000; Stevenson, 2000; Long, 2001; Huang, 2002; Rahkamaa-Tolonen,2005) & HCs (Cant,2000) though the reactions that follow NO_2 production are different)**

Observations relevant to modeling (2)

- **Metals oxidize NO on ZSM-5 catalysts**
  - **HZSM-5 oxidizes NO but only in absence of NH_3 (Stevenson, 2000)**
  - **Except for NO oxidation, metal-ZSM-5 catalysts have the same kinetics as HZSM-5 (Long,2000; Long,2002)**
  - **NO & NO_2 reach equilibrium around 350^oC on metal-ZSM-5 (typical SV), equilibrium is not reached even at 500^oC on HZSM-5 (Long,2000)**
  - **kinetics for HZSM-5 (Long,2002; Stevenson, 2002) catalysts can be used for Fe-ZSM-5 by adding NO-NO_2 inter-conversion steps**

- **1:1 ratio of NO:NO_2 is optimal**
  - **$NO+NO_2 > NO_2 >> NO + O_2$**
  - **$(NH_3/NOx)_{stoic} > 1$ when $NO_2 > 50\%$**

SCR mechanisms

- **NO SCR (Eng,1997; Long, 2000; Stevenson,2000; Long*, 2001)**
  - **NO + 1/2 O_2 <=> NO_2 (rate limiting step)**
  - **NO_2 + 2NH_4^+ <=> (NH_4^+)$_2NO_2$**
  - **(NH_4^+)$_2NO_2$ + NO <=> 2N_2 + 3H_2O + 2H^+**
  - **With 50% NO & 50% NO_2**
    - reactions 2 & 3 can proceed without reaction 1
    - metal-ZSM-5 and HZSM-5 catalysts behave similarly
  - **1:1 ratio of NH_3:NO**
  - **negligible N_2O**
  - **Models based on a global NO conversion rate have been developed(Komatsu, 1994; Eng, 1997; Stevenson, 2000; Huang, 2002)**
    - E_a : 35kJ/mol - 61 kJ/mol (~ 54kJ/mol in most cases)
    - all but one study (Stevenson, 2000) ignored NH_3 oxidation
    - mostly steady state experiments

SCR mechanisms

- **NO$_2$ SCR** **(Stevenson, 2002)**
  - $(NH_4^+)_2NO_2 + NO_2 <=> N_2 + N_2O + 3H_2O + 2H^+$ (~500-900 times faster than NO oxidation in 300°C-400°C range)
  - N_2O can participate in many likely reactions, e.g.,
    - $3N_2O + 2NH_4^+ <=> 4N_2 + 3H_2O + 2H^+$
    - $N_2O + NO_2 <=> 3NO$
  - stoichiometry varies with T (and perhaps from one catalyst to another) from 1.2:1 - 2:1 (median:1.4-1.5)
  - > 50% N_2O selectivity (300°C-400°C) ! How ?
  - modeling global NO_2 conversion rate more difficult
    - reaction orders change rapidly (order in [NH_3] changes from 0.13 to 0.82 in 300°C-350°C range)
  - Conclusion : Modeling can become really complex when N_2O starts to form (NO_2>NO in the flow)

Kinetic models for NO SCR

- **Global single step model : $r_{NO} = K_{NO}\,[NO]^x[NH_3]^y[O2]^z$**
  - $E_{NO} \sim 54$ kJ/mol
  - [x,y,z] :
    - [1,0,0.5] **(Komatsu,1994)**
    - [0.73,-0.61,1.06] **(Eng, 1997)**
    - [1,-0.45,1] **(Stevenson, 2000)**
    - [0.9,-0.12,0.4] **(Huang, 2002)**
  - y has negative values and varies most with temperature
- **Adsorbed NH_3 inhibits NO oxidation : surface reactions model(Stevenson, 2000, Wallin,2003)**
  - $r_{NO} = K_{NO}\,[NO][O_2]^{0.5}/\{1 + K_a\,[NH_3]\}$
  - $r_{OX} = K_{OX}\,K_a[NH_3]/\{1 + K_a[NH_3]\}$,
    - $E_{OX} = 88$kJ/mol**(Long, 2001)** , $E_a = 19$kJ/mol - 45 kJ/mol
  - NH_3 storage capacity is needed

Models for NO+NO$_2$ SCR

- **Separate out NO oxidation from SCR**
  - **NO + 1/2 O$_2$ <=> NO$_2$**
  - **NO$_2$ + 2NH$_4^+$ <=> (NH$_4^+$)$_2$NO$_2$ (equilibrium)**
  - **NO + (NH$_4^+$)$_2$NO$_2$ <=> 2N$_2$ + 3H$_2$O + 2H+**
  - **H$^+$ + NH$_3$ <=> NH$_4^+$ (equilibrium)**
  - **should work as long as NO > NO$_2$ at inflow**
    - **lot of other reactions involving N$_2$O need to be added otherwise**

Unresolved issues

- **Urea to ammonia conversion on zeolites**
  - sprays : hydrodynamics, heat & mass transfer, uniformity
  - No problem was reported with use of urea **(Xu, 2002)**
  - Thermal pre-treatment needed for urea decomposition below 250°C, formation of melamine suggested as a possibility **(Jones, 2004).**
  - Reactions involving species like HNCO and NOx need to be studied

- **Model for self-inhibition of SCR at low T (< 250°C)**
  - NOx adsorption blocks NH_3 adsorption **(Xu, 2002)**
    - NOx storage : 0.02 - 0.05 mol/m³ (170°C-350°C range)
    - NH_3 adsorption at least 2 orders of magnitude higher
    - how does NOx prevent NH_4^+ formation despite the huge differences in propensities for storage

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