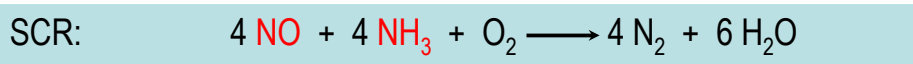
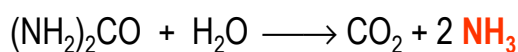
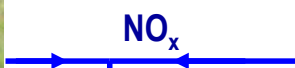
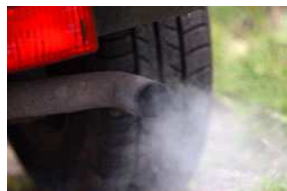


# The selective catalytic reduction (SCR) of NO<sub>x</sub> by ammonia



In diesel vehicles:

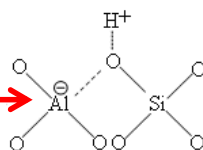
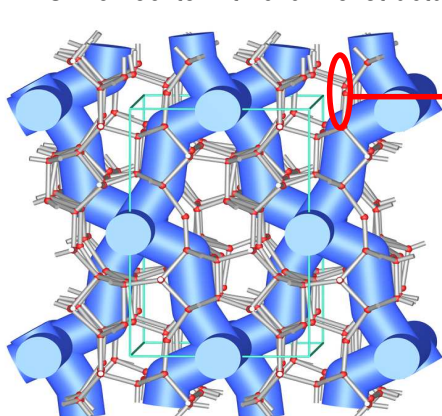


SCR mechanism over Fe-ZSM-5:



## Structure of iron sites in Fe-ZSM-5

ZSM-5 zeolite with channel structure:

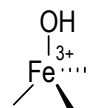
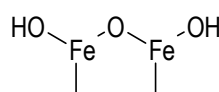


Exchange of H<sup>+</sup> with Fe: a large variety of Fe species are formed in Fe-ZSM-5:

Size

Fe<sub>2</sub>O<sub>3</sub> particles

Fe<sub>x</sub>O<sub>y</sub> clusters



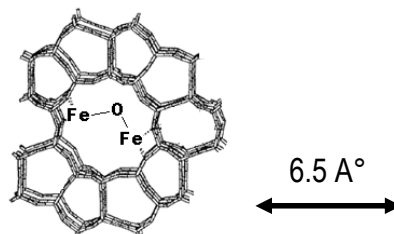
Which one is the active species?

## Problem: Identification of the SCR active sites in Fe-ZSM-5

**Reason:** No method (e.g. UV/VIS, IR, EPR, EXAFS, XPS, XRD) can definitively distinguish between isolated iron species and iron oxide clusters of different nuclearity in the same sample

**Solution:** A statistical approach

**Idea:** At least two iron ions, located on Al -sites, must be present within a sphere with  $r = 6.5 \text{ \AA}$  to form an oxygen bridged Fe-O-Fe species



**Procedure:** Calculating of the averaged number of Al sites bearing an iron ion =  $N_{Fe}$ ;  $N_{Fe} = f(\text{Si/Al}, \text{Fe/Al})$

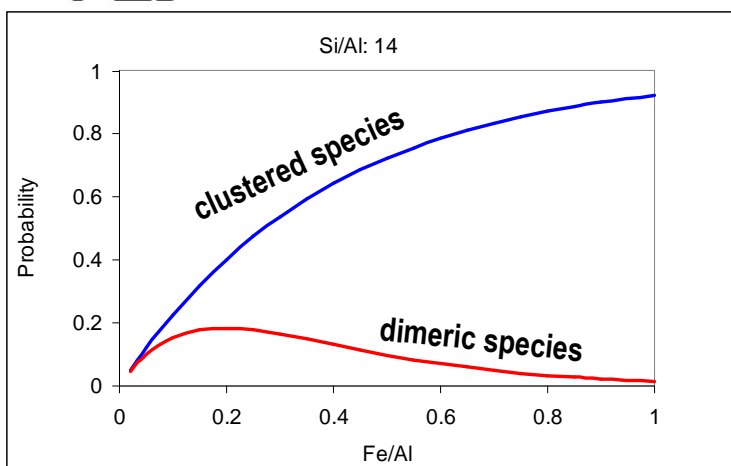
Assumption: Al Atoms are statistical distributed and the variation of the local Si/Al ratio can

be described by a Poisson distribution: 
$$P(x; N_{Fe}) = \frac{N_{Fe}^x \cdot e^{-N_{Fe}}}{x!}$$

Rice, M.J., Chakraborty, A.K., and Bell, A.T., J. Catal. 186 (1999) 222.

Goodman, B.R., Hass, K.C., Schneider, W.F., and Adams, J.B., Catal. Lett. 68 (2000) 85.

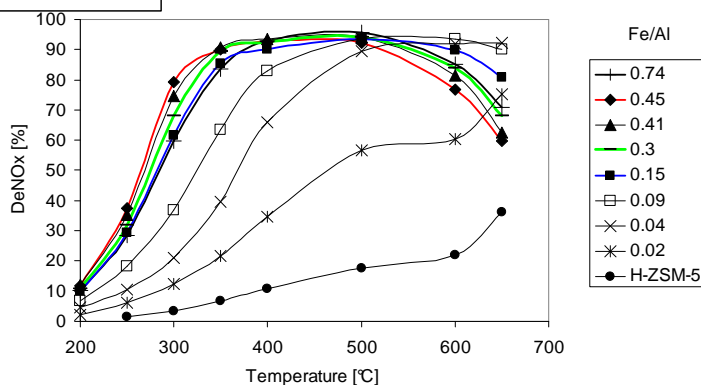
S. Brandenberger, October 2008



$$1 - P(x=0; N_{Fe}) = 1 - \frac{N_{Fe}^0 \cdot e^{-N_{Fe}}}{0!} = 1 - e^{-N_{Fe}}$$

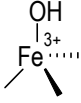
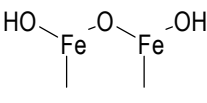
$$P = \frac{N_{Fe}^1 \cdot e^{-N_{Fe}}}{1!} \cdot e^{-N_{Fe}}$$

Correlation of the **measured** SCR activity with the **calculated** concentration of different species



S. Brandenberger, October 2008

## SCR activity of the different iron species

Temperature	Isolated species 	Dimeric species 	Oligomeric species $Fe_xO_y$	Particles $Fe_2O_3$
200-300 °C	<b>Active</b> TOF $\approx 14 \text{ s}^{-1}$ (250 °C)	-	-	-
$\approx 350 \text{ °C}$	<b>Active</b> TOF $\approx 46 \text{ s}^{-1}$ (350 °C)	<b>Active</b> TOF $\approx 120 \text{ s}^{-1}$ (350 °C)	-	-
$\approx 400 \text{ °C}$	<b>Active</b> TOF $\approx 100 \text{ s}^{-1}$ (400 °C)	<b>Active</b> TOF $\approx 170 \text{ s}^{-1}$ (400 °C)	<b>Active</b>	-
$\geq 450 \text{ °C}$	<b>Active</b>	<b>Active</b>	<b>Active</b>	<b>Active</b> TOF $\approx 27 \text{ s}^{-1}$ (500 °C)