Seltene Erden in der SCR-Katalyse

(Vortrag im Rahmen des Workshops „Seltene Erden -Ihre Bedeutung für die Industrialisierte Welt“ des Materials Valley)

Rare Earths in S(elective) C(atalytic) R(eduction)

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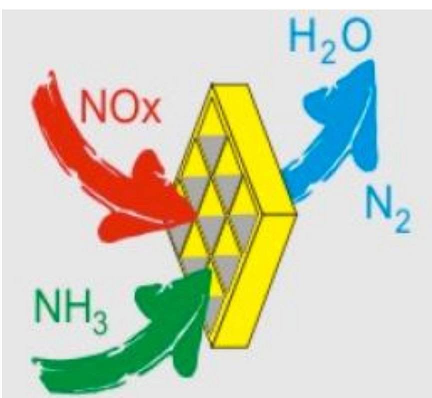
Content

- What is SCR ?
- Driving forces for SCR
- Materials applied in SCR – state of the art
- Innovative materials for SCR containing Rare Earths and their properties
- Summary, Conclusions and Outlook

What is SCR ?

- SCR stands for **S**elective **C**atalytic **R**eduction
- Wideley employed technology for removal of NOx out of exhaust gases
- NOx is converted by ammonia (NH3) into water and nitrogen according to the reaction



$$4\,NH_3 + 4\,NO + O_2 \Rightarrow 4\,N_2 + 6\,H_2O$$

$$8\,NH_3 + 6\,NO_2 \Rightarrow 7\,N_2 + 12\,H_2O$$

What is SCR ?

- **Technology known already since the 1970s; applied at stationary sources (eg. fossil fuel power plants)**
- **Technology was successfully adopted to stationary diesel engines by substitution of ammonia by urea (urea-SCR), which is a precursor for NH3**

$$(NH_2)_2CO + H_2O \longrightarrow 2\,NH_3 + CO_2$$

- **Nowadays urea-SCR is an emerging technology for the NOx reduction of exhausts of diesel engines of heavy-duty and light-duty vehicles as well as passenger cars and non-road applications**



Driving Forces for promoting technologies for exhaust gas emissions = worldwide emission standards

http://www.altenergystocks.com/archives/2010/03/

Global Regulation Timeline by Region

*Phased in
**Proposed

CVS - Commercial Vehicle Systems
LVS - Light Vehicle Systems

	2007	2008	2009	2010	2011	2012	2013	2014
U.S.	US-07 CVS	Locomotive & Marine Tiers 0-2	CA CVS Retrofit**	US-10 CVS On-Highway Motorcycle Rule Tier 2	US off-road diesel Tier-4A*	Locomotive & Marine Tier 3 CA LEV III	US Tier 3 LVS** R.I.C.E. Stationary** Locomotive & Marine Tier 4*	US off-road diesel Tier-4B*
EUROPE		EU Euro-5 CVS	EU Euro-5 LVS*	Netherlands Marine OE/Retrofit	EU off-road Stage 3B*	EU CO2/GHG 120g PM # LVS	EU-6 CVS**	EU off-road Stage 4 EU Euro-6 LVS*
CHINA	Euro-3 LVS	Euro-3 Two-wheel Beijing Euro-4 LVS	Beijing CVS Yellow Label		Euro-4 LVS/CVS	Euro-5 LVS*		Euro-5 CVS**
JAPAN		Cold-start restrictions LVS	Japan-09 LVS/CVS		NO_x reductions LVS		JP-13 CVS	
BRAZIL			US Tier 2 LVS* Motorcycle Rule*			Euro-5 CVS		
RUSSIA		Euro-3 LVS			Euro-4 LVS/ CVS			Euro-5 CVS
INDIA				Euro-4 LVS* & motorcycle rule*	Euro-4 CVS 11 Cities			

Stricter Emission Regulations

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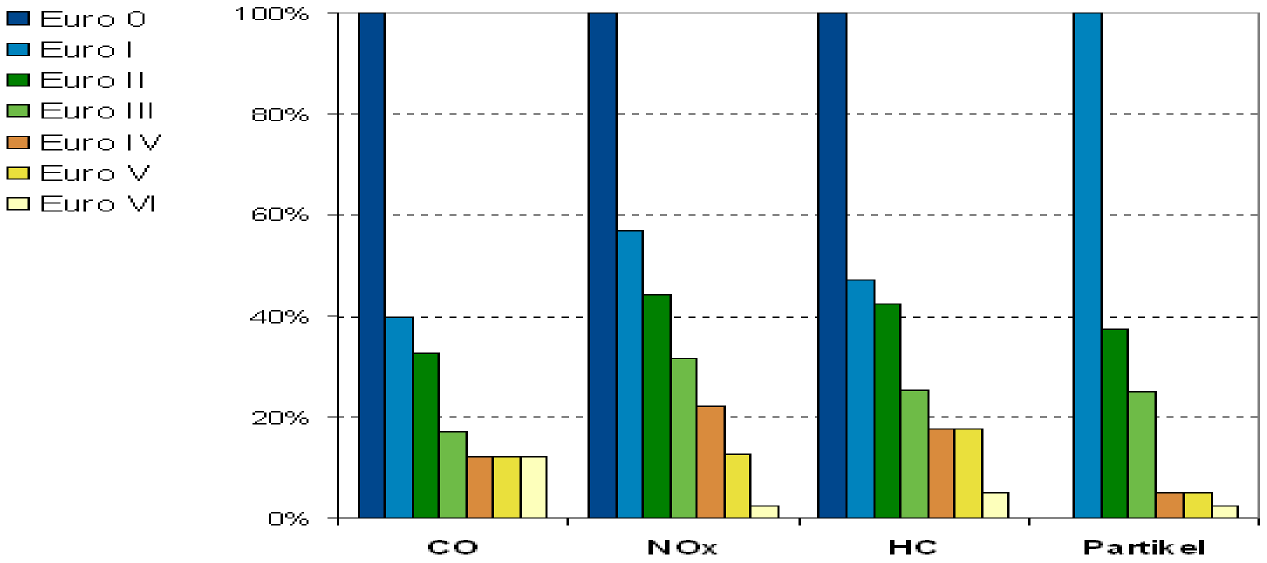
Future Emission Limits
Heavy Duty Diesel (Europe)

Source: LUBW, Baden-Württemberg

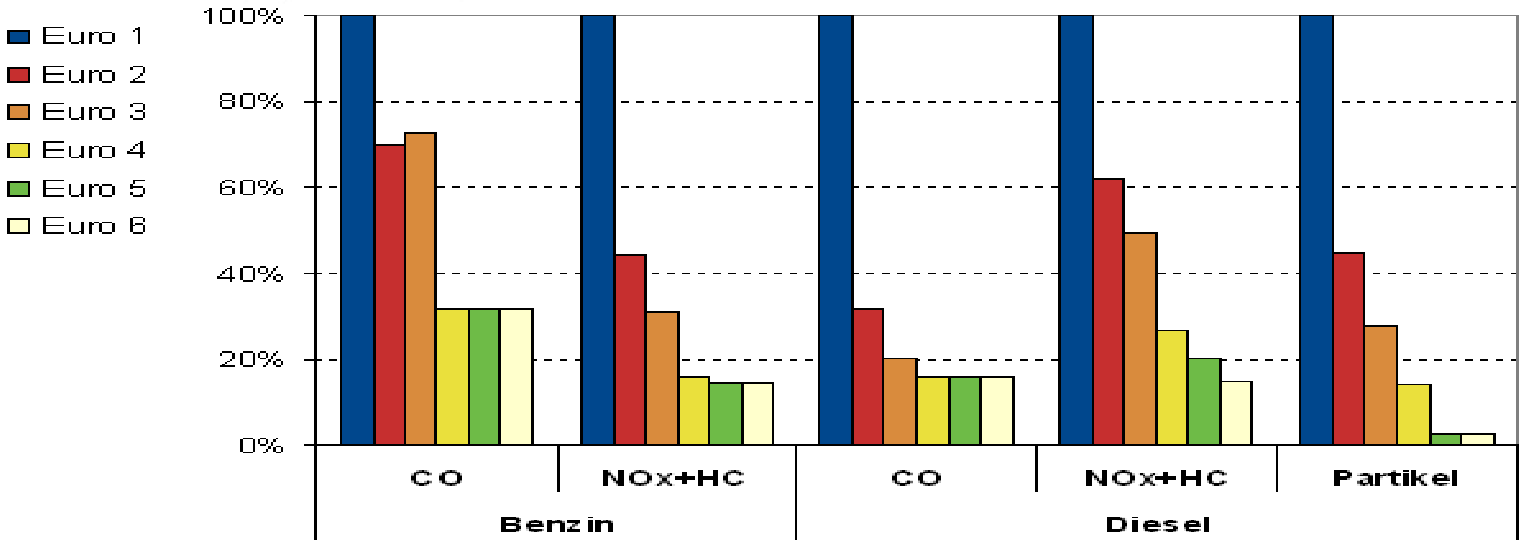


	gültig ab *	CO	NOx	HC	Partikel
		in g/kWh			
Euro 0	1988/90	12,3	15,8	2,6	-
Euro I	1992/93	4,9	9	1,23	0,4
Euro II	1995/96	4	7	1,1	0,15
Euro III	2000/01	2,1	5	0,66	0,1
Euro IV	2005/06	1,5	3,5	0,46	0,02
Euro V	2008/09	1,5	2	0,46	0,02
Euro VI	2012/13	1,5	0,4	0,13	0,01

Future Emission Limits

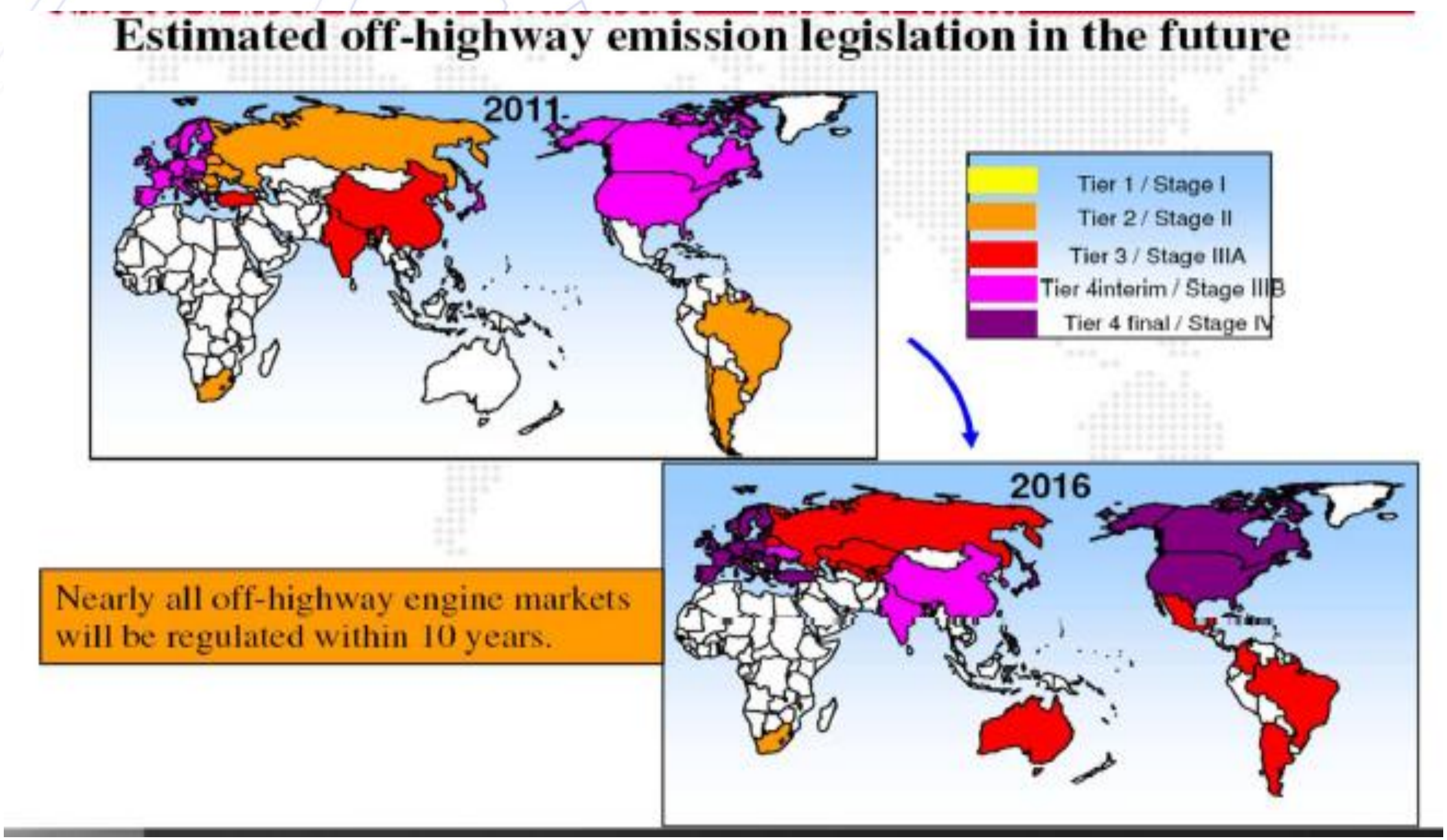
Passenger Cars (Europe)

Source: LUBW, Baden-Württemberg



	gültig ab	Benzin			Diesel			
		CO	NOx	HC	CO	NOx	HC+NOx	Partikel
		in g/km						
Euro 1	1.7.1992	3,16	HC+NOx 1,13		3,16		1,13	0,18
Euro 2	1.1.1996	2,2	HC+NOx 0,5		1,0		0,7	0,08
Euro 3	1.1.2000	2,3	0,15	0,2	0,64	0,5	0,56	0,05
Euro 4	1.1.2005	1,0	0,08	0,1	0,5	0,25	0,3	0,025
Euro 5	1.9.2009	1,0	0,06	0,1	0,5	0,18	0,23	0,005
Euro 6	1.9.2014	1,0	0,06	0,1	0,5	0,08	0,17	0,005

Future Emission Limits
NON Road



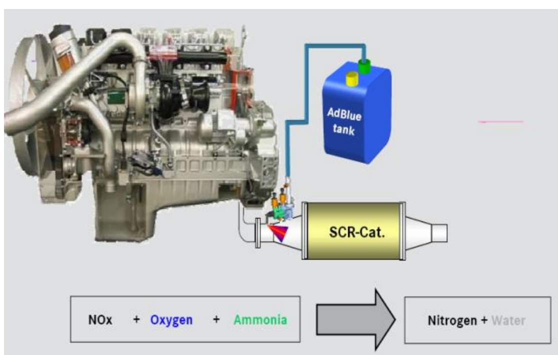
Source: AGCO SISU POWER, Dez. 2008

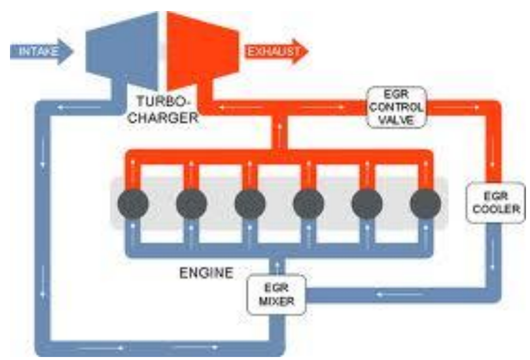
Technologies for NOx removal in mobile application

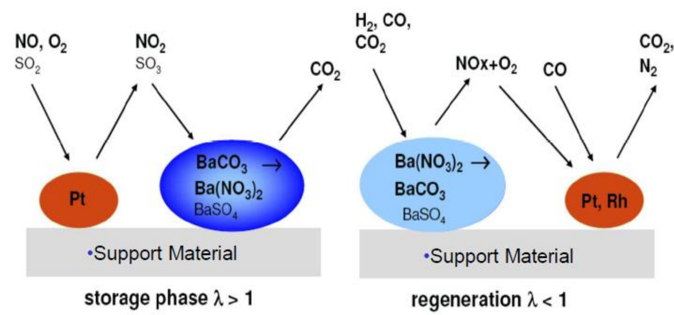
Selective Catalytic Reduction by NH3 (NH3-SCR)

(NH3 generated out of urea solution (Ad Blue) on board of the vehicle)

- *Selective Catalytic Reduction by CH (CH-SCR)*
- ***EGR** (Exhaust Gas Recirculation)*
- ***NOx Storage** –Technology (Nox Absorber, NOx Trap, Lean NOx Trap)*







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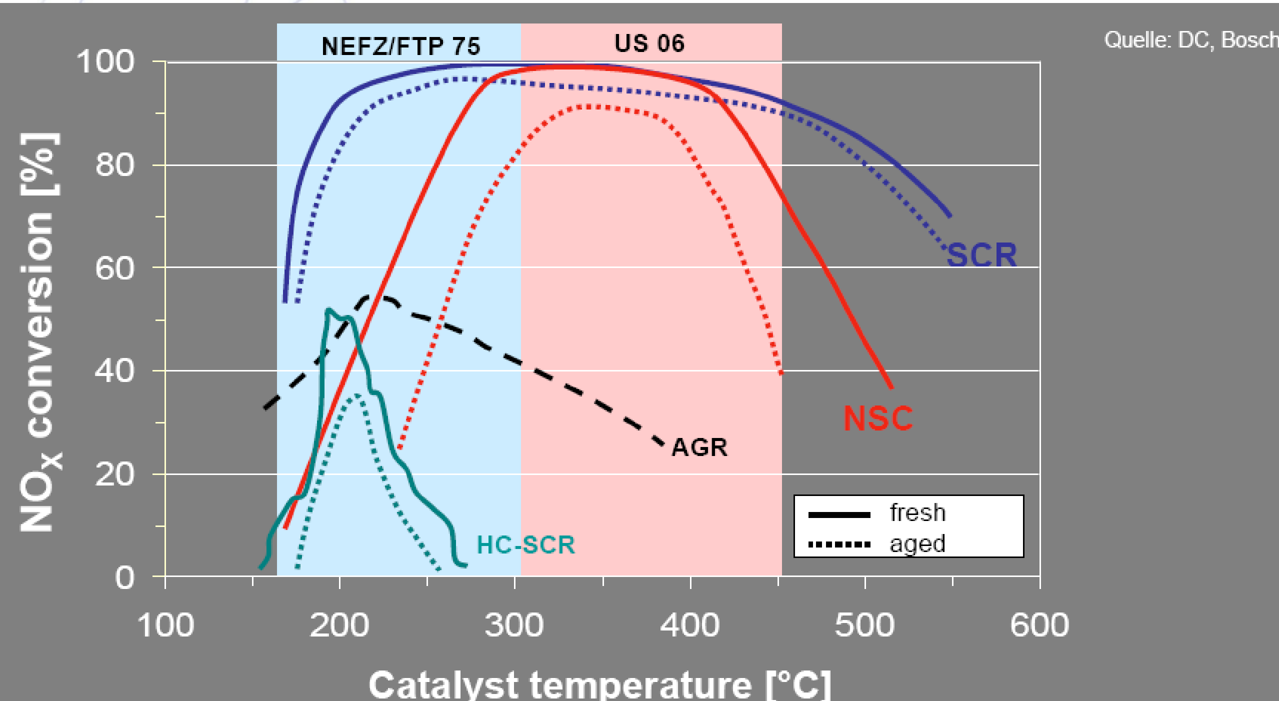
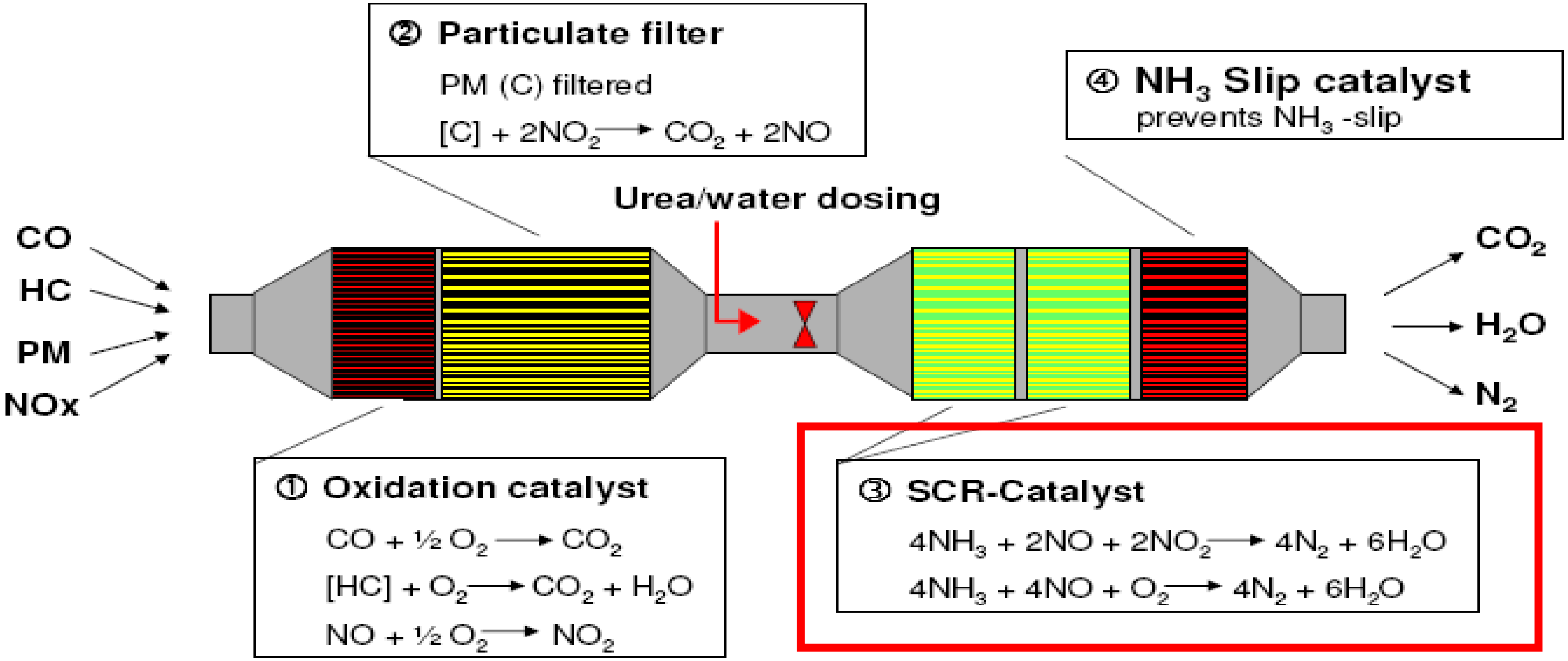
NOx Control –Technologies and their Efficiencies



Results:

- SCR system shows higher efficiency as NO_X adsorber
- SCR system operates in a wide temperature range
- SCR technology: Robust method over running time
- Low influence of fuel quality (e.g. sulphur amount) on SCR methods.

Main Components of an Exhaust Gas Aftertreatment System (Diesel)



SCR Catalysts – Materials applied in SCR Catalysis

Vanadium Oxide based Catalysts

TiO_2 / WO_3 : (SiO_2) based materials doped with Vanadium-Oxide Species, applied as

FULL CATALYST (FULL EXTRUDATE)

COATED CATALYST

Heavy Duty Diesel and Non Road Applications

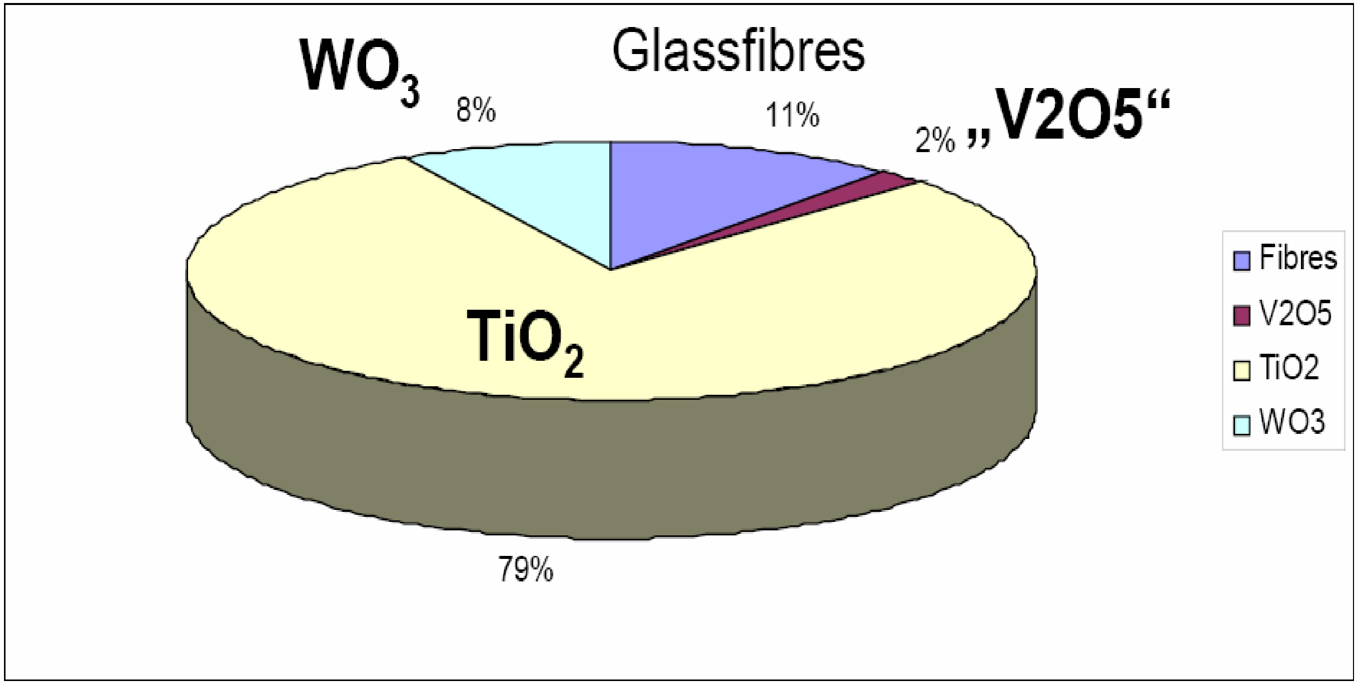
Disadvantages:

Health concern on possible release of V_2O_5 out of catalyst

Not stable above 650° C (dramatic loss on activity > 650° C)

Not applicable downstream a DPF

Composition of commercial TiO2/ WO3 / V-Oxid "Full Catalyst " (Extrudate)



Source: 6.CTI Forum Stuttgart, 2010

Classification of V2O5

· *Classification according to Directive 67/548/EEC or Directive 1999/45/EC*

T; Toxic

R48/23: *Toxic: danger of serious damage to health by prolonged exposure through inhalation.*

Xn; Harmful

R20/22-63: *Harmful by inhalation and if swallowed. Possible risk of harm to the unborn child.*

Xi; Irritant

R37-41: *Irritating to respiratory system. Risk of serious damage to eyes.*

N; Dangerous for the environment

R51/53: *Toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment.*

SCR Catalysts – Materials applied in SCR Catalysis

Zeolites (Fe- und Cu-Zeolite) applied as

COATED CATALYST (Heavy duty, passenger car, non road)

Disadvantages:

sensitive against hydrothermal ageing

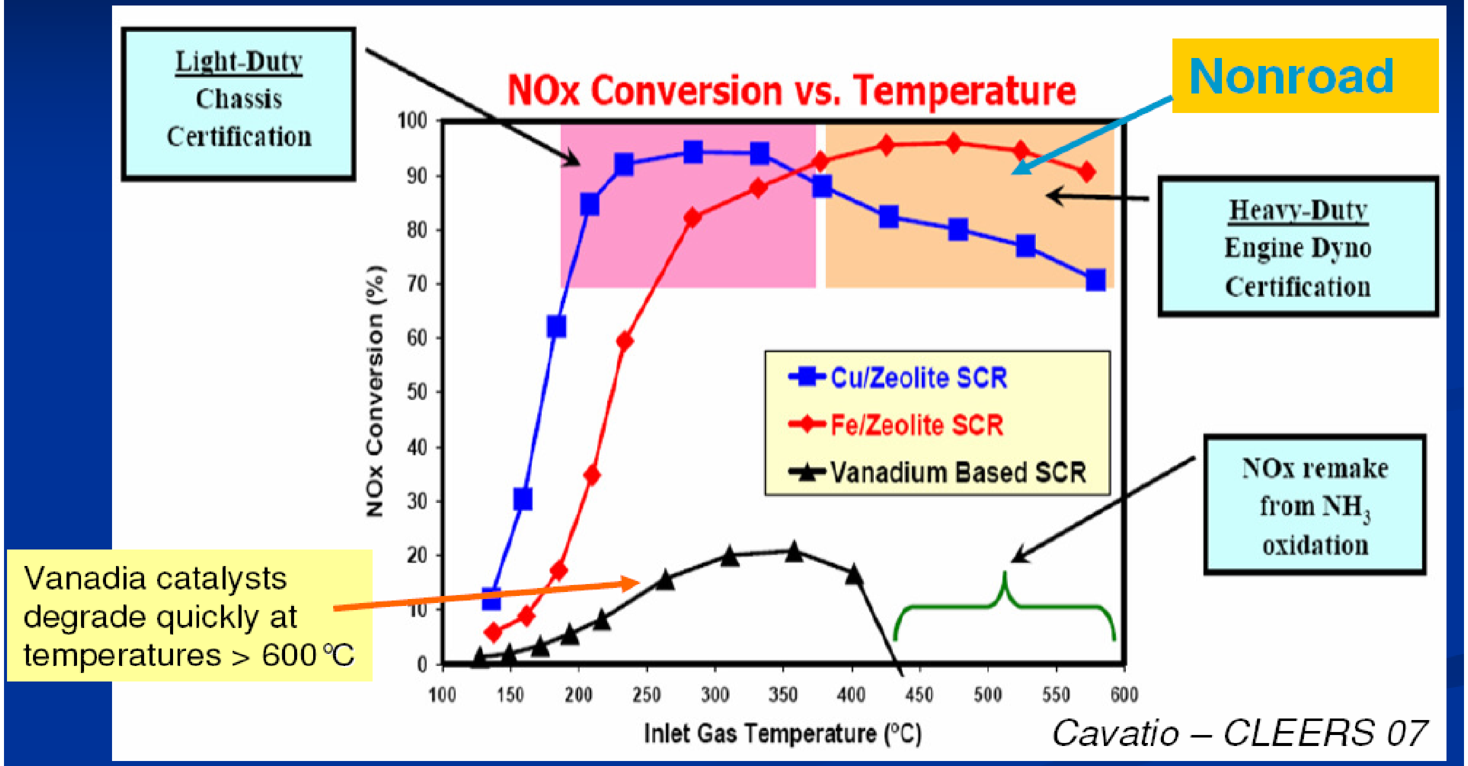
Sulfur sensitive

Selectivity problems (N2O formation particularly Cu-Zeolite)

Costs >> compared to Vanadium based SCR catalyst

Catalyst Performance – Zeolite vs Vanadia

Catalysts Aged 64 hrs @ 650 °C*



*Typical temperature exposure during active DPF regeneration

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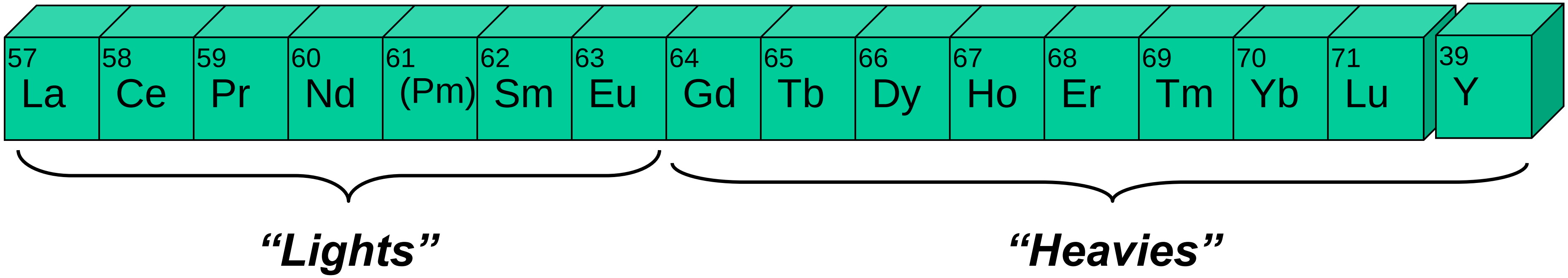
Rare Earths in SCR

How may Rare Earths Contribute to the Application in SCR ?



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Benefits of Rare Earths in SCR

Combination of:

Rare Earth(s) + Iron + Vanadium =

Environmental friendly non toxic Vanadium based Compounds ‚so called

„ Iron- Rare Earth(s)- Vanadates“

„Fe(x)RE(1-x)VO4“ (x = 0 – 1)

applicable as dopants for making SCR catalysts

Benefits of Rare Earth (Fe) Vanadates in SCR formulations

Properties of SCR Catalyst (TiO_2 based materials)

Contains environmental friendly Rare Earths based Vanadate dopants

Rare Earth Vanadates considered not to be detrimental

Rare Earths in the Vanadate contribute to significant higher thermostability (up to approx. 800°C) compared to V-Oxide based SCR Materials (stable up approx. 650°C)

High catalytic activity remains after severe hydrothermal Ageing (700°C/ 100 hrs)

Rare Earth (Fe) Vanadates in SCR formulations

Properties of SCR Catalyst (TiO_2 based materials)

High selectivity, no N_2O formation in SCR reaction
(N_2O = hazardous gas , emission will be most likeley regulated in future)

Insensitive against Sulfur, applicable for S-containing fuel (Emerging countries !)

Provides cost efficient alternative to other SCR materials such as Zeolites and Mixed Oxides.

Toxicological Investigations on Rare Earth Vanadates

Bioeffect Screening

In vitro assays on various cells (eg embryonic tem cells in stead of animal testing)

aquatic organisms (Exotoxicological test against Daphnia and Desmodesmus)

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Toxicological Profile of Rare Earth Vanadates compared to V2O5

	Cytotoxicity	Embryotoxicity	Genotoxicity
V2O5	**pos.**	**pos.**	negative
RE-Vanadate (REVO4)	negative	negative	negative
Fe-RE-Vanadate (Fe(0,5)RE(0,5)VO4)	negative	negative	negative

Interreg IV

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Ecotoxicological Test of Vanadates in comparison to V2O5 (Test Item Daphnia Magna)

	NOEC 24h mg/Liter	24h EC 50 mg/Liter	24 h EC 100 mg/Liter	NOEC 48h mg/Liter	48h EC 50 mg/Liter	48 h EC 100 mg/Liter	Test Procedure
V_2O_5							OECD 202/EUC2/EN ISO 6341
Sample	dissolved	dissolved	dissolved	dissolved	dissolved	dissolved	
Result	**2,2**	**4,6**	> 100	**0,22**	**1,38**	**4,6**	
RE-Vanadate ($REVO_4$)							
Sample	dissolved	dissolved	dissolved	dissolved	dissolved	dissolved	OECD 202/EUC2/EN ISO 6341
Result	100	> 100	> 100	100	> 100	> 100	
Sample (> 1g Liter !!)	Suspension	Suspension	Suspension	Suspension	Suspension	Suspension	OECD 202/EUC2/EN ISO 6341
Result	1000	> 1000	> 1000	> 1000	> 1000	> 100	
Iron-RE-Vanadate ($Fe_{0,5}RE_{0,5}VO_4$)							
Sample	dissolved	dissolved	dissolved	dissolved	dissolved	dissolved	OECD 202/EUC2/EN ISO 6341
Result	100	> 100	> 100	100	> 100	> 100	

EC50 higher than a conc. of 100 mg/Liter are considered to be non toxic to the environment !!

$K_2Cr_2O_7$ - Reference		**0,6 - 2,1**

NOEC — **OBSERVED NO EFFECT CONCENTRATION**

EC 50 — **HALF MAXIMUM EFFECT CONCENTRATION**

EC 100 — **MAXIMUM EFFECT CONCENTRATION**

Interreg IV

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Ecotoxicological Test of Vanadates in comparison to V_2O_5 (Test Item Desmodesmus subspicatus)

	NOEC 72h mg/Liter	72h EC 50 mg/Liter	72h EC 100 mg/Liter	Test Procedure
V_2O_5				
Sample	dissolved	dissolved		OECD 201/EUC3/EN ISO 8692
Result	**2,2**	**1,67**	**na**	
RE-Vanadate ($REVO_4$)				
Sample	dissolved	dissolved	dissolved	OECD 201/EUC3/EN ISO 8692
Result	100	> 100	> 100	
Iron-RE-Vanadate ($Fe_{0,5}RE_{0,5}VO_4$)				
Sample	dissolved	dissolved	dissolved	OECD 201/EUC3/EN ISO 8692
Result	100	> 100	> 100	

NOEC **OBSERVED NO EFFECT CONCENTRATION**
EC 50 **HALF MAXIMUM EFFECT CONCENTRATION**
EC 100 **MAXIMUM EFFECT CONCENTRATION**

EC50 higher than a conc. of 100 mg/Liter are considered to be non toxic to the environment !!

Additional Properties of „$Fe_{(x)}RE_{(1-x)}VO_4$“

- Stable up to > 1000°C without any release of V_2O_5 according to the chemical reactions

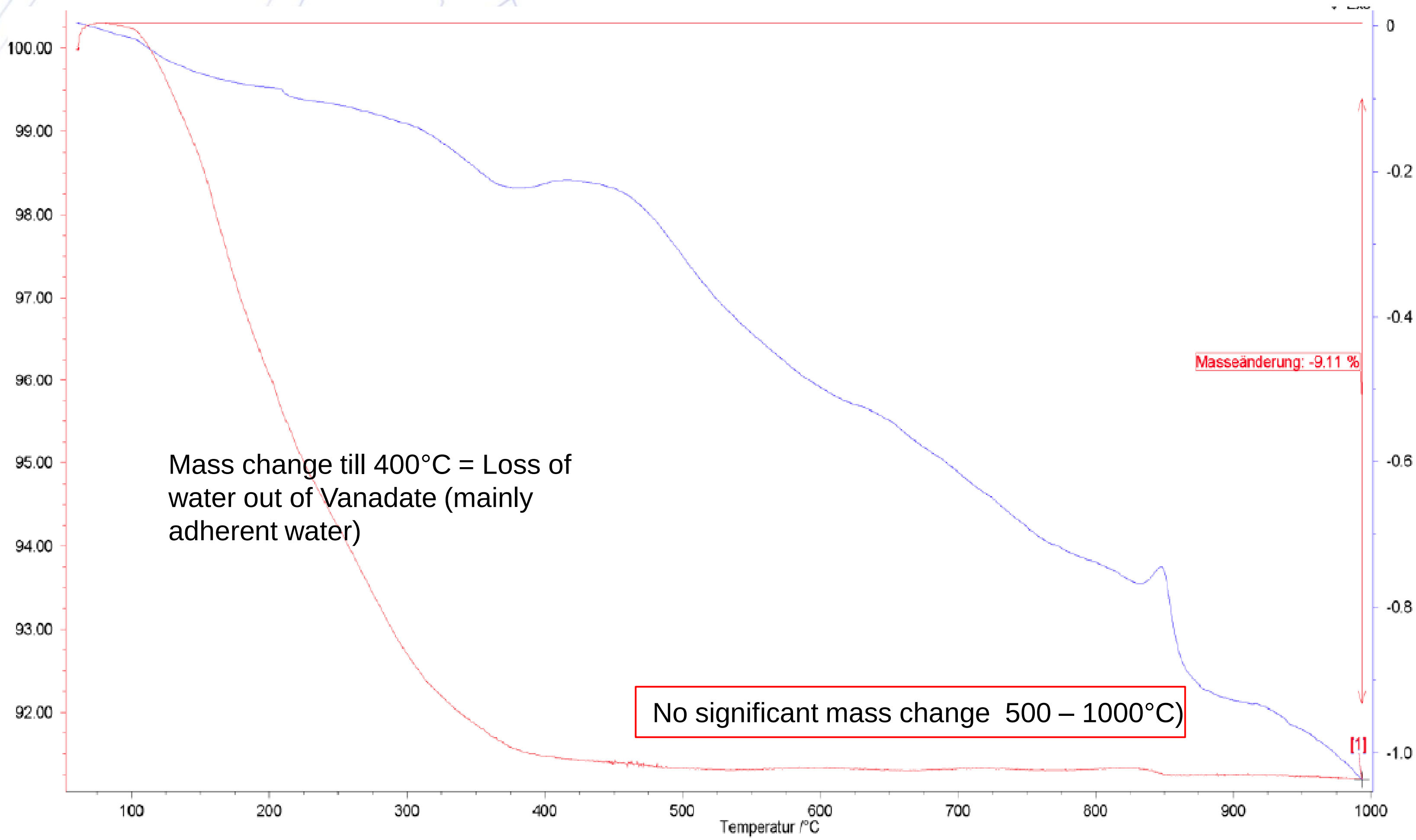
[T= > 600°C]

$RE_2O_3 + V_2O_5 \rightarrow 2\,REVO_4$ (RE = Ce, Pr, Sm, Er, Dy, Gd, Tb)

$Fe_2O_3 + V_2O_5 \rightarrow 2\,FeVO_4$

- Stability of Rare Earth Vanadates confirmed by Differential thermoanalysis

DTG of a FeRE-Vanadate



Functional Testing of SCR catalysts formulations – different conditions

- based on **powders** in a microreactor
- based on **coated honeycomb**
- based on **“full catalyst”** (Extrudate)
- Test conditions: various types of feedgas (NO, NO/NO2, NO2)
- Ageing: dry ageing (powders) and hydrothermal ageing (real catalysts)

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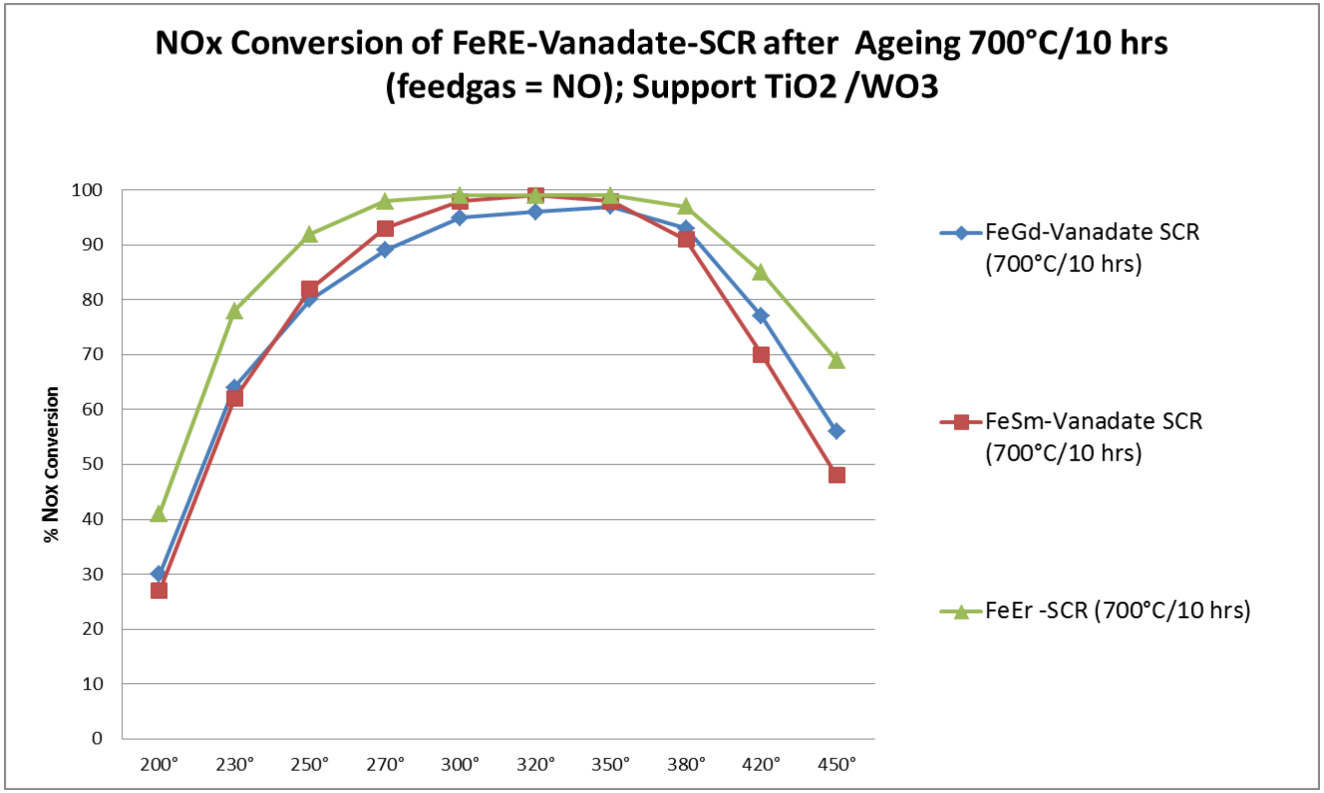
Catalytic Activity of various Rare Earth Vanadate-SCR Catalysts

(Support = $TiO_2/WO_3/SiO_2$)

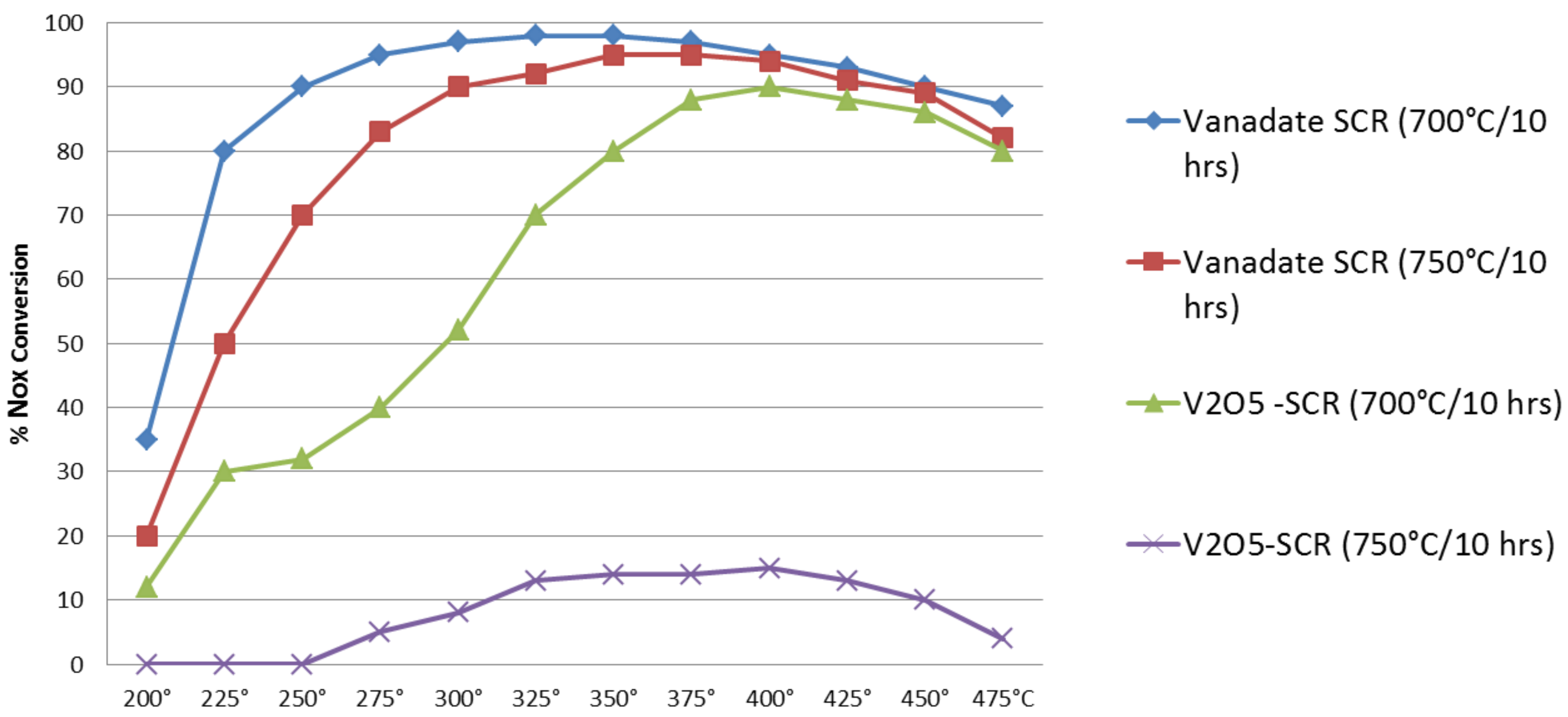
Conditions: SV [h^{-1}] = 180.000, feedgas = NO = 100%, powder sample



Catalytic Activity after Hydrothermal Ageing of Catalyst – V2O5-SCR versus Rare Earth Vanadate-SCR

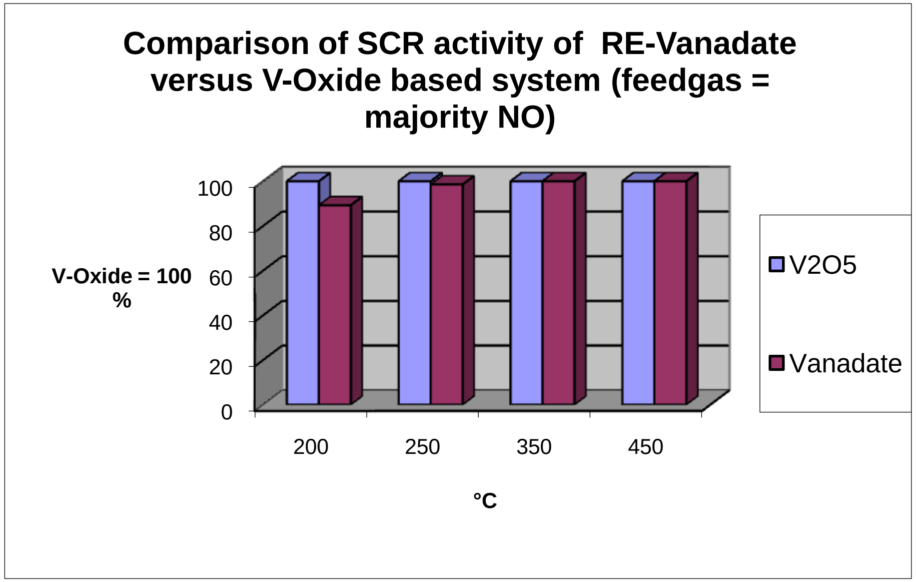
(Support = $TiO_2/WO_3/SiO_2$ based)

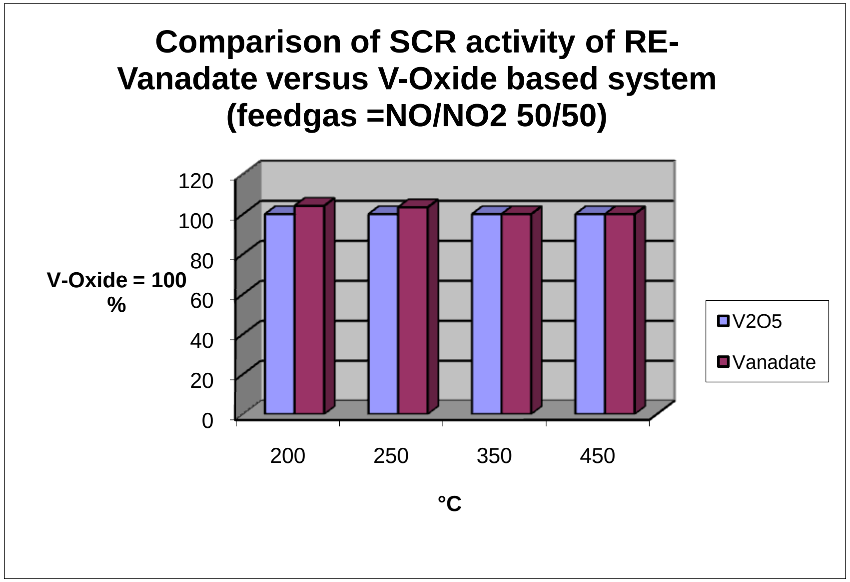
Conditions: Washcoated catalyst, SV [h^{-1}] = 30.000, feedgas = NO/NO_2 = 50/50



Catalytic Activity –V2O5 -SCR versus Rare Earth Vanadate - SCR –

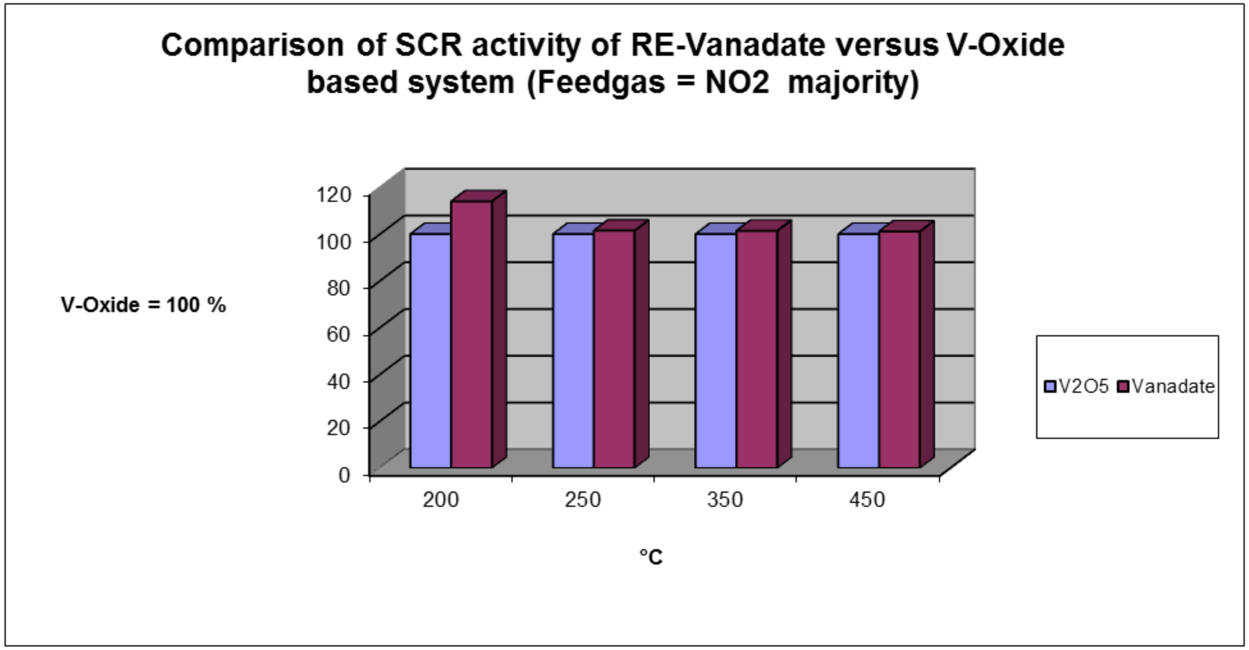
Conditions: Industrial Catalyst, 10 ppm NH_3 slip, SV [h^{-1}] = 60.000



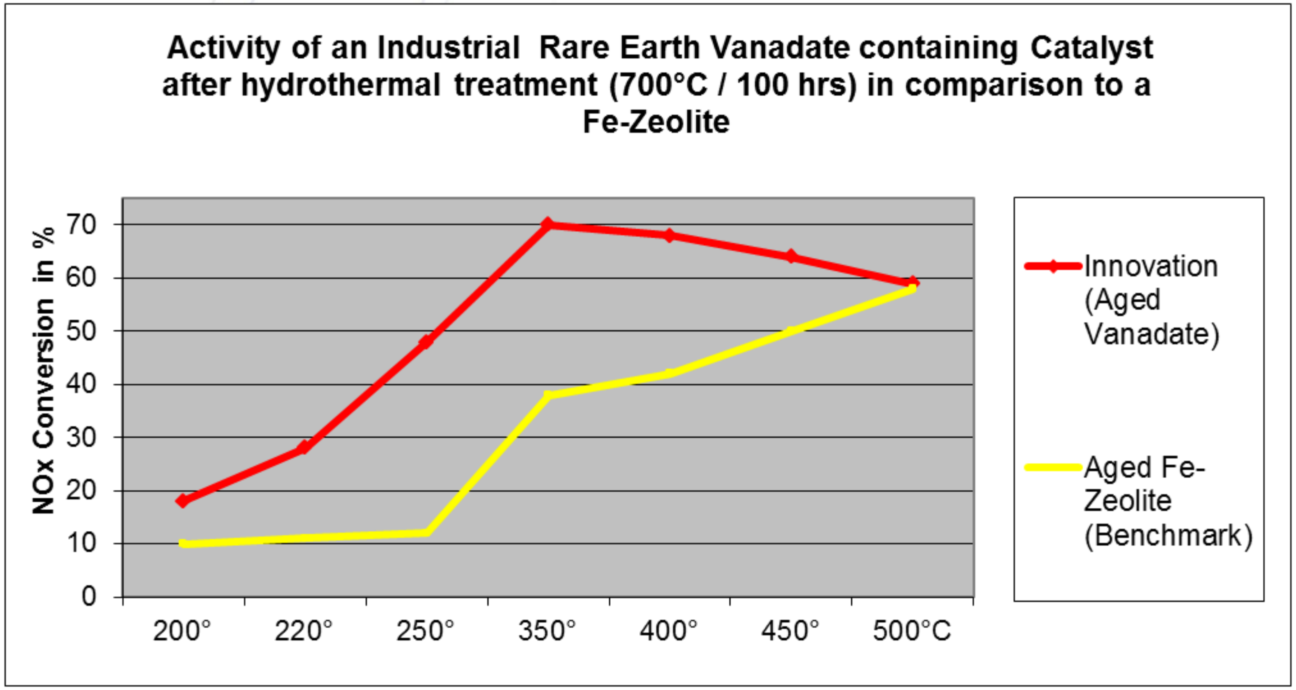


Catalytic Activity –V2O5 versus Rare Earth Vanadate – Industrial Catalyst (Support = TiO2/WO3)

Conditions: 10 ppm NH3 slip, SV (-1) = 60.000

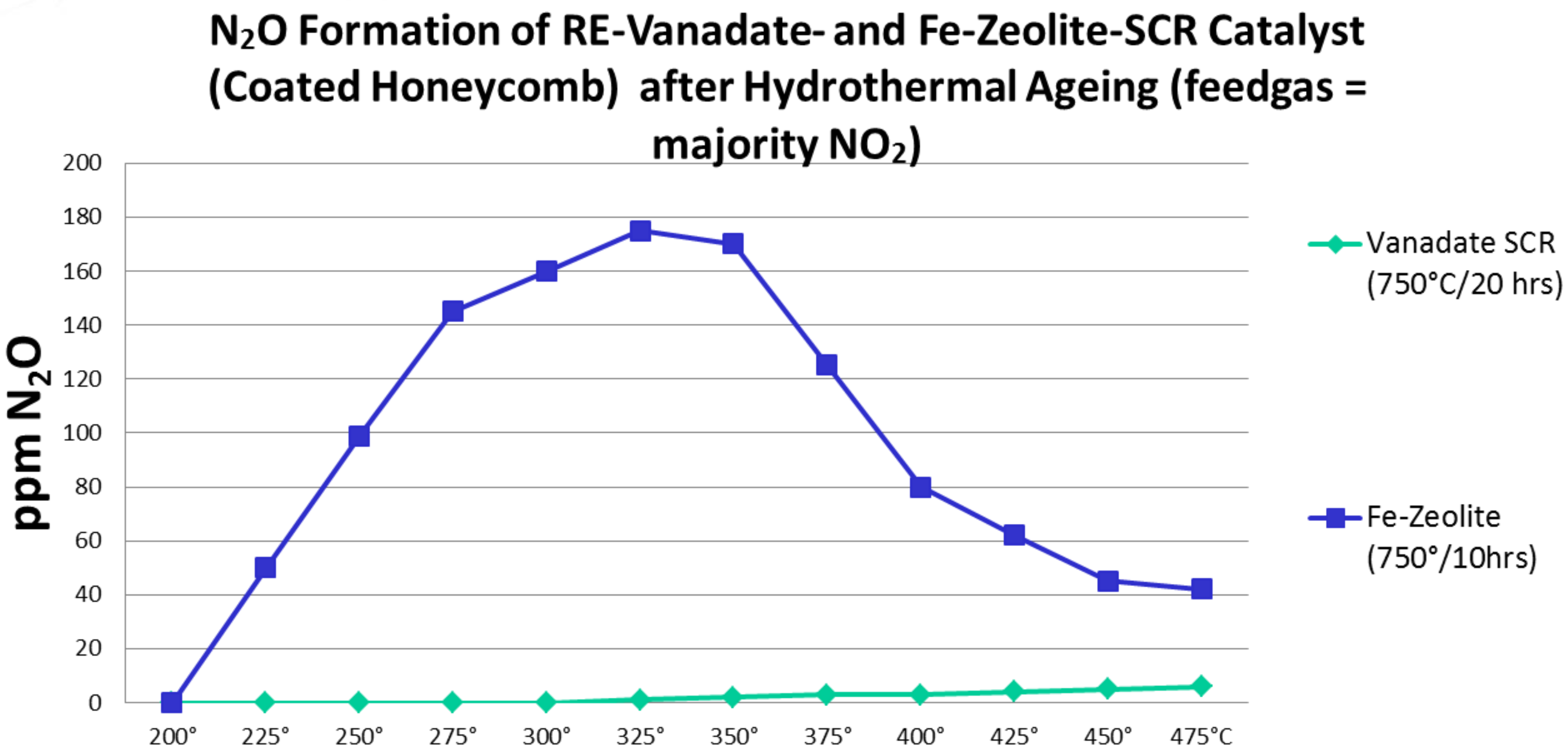


Catalytic Activity of a Rare Earth Vanadate based Catalyst after severe hydrothermal ageing



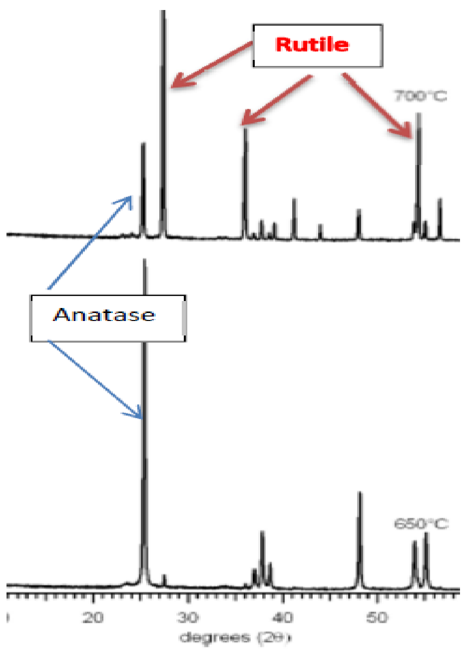
Source: 6. CTI Forum SCR Systems, Stuttgart 5.- 8.7.2010, CERAM Frauenthal

N$_2$O Formation – Fe-Zeolite versus Vanadate-SCR

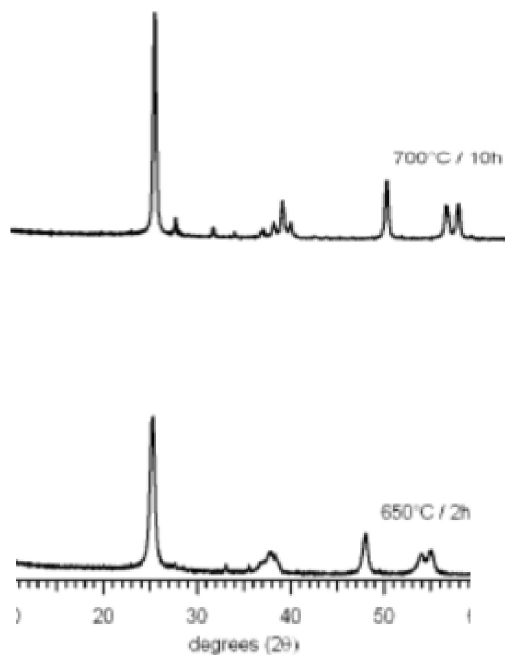


Thermal Stability of Vanadat containing SCR formulation
(TiO2/WO3 based)

- **Thermal stability is attributed to the inhibition of the formation of Rutile out of Anatase caused by the Rare Earths**



RE-Vanadate free SCR



RE-Vanadate SCR

Summary and Conclusions

Rare Earths in a TiO_2 based SCR system contribute siginifcantly

to a postive toxicological behaving (SCR catalyst and dopant !)

to a significant higher thermostability combined with a remaining high catalytic activity after hydrothermal ageing

to a significant decrease of the greenhouse gas N_2O in the SCR reaction

Summary and Conclusions

The catalyst and the Vanadate-based dopants applied in it are environmetal friendly

Catalysts are applicable either as full catalysts or as coated catalyst

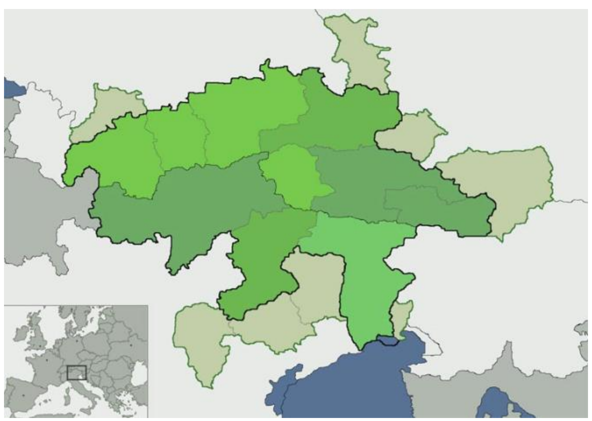
Application areas:

On-Road and Non-Road Applications

Markets: globally

Acknoledgements

The work is partly supported in the frame of Interreg IV in a co-operation between Treibacher Industrie AG (Austria) and the Department of Science and Technology of the University of Udine (Italy)



Thank you for yor attention !

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