Final report

1.1 Project details

Project title	**Low temperature deNOx technologies for biomass and waste fired power plants**
Project identification (program abbrev. and file)	**Energinet.dk project no. 12096**
Name of the programme which has funded the project	**ForskEl**
Project managing company/institution (name and address)	**DTU-Chemistry**
Project partners	**DTU Chemical Engineering** **LAB, S.A., Lyon, France** **DONG Energy A/S, Denmark**
CVR (central business register)	
Date for submission	**28.Oktober 2017**

1.2 Short description of project objective and results

The objective was to develop technologies for deNO$_x$ of flue gases at temperatures <200 °C for end-of-pipe installations. Thus development of deNOx catalysts sufficiently active at low temperatures in addition to converting NO$_x$ into HNO$_3$ by an alternative ionic liquid based process was attempted.

Increased activity of our low temperature catalysts was obtained but SO$_2$ poisoning and inhibition by H$_2$O are still issues for application in fossil fuel fired power plants. However, our industrial partner LAB S.A. aims now at a full industrial installation in one of their customers waste incineration plants.

Fast-SCR at 150 °C was demonstrated to enhance low temperature activity of the state-of-the-art catalyst sufficiently but partial oxidation of NO upstream is still a challenge.

The enhanced conversion of NO$_x$ to HNO$_3$ using SILP materials promoted by methanol is shown to be promising for future industrial tail-end deNOx applications.

Danish version :

Formålet er at udvikle deNOx teknologier til røggasrensning ved temperaturer under 200 C brugbare for end-of-pipe installationer. Således er lavtemperaturkatalysatorer med tilstrækkelig aktivitet samt alternative ionisk væske baserede processer forsøgt udviklet.

Der blev opnået forbedret aktivitet af lavtemperaturkatalysatorerne men SO2 og H2O hæmmer aktiviteten for meget til umiddelbar anvendelse i fossilt fyrede kraftværker. Vores industrielle partner LAB S.A. er imidlertid i færd med at etablere en fuld industriel installation i et af deres kunders affaldsforbrændingsanlæg.

Fast-SCR ved 150 C blev vist at forøge lavtemperaturaktiviteten af standard katalysatorer i tilstrækkelig grad men ovenstrøms delvis oxidation af NO er stadigvæk en udfordring.

Den forøgede omsætning af NOx til HNO3 opnået med SILP materialer promoteret af methanol er lovende for fremtidige industrielle end-of-pipe installationer.

1.3 Executive summary

This project aimed at developing efficient and economic NO_x removal technologies to be used at waste incineration plants and at biomass- and waste-fired power plants. Both types of plants can provide base-load electricity and hot water that comes with a relatively low CO_2 footprint, which is a very important aspect of the transformation of the electricity market. Flue gases from both types of plants are considered challenging because they typically lead, among other things, to accelerated catalyst deactivation in the SCR (Selective Catalytic Reduction) unit, which is responsible for removal of NO_x. By placing the SCR unit at the so-called tail-end position, just upstream of the stack, the catalyst is exposed to a much cleaner flue-gas than at the commonly used high-dust position, which is located right after the boiler. The difference is because the gas has already passed the dust- and SO_2-removal units. The major disadvantage of the tail-end placement is that the temperature of the flue gas has dropped to about 150 °C, which is too low for the traditional VWT (vanadia-tungsta-titania) catalyst to work efficiently. Currently waste-incineration plants make use of heat exchangers and gas burners to re-heat the flue gas from 150 to about 200-250 °C where the catalytic activity is just about sufficient. Although re-heating solves the problem of insufficient catalytic activity, it is problematic in terms of both capital and running costs, space requirements and engineering complexity.

Essentially two strategies were followed:

    i) NH_3-SCR using affordable metal oxides at 150 °C.
    ii)   Transformation of NO_x into HNO_3 using ionic liquid SILP materials at ≤ 150 °C.

The SCR based subproject was founded on our discovery that $MnFeO_x/TiO_2$ catalysts, when prepared by the deposition precipitation (DP) method, vastly outperform the commercial VWT catalyst at 150 °C. However, inhibition by high (10 – 20 vol. %) levels of water and deactivation even by very low (5 ppmv) levels of SO_2 required significant catalyst improvements for commercialization to be a realistic goal. Doping the catalyst with Ce or heteropoly acids does not suppress the formation of metal sulfates, which is the major mode of poisoning. Furthermore, significant increase in the resistance towards high levels of water was not observed. Therefore, only slight activity enhancements (≈30 %) were realized by optimizing the composition of $Mn_{1-x-y}Fe_xCe_y/TiO_2$ in collaboration with our partners. The activity benchmark, which is a commercial VWT catalyst tested at 220 °C, is still missed by about a factor of two excluding the effect of SO_2. Nonetheless, one of our partners (LAB S.A.) attempted shaping of $Mn_{1-x-y}Fe_xCe_y/TiO_2$ into monolithic form and up-scaling in collaboration with industrial catalyst producers, which is an ongoing further step towards commercialization. Because of the severe sulphur poisoning of manganese based catalysts, we investigated the activity of highly loaded V_2O_5/TiO_2 and sulphated $MnFeO_x/TiO_2$ under so-called fast SCR (50:50 NO/NO_2) conditions at 150 °C. Activity enhancements of a factor of 5-10 were observed. However, lack of efficient NO to NO_2 oxidation at 150 °C still poses a serious barrier at the moment. The characterization results of DP prepared manganese based catalysts suggest that they alternatively might be promising for total oxidation of volatile organic compounds (VOCs), a field of application that typically does neither involve sulphur nor water in excessive concentrations. However, this could not be further persuided in the present project. A minor side project was dedicated to developing catalysts capable of withstanding moderate levels of potassium at 200-250 °C which is the temperature of operation of traditional tail-end units. Biomasses contain potassium and other alkali and alkali-earth metal containing salts in large amounts, which probably causes problems even at the tail-end position. V_2O_5/TiO_2 doped with Mo or W containing heteropoly acids can withstand low amounts (100 µmol/$g_{catalyst}$) of potassium, however, even moderate loadings (200 µmol/$g_{catalyst}$) cause unfortunately significant deactivation.

The SILP based subproject was aimed at advancing a waste to chemical process converting harmful NO_x gases into HNO_3, which is a salable bulk chemical. The project was founded on former projects suggesting that some ionic liquids (ILs) like [BMIM][NO_3] are capable of converting NO to NO_2 and HNO_3 at temperatures far below 100 °C. Conversion of NO into NO_2 under continuous flow conditions was regarded a versatile building block in the pursuit of achieving fast-SCR conditions at low temperatures without the need for costly reheating. However, we found out that some of the previous studies were inaccurate and that continuous oxidation of NO into NO_2 is not feasible. It was however discovered late in the project that transformation of NO into HNO_3 can be promoted by small amounts (molar alcohol/NO = 20:1) of short chained alcohols (e.g. methanol). This is neither prohibitive from an economic nor from a safety or environmental point of view. Our studies showed that the oxidation is almost insensitive to temperature between 30 and 150 °C and works efficiently even at NO concentrations as low as 500 ppm. The reaction is quite insensitive to increases in space velocity with NO conversions of 55 and 40 % at space velocities of 15,000 and 95,000 h^{-1}, respectively. This discovery was patented at the end of the project and may prove very useful for establishment of both fast SCR and ionic liquid absorption deNOx facilities at the tail-end of industrial installations.

1.4 Project objectives

The overall objective was to develop NO_x-removing technologies capable of operating economically in installations like e.g. waste incinerators and biomass-fired power plants, which typically produce challenging flue gases. Since both types of plants can contribute to baseload electricity generation with a relatively low carbon footprint, they play an important role in making power generation more climate friendly. If successful, the project could have helped Danish industry to enter a market worth an estimated 2 billion DKK per year.

The goal should have been achieved by technologies able to function at low to very low temperatures, thus making so-called "tail-end" or "end-of-pipe" placement of the NH_3-SCR unit more economic by removing the need for re-heating large volumes of flue gas. Furthermore, a novel waste to chemical process using ionic liquids to convert NO into nitric acid was investigated.

The major risks associated with the project are that the market potential fails to materialize and that the researchers fail to develop catalysts able to perform satisfactorily under realistic conditions. A possible disappearance of the market potential could be caused by decreasing biomass- and waste firing. The former might be caused by technologies able to use waste-biomasses for higher value products than electricity like e.g. chemicals, or by development of inexpensive energy storage systems and/or transnational power grids that would reduce the need for thermal power plants to cope with the fluctuating output of renewables like wind and solar. So far, both scenarios have not come true. Reduced waste incineration can practically only be caused by drastically increased rates of recycling. In terms of market potential, the risks associated with the project have not materialized. The risk of not delivering sufficiently active catalysts is mostly connected to poisons like SO_2, alkali metals and inhibitors like water, which are all present in flue gases, even at the tail-end position. Upscaling of catalyst production not based on the simple impregnation (IMP) method can also be a risk. The background knowledge generated in the previous PSO 10521 "Hydrocarbon-SCR" project revealed that the more cumbersome deposition precipitation (DP) method can produce significantly more active catalysts. The drawbacks of DP are the high volume of liquids used, consumption of base and possible foam formation. Shaping of catalyst powders into monolithic form, which is required for the catalysts to be used at high space velocities, poses another hurdle and risk factor. A risk factor associated with the waste to chemical subproject is dwindling demand and prices for nitric acid. Since the main use of nitric acid is for fertilizers and food production needs to keep up with global population growth, this risk was deemed

unrealistic. Lack of long term stability of the ionic liquids, which convert NO to HNO_3, is a more serious risk factor.

The project implementation developed only partially as foreseen. Both the NH_3-SCR and the waste to chemicals subprojects have experienced unforeseen difficulties. According to some of the collected background knowledge, it should be possible to make manganese based NH_3-SCR catalysts relatively sulphur and water tolerant [1-8]. However, our own tests revealed that increasing the catalyst's acidity neither by doping with e.g. heteropoly acids nor doping with metals like Ce causes significantly enhanced tolerance towards the mentioned poisons and inhibitors. Another problem was use of large volumes of liquid (20 m^3_{liquid}/$ton_{catalyst}$) during catalyst preparation. This results in low space time yields and large volumes of waste liquid. Modification of parameters like base concentration, speed of base addition and temperature did not solve the problem. Therefore, our consortium could not deliver a sufficiently active and stable catalyst at reasonable costs, and technology transfer to end users facilities was therefore not possible. The waste to chemicals subproject experienced several revelations. Absorption of NO into the formerly tested [BMIM][NO_3] and oxidation of NO to NO_2 turned out to be too slow. However, late in the project, it was discovered that presence of small amounts of short chained alcohols enhances the transformation of NO to NO_2 and HNO_3. This finding means that the investigated materials might be used to create fast SCR conditions at low temperatures which could have made a big difference for the NH_3-SCR subproject if discovered earlier. The need to add small amounts of alcohol (e.g. methanol) is not prohibitive from a cost perspective; however, it complicates the engineering task. Of late, we also realized that the alcohol assisted oxidation reaction probably only takes place if the relative humidity is high. Although this always is the case in most flue gases it might impose additional restrictions on the reaction control. Further experimental campaigns are needed to clarify these issues. These experiments should also cover the effects of possible poisons like SO_2. Because of the immatureness of this technology it did not make sense to test SILP materials at the end users facilities. However a SILP sample was exposed to flue gas in one of LAB S.A.'s facilities and the NOx absorption capacity was not altered by this indicating that the SILP material was stable in the flue gas.

The project has had the following work packages:

WP1. Literature review of the current state-of-the-art
WP2. Synthesis of promising low temperature deNOx catalysts
WP3. Selection/synthesis and absorption screening of task-specific NO absorbing ionic liquids
WP4. Catalyst test rig construction/modification and low temperature catalyst activity screening
WP5. Synthesis of Supported Ionic Liquid Phase (SILP) NO gas absorbers
WP6. Test and characterization of catalysts and SILP absorber materials at the industrial partners facilities
WP7. Transfer to industrial actors regarding the deNOx technology evolved
WP8. Delivery of final project report, recommendations and PhD thesis

Time schedule:

The numbers of the activities in the table below refer to the WP numbers mentioned above. Large X indicates a milestone.

	Year 1				Year 2				Year 3				Year 4			
	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3	Q4
1.	x	X														
2.	x	x	X	x	x	x	X	x	x	x	x	x	x	x	X	
3.		x	x	x	x	x	X									
4.	x	x	X	x	x	x	x	x	x	X						
5.		x	x	x	x	x	x	X								
6.							x	x	x	x	x	x	x	x	X	
7.		x	x	x	x	x	x	x	x	x	x	x	x	x	X	
8.														x	X	

The project has followed the plan and all milestones have been reached as described in this report and the 4 previous interim reports submitted to energinet.dk.

The documentation is further found in the results of dissemination, see 1.5.3.

1.5 Project results and dissemination of results

Essentially two research strategies were followed:

1) Metal oxide (heterogeneous) catalyst used for the selective catalytic reduction of NO with NH_3 (NH_3-SCR) at 150 °C.
2) Transformation of NO to HNO_3 using supported ionic liquid phase (SILP) materials at low temperatures.

The two subprojects were conducted mostly independent from each other. The only overlap was based on the assumption that SILP materials without promoters could be used as efficient NO to NO_2 catalysts at 150 °C thus facilitating fast-SCR using metal oxide catalysts at that temperature. An introduction to the NH_3-SCR technology can be found in our previous project report "PSO 10521".

1.5.1 NH₃-SCR at 150 °C using metal oxide catalysts

In the period 2011-2014, we have demonstrated that $MnFeO_x/TiO_2$ prepared by the deposition precipitation (DP) method is about three times as active as when synthesized with the more commonly used impregnation (IMP) method [9-10]. Already during that period, we realized that manganese containing catalysts are severely deactivated by levels of SO_2 and water typically present at the tail-end position. Therefore, our focus was initially directed at improving the sulphur and water tolerance. As we did not succeed in doing this, we also tried to boost the activity of $MnFe/TiO_2$ by precursor selection and Ce doping. Other side projects dealt with fast-SCR at 150 °C and potassium tolerance of V_2O_5-WO_3/TiO_2 at 220 °C.

1.5.1.1 SO₂ tolerance of MnFeX/TiO₂ at 150 °C

The SO_2 studies of the PSO 10521 "Hydrocarbon-SCR" project revealed that even low (10 ppm) levels of SO_2 cause severe and practically irreversible deactivation of $MnFe/TiO_2$ by formation of metal sulphates. Therefore, we have exposed DP prepared $MnFe/TiO_2$ doped with Ce or $H_3PW_{12}O_{40}(H_2O)_x$ to a simulated flue gas containing 5-10 ppm of SO_2 for up to 87 hours and compared the results to $MnFe/TiO_2$ synthesized by both the DP and IMP methods, see figure 1. The first order rate constants of the sulphurated catalysts in presence of a realistic water level (17.5 vol. %) are all modest and do not spread out much (8.4 to 11.7 $cm^3s^{-1}g^{-1}$). The benchmark value of the commercial V_2O_5-WO_3/TiO_2 at 220 °C of roughly 48 $cm^3g^{-1}s^{-1}$ is missed by a large margin. H_2-TPR performed on small (30 mg) batches withdrawn after specific time intervals is an effective method to observe the formation of metal sulphates, see figure 1. The signals corresponding to metal oxides at roughly 100 to 450 °C decrease upon SO_2 exposure and a new reduction peak at about 450 to 600 °C increases in size and can be attributed to metal sulphates. This happens irrespective of the presence of dopants or the preparation method. The fact that both DP and IMP prepared metal oxides are transformed into seemingly similar metal sulphates is putting a serious question mark over the use of the more expensive and complicated DP method.
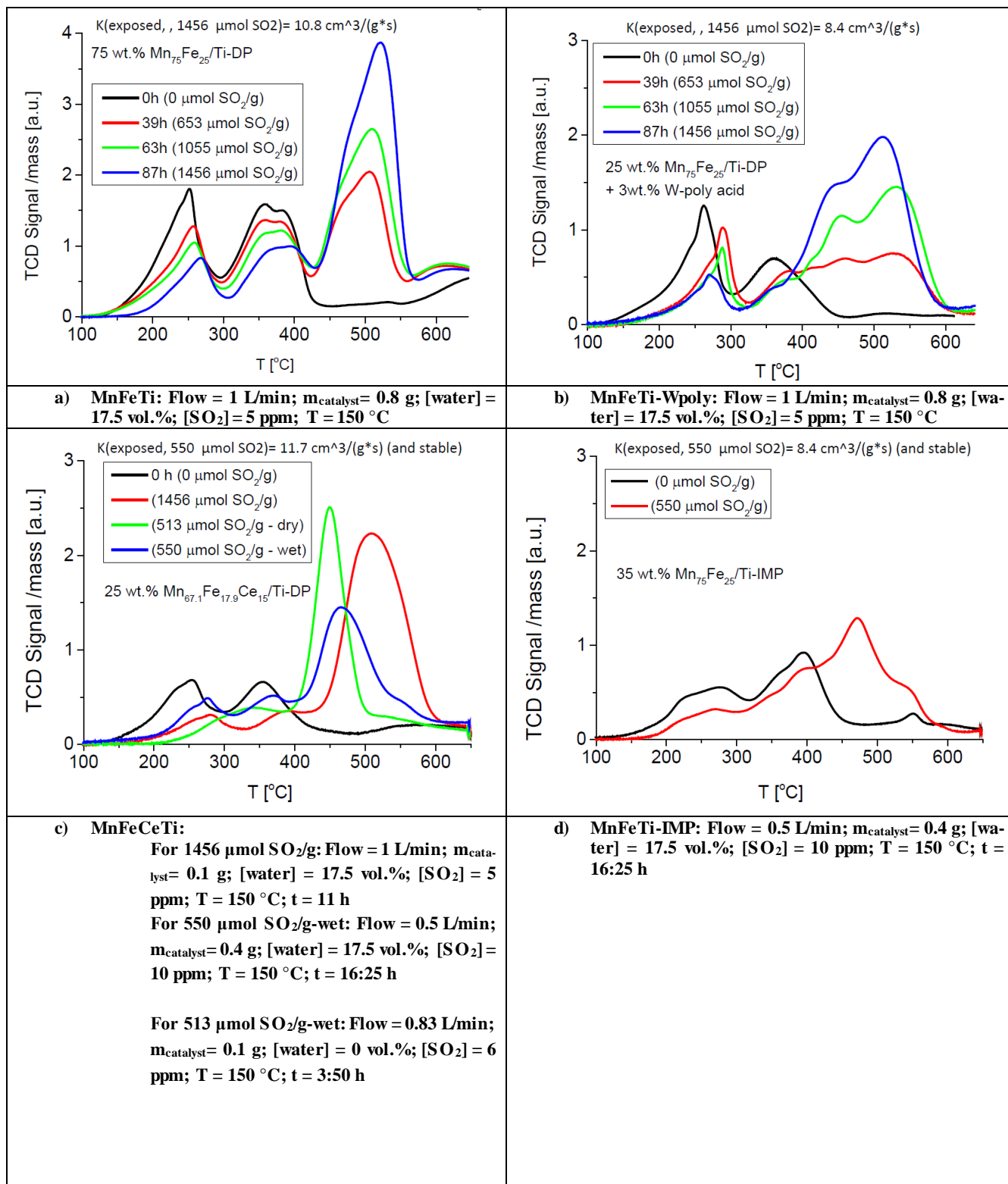
a) MnFeTi: Flow = 1 L/min; $m_{catalyst}$= 0.8 g; [water] = 17.5 vol.%; [SO$_2$] = 5 ppm; T = 150 °C

b) MnFeTi-Wpoly: Flow = 1 L/min; $m_{catalyst}$= 0.8 g; [water] = 17.5 vol.%; [SO$_2$] = 5 ppm; T = 150 °C

c) MnFeCeTi:
For 1456 µmol SO$_2$/g: Flow = 1 L/min; $m_{catalyst}$= 0.1 g; [water] = 17.5 vol.%; [SO$_2$] = 5 ppm; T = 150 °C; t = 11 h

For 550 µmol SO$_2$/g-wet: Flow = 0.5 L/min; $m_{catalyst}$= 0.4 g; [water] = 17.5 vol.%; [SO$_2$] = 10 ppm; T = 150 °C; t = 16:25 h

For 513 µmol SO$_2$/g-wet: Flow = 0.83 L/min; $m_{catalyst}$= 0.1 g; [water] = 0 vol.%; [SO$_2$] = 6 ppm; T = 150 °C; t = 3:50 h

d) MnFeTi-IMP: Flow = 0.5 L/min; $m_{catalyst}$= 0.4 g; [water] = 17.5 vol.%; [SO$_2$] = 10 ppm; T = 150 °C; t = 16:25 h

Figure 1: H₂-TPR of fresh and SO₂ exposed catalysts. All exposures were conducted in the presence of circa 500 pmm NO and 550 ppm NH₃.

Figure 2 shows the TGA curves and XRD diffractograms of undoped and H$_3$PW$_{12}$O$_{40}$(H$_2$O)$_x$ doped MnFe/TiO$_2$ after SO$_2$ exposure. From the TGA curves it can be seen that not only metal sulphates but also relatively easily decomposable products, which are most likely NH$_4$HSO$_4$ and (NH$_4$)$_2$SO$_4$, are formed. The presence of (NH$_4$)$_2$Mn$_2$(SO$_4$)$_2$ is ascertained by XRD and corroborates the H$_2$-TPR findings.
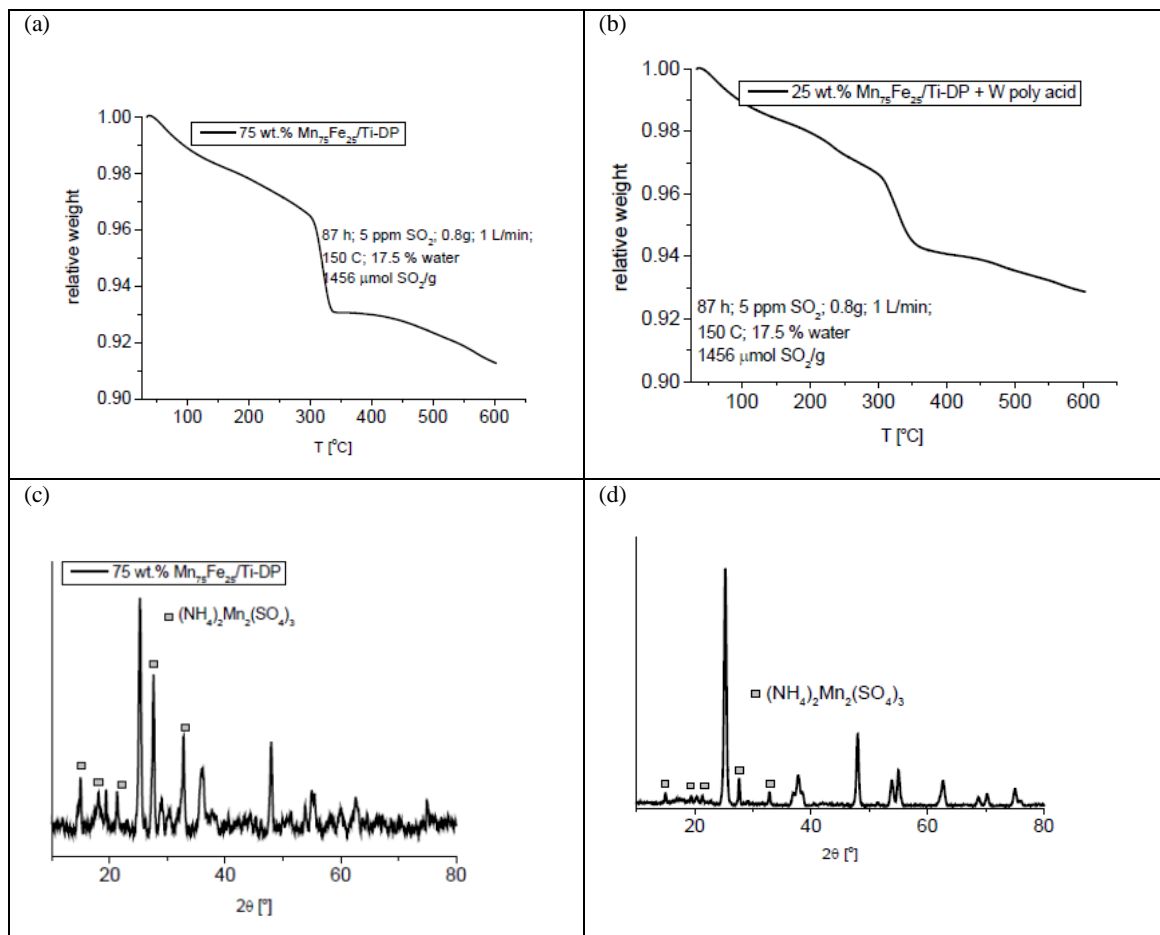
Figure 2: (a) TGA of spent MnFeTi; (b) TGA of spent MnFeTi-Wpoly; (c) XRD of spent MnFeTi; (d) XRD of spent MnFeTi-Wpoly

In summary, we did not manage to suppress formation of metal sulphates and their activity reducing effect by doping the MnFe/TiO$_2$ catalyst. Use of the elaborate DP technique might not be justifiable because SO$_2$ exposure converts DP and IMP prepared manganese oxides into sulphates.

1.5.1.2   Water tolerance of MnFeX/TiO$_2$ at 150 °C

Figure 3 shows that water levels of 10 vol. % and above cause the relative activities of manganese based catalysts to drop by almost a factor of 10. The presence of Ce makes practically no difference. Two values for Mn$_{0.3}$Ce$_{0.7}$ at 5 vol. % water found in the literature [11-12] are located close to our curve meaning that even high contents of Ce do not enhance the water tolerance.

H$_2$O: Effect of Ce @ 150 ^{0}C

F=830 mL/min (NO = 481 ppm; NH3 = 530 ppm)
+ H$_2$O

0.1g
0.2g
0.3g
0.8g

- ■ 25 Mn$_{75}$Fe$_{25}$/Ti
- ● 25 Mn$_{75}$Fe$_{20}$Ce$_5$/Ti
- ▲ Mn$_{0.3}$Ce$_{0.7}$ (China) *J. Phys. Chem. C 2015, 119, 4180–4187*
- ▼ Mn$_{0.3}$Ce$_{0.7}$ (Kröcher) Applied Catalysis B: Environmental 88 (2009) 413–419

k$_{water}$/k$_{dry}$

H$_2$O [vol. %]

6
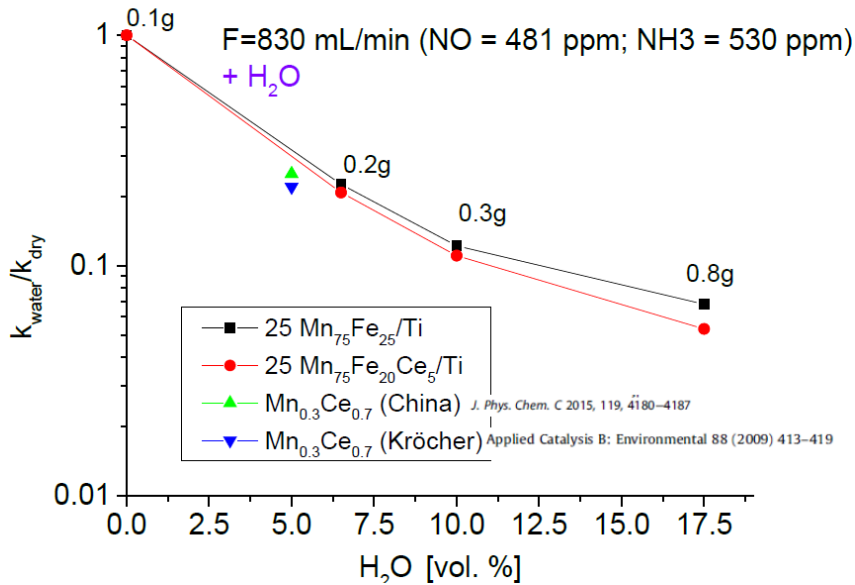
Figure 3: Activity of Mn containing catalyst at 150 ˚C as function of the water content relative to their activity in dry gas.

As the inhibiting effect of water is mostly ascribed to competitive adsorption of H$_2$O and NH$_3$, increasing the number of acid sites on the catalyst's surface should dampen the effect of water because NH$_3$ is a much stronger base than H$_2$O. Impregnation with H$_3$PW$_{12}$O$_{40}$(H$_2$O)$_x$ (W-poly acid) was used to enhance the acidity of DP prepared 25 wt. % Mn$_{0.75}$Fe$_{0.25}$/TiO$_2$. Figure 4 shows that doping with 5 wt. % H$_3$PW$_{12}$O$_{40}$(H$_2$O)$_x$ indeed increases the water tolerance, however, at the cost of a much decreased base (dry) activity. At 17.5 vol. % water, the activity was only marginally increased by W poly acid.

H$_2$O: Effect of W poly acid @ 150 ^{0}C
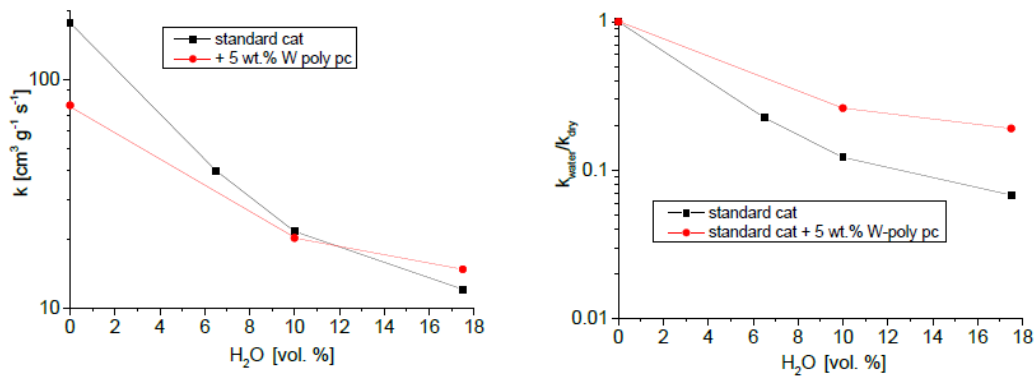
Figure 4: Absolute (left) and relative (right) activities of DP prepared 25 wt. % Mn$_{0.75}$Fe$_{0.25}$/TiO$_2$ with and without 5 wt. % % H$_3$PW$_{12}$O$_{40}$(H$_2$O)$_x$ as a function of the water content.

A H$_3$PW$_{12}$O$_{40}$(H$_2$O)$_x$ loading optimization at a water level of 17.5 vol. % was performed and the absolute activities are shown in figure 5. No dramatic activity enhancements were ob-

tained and even the most active sample misses the activity benchmark by a factor of almost 3. Note that all experiments were conducted in the absence of SO_2.

Poly acid loading optimizaton @ 150 °C
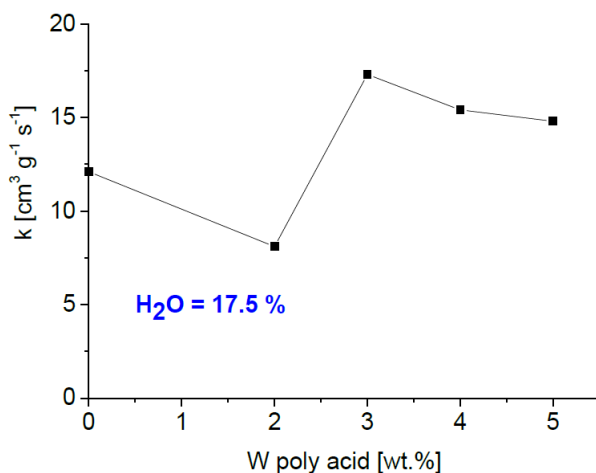
Figure 5: First order rate constant of 25 wt. % $Mn_{0.75}Fe_{0.25}/TiO_2$ as a function of the $H_3PW_{12}O_{40}(H_2O)_x$ concentration.

In summary, water levels of 10-20 vol. % in the flue gas cause activity drops of a factor of about 5 to 15 resulting in too low activities for real-life applications. Cerium has no effect on the water tolerance while $H_3PW_{12}O_{40}(H_2O)_x$ dampens the relative inhibition though at the cost of a lower base value.

1.5.1.3   Effect of Mn, Fe and Ce precursors

Several sources have reported that the metal precursor can have a substantial influence on the catalyst's activity [13-15]. We have used combinations of the following manganese and iron precursors: $Mn(II)*(NO_3)_2$, $Mn(II)*(acetate)_2$, $Fe(III)*(NO_3)_3$, $Fe(III)*(acetate)_3$. The resulting NO conversion profiles are plotted in figure 6. The precursor combination has a pronounced effect on activity, not least at 150 °C, as seen in figure 7. Further activity enhancements might be obtainable by varying the share of nitrate precursor around 25 %. The reason for the difference in activity might be a change in ion coordination before precipitation which would change the nature of the resulting surface oxides.
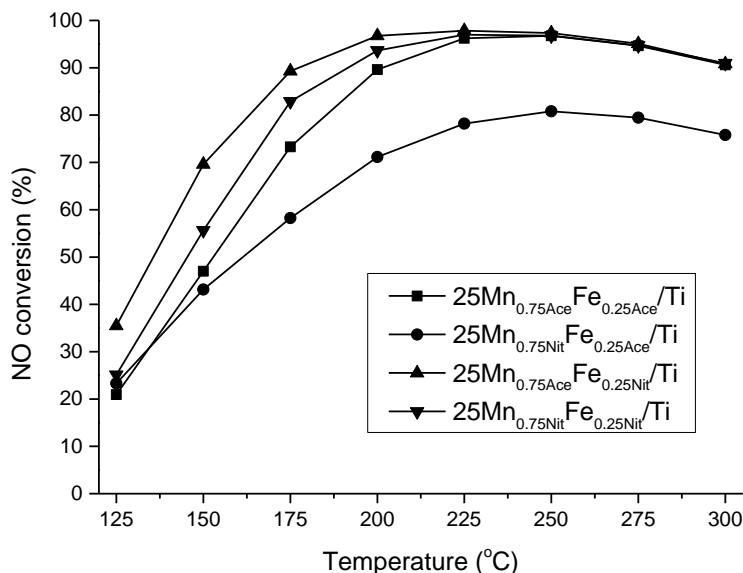
Figure 6: NO conversion as a function of temperature of 25 wt. % $Mn_{0.75}Fe_{0.25}/TiO_2$ prepared by deposition precipitation with acetate or nitrate precursors. Conditions: F = 300 mL/min, $m_{catalyst}$ = 50 mg, [NO]=[NH₃] = 1000 ppm, [O₂] = 4 %, [H₂O] = 2.3 %.
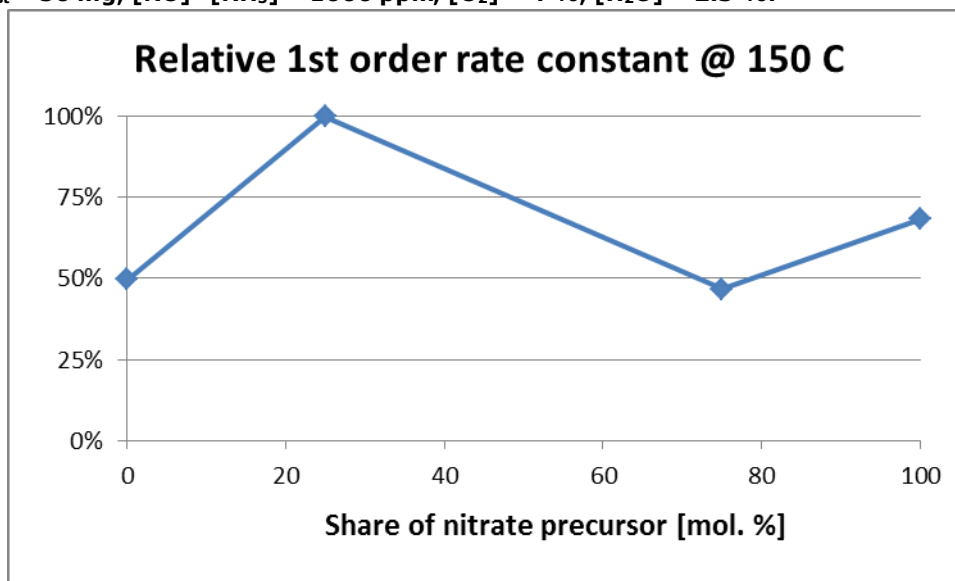

Figure 7: Relative pseudo first order rate constants derived from Figure 6; k = (F/w)*ln(1/(1-X_{NO})) with F = gas flow, w = catalyst weight, X_{NO} = fractional NO conversion.

To further investigate the redox properties H_2-TPR measurements were conducted, see figure 8. The most active catalyst, 25 $Mn_{0.74Ace}Fe_{0.25Ni}/Ti$, also exhibits the most favorable redox properties with the two reduction peaks occurring at the lowest temperatures and the low temperature peak being highest relative to the high temperature peak. The latter feature is also seen in the profile of the second most active catalyst.
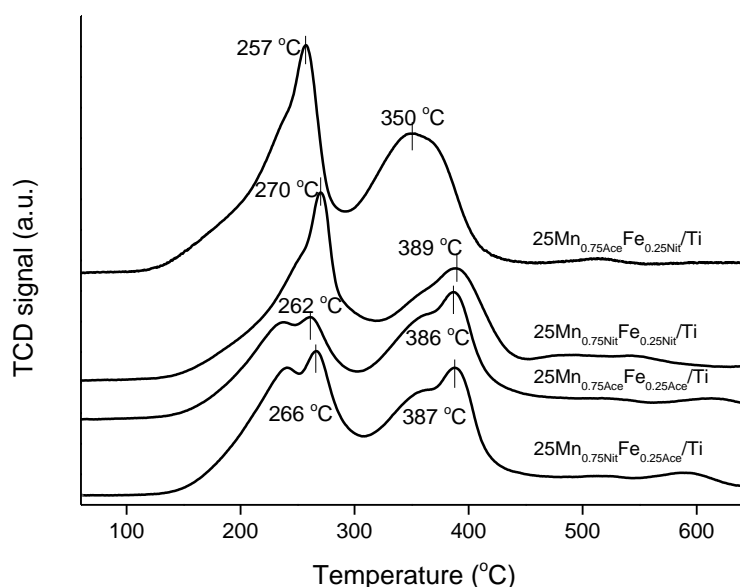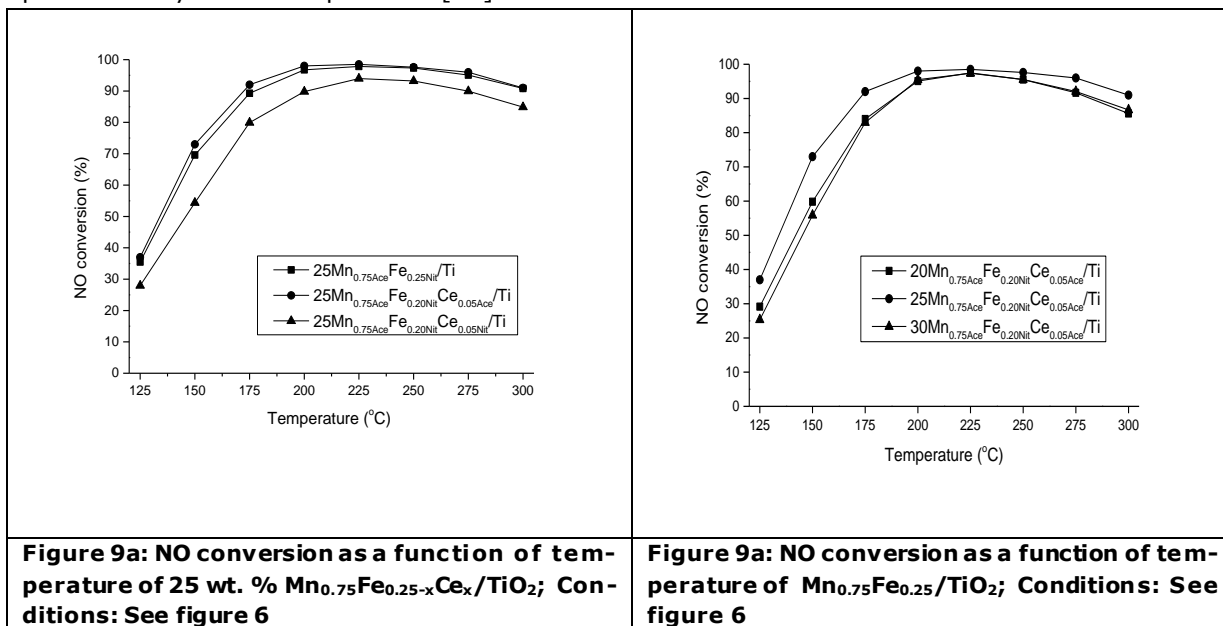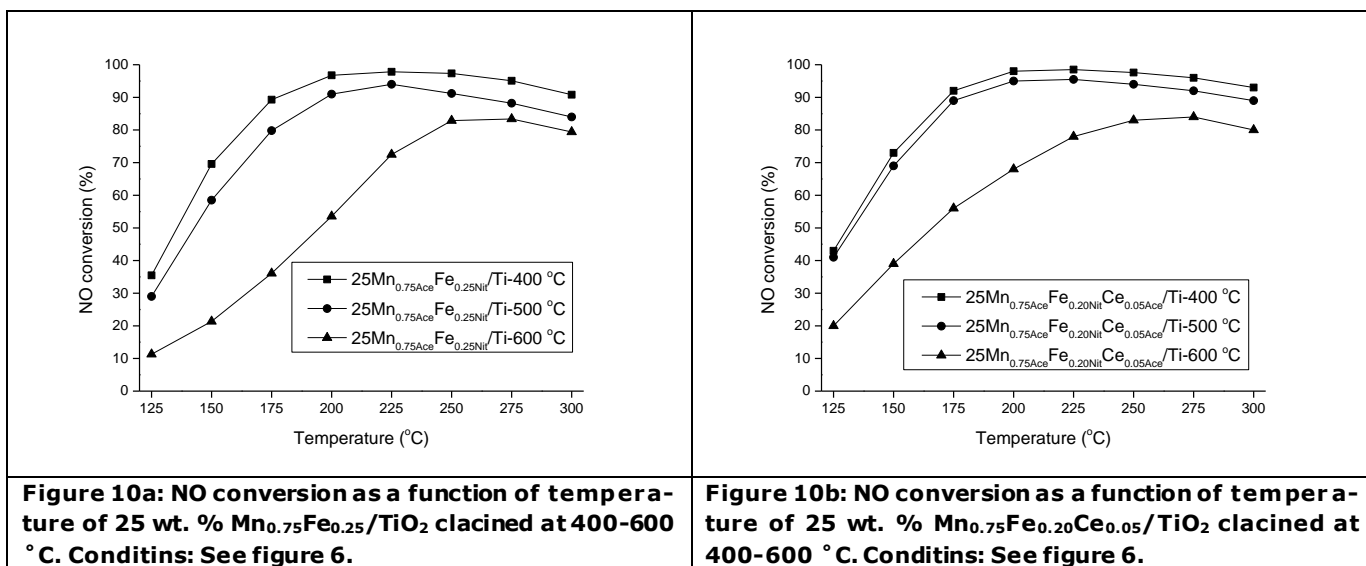

Figure 8: H_2-TPR of 25 wt. % $Mn_{0.75}Fe_{0.25}/TiO_2$ prepared with various combinations of metal precursors.

The effect of substituting Fe partially with Ce was investigated, see figure 9a. This causes only a marginal activity enhancement and only if Ce(III)*(acetate)₃ was used as precursor. The effect of metal loading of $Mn_{0.75}Fe_{0.20}Ce_{0.05}/TiO_2$ is shown in figure 9b. No improvement

relative to 25 wt. % was realized. A more thorough optimization of this catalyst system was performed by one of our partners [16].

| **Figure 9a: NO conversion as a function of temperature of 25 wt. % $Mn_{0.75}Fe_{0.25-x}Ce_x/TiO_2$; Conditions: See figure 6** | **Figure 9a: NO conversion as a function of temperature of $Mn_{0.75}Fe_{0.25}/TiO_2$; Conditions: See figure 6** |

SCR catalysts are expected to last for years and frequent heating to about 350 °C is necessary to decompose $(NH_4)_2SO_4$. Therefore, their thermal stability is of paramount importance. One way to rapidly test Ce's effect on the thermal stability is to increase the calcination temperature to which the catalyst is exposed to for 2h. Figure 10 shows the NO conversion profiles of 25 wt. % $Mn_{0.75}Fe_{0.25}/TiO_2$ and 25 wt.% $Mn_{0.75}Fe_{0.20}Ce_{0.05}/TiO_2$ calcined at 400, 500 and 600 °C. Increasing the calcination temperature lowers the activity of both catalysts; however, the Ce containing one is less affected. XRD analysis confirmed that Ce suppresses the thermally induced formation of crystalline Mn_2O_3.

| **Figure 10a: NO conversion as a function of temperature of 25 wt. % $Mn_{0.75}Fe_{0.25}/TiO_2$ clacined at 400-600 °C. Conditins: See figure 6.** | **Figure 10b: NO conversion as a function of temperature of 25 wt. % $Mn_{0.75}Fe_{0.20}Ce_{0.05}/TiO_2$ clacined at 400-600 °C. Conditins: See figure 6.** |

Lastly, the effect of space velocity on the conversion profiles was tested, see figure 11. The pseudo first order constants at 150 °C are between 121 and 127 $cm^3g^{-1}s^{-1}$.
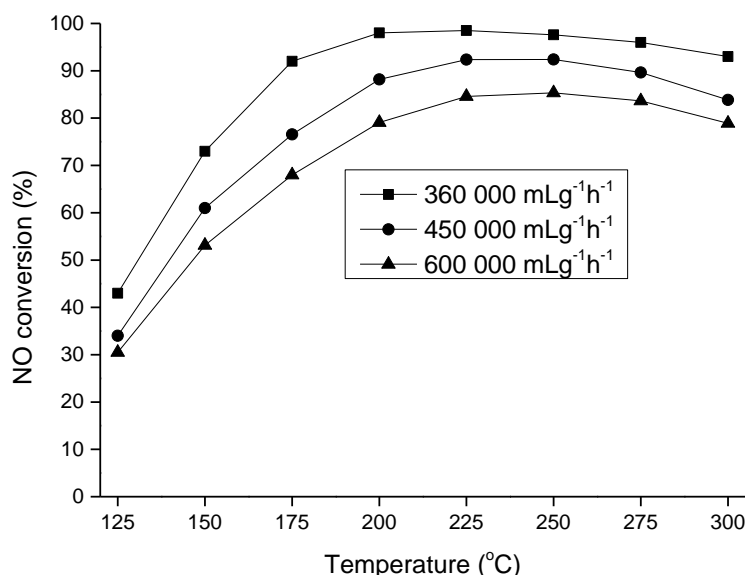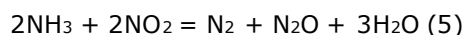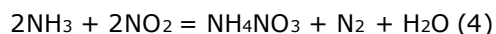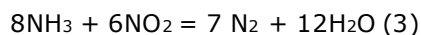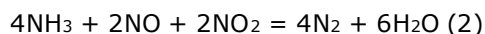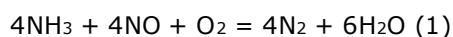
Figure 11: NO conversion as a function of temperature of 25 wt. % $Mn_{0.75}Fe_{0.20}Ce_{0.05}$ / TiO_2 at various space velocities.

In summary, precursor choice has a profound effect on the activity due to improved redox properties. Small amounts of Cerium can increase the thermal stability by suppressing formation of crystalline Mn_2O_3.

1.5.1.4 Fast SCR at 150 °C

Since manganese based catalysts are severely deactivated by SO_2 levels as low as 5 ppm we have explored the effect of fast-SCR conditions at 150 °C. Fast SCR means that NO_2 accounts for up to 50 mol. % of NO_x. Reaction (1) and (2) represent standard- and fast-SCR, respectively. The latter is typically much faster than the former. Reaction (3) is typically reported to be slower than reaction (1). Therefore, one would expect the NO conversion to be higher than the NO_2 conversion when using an equimolar mixture. Reactions (4) and (5) are unwanted side reactions, which increase the NO_2 conversion.

$$4NH_3 + 4NO + O_2 = 4N_2 + 6H_2O \quad (1)$$

$$4NH_3 + 2NO + 2NO_2 = 4N_2 + 6H_2O \quad (2)$$

$$8NH_3 + 6NO_2 = 7 N_2 + 12H_2O \quad (3)$$

$$2NH_3 + 2NO_2 = NH_4NO_3 + N_2 + H_2O \quad (4)$$

$$2NH_3 + 2NO_2 = N_2 + N_2O + 3H_2O \quad (5)$$

In typical flue gases, NO_2 stands only for about 5 mol. %. We have exposed the following four catalysts to both standard and fast SCR conditions: 25 wt. % $Mn_{75}Fe_{20}Ce_5/TiO_2$ (MnFeCe), 25 wt. % $Mn_{75}Fe_{25}/TiO_2$ (MnFe), 25 wt. % $Mn_{75}Fe_{25}/TiO_2$ impregnated with 656 µmol g^{-1} $(NH_4)_2SO_4$ followed by calcination at 350 °C (MnFe-SO_2) and 20 wt.% V_2O_5/TiO_2 prepared by a sol-gel route [17] (20 % V2O5). Figure 12 gives the NO_x conversions under both standard and fast SCR conditions. The performance of all catalysts is enhanced by increasing the NO_2 share to 50 mol. %. All catalysts have in common that the NO_2 conversion under fast-SCR conditions is higher than the corresponding NO conversion. This fact might hint at undersired side reactions, namely formation of N_2O (potent green house gas) and NH_4NO_3 (explosive and catalyst inhibiting).
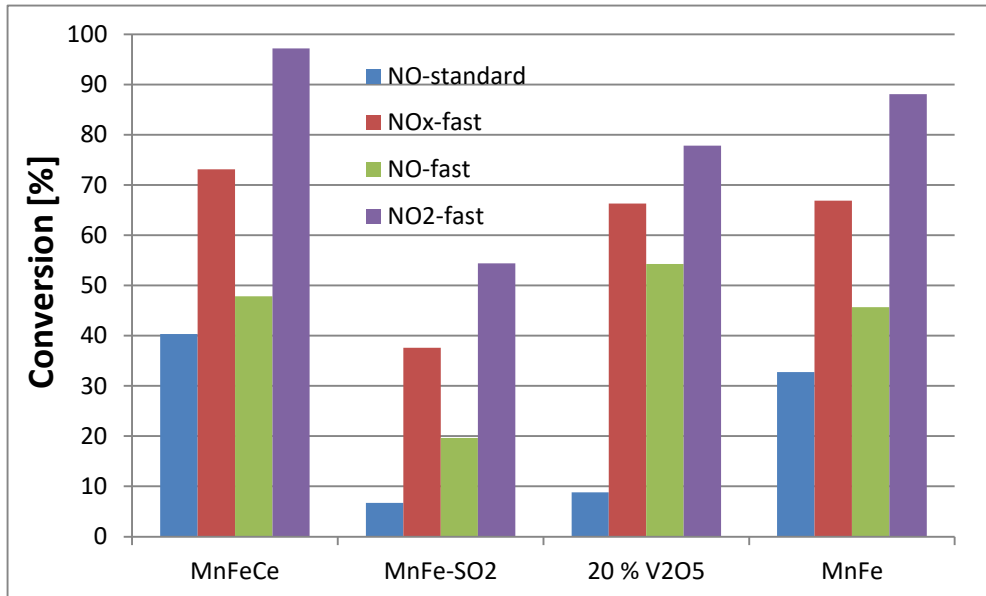
Figure 12: Conversion of NO$_x$ components under standard- and fast-SCR conditions; Conditions: F = 1000 mL/min, m$_{catalyst}$ = 120 mg, [NO]= 500 pppm (standard SCR) [NO] = [NO$_2$] = 250 ppm (fast SCR), [NH$_3$] = 500 ppm, [O$_2$] = 4 %, [H$_2$O] = 5 %, T = 150 ˚C.

Figure 13 represents both the "acceleration" and the "non-stoichiometry" of the fast-SCR reaction. The "acceleration" is represented by the blue line and gives the ratio of the pseudo first order rate constant under fast- and standard-SCR conditions. The vanadia based catalysts benefits the most and the activity ratio of 12 is close to other reports [18-20]. The two manganese based catalyst, which do not contain sulfur (MnFeCe, MnFe) experience activity boosts of less than a factor of 3. This might be because this kind of catalyst is reported to have very good oxidation abilities [6, 22-25] and hence already performs some kind of fast-SCR on its own. The sulfated manganese catalyst's (MnFe-SO$_2$) activity increases by a factor 7. This might indicate that metal sulfation decreases the catalyst's ability to oxidize NO. The fact that the NO$_x$-fast conversion of MnFe-SO2 is higher than NO-standard of MnFe is very enchouraging. However, the reader should keep in mind that this study was conducted with a relatively low water content (5 %) due to equipment constraints. At more realistic water levels (10-20 %) the adsorption of ammonia might become the bottleneck of the reaction and thus reducing the effect of fast-SCR conditions.
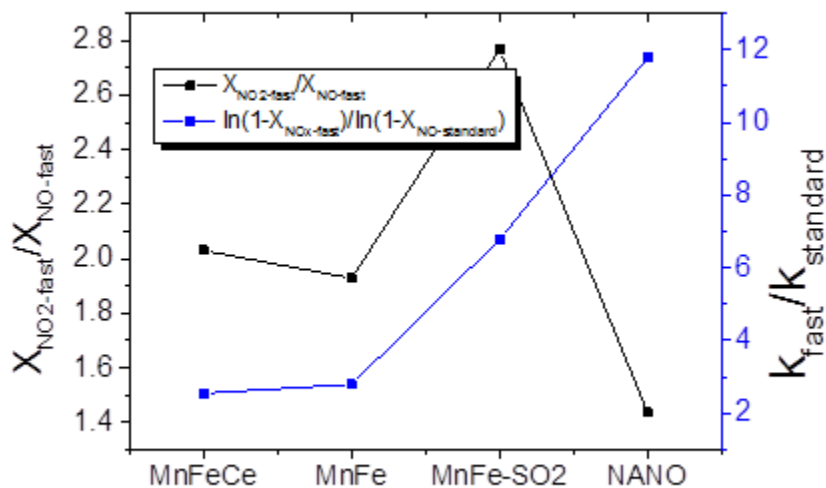

Figure 13: Effect of fast-SCR conditions on the relative activity (k$_{fast}$/k$_{standard}$) and non-stochiometry (X$_{NO2-fast}$/X$_{NO-fast}$) under fast-SCR conditions. Values are derived from figure 12.

Figure 14 shows that the selectivity towards N₂O increases only marginally when switching from standard- to fast-SCR and that 20% V2O5 generates the least amount of this very undesirable byproduct.
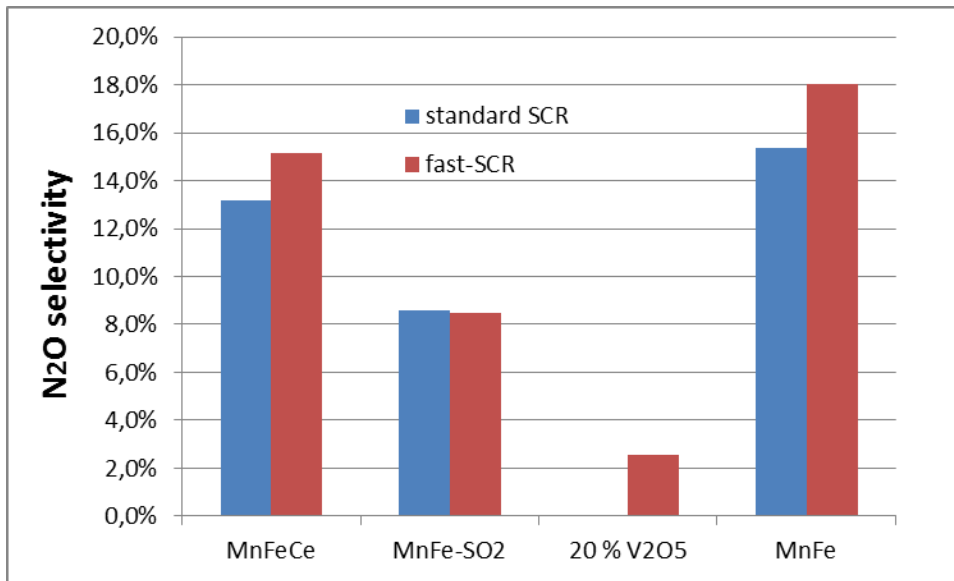

Figure 14: N$_2$O selectivities under standard- and fast-SCR conditions; Conditions: see figure 12.

Figure 15 shows that N$_2$O formation only partly accounts for the difference between the NO and NO$_2$ conversions of fast-SCR experiments.
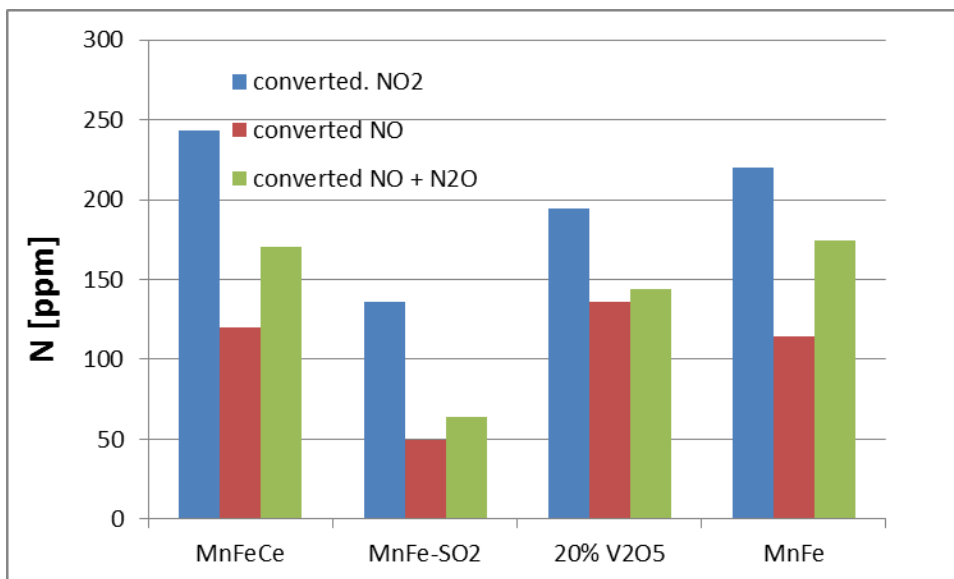

Figure 15: N balance of fast-SCR experiments; Conditions: see figure 12.

Thermogravimetric analysis (TGA) was used to test for NH_4NO_3 deposits on a sulphated 25 wt. % $Mn_{67.1}Fe_{17.9}Ce_{15}/TiO_2$ and 20% V2O5 after 4 hours of exposure to fast-SCR conditions, see figure 16. 20% V2O5 lost less than 2 wt. % upon heating to 400 ˚C. A fresh 20% V2O5 sample was impregnated with 400 µmol g^{-1}$_{catalyst}$ of NH_4NO_3. This is the theoretical amount of NH_4NO_3 formed if it were to stand for 5 % of the converted NO_x. Comparison of the two curves of figure 16 a reveals that NH_4NO_3 formation definitely does not explain the high X_{NO2}/X_{NO} ratios and is not an impediment to the use of fast-SCR. Hence we can conclude that that reaction (3) is faster than reaction (1) under the experimental conditions used.
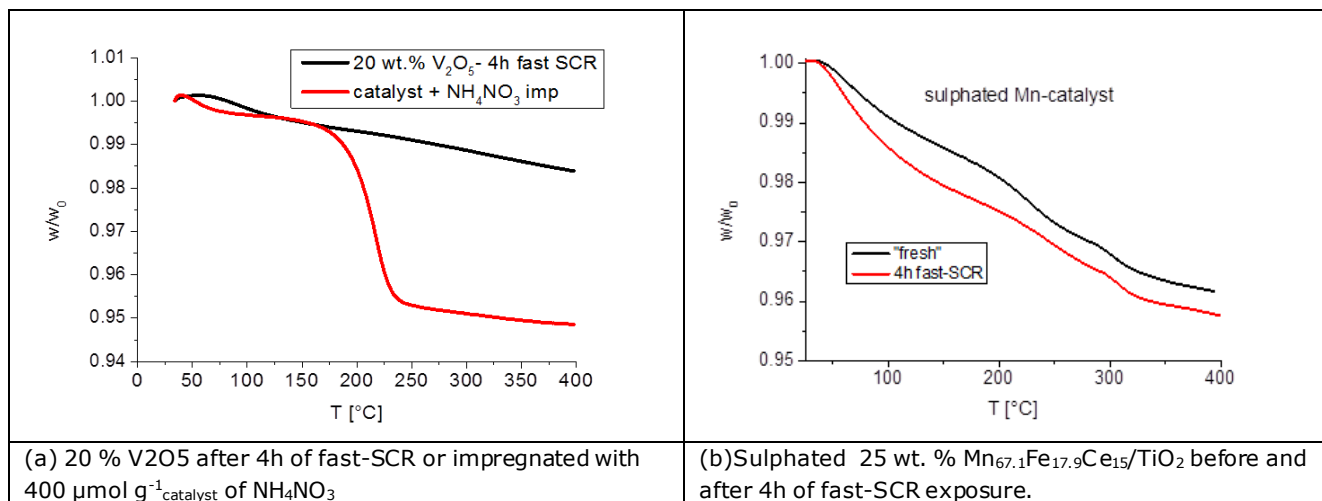
| (a) 20 % V2O5 after 4h of fast-SCR or impregnated with 400 µmol g$^{-1}_{catalyst}$ of NH₄NO₃ | (b)Sulphated 25 wt. % $Mn_{67.1}Fe_{17.9}Ce_{15}/TiO_2$ before and after 4h of fast-SCR exposure. |

Figure 16:TGA. Conditions: Flow = 20 mL/min of N₂, ΔT = 10 °C/min

Due to its superior sulfur tolerance and lower selectivity towards N₂O, 20 % V2O5 seems to be the most promising catalyst under fast-SCR conditions at 150 ˚C. Therefore, we have tested the effects of a possible promoter (Fe) [26] and of a known catalyst poison (K) [17, 27], see figure 17. Iron has no promotional effect and potassium is only a very mild poison. 1.41 wt.% K₂O, which corresponds to a loading of 300 µmol K g$^{-1}_{catalyst}$ causes less than 10 % deactivation. Another of our studies [28] showed that 200 µmol K g$^{-1}_{catalyst}$ can cause 70 % deactivation on a commercial VWT catalyst when tested at 220 ˚C under standard-SCR conditions. The reference activities were close to each other. This makes fast-SCR at 150 ˚C very promising for biomass-fired plants.
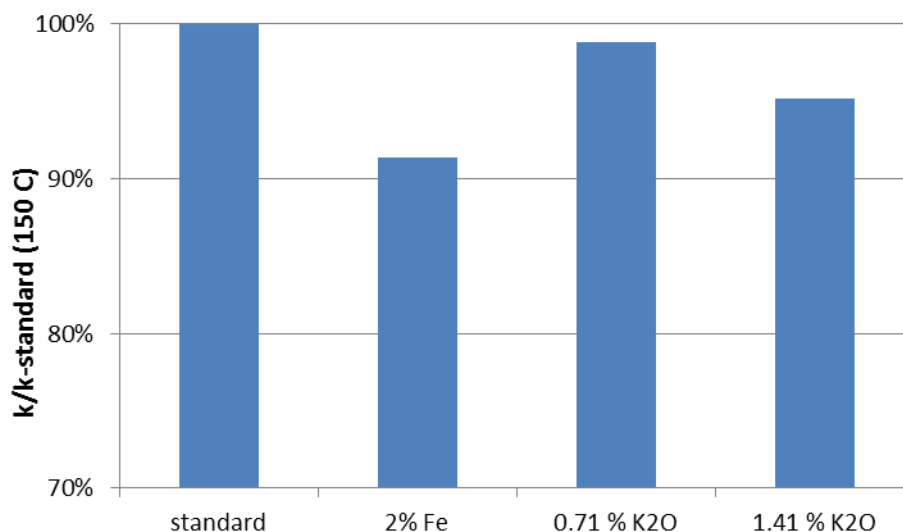

Figure 17: Relative fast-SCR pseudo first oder rate constants of 20 wt. % V₂O₅/TiO₂: pure (standard) and impregnated with Fe(NO₃)₃ or KNO₃ followed by calcination. Conditions: See figure 6.

In summary, we have demonstrated that fast-SCR at 150 °C is very promising in terms of activity and selectivity. Sol-gel prepared 20 wt. % V₂O5/TiO₂ is the most promising candidate due to its sulfur tolerance, low selectivity towards N₂O and extreme tolerance towards potassium. However, the necessary oxidation of NO to NO₂ presently presents a serious hurdle to use low temperature fast-SCR in most plants. To the best of our knowledge there is currently no catalyst available that can efficiently oxidize NO at 150 °C in the presence of both water and SO₂. Oxidation at higher temperatures would have to be carried out upstream of the desulfurization unit. This would probably lead to the undesired oxidation of SO₂ to SO₃ which in turn can react with water to form H₂SO₄ and cause corrrosion and acid slip via the stack.

1.5.1.5   Potassium tolerance of promoted V_2O_5/TiO_2 at 225 °C

Tail-end placement of the SCR unit can make sense in biomass-fired plants because the dust and sulfur removing units reduce the amount of potassium containing particles in the flue gas and hence reduce catalyst deactivation [29]. Therefore, a moderate potassium tolerance might be sufficient to be of industrial relevance. We have conducted this study at a temperature which requires re-heating after the desulphurization unit because finding a catalyst with sufficient activity at 150 °C under realistic conditions was not accomplished so far. Previous studies have shown that promoting V_2O_5/TiO_2 with heteropoly acids (HPAs) instead of WO_3 can make it more potassium tolerant [30, 31].

In the first part of the study we have tested the effect of three HPAs: $H_3PW_{12}O_{40}$(TPA), $H_4SiW_{12}O_{40}$(TSiA) and $H_3PMo_{12}O_{40}$(MPA) on the low-temperature activity of 3-6 wt. % V_2O_5/TiO_2 [32]. The catalysts were prepared by sequential impregnation with the HPA being introduced during the first step followed by calcination. The HPA loading was 15 wt.%. We also prepared catalysts containing 10 wt. % WO_3 to make comparison to traditional VWT catalysts possible.

The catalysts containing 5 wt. % V_2O_5 are more active and potassium tolerant than the corresponding 3 wt. % V_2O_5 ones, regardless of the promoter see table 1. Compared to the WO_3 promoted catalysts all HPA promoted ones are more active and potassium tolerant. The 5 wt. % V_2O_5 samples promoted by HPA are practically not affected by 100 µmol K g^{-1}.

	1st order k [$cm^3s^{-1}g^{-1}$]				1st order (-K/fresh)[%]	
	3V	5V	3V-K	5V-K	3V-K	5V-K
WO3	31.6	54.6	17.4	50.3	55	92
MPA	36.5	57.8	33.6	57.8	92	100
TPA	34.1	77.2	27.6	77.2	81	100
TSiA	34.0	72.6	27.2	68.9	80	95

Table 1:Activities of fresh and K loaded (100 µmol K g^{-1}) catalysts at 225 °C Reproduced from [32]

Extensive characterization encompassed NH_3-TPD, H_2-TPR, Raman spectroscopy, FTIR, XRD and EPR revealed that the improved potassium tolerance of HPA containing samples is probably due to an increased number of acid sites, see figure 18.
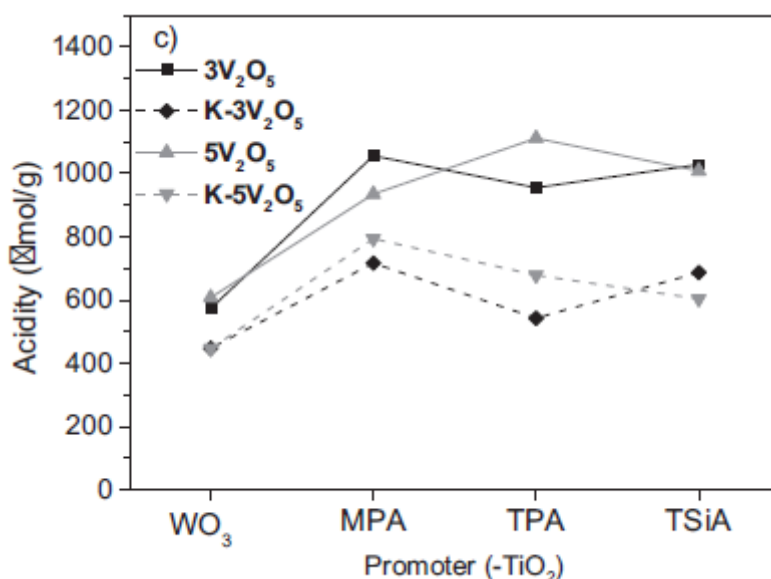

Figure 18: Number of surface acid sites in µmol g^{-1} as determined by NH_3-TPD as a function of promoter, vanadia concentration and presence of 100 µmol K g^{-1}. [32]

XRD and Raman spectroscopy showed that no crystalline V_2O_5 is present which means that N_2O formation is unlikely. Indeed, none of the catalysts generated N_2O, even at 300 °C.

In the second part of the study, both the vanadia and the HPA (MPA) loading were varied and a higher potassium loading (200 µmol K g^{-1}) was used. All catalysts experienced significant deactivation, also those with high vanadia loadings. Therefore, it is questionable if the combination of high vanadia loadings and use of HPAs, which leads to a high number of acid sites, is of practical use. Studies by Haldor Topsøe A.S. and DTU [33, 34] have shown that increasing the number of acid sites simply leads to increased capture of potassium and hence no enhancement in the potassium tolerance is observed. Combining the highly acidic catalysts with a potassium repelling protective layer might solve this problem [17, 35].
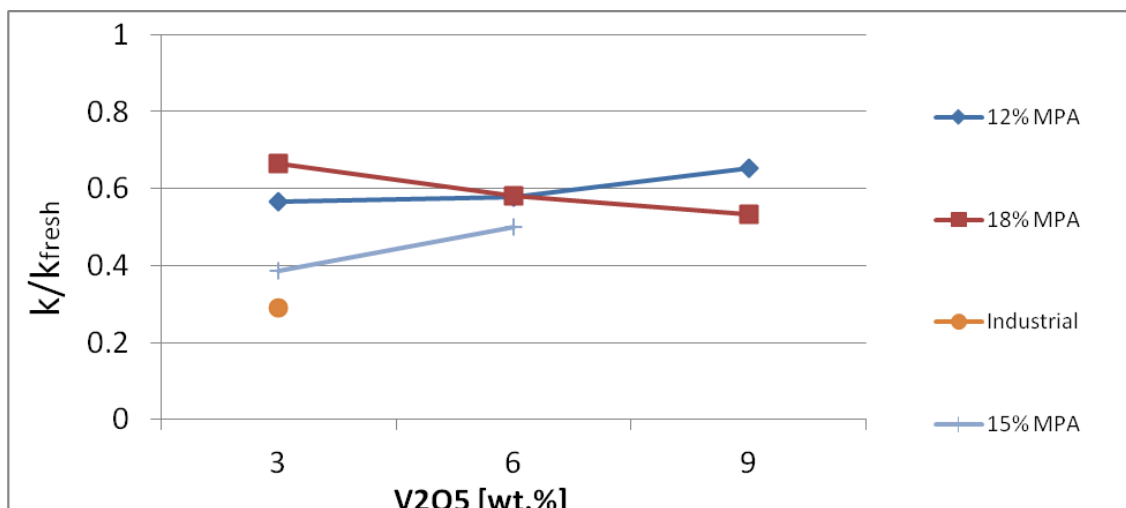

Figure 19: Activity of catalyst loaded with 200 µmol K g^{-1} at 225 °C. Indusatrial ≈ 3 wt. % V_2O_5 - 7 wt. % WO_3/TiO_2.

1.5.1.6   Conclusion on "NH_3-SCR at 150 °C"

Manganese based catalysts proved to be too much affected by realistic water and SO_2 concentrations to be sufficiently active at 150 °C. Doping with both ceria and HPAs does not solve the issue. Fast-SCR at 150 °C using highly loaded, sol-gel prepared V_2O_5/TiO_2 is promising in terms of activity and selectivity, however, the current lack of an efficient low-temperature NO oxidation catalysts makes industrial implementation unrealistic. Significant catalyst development would be required to potentially find a catalyst with sufficient activity under the conditions present at the tail-end position. Furthermore, the cost of oxidation of NO might be higher than the cost of re-heating the flue gas from 150 to 200-250 °C which is the current practice. Some progress was made in making vanadia based low-temperature (200-250 °C) catalysts more potassium tolerant by using high vanadia contents and substituting WO_3 with HPAs. The improved potassium tolerance is based on an increased number of acid sites and must therefore be combined with protective layers in order not to be cancelled by increased alkali capture from the flue gas.

Commercialization resulting in increased turnover, exports and employment has not happened so far due to the difficulties encountered during the project.

Future projects could focus on the sulphur and water tolerance of catalysts not based on manganese which are still sufficiently active under the conditions present at the outlet of dry FGD units.

1.5.1.7   Bibliography

1.   Chang H, Li J, Chen X, et al (2012) Effect of Sn on MnO x-CeO 2 catalyst for SCR of NO x by ammonia: Enhancement of activity and remarkable resistance to SO 2. Catalysis Communications 27:54–57. doi: 10.1016/j.catcom.2012.06.022

2.   Hu P, Huang Z, Hua W, et al (2012) Applied Catalysis A : General Effect of H 2 O on catalytic performance of manganese oxides in NO reduction by NH 3. "Applied Catalysis A, General" 437–438:139–148. doi: 10.1016/j.apcata.2012.06.025

3.   Lee SM, Park KH, Hong SC (2012) MnOx/CeO2–TiO2 mixed oxide catalysts for the selective catalytic reduction of NO with NH3 at low temperature. Chemical Engineering Journal 195–196:323–331. doi: 10.1016/j.cej.2012.05.009

4.   Wu Z, Jin R, Wang H, Liu Y (2009) Effect of ceria doping on SO2 resistance of Mn/TiO2 for selective catalytic reduction of NO with NH3 at low temperature. Catalysis Communications 10:935–939. doi: 10.1016/j.catcom.2008.12.032

5.   Yu J, Guo F, Wang Y, et al (2010) Sulfur poisoning resistant mesoporous Mn-base catalyst for low-temperature SCR of NO with NH3. Applied Catalysis B: Environmental 95:160–168. doi: 10.1016/j.apcatb.2009.12.023

6.   Qi G, Yang RT (2003) Performance and kinetics study for low-temperature SCR of NO with NH 3 over MnOx-CeO2 catalyst. Journal of Catalysis 217:434–441. doi: 10.1016/S0021-9517(03)00081-2

7.   Qi G, Yang RT (2003) Low-temperature selective catalytic reduction of NO with NH3 over iron and manganese oxides supported on titania. Applied Catalysis B: Environmental 44:217–225. doi: 10.1016/S0926-3373(03)00100-0

8.   Yu J, Guo F, Wang Y, et al (2010) Sulfur poisoning resistant mesoporous Mn-base catalyst for low-temperature SCR of NO with NH3. Applied Catalysis B: Environmental 95:160–168. doi: 10.1016/j.apcatb.2009.12.023

9.   Schill L, Putluru SSR, Jensen AD, Fehrmann R (2015) MnFe/Al2O3 Catalyst Synthesized by Deposition Precipitation for Low-Temperature Selective Catalytic Reduction of NO with NH3. Catalysis Letters 145:1724–1732. doi: 10.1007/s10562-015-1576-6

10.   Putluru SSR, Schill L, Jensen AD, et al (2015) Mn/TiO2 and Mn-Fe/TiO2 catalysts synthesized by deposition precipitation-promising for selective catalytic reduction of NO with NH3 at low temperatures. Applied Catalysis B: Environmental 165:628–635. doi: 10.1016/j.apcatb.2014.10.060

11.   Casapu M, Kröcher O, Elsener M (2009) Screening of doped MnOx-CeO2 catalysts for low-temperature NO-SCR. Applied Catalysis B: Environmental 88:413–419. doi: 10.1016/j.apcatb.2008.10.014

12.   Xiong S, Liao Y, Xiao X, et al (2015) Novel effect of H2O on the low temperature selective catalytic reduction of NO with NH3 over MnOx-CeO2: Mechanism and kinetic study. Journal of Physical Chemistry C 119:4180–4187. doi: 10.1021/jp512407k

13.   Peña DA, Uphade BS, Smirniotis PG (2004) TiO2-supported metal oxide catalysts for low-temperature selective catalytic reduction of NO with NH3: I. Evaluation and characterization of first row transition metals. Journal of Catalysis 221:421–431. doi: 10.1016/j.jcat.2003.09.003

14.   Li J, Chen J, Ke R, et al (2007) Effects of precursors on the surface Mn species and the activities for NO reduction over MnOx/TiO2 catalysts. Catalysis Communications 8:1896–1900. doi: 10.1016/j.catcom.2007.03.007

15.   Singoredjo L, Korver R, Kapteijn F, Moulijn J (1992) Alumina Supported Manganese Oxides for the Low-Temperature Selective Catalytic Reduction of Nitric-Oxide with Ammonia. Applied Catalysis B-Environmental 1:297–316. doi: 10.1016/0926-3373(92)80055-5

16.   Patent: Siret B, Tabaries F,, CATALYSEUR DE DÉNITRIFICATION, PROCÉDÉ DE DÉNITRIFICATION DE FUMÉES UTILISANT UN TEL CATALYSEUR ET PROCÉDÉ DE FABRICATION D'UN TEL CATALYSEUR, EP 2933018 A1,

17.   Kristensen SB (2013) deNOx catalysts for biomass combustion. April 2013. PhD thesis, Technical University of Denmark.

18.   Forzatti P, Nova I, Tronconi E, et al (2012) Effect of operating variables on the enhanced SCR reaction over a commercial V 2O 5-WO 3/TiO 2 catalyst for stationary applications. Catalysis Today 184:153–159. doi: 10.1016/j.cattod.2011.11.006

19.   Koebel M, Elsener M, Madia G (2001) Reaction Pathways in the Selective Catalytic Reduction Process with NO and NO_2 at Low Temperatures. Ind Eng Chem Res 59:52–59.

20.   Madia G, Koebel M, Elsener M, Wokaun A (2002) The effect of an oxidation precatalyst on the NOx reduction by ammonia SCR. Industrial and Engineering Chemistry Research 41:3512–3517. doi: 10.1021/ie0200555

21.   Wu S, Yao X, Zhang L, et al (2015) Improved low temperature NH3-SCR performance of FeMnTiOx mixed oxide with CTAB-assisted synthesis. Chemical Communications 51:3470–3473. doi: 10.1039/c4cc09719j

22.   Schill L (2014) Alternative catalysts and technologies for NO_x removal from biomass- and wate-fired plants. February 2014. PhD thesis, Technical University of Denmark.

23.   Chen Z, Yang Q, Li H, et al (2010) Cr-MnOx mixed-oxide catalysts for selective catalytic reduction of NOx with NH3 at low temperature. Journal of Catalysis 276:56–65. doi: 10.1016/j.jcat.2010.08.016

24.   Chen Z, Wang F, Li H, et al (2012) Low-Temperature Selective Catalytic Reduction of NO x with NH 3 over Fe À Mn Mixed-Oxide Catalysts Containing Fe 3 Mn 3 O 8 Phase. Industrial & Engineering Chemistry Research 202–212.

25.   LI H, TANG X, YI H, YU L (2010) Low-temperature catalytic oxidation of NO over Mn-Ce-Ox catalyst. Journal of Rare Earths 28:64–68. doi: 10.1016/S1002-0721(09)60052-1

26.   Gao R, Zhang D, Liu X, et al (2013) Enhanced catalytic performance of V2O5–WO3/Fe2O3/TiO2 microspheres for selective catalytic reduction of NO by NH3. Catalysis Science & Technology 3:191. doi: 10.1039/c2cy20332d

27.   Putluru SSR, Kristensen SB, Due-Hansen J, et al (2012) Alternative alkali resistant deNOx catalysts. Catalysis Today 184:192–196. doi: 10.1016/j.cattod.2011.10.012

28.   Promoted V_2O_5/TiO_2 catalysts for selective catalytic reduction of NO with NH_3 at low temperatures, Europacat conference- August 2017, Florence, Italy

29.   Wieck-Hansen K, Overgaard P, Larsen OH (2000) Cofiring coal and straw in a 150 MWe power boiler experiences. Biomass and Bioenergy 19:395–409. doi: 10.1016/S0961-9534(00)00051-9

30.   Putluru SSR, Jensen AD, Riisager A, Fehrmann R (2011) Heteropoly acid promoted V2O5/TiO2 catalysts for NO abatement with ammonia in alkali containing flue gases. Catalysis Science & Technology 1:631. doi: 10.1039/c1cy00081k

31.   Putluru SSR, Mossin S, Riisager A, Fehrmann R (2011) Heteropoly acid promoted Cu and Fe catalysts for the selective catalytic reduction of NO with ammonia. Catalysis Today 176:292–297. doi: 10.1016/j.cattod.2010.11.087

32.   Putluru SSR, Schill L, Godiksen A, et al (2016) Promoted V2O5/TiO2 catalysts for selective catalytic reduction of NO with NH3 at low temperatures. Applied Catalysis B: Environmental 183:282–290. doi: 10.1016/j.apcatb.2015.10.044

33.   Olsen BK, Kügler F, Castellino F, Jensen AD (2016) Poisoning of vanadia based SCR catalysts by potassium: influence of catalyst composition and potassium mobility. Catal Sci Technol 6:2249–2260. doi: 10.1039/C5CY01409C

34.   Jensen-holm H, Castellino F, White TN (2012) SCR DeNOx catalyst considerations when using biomass in power generation. Power Plant Air Pollutant Control "MEGA" Symposium 1–27.

35. Olsen BK, Kügler F, Castellino F, Schill L, Jensen AD (2017) Deactivation of SCR catalysts by potassium: A study of potential alkali barrier materials. In: VGB PowerTech, 2017, p. 56-64.

1.5.1.8   List of abbreviations

DP	Deposition Precipitation
EPR	Electron Paramagnetic Resonance
FTIR	Fourier Transfrrom Infrared Spectroscopy
H2-TPR	Hydrogen Temperature Programmed Reduction
HPA	Heteropoly Acids
IL	Ionic Liquid

IMP	Incipient Wetness Impregnation
MPA	$H_3PMo_{12}O_{40}$
NH3-TPD	Ammonia Temperature Programmed Desorption
SCR	Selective Catalytic Reduction
SILP	Supported Ionic Liquid Phase
TGA	Thermo Gravimetric Analysis
TPA	$H_3PW_{12}O_{40}$
TSiA	$H_4SiW_{12}O_{40}$
VOC	Volatile Organic Compounds
VWT	Vanadia-Tungsta-Titania
XRD	X Ray Diffraction

1.5.2 Transformation of NO to HNO_3

Results of this subproject can be found in the PhD thesis "Low Temperature DeNOx Technologies for Power and Waste Incineration Plants" submitted by Peter Westergaard Jakobsen in 2017 (Enclosure 1).

1.5.3 Dissemination

The project dissemination comprises 11 peer reviewed international journal articles, 2 patents/patent applications, 15 oral contributions at international conferences, 1 PhD thesis and 3 Bachelor and Master thesis which all together is considered as a very satisfactory output of the project.

Peer reviewed articles:

1. Kaas-Larsen PK, Thomassen P, Schill L, et al (2016) Selective Reversible Absorption of the Industrial Off-Gas Components CO2 and NO. ECS Trans 75:3–16. doi: 10.1149/07515.0003ecst

2. Putluru SSR, Schill L, Godiksen A, et al (2016) Promoted V2O5/TiO2 catalysts for selective catalytic reduction of NO with NH3 at low temperatures. Applied Catalysis B: Environmental 183:282–290. doi: 10.1016/j.apcatb.2015.10.044

3. Olsen BK, Kügler F, Castellino F, Schill L, Jensen AD (2017) Deactivation of SCR catalysts by potassium: A study of potential alkali barrier materials. In: VGB PowerTech, 2017, p. 56-64.

4. Kunov-Kruse AJ, Thomassen PL, Riisager A, et al (2016) Absorption and Oxidation of Nitrogen Oxide in Ionic Liquids. Chemistry - A European Journal 22:11745–11755. doi: 10.1002/chem.201601166

5. Kolding H, Thomassen P, Mossin S, et al (2014) Absorption of Flue-Gas Components by Ionic Liquids. ECS Trans 64:97–108. doi: 10.1149/06404.0097ecst

6. S. S. R. Putluru, L. Schill, A. D. Jensen, B. Siret, F. Tabaries, R. Fehrmann (2015) Mn/TiO2 and Mn-Fe/TiO2 catalysts synthesized by deposition precipitation-promising for selective catalytic reduction of NO with NH3 at low temperatures, Appl. Catal. B 165, p. 628-635.

7. L. Schill, S. S. R. Putluru, R. Fehrmann, A. D. Jensen (2014) Low-Temperature NH3–SCR of NO on Mesoporous Mn0.6Fe0.4/TiO2 Prepared by a Hydrothermal Method, Catal. Lett. 144, p. 395-402.

8. S. S. R. Putluru, L. Schill, D. Gardini, S. Mossin, J. B. Wagner, A. D. Jensen, R. Fehrmann (2014) Superior DeNOx activity of V2O5–WO3/TiO2 catalysts prepared by deposition–precipitation method, J Mater Sci 49, p. 705-2713.

9. S. S. R. Putluru, L. Schill, R. Fehrmann, A. D. Jensen (2014) Hydrothermally Stable Fe–W–Ti SCR Catalysts Prepared by Deposition–Precipitation, Catal. Lett 144, p. 1170-1077.

10. L. Schill, S. S. R. Putluru, A. D. Jensen, R. Fehrmann (2014) Effect of Fe doping on low temperature deNOx activity of high-performance vanadia anatase nanoparticles, Catal. Commun. 56, p. 110-114.

11. L. Schill, S. S. R. Putluru, A. D. Jensen, R. Fehrmann (2015) MnFe/Al$_2$O$_3$ Catalyst Synthesized by Deposition Precipitation for Low-Temperature Selective Catalytic Reduction of NO with NH$_3$, Catal. Lett. 145, p. 1724-1732.

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Patents

1. Fehrmann, R., Riisager, A., Mossin, S., Thomassen, P. L., Madsen, A. T., and Kunov-Kruse, A. J. (2015). IPC No. B01D 53/ 04 A I. Combined oxidation and absorption of NOx by an ionic liquid tandem process. (Patent No. WO2015158849)

2. Patent Application: Methanol promoted low temperature oxidation of NO, promotional tenique for use in tail-end, low temperature fast SCR, P. W. Jakobsen, S. Mossin and R. Fehrmann, patent application filed by DTU 7.September 2017

Conference Contributions

1. MnFe/Al$_2$O$_3$ Catalysts Synthesized by Deposition Precipitation for Low-Temperature Selective Catalytic Reduction of NO with NH$_3$ (Europacat X conference, August 2017 in Florence (Italy)). Oral Presentation

2. Promoted V$_2$O$_5$/TiO$_2$ catalysts for selective catalytic reduction of NO with NH$_3$ at low temperatures (Europacat X conference, August 2017 in Florence (Italy)). Poster Presentation

3. MnFe/Al$_2$O$_3$ Catalysts Synthesized by Deposition Precipitation for Low-Temperature Selective Catalytic Reduction of NO with NH$_3$ (NordicSymposium on Catalysis, June 2016 in Lund (Sweden)). Poster Presentation

4. Promoted V$_2$O$_5$/TiO$_2$ catalysts for selective catalytic reduction of NO with NH$_3$ at low temperatures (Nordic Symposium on Catalysis, June 2016 in Lund (Sweden)). Poster Presentation

5. Effect of dopants on NH$_4$NO$_3$ formation over vanadia-based SCR catalysts under fast-SCR conditions at 150 °C (251st ACS National Meeting, March 2016 in San Diego, California (USA)). Oral Presentation

6. Mn/TiO2 and Mn-Fe/TiO2 Catalysts Synthesized by Deposition Precipitation – Promising for Selective Reduction of NO with NH3 at Low Temperatures (24th North American Catalysis Society Meeting, June 2015 in Pittsburgh, Pensylvania (USA)). Poster Presentation

7. Effect of Fe doping on low temperature deNOx activity of high performance vanadia-anatase nanoparticles(247th ACS National Meeting & Exposition (Chemistry & Materials for Energy), March 2014 in Dallas, Texas (USA)). Oral presentation

8. Synthesis of Poly Ionic Liquids in Nano-Sized Hollow-Sphere Silica (26th EuChem Conference on Molten Salts and Ionic Liquids, July 2016 Vienna (Austria)). Oral presentation

9. Advances in Gas Phase Separation of NOx with Supported Ionic LiquidPhase Using Hollow-Sphere Silica (251st ACS National Meeting, March 2016 in San Diego (USA)). Oral presentation

10. Absorption and Oxidation of NOx to Nitric Acid - An Atom-Efficient Method for NOx Removal Using Ionic Liquids (EuropacatXII, September 2015 in Kazan (Russia)). Oral presentation

11. Atom-Efficient NOx Removal Using SILP Absorbers (26th EuChem Conference on Molten Salts and Ionic Liquids, July 2016 in Vienna (Austria)). Poster presentation

12. Advances in Absorption and Oxidation of NO in flue gas to form Nitric Acid (17th Nordic Symposium on Catalysis, June 2016 in Lund (Sweden)). Poster presentation

13. NOx Absorption and Oxidation in Supported Ionic Liquid Phase (SILP) (25th EuChem Conference on Molten Salts and Ionic Liquids, July 2014 inTallinn (Estonia)). Poster presentation

14. Absorption and Catalytic Conversion of NO to HNO_3 Using Ionic Liquid (16th Nordic Symposium on Catalysis, June 2014 in Oslo (Norway)). Poster presentation

15. NO Absorption and Oxidation in Supported Ionic Liquid Phase Materials; NO Absorption and Oxidation in Supported Ionic Liquid Phase (247th ACS National Meeting, March 2014 in Dallas, Texas (USA)). Poster presentation

Thesis

1 ."Low Temperature DeNOx Technologies for Power and Waste Incineration Plants" ,Peter Westergaard Jakobsen, PhD thesis, DTU Chemistry, DTU, June 2017(Enclosure 1)

2." Low Temperature DeNOx with Supported Ionic Liquid Phase Materials", Andreas Juul Jacobsen and David Nielsen , Bachelor thesis, DTU Chemistry, DTU, June 2015

3. "Low Temperature Sulphur Resistant DeNOx Technologies(1)", Andreas Juul Jacobsen, Master Thesis, DTU Chemistry, DTU, June 2017

4. "Low Temperature Sulphur Resistant DeNOx Technologies(2)", Frederik Bojsen Kværndrup, Master Thesis, DTU Chemistry, DTU, August 2017

1.6 Utilization of project results

The promising low temperature catalysts optimized in this project are right now attempted commercialized by our partner LAB S.A. for installation in full scale at a waste incineration plant under construction for a customer of LAB S.A.
However, our institute will probably not be taking part in a possible commercialization of these manganese based low temperature SCR catalysts because the relevant patents are now owned by our project partners, CNIM group of France (LAB S.A.) due to protection of commercially sensitive know-how.
The NO to HNO_3 alcohol promoted oxidation project is not yet ready for commercialization and funding for further investigations that might move it towards commercialization might be sought. This includes both the perspective of waste-to-value production of nitric acid as well as the use of the invention for fast-SCR utilizing standard sulfur and water resistant catalysts at tail-end installations.

So far, no results have been transferred to other institutions which gives the project participants much leeway in possible future projects. Some of the project participants (Rasmus Fehrmann, Susanne Mosin and Peter Westergaard Jakobsen) are currently applying for a patent (covering the methanol assisted oxidation of NO to NO_2 and HNO_3) in order to secure any possible future commercial developments.

The results of the PhD thesis describing the oxidation of NO to HNO_3 will be used in our teaching activities. The major beneficiary of the latest results is the course "26510- Catalysis and Sustainable Chemistry". This will include lecture material and possibly a laboratory exercise. In addition bachelor and master projects during the project and later on have been and will be inspired by the now expired project.

1.7 Project conclusion and perspective

We conclude that the search for a low-temperature (150 °C) SCR catalyst is very challenging and no practical global solution for all possible applications is at hand at the moment. Manganese based catalysts are too much affected by sulphur and water(but may find special applications as persued by LAB S.A.), while vanadia based ones so far have too low basic activities. Future activities could include boosting the activity of vanadia containing catalysts by e.g. doping with other metals like e.g. Cu, Nb, Ta etc. Investigating Cu based catalysts might be another option. However, based on the current literature findings it is not very likely that a suitable catalyst can be found easily. But the late discovery – now patented- of the SILP material and promoters enhancing the oxidation of NO at low temperatures may prove very useful for future design of low temperature catalytic deNOx technologies.

The transformation of NO into HNO_3 might have commercial potential but needs further investigation, especially regarding space velocities, stepwise methanol injection and HNO_3 collection.
Funding for all these investigations might be applied for in the future-