Hg and NO$_x$ removal from flue gases by supported MnO$_x$ sorbents/catalysts

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Abstract
Supported MnO$_x$ catalysts/sorbents have been investigated for the simultaneous removal of NO$_x$ and elemental Hg from flue gases in the temperature range 50 – 250°C. In particular, the effect of the type of support (TiO$_2$ vs. Al$_2$O$_3$) on both NO$_x$ conversion via NH$_3$-SCR and Hg capture efficiency has been addressed. The two catalysts display significant and quite similar NH$_3$-SCR activity with an optimal performance in the range 80 – 140°C. On the contrary, the Mn-based sorbent over TiO$_2$ shows a much better Hg capture performance than that supported over Al$_2$O$_3$. The most likely reason was the higher proportion of Mn^{4+} sites, as revealed by H$_2$-TPR and XRD analysis.

Introduction
Mercury is a global threat to human and environmental health. Coal combustion on its own contributes to about 30% of the global anthropogenic Hg emissions. Elemental mercury (Hg^0) is the most difficult species to remove with conventional air pollution control devices due to its high volatility and insolubility in water. Oxides of transition metals (in particular Mn) have been recently indicated as possible alternatives to activated carbon as regenerable sorbents for Hg removal from combustion flue gas [1]. In fact MnO$_x$-based sorbents have been found to perform better than a number of commercially (impregnated) activated carbons. Moreover MnO$_x$ based catalysts are widely studied for their high activity and selectivity for NO$_x$ reduction in flue gases via the low temperature (<200°C) NH$_3$-SCR reaction [2,3], which is a typical redox process. This observation opens the possibility of simultaneous SCR and mercury capture in a single process unit in tail-end configuration [2]. Following previous studies [4,5] in this work we investigated the effect of the type of support (TiO$_2$ vs. Al$_2$O$_3$) on the elemental mercury removal performance of MnO$_x$-based catalysts, which can be suited for the low temperature NH$_3$-SCR process.

Experimental
Catalysts preparation and characterization
MnO$_x$-based catalysts/sorbents with a Mn loading of ca. 6% were prepared via two repeated cycles of incipient wetness impregnation onto two commercial supports: i)

TiO$_2$ powder by Tioxide, predominantly anatase phase, 125 m^2/g, mean pore size 3.6 nm; γ-Al$_2$O$_3$ spheres of 1 mm diameter by Sasol, 173 m^2/g, mean pore size 8.0 nm. Impregnations were performed with aqueous solutions of Mn (CH$_3$COO)$_2$·4H$_2$O (Aldrich), after which the samples were first dried in a stove at 120°C and then calcined in air at 550°C for 3h. The catalysts/sorbents were fully characterized by means of ICP-MS, XRD, BET, H$_2$-TPR, and Hg-TPD [5].

Catalysts testing
NH$_3$-SCR activity tests were performed on powder catalysts (300 mg, particle size: 200–300 μm) loaded in a down-flow quartz reactor with annular section (inner d =6 mm, outer D=10 mm). The reactor was placed in a tubular furnace and operated at atmospheric pressure in the temperature range 50–250°C. The feed contained 500 ppmv NO, 500 ppmv NH$_3$ and 8% vol. O$_2$ (balance He) at a total inlet flow rate of 30 Sl/h, corresponding to a GHSV = 6.6·10^4 h^{-1}. The concentrations of NO, NO$_2$ and N$_2$O were measured with an Emerson X-Stream XEGP analyzer after removing H$_2$O and unconverted NH$_3$ using a Sycapent (P$_2$O$_5$) trap.
Hg removal tests were performed in a similar labscale reactor [4] equipped with a CVVA continuous Hg^0 analyzer, by employing 10 – 100 mg of sorbent (size: 200–300 μm), and a total flow rate of 78 Sl/h (max GHSV = 5.1·10^6 h^{-1}). Capture tests were performed with an inlet Hg^0 concentration in the range 50-250 μg/m^3 in air or in a simulated flue gas containing 100 ppmv of both NO and NH$_3$, and 18% O$_2$. Hg-TPD tests were carried out in the same experimental set up, by heating samples up to 550°C at 10°C/min in air flow.

Results and Discussion
Catalysts characterization
XRD spectra of Mn/A and Mn/T materials calcined at 550°C (not reported) show only the characteristic peaks of the two supports, probably due to the low loading and high dispersion of the active phase. Mn/A sample preserved a BET value as high as 165 m^2/g after calcination at 550°C. On the other hand, the surface area of Mn/T dropped to ca. 70 m^2/g, accompanied by a significant enlargement of the average pore size of the TiO$_2$ support. H$_2$-TPR revealed that the average oxidation state of Mn was significantly higher when supported on TiO$_2$ (3.5) rather than on Al$_2$O$_3$ (3.2). Thus, for Mn/T sample as much as 70% of Mn is present as Mn^{4+} species (as MnO$_2$), the rest being Mn^{3+} (as Mn$_2$O$_3$). On the other hand, the percentage of easily reducible Mn^{4+} decreases to ca. 20% for Mn/A. Such a difference is possibly related to the stabilization of Mn^{4+} through a partial dissolution of MnO$_2$ in TiO$_2$.
In Figure 1 the catalytic performances of Mn/A and Mn/T for the NH$_3$-SCR reaction are compared with that of a commercial V$_2$O$_5$-WO$_3$/TiO$_2$ sample tested under identical conditions in the temperature range 50-250°C. In agreement with several previous reports [2,3], Mn-based catalysts displayed significant SCR activity already at low temperatures where the commercial V-based catalyst gave

poor performance: at 130°C the NO_x conversion over V_2O_5-WO_3/TiO_2 catalyst was below 10%, whilst it was ca. 80% over both of the two supported MnO_x catalysts. Mn/A and Mn/T catalysts displayed quite similar NH_3-SCR activity as a function of temperature and optimal catalytic performance was achieved in the range between 80 - 140 °C: for higher temperatures the NO_x conversion levelled off up to 225 °C, whereas the N_2 selectivity started to decrease progressively. This circumstance reflected the detection in the products of increasing amounts of N_2O (and to a lower extent NO_2), which, on the other hand were not formed over the commercial vanadium based catalyst.
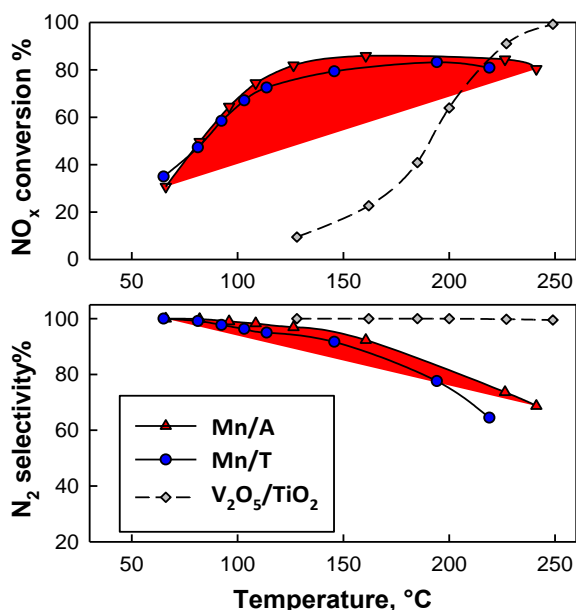

Figure 1 NO_x conversion and N_2 selectivity during the NH_3-SCR over Mn/A, Mn/T and a commercial V_2O_5- WO_3/TiO_2 reference catalyst as a function of temperature. Feed: NO=NH_3=500ppmv, O_2=8%, GHSV =66000 h^{-1}

Hg removal tests
Preliminary tests, performed with a fixed bed of each of the two raw supports, revealed that both γ-Al_2O_3 and TiO_2 have negligible Hg removal activity [4,5] (capture or oxidation) in the explored experimental conditions. On the other hand, Mn/A and Mn/T sorbents removed elemental Hg from an air stream already at room temperature, and their removal efficiency increased (slowly) up to roughly 200°C, before starting to decrease beyond that temperature level. Further tests conducted at fixed temperature showed that the removal efficiency remained constant by varying the inlet mercury concentration, indicating for both materials a first order dependency of the apparent capture rate [5]. Figure 2-a reports the kinetic constant for the initial Hg removal rate over Mn/A and Mn/T obtained from experimental data under the assumption of ideal isothermal plug flow reactor. It

should be mentioned that, due to the higher activity of Mn/T, experimental tests had to be run with a lower quantity of sorbent (10 mg mixed with inert TiO_2, as opposed to the 100 mg for Mn/A), in order to keep the measured Hg removal efficiency below 90%. Comparing the apparent rates of Hg capture per gram of sorbent in Fig. 2a it appears that the process was as much as 10 times faster on Mn/T than on Mn/A. The Arrhenius plots show that the apparent Hg capture rates on both catalysts displayed a rather low dependency on the reaction temperature, and in fact almost levelled off above ca. 100°C, thus suggesting a significant effect of mass transfer limitations. This was confirmed by the estimation of the Weisz modulus ψ[5], which is the ratio of time constants of intraparticle diffusion and reaction: for Mn/A and Mn/T (assumed spherical with average d = 250 μm), ψ was always above 1, and increased respectively from 2 to 11 and from 16 to 100 along with temperature in the range 20 - 200°C. Under pore diffusion control, the apparent activation energy calculated from the low temperature branch of the Arrhenius plots in Fig 2a is halved with respect to that of the intrinsic surface reaction, which, therefore, could be estimated at about 85 kJ/mol for both Mn/T and Mn/A. In fact, Hg-TPD experiments (Fig. 2b for Mn/T) revealed that most mercury removed from the flue gas was captured and stored on the catalyst [5]; desorption of elemental mercury previously adsorbed on Mn/A or Mn/T occurred above 320°C and peaked at temperatures around 430°C. Mn/A material also showed some limited desorption of more weakly bound Hg species for T≥ 150°C [5], which was absent in the case of Mn/T sorbent. It can be argued that chemisorption and chemical reaction is the most likely binding mechanism for Hg-MnO_x also when the active phase was dispersed on both supports. However, titania guaranteed a much larger number of superficial Mn active sites with respect to alumina, even if its BET surface area was lower.
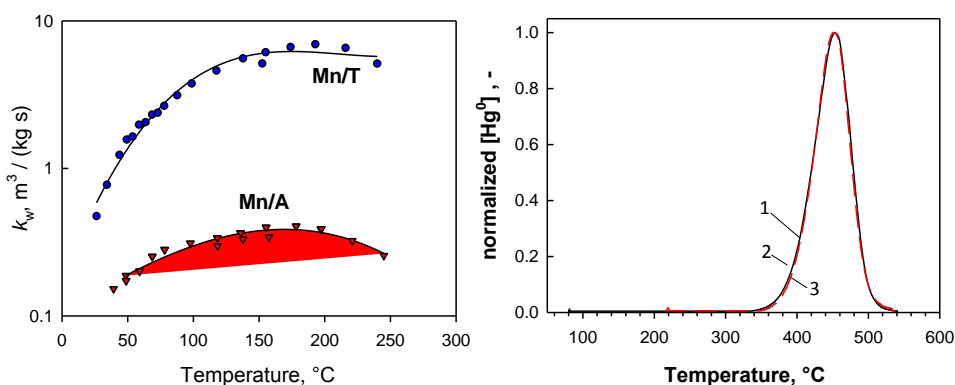

Figure 2 a) Kinetic constant for the initial Hg capture rate referred to the weight of Mn/A and Mn/T catalysts. [Hg]= 150 – 250 μg/m³. Mn/A=100mg; Mn/T=10mg. b) Hg-TPD profiles from a single batch of Mn/T following a corresponding Hg capture test in air at 80°C (1), 90°C (2) and 215 °C (3).

In particular, it was previously demonstrated by XPS measurements that Hg was stored on MnO_x sorbents in an oxidized form also when mercury was captured under N_2, and that some Mn^{4+} was converted to Mn^{3+} by reacting with Hg^0 during the adsorption process [2]. Therefore the maximum reactivity should be associated to the more easily reducible Mn^{4+} sites, which in turn were significantly more abundant when the active phase was dispersed on TiO_2 rather than on γ-Al_2O_3. No evident sign of degradation of the initial Hg capture rate could be detected for supported Mn/T and Mn/A sorbents during a few adsorption/desorption cycles with regeneration temperatures of 550°C. As an example, Hg-TPD profiles reported in Fig. 2b correspond to 3 sets of repeated adsorption tests performed on the same batch of Mn/T catalyst, which was completely regenerated during the previous desorption phase at 550°C.

Hg removal tests with NO and NH₃
In order to investigate the possibility of simultaneous low temperature NH_3-SCR and mercury capture over a single catalytic system, Hg removal tests were repeated under a flow of a simulated flue-gas containing also NO or NO + NH_3 in addition to Hg (and O_2). At a space velocity as high as $5.1 \cdot 10^5$ h^{-1} Mn/T displayed 100% removal efficiency in air in the whole temperature range explored. It should be noticed that such a GHSV is roughly one order of magnitude larger than what used for NH_3-SCR tests and it was selected in order to appreciate some possible effects of NO and NH_3. In fact, the presence of 100 ppmv of NO in the flue gas determined a moderate decrease in the capture efficiency of Mn/T for temperatures up to 100°C and possibly above 220°C. However, the simultaneous presence of equal amounts of NO and NH_3 induced a small further reduction of the capture efficiency at low temperatures, which vanished above 115°C, where 100% removal was re-attained. In line with the lower Hg capture rate observed when the active MnO_x phase was dispersed on alumina, Mn/A catalyst displayed removal efficiencies comprised in the range 50-70% under identical experimental conditions in air. Similarly to Mn/T, the addition of NO caused a reduction in the measured Hg capture, which was lowered by 10-20 % throughout the temperature range with respect to the reference case, with a higher impact at T< 115 °C.
It should be noticed that according to previous literature data [3,4], the critical species for the catalyst operation both for the low temperature NH_3-SCR and for the Hg capture remains SO_2, which can irreversibly poison the manganese active phase by forming stable sulphate species.

Conclusions
MnO_x-TiO_2 catalysts show promising results for the simultaneous low temperature NH3-SCR and Hg capture in a tail-end configuration after particle removal and desulphurization units, thus working with relatively clean flue gases.

References

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