COMBINED MERCURY REMOVAL AND LOW TEMPERATURE NH₃-SCR OF NO WITH MnOₓ/TiO₂ SORBENTS/CATALYSTS

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Abstract
MnOₓ/TiO₂ catalysts/sorbents were investigated for flue gas purification via the simultaneous low-temperature NH₃-SCR of NO and elemental Hg capture, in the temperature range 25-300 °C. In particular, the effects of the Mn precursor salt (acetate vs. nitrate) and of the TiO₂ textural properties (nanotubes vs. random mesopores) on both deNOₓ and Hg capture efficiencies were addressed. The catalysts/sorbents were also characterized by means of ICP-MS, XRD, BET, H₂-TPR, NH₃ adsorption, and TPD of both NH₃ and Hg. Catalysts prepared by acetate precursors generally displayed a higher reducibility and oxidation activity, which was beneficial to improve mercury capture rate, but adversely impacted on the selectivity of the SCR process at temperatures above 150 °C. In the absence of HCl in the flue gas, Hg was effectively captured up to 250 °C and stored on the catalysts, most probably in an oxidized form. The original sorption properties of the catalysts could be fully restored by a simple thermal treatment at temperatures between 400-500 °C, releasing elemental mercury. The use of TiO₂ nanotubes as the support for the MnOₓ active phase increased the strength of the Hg bond.

Introduction
Mercury and nitrogen oxides represent major pollutants released from coal-fired power plants [1,2]. Mercury is well known to cause adverse effects to the environment and to the food chain. Recent studies recognized that about 30% of the global anthropogenic Hg emissions are caused by coal combustion, mainly in the elemental form (Hg⁰), which is less effectively captured due to its high volatility and insolubility in water [3]. Activated carbon injection in flue gas upstream of a particulate matter control device represents the best available technology for elemental mercury capture. However, low temperatures (< 150 °C) and high carbon-to-mercury ratios must be used to achieve acceptable removals, and spent sorbents cannot be regenerated and require proper disposal, thus leading to costly operation [4,5]. Oxides of transition metals have been recently proposed as possible alternatives to activated carbon as cheap and regenerable sorbents for Hg removal from combustion flue gas. In particular, they are able to perform Hg capture at higher temperatures (100-400 °C) and they can be thermally regenerated [6,7]. Among the transition metal oxides, MnOₓ-based sorbents have shown a good mercury capture potential [8-12].

Among the different commercial technologies for NOₓ abatement from power plants, the selective catalytic reduction (SCR) of NOₓ by NH₃ is the most widespread method due to its efficiency, selectivity and economics. Industrially adopted SCR catalysts are based on V₂O₅-WO₃/TiO₂ systems [13-15]. Due to relatively high operating temperatures required (> 250 °C) by this catalyst and its sulphur tolerance, the SCR unit is generally located upstream of the desulfurizer and/or the particulate control device to avoid (costly) reheating the flue gas. Efforts have been made to develop catalysts capable of operating in the low temperature range...
(100-200 °C) in a tail-end configuration of the deNOx unit. Manganese oxides are of interest as SCR catalysts at low temperature under sulfur-free conditions because they contain various types of labile oxygen that are necessary to promote the adsorption and activation of NH3 on the catalysts surface to fulfill the SCR cycle [16-19]. This observation opens the possibility of simultaneous CR and mercury capture in a single process unit in tail-end configuration [11,20]. In particular, we recently showed that MnOx-based catalyst/sorbent prepared by dispersing the active phase onto high surface area TiO2 or Al2O3 supports can effectively remove and store mercury up to 250 °C and displays a significant SCR activity in the range 100–200 °C [21-23]. Overall, the type of support was found to have a limited impact on the NH3-SCR performance, whereas the Hg capture rate was highly enhanced when the active phase was supported on TiO2.

Following previous studies, in this work we investigated the effects of the Mn precursor salt (acetate vs. nitrate) and of the TiO2 textural properties (nanotubes vs. random mesopores) on both deNOx and Hg capture efficiencies. In particular, titania nanotubes, prepared by Microwave-Assisted Hydrothermal synthesis, provide a higher surface area and a unique nanotubular structure that can be beneficial to enhance the dispersion of the active phase and to improve SCR performance [24,25].

**Experimental Section**

**Catalysts Preparation**

Three kinds of MnOx-based catalysts/sorbents were prepared using two kind of supports: (i) a commercial TiO2 powder (denoted as T) with predominant anatase phase; (ii) TiO2 nanotubes (denoted as TNT) prepared by Microwave-Assisted Hydrothermal (MAH) synthesis [26,27] starting from the same TiO2 powder. In particular, 0.42 g of TiO2 was added to a 10 mol water solution of NaOH to obtain a suspension volume of 50 mL that was microwave-irradiated in a sealed Teflon vessel at 150 °C for 2.5 h. After washing, the resulting nanotubes were dried at low temperature of 120 °C in order to avoid agglomeration of the structure, (denoted as TNT 120 °C) and finally calcined at 500 °C for 4h (TNT 500 °C). The reference catalyst/sorbent (denoted as Mn/T-Ac) was prepared via incipient wetness impregnation onto TiO2 powder support, previously calcined in air at 550 °C (T 550 °C), using manganese acetate as the precursor salt and a target loading of roughly 6% wt. of Mn [21]. Two other catalysts with identical nominal composition were prepared by the same method using a manganese nitrate aqueous solution and the two types of TiO2 supports (T and TNT): they were labelled as Mn/T-Nit and Mn/TNT-Nit, respectively. After the impregnation step, the samples were first dried in a stove at 120 °C and calcined in air for 3 h at 500 °C. All samples were ground and sieved (125-250 μm) to obtain a homogeneous powder.

**Catalysts Characterization**

The actual content of manganese in the materials was determined by inductively coupled plasma spectrometry using an Agilent 7500 ICP-MS instrument, after microwave-assisted acid digestion. The textural properties of the supports and the resulting MnOx-based sorbents were determined with a Quantachrome Autosorb 1-C by N2 adsorption at 196 °C, after degassing samples for 2 h at 150 °C. The Brunauer-Emmett-Teller (BET) method was adopted for the calculation of the specific surface area, while cumulative surface area as a function of the pore diameter was evaluated by means of Barret-Joyner-Halenda (BJH) for mesopores. Powder X-ray diffraction (XRD) patterns were acquired with a Bruker D2 Phaser instrument operated at diffraction angles 2θ between 20 and 80 ° and scan rate of 0.02 ° 20 s⁻¹. The crystalline phases of the materials were determined by comparing the XRD pattern to the reference data from International Center for Diffraction Data (ICDD) files. Hydrogen-
Temperature Programmed Reduction (H₂-TPR) tests were carried out with a Micromeritics Autochem II TPD/TPR analyzer equipped with a TCD. The samples (200 mg) were preliminarily treated for 1 h at 400 °C under air flow, cooled down to room temperature and then analyzed under a 2 % H₂/Ar flow, by heating up to 700 °C at 10 °C min⁻¹. The hydrogen consumption of the materials in the temperature range 100-700 °C was obtained by integrating the thermal conductivity detector (TCD) signal.

Ammonia was used as probe molecule in the adsorption and Temperature Programmed Desorption (TPD) experiments because it is both a basic molecule to test surface acidity, and it is one of the reactants for SCR. Experiments were carried out in the same apparatus used for SCR tests with 125 mg samples. After a pretreatment under He/O₂ flow at 250 °C, the furnace temperature was reduced to 100 °C, and the samples were then saturated with 500 ppm NH₃ in He at a flow rate of 20 L h⁻¹. Physisorbed NH₃ was removed by flushing the sample in He at 100 °C. Thereafter, the sample was heated at 10 °C min⁻¹ up to 500 °C under He flow and the evolved gas were continuously analyzed to measure the concentration of NH₃, NO, N₂O and NO₂.

**Catalysts Testing**

Hg removal and NH₃-SCR activity tests were performed in lab scale quartz reactors [21-23]. Hg capture tests were performed in the temperature range 25-300 °C with an inlet Hg⁰ concentration of 150 μg m⁻³ in air and total flow rate of 60 NL h⁻¹, using 20-100 mg samples (particle size: 125-250 μm). The concentration of elemental Hg in the gas was measured by a cold vapor atomic adsorption continuous Hg⁰ analyzer. Hg-TPD tests were carried out in the same experimental setup, by heating samples up to 500 °C at 10 °C min⁻¹ under air flow (60 NL h⁻¹). NH₃-SCR tests were conducted with a feed containing 400 ppmv NO, 400 ppmv NH₃ and 8 %vol. O₂ (balance He) at a total flow rate of 25 NL h⁻¹, using 125 mg of catalyst (particle size: 125-250 μm). Two continuous analyzers in series with specific detectors were used to measure the concentration of NH₃ (GEIT) and that of NO, N₂O and NO₂ (Emerson X-Stream XEGP).

**Results and Discussion**

**Catalysts Characterization**

In Table 1 the list of catalysts used in the tests is reported with their actual Mn loading, measured by ICP-MS tests, which was ca. 6 %wt. for all of them. XRD spectra of the TiO₂ support (T) indicated that it consisted of a mixture of anatase and brookite phases, in agreement with previous reports [28]. The MAH treatment and the following calcination at 500 °C returned a pure anatase phase with the disappearance of the brookite phase. The dispersion of the MnOₓ active phase onto those supports gave rise to small and not well resolved additional peaks in the XRD pattern of Mn/T-Ac, Mn/T-Nit and Mn/TNT-Nit materials (not reported) that could be possibly assigned to MnO₂.

**Table 1.** Catalysts/sorbents and parent support properties.

<table>
<thead>
<tr>
<th></th>
<th>Mn %wt.</th>
<th>S₅₂</th>
<th>qₚ(BJH)</th>
<th>Vₚ(BJH)</th>
<th>H₂/Mn</th>
<th>NH₃ ads</th>
<th>Eₐ(Hg)</th>
<th>Eₐ(SCR)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T 550 °C</td>
<td>5.9</td>
<td>70</td>
<td>125</td>
<td>0.24</td>
<td>0.86</td>
<td>0.26</td>
<td>46.6</td>
<td>42.9</td>
</tr>
<tr>
<td>TNT 500 °C</td>
<td>5.8</td>
<td>90</td>
<td>49</td>
<td>0.27</td>
<td>0.90</td>
<td>0.38</td>
<td>45.5</td>
<td>37.8</td>
</tr>
<tr>
<td>Mn/T-Ac</td>
<td>5.5</td>
<td>104</td>
<td>97</td>
<td>0.46</td>
<td>1.02</td>
<td>0.43</td>
<td>-</td>
<td>38.2</td>
</tr>
</tbody>
</table>
Errore. L'origine riferimento non è stata trovata.

*a* shows the H\textsubscript{2}-TPR traces recorded for Mn/T-Ac, Mn/T-Nit and Mn/TNT-Nit in comparison to those of two reference pure manganese oxides. The reduction process started at ca. 250 °C for those catalysts prepared from nitrate precursor, whereas it was anticipated at ca. 150 °C for Mn/T-Ac sample. Mn/T-Nit and Mn/TNT-Nit displayed a main reduction event peaking at 380 °C, with a shoulder at 470 °C; Mn/T-Ac showed a broad peak centered at ca. 370 °C, which ended at ca. 500 °C. Based on the characteristic reduction temperatures during H\textsubscript{2}-TPR and the total amount of H\textsubscript{2} consumed (considering that all of the Mn is finally reduced to Mn\textsuperscript{2+} [17,29]), it was possible to calculate the average oxidation state of Mn in the system (Errore. L'origine riferimento non è stata trovata.). In particular, Mn/T-Nit and Mn/TNT-Nit samples mostly contained Mn\textsuperscript{4+} species as in MnO\textsubscript{2} (98 and 100 %, respectively), whereas Mn/T-Ac sample also contained a fraction (29 %) of Mn\textsuperscript{3+} species (as in Mn\textsubscript{2}O\textsubscript{3}).

![Figure 1](image)

**Figure 1.** a) H\textsubscript{2}-TPR profiles for Mn/T-Ac, Mn/T-Nit and Mn/TNT-Nit materials and reference bulk manganese oxides; b) cumulative BJH surface area as a function of pore diameter for Mn/T-Nit and Mn/TNT-Nit materials and their corresponding supports.

The textural properties of catalysts/sorbents and their corresponding supports are collected in **Table 1** while the plots of the cumulative surface area as a function of the pore diameter are presented in **Figure 1-b.** The BET surface area of titania nanotubes prepared at 120 °C (485 m\textsuperscript{2} g\textsuperscript{-1}) dropped to 114 m\textsuperscript{2} g\textsuperscript{-1} after the heat treatment at 500 °C. This value was still significantly higher than the surface area retained by the TiO\textsubscript{2} support treated at 550 °C (87 m\textsuperscript{2} g\textsuperscript{-1}). Both supports were characterized by the predominance of mesopores with a mean dimension of ca. 50 and 100 Å respectively for T and TNT. Dispersion of active phase on both supports and subsequent calcination did not significantly modify the textural properties of the parent support, so that Mn/T-Ac, Mn/T-Nit and Mn/TNT-Nit samples preserved a BET value as high as 70, 90 and 104 m\textsuperscript{2} g\textsuperscript{-1} respectively. The mean pore size was estimated equal to 125, 97 and 49 Å for Mn/T-Ac, Mn/TNT-Nit and Mn/T-Nit catalysts/sorbents. Therefore, the use of the acetate precursor salt induced some enlargement of the characteristic dimension...
of the pores that was reflected by a loss of specific surface area. On the other hand, nitrate precursors did not alter the textural properties of the titania supports. The quantity of NH₃ adsorbed at 100 °C increased in the order Mn/TNT-Nit > Mn/T-Nit > Mn/T-Ac following the same trend of the exposed surface area (Table 1), which determined the number of Ti⁴⁺ Lewis acid sites on the surface [30].

**Hg removal test**

Preliminary tests, performed with a fixed bed of each of the two raw supports, revealed that both T and TNT had negligible Hg removal activity (capture or oxidation) in the explored experimental conditions. Results of the sorbent Hg removal tests are presented in Figure 2-a in terms of the Hg removal efficiency for Mn/T-Ac, Mn/TNT-Nit and Mn/T-Nit as a function of temperature. Mn/T-Ac sorbent removed elemental Hg from an air stream already at room temperature, and its removal efficiency approached 100 % for T≥ 70 °C and up to 300 °C. Under identical experimental conditions, Mn/TNT-Nit and Mn/T-Nit sorbents shared a similar trend of performance and removed less mercury than the reference Mn/T-Ac sample: their capture efficiency increased more slowly with temperature up to 200 °C and levelled-off or eventually decreased above this level. Moreover, in the temperature range from 25 to 45 °C, the mercury removal efficiency with all of the sorbents remained constant while varying the inlet mercury concentration, thus indicating a first order dependency of the apparent removal rate [22].

![Figure 2](image)

**Figure 2.** a) Initial Hg capture efficiency over Mn/T-Ac, Mn/TNT-Nit and Mn/T-Nit catalysts as a function of temperature in air. Feed: [Hg⁰] = 150 µg m⁻³ e Qₜ = 60 NL h⁻¹. b) Hg-TPD profiles obtained of Mn/TNT-Nit, Mn/T-Ac and Mn/T-Nit following a corresponding Hg capture test in air at 150 °C.

Hg-TPD profiles (shown in Figure 2-b), obtained after a Hg capture test in air at 150 °C for 2 h, revealed that most of the mercury, which had been previously removed from the flue gas, was captured and stored on the catalyst, and then thermally released as elemental mercury. In fact, the Hg⁰ balance was closed within 10 % for all materials: therefore, the release of HgO(g) during adsorption and desorption was substantially negligible [21,22]. The desorption of elemental mercury previously adsorbed on Mn/T-Ac and Mn/T-Nit occurred above 320 °C and peaked at temperatures around 430 °C. Mn/TNT-Nit began to desorb elemental mercury only above 400 °C, peaked around 490 °C, indicating that the nanotubular morphology of the support increased the strength of the Hg bond. For all sorbents, there was a complete regeneration for temperatures ≤ 500 °C. Repeating Hg-TPD experiments for the same batch of sorbents after three adsorption tests at different temperatures gave substantially superimposed profiles. It can be argued that mercury was strongly bound to the MnOₓ active phase (by
chemisorption) already at low temperatures, and the thermal regeneration of the sorbents restored the same type of active sites and capture mechanism.

Arrhenius plots for the initial Hg removal rate (not shown) over Mn/T-Ac and Mn/TNT-Nit were obtained from experimental removal data under the assumption of ideal isothermal plug flow reactor [21,22]. The apparent activation energy calculated from the low temperature branch of the Arrhenius plots is estimated at about 45 kJ mol\(^{-1}\) for both Mn/TNT-Nit and Mn/T-Ac. Considering the presence of pore diffusion limitations, the apparent activation energy is halved with respect to that of the intrinsic surface reaction, which, therefore, compares well with the value (ca. 78 kJ mol\(^{-1}\)) for Hg\(^{0}\) adsorption on a MnO\(_2\) (110) surface estimated from first principle calculations [31]. This is consistent with a binding mechanism for Hg-MnO\(_x\) based on chemisorption (or chemical reaction) also when the active phase was dispersed on T and TNT supports.

However, a comparison of the apparent rates of Hg capture per gram of sorbent shows that the process was as much as 8 times faster on Mn/T-Ac than on Mn/TNT-Nit, in spite of the lower BET surface area of the former. In particular, it was previously demonstrated by XPS measurements that Hg was stored on MnO\(_x\) sorbents in an oxidized form [20] 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 [8,9]. Therefore, the higher reactivity of Mn/T-Ac should be associated to the easier reducible Mn\(^{4+}\) sites [8,32] (see Figure 1-a). The increased fraction of Mn\(^{3+}\) in sorbent prepared from acetate precursor appears to facilitate the reduction Mn\(^{4+}/\)Mn\(^{3+}\) increasing oxygen mobility/availability for mercury oxidation.

To sum up, these results showed that both support morphology and Mn-precursor influenced considerably the elemental mercury capture of sorbents. In particular, the use of acetate precursor increased the removal rate in the whole temperature range, most probably due to the occurrence of Mn\(^{4+}\) species easily reducible to Mn\(^{3+}\) already at low temperature [30,33].

**NH\(_3\)-SCR tests**

**Figure 3** presents the results NH\(_3\)-SCR tests performed with Mn/T-Ac, Mn/TNT-Nit and Mn/T-Nit in comparison with a commercial V\(_2\)O\(_5\)-WO\(_3\)/TiO\(_2\) catalyst in the temperature range 50-300 °C. In agreement with several previous reports, Mn-based catalysts displayed significant SCR activity already at low temperatures where the commercial V-based catalyst gave poor performance [17-19,29]: at 150 °C the NO\(_x\) conversion over V\(_2\)O\(_5\)-WO\(_3\)/TiO\(_2\) catalyst was below 15 %, whilst it was ca. 60 % over Mn/T-Ac catalyst, above ca. 22 and 30 % over Mn/TNT-Nit and Mn/T-Nit respectively. Catalysts prepared from acetate precursor displayed a different NH\(_3\)-SCR activity as a function of temperature and showed an optimal catalytic performance in the range between 50-200 °C. At elevated temperature (> 200 °C), the NO\(_x\) conversion of the catalysts decreased: this circumstance reflected the detection in the products of increasing amounts of NO\(_2\) and N\(_2\)O, which, on the other hand were not formed over the commercial vanadium based catalyst [29].

Arrhenius plots for the NH\(_3\)-SCR rate over Mn/T-Ac, Mn/T-Nit and Mn/TNT-Nit were obtained from experimental conversion data under the assumption of ideal isothermal plug flow reactor and first order reaction rate with respect to NO. Comparing the apparent rates of reaction per gram of sorbent, it appears that the process was as much as 5 and 3 times faster over Mn/T-Ac than over Mn/TNT-Nit and Mn/T-Nit respectively. The apparent activation energy was calculated from the low temperature branch of the Arrhenius plots (under kinetic control): all MnO\(_x\)-based catalysts showed similar values of about 40 kJ mol\(^{-1}\), in agreement with literature data. Though being less active, Mn/T-Nit and Mn/TNT-Nit gave a slightly better N\(_2\) selectivity with respect to Mn/T-Ac, indicating a higher oxidation tendency of the latter catalyst, which probably resulted from the higher oxygen availability from MnO\(_x\) species.
**Figure 3.** NO\textsubscript{x} conversion (a) and N\textsubscript{2} selectivity (b) during the NH\textsubscript{3}-SCR over Mn/T-Ac, Mn/TNT-Nit, Mn/T-Ac and a commercial V\textsubscript{2}O\textsubscript{5}-WO\textsubscript{3}/TiO\textsubscript{2} reference catalyst as a function of the reaction temperature. Feed: NO = NH\textsubscript{3} = 400 ppm; O\textsubscript{2} = 8\% vol; Q\textsubscript{t} = 25 NL h\textsuperscript{-1}.

Those results were also confirmed by NH\textsubscript{3}-TPD experiments, during which N\textsubscript{2}O and NO were formed by reaction of adsorbed ammonia and lattice oxygen from the MnO\textsubscript{x} active phase, and released in addition to some residual NH\textsubscript{3}. In fact, the NH\textsubscript{3}-SCR catalytic activity of the samples was directly related to the mobility/availability of oxygen in MnO\textsubscript{x}, which was able to react with adsorbed ammonia.

**Conclusions**

The experimental results reported in this work clearly show that Mn-based catalysts/sorbents are well suited for the low-temperature NH\textsubscript{3}-SCR and for the Hg capture in the temperature range 80-150 °C. Below this range both the NO conversion and the Hg capture efficiency decrease, while above this range the N\textsubscript{2} selectivity decreases. In particular, elemental mercury in flue gas was chemisorbed on the MnO\textsubscript{x} phase and stably stored in an oxidized form, which could be thermally decomposed in air above 320 °C, thus allowing a complete regeneration of the sorbent. The morphology of support (TiO\textsubscript{2} powder vs. TiO\textsubscript{2} nanotubes) was found to have a limited impact on the SCR performance, while the elemental mercury was more strongly chemisorbed when the MnO\textsubscript{x} active phase was supported on TiO\textsubscript{2} nanotubes. Therefore, the influence of the precursor salt (acetate vs. nitrate) was found to be significant. Overall, the MnO\textsubscript{x}-based sorbent prepared from acetate precursor salt shows promising results for the simultaneous low temperature NH\textsubscript{3}-SCR and Hg capture in a tail-end configuration after particle removal and desulphurization units, thus working with relatively clean flue gases. This was explained by the simultaneous presence of Mn\textsuperscript{4+} and Mn\textsuperscript{3+} sites present on this sorbent, which increased the mobility/availability of oxygen in active phases, facilitating NH\textsubscript{3} and Hg oxidation. Acetate aqueous solution promoted a significantly higher MnO\textsubscript{x} dispersion, due to the more acid character of the sorbent for a smaller fraction of Ti\textsuperscript{4+} acid sites.

It should be noticed that according to literature data [20,22,34-36], the critical species for catalyst operation in either processes (low temperature NH\textsubscript{3}-SCR and Hg capture) remains SO\textsubscript{2}, which can irreversibly poison the manganese active phase by forming stable (inactive) sulphate species. This aspect clearly deserves further investigation to bring this catalyst/sorbent to the commercial stage.

**References**


