NANOSTRUCTURED MnO$_x$ CATALYSTS FOR LOW-TEMPERATURE NO$_x$ SCR

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Abstract
Manganese oxides in different structures and morphology have been investigated as catalysts for low temperature SCR by preparing a series of samples by both SCS (Solution Combustion Synthesis) and co-precipitation methods. The samples have been characterized and their catalytic activity tested for NO$_x$ removal in the range of temperature of interest. The different preparation procedures allowed to obtain MnO$_x$ systems with variable average oxidation state that can be put in correlation with the porosity and the morphology and the resulting catalytic performances in the SCR. The presence of Mn$_3$O$_4$ in the resulting material with low degree of crystallinity seemed to be the key factor to get the best catalyst among those prepared, being this phase not only active, but very selective towards the production of N$_2$.

Introduction
Nitrogen oxides are by-products emitted by stationary and mobile sources in high-temperature combustion and constitute well-known atmospheric pollutants that can contribute to the ozone depletion, acids rains, photochemical smog and greenhouse effects [1].

In large stationary applications, the issue of the NO$_x$ removal is accomplished through the post-treatment of the exhaust gases by means of the selective catalytic reduction (SCR) method. The main advantages got from the exploitation of this technology are its high efficiency and its reliability as well as stability of the catalytic reaction, but the high cost represents a considerable drawback as well as the need to have a proper temperature range of effective performances that obliges to place SCR unit. SCR devices could be even employed to perform the abatement of nitrogen oxides in mobile sources after adequate and calibrated system revision and modification.

Research is hence now focused on the development of novel catalysts for the SCR process, which are characterized by low cost and low-T performance. In the last decade different types of catalysts have been developed for low temperature (LT) NH$_3$-SCR [2-4] and MnO$_x$ holds a place of pride because of its lower cost, versatility, environment-friendly nature and, of course, performances. Several works investigated the activity and selectivity in low temperature NH$_3$-SCR of manganese oxides [5,6]. From these studies, it can therefore be concluded that the
SCR activity and the selectivity for nitrogen of unsupported manganese oxides is mainly affected by the Mn oxidation state, the degree of crystallinity and the specific surface area.

In this work, manganese oxides were investigated as catalysts for low-T SCR. Different MnOₓ catalysts were prepared by means of different operating conditions and characterized, as well as tested in the SCR process under lab-scale conditions. The goal was thereafter to understand the suitable Mn oxidation state necessary for SCR performances and to study the nature of active sites.

**Experimental**

For the synthesis of manganese oxides, the route investigated in this work is the comparison between two different methods: Co-precipitation [7] and Solution Combustion Synthesis [8].

Catalysts synthesized by the SCS method are labelled according to the glycine (C₂H₅NO₂)/nitrate (Mn(NO₃)₂) ratio: G1N2 for a glycine/nitrate ratio equal to 1:2 and G2N1 for a glycine/nitrate ratio of 2:1.

Two catalysts were prepared by means of co-precipitation synthesis: the reaction occurred between potassium permanganate KMnO₄ and ascorbic acid C₆H₈O₆ (AA_400) or maleic acid C₄H₄O₄ (AM_600).

All samples prepared were then characterized. X-ray diffraction (XRD) was performed in order to identify the present phases. Field Emission Scanning Electron Microscopy (FESEM) was carried out in order to study the morphology of the crystal aggregates of the materials. BET specific surface area was calculated from the N₂ desorption plots of the catalysts by using a Micromeritics Tristar 3020 analyzer. The reducing capacities of the catalysts have been deeply investigated by means of H₂-TPR analysis of the samples through the use of a TPD/R/O 1100 ThermoQuest instrument. The NH₃-TPD analysis was carried out in the same TPD/R/O apparatus in order to evaluate Bronsted and Lewis acids searching for the interaction between ammonia and MnOₓ porous sites.

The measurements of the SCR activity were performed in a pilot plant under a reacting gas with the following composition: 800 ppm NO, 800 ppm NH₃, 3% O₂, and balance He. The NOₓ concentration was analyzed by means of a NO/NO₂ UV Limas gas analyzer, whereas the N₂O and NH₃ concentrations in a Uras nd-IR gas analyzer.

**Results and Discussion**

The XRD patterns of all samples synthesized are illustrated in Fig. 1. All the peaks identified in the patterns corresponded to MnOₓ phases. In particular the peaks of the G1N2 samples matched well with the standard pattern of Mn₂O₃, whereas the G2N1 and the AA_400 samples presented the characteristic peaks of the Mn₃O₄ phase. The AM_600 sample was the only one showing the characteristic peaks of the MnO₂ phase.
In general, the XRD patterns of the samples obtained by SCS at the lowest temperature revealed a more weakly crystallized structures than the catalysts synthesized at higher temperatures. The difference of crystallinity among the samples was consistent with the values of the BET surface area (not shown here). The G1N2 samples, showing the higher degree of crystallinity, were characterized by very similar BET values (40-50 m$^2$/g). On the other hand, the G2N1 samples showed a significant change in the surface area depending on the synthesis temperature. The samples obtained by the co-precipitation method showed very different behaviours.

The FESEM analysis conducted for the samples obtained by SCS showed large agglomerates of nanoparticles with spherical shape. All samples presented a sponge structure with large alveoli. The samples obtained by means of co-precipitation showed different behaviours: the AM_600 sample was characterized by squared and strongly agglomerated primary particles and the AA_400 sample exhibited a needle-like structure with a marked presence of porosities. The TPR curves of H$_2$-consumption in the range 180-650 °C, temperature range in which the MnO phase is no more reducible under such levels of H$_2$ partial pressure, are illustrated in Fig. 2.

For the samples synthesized at 600 °C the reduction of MnO$_x$ is proved to occur between 370 and 470 °C: the reduction of MnO$_2$ presents two peaks at 365 and 475 °C, the reduction of Mn$_2$O$_3$ exhibits only one peak at 490 °C with a shoulder at a
lower temperature as well as the Mn$_3$O$_4$ phase, with one peak at 520 °C. In the case of the samples constituted by Mn$_2$O$_3$, only the G1N2_600 one showed reduction of the MnO$_x$ phase. The sample G1N2_400 showed two reduction peaks, at 315 °C and 487 °C respectively. Considering the samples G2N1, the average oxidation state was practically equal to 8/3, leading to state that the main phase was Mn$_3$O$_4$. The sample G2N1_600 followed the same trend of the standard sample, characterized by only one peak representing the reducing step Mn$_3$O$_4 \rightarrow$ MnO. The sample G2N1_400 seemed to show the peaks related to the reduction of the γ-MnO$_2$ phase. The AA_400 sample showed a value higher than that of the G2N1 samples and the sample AM_600 reported a value higher than 4, corresponding to the presence of Mn in the +4 oxidation state.

![Figure 2. H$_2$-TPR profiles of the samples: (a) G1N2_400; (b) G1N2_600; (c) AM_600; (d) commercial Mn$_2$O$_3$; (e) G2N1_400; (f) G2N1_600; (g) AA_400; (h) commercial Mn$_3$O$_4$.](image)

The NH$_3$-TPD analysis was performed in order to compare the adsorption properties of the samples prepared by SCS and co-precipitation method and titrate the acid sites. The feature of adsorption capacity is close connected to the surface reactivity of the metal oxide.

Regarding the co-precipitation samples, the AM_600 showed one well-defined peak at almost 140 °C, whereas the AA_400 sample was characterized by the absence of desorption. Among the catalysts obtained by means of SCS, the G2N1_400 sample was the only showing a large and low-intense NH$_3$ desorption peak in the range 120-200 °C. The other catalysts were characterized by a negligible or null desorption of ammonia.
The curves of the catalytic activity are illustrated in Fig. 3.

**Figure 3.** Catalytic activity of the synthesized samples: (a) NO\(_x\) conversion; (b) Selectivity; (c) NH\(_3\) conversion; (d) Selectivity vs NO\(_x\) conversion (red = G1N2_400; dark cyan = G2N1_400; blue = G1N2_600; black = G2N1_600; violet = AA_400; magenta = AM_600).

In general, the results showed that all samples synthesized by SCS showed a good performance in a sufficient range at low temperatures as well as the AA_400 sample does. Conversely, AM_600 showed a very poor NO\(_x\) conversion (max 5%). The selectivity to N\(_2\) obtained in the range from 120 to 300 °C seemed to be the highest among all samples. In Fig. 5d the selectivity vs conversion graph dramatically revealed the scarce interest that we can give to the AM_600 catalyst. However, all other investigated catalysts are active in the temperature range 120-350 °C and therefore can be considered suitable for working at low temperature region of SCR process. More specifically, the NO\(_x\) conversion data showed that the G2N1_400 sample presented the highest values, the best N\(_2\)-selectivity and also the best behaviour in the selectivity vs NO\(_x\) conversion graph, with a higher and wider curve. All the curves followed the same trend, where the conversion presented a maximum and subsequently decreased obtaining a bell curve on the graph.

The oxidation state of manganese was the main element that governed the N\(_2\)O selectivity during the oxidation reaction of NH\(_3\) on the manganese oxides catalysts. The higher selectivity to N\(_2\)O was obtained over samples characterised by higher values of Mn average oxidation state, in particular it seemed that the Mn\(_3\)O\(_4\) phase could give benefits to the activity with respect to the other MnO\(_x\) phases synthesized.
From the conversion curves, it can be deduced for the samples synthesized by SCS that the increased surface area led to higher catalytic activity at low temperatures. In fact, the G2N1_400 sample showed the highest value of SSA and the conversion is 100% in a wide range at low temperatures.

Actually, the comparison between G2N1_400 and AA_400 samples was particularly interesting, because they should be characterised by the same MnO$_x$ phase and almost the same specific surface area, but the co-precipitated sample showed a lower NO$_x$ conversion and a lower selectivity, demonstrating that the synthesis method is strongly affecting the catalytic performance.

**Conclusions**

Manganese oxides prepared in different structures and morphology generally confirmed to possess very interesting properties for Low-Temperature SCR of nitrogen oxides. The presence of Mn$_3$O$_4$ in the catalyst seemed to be the key factor to get the active and, most of all, selective sample. The crystallinity degree also played a relevant and obvious role, because too crystalline catalysts with low surface area perform much worse than more amorphous sample.

**References**


doi: 10.4405/39proci2016.IV1