Mn-Ce-Fe/TiO$_2$ catalysts for NOx SCR at low temperature

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Highlights

- Mn-Ce-Fe systems supported on TiO$_2$ were developed for low temperature NO$_x$ SCR.
- Different compositions of active oxides and titania phases as support were tested.
- The Mn-Ce system showed a complete conversion in a wide range of temperature.

1. Introduction

Nitrogen oxides are among the most dangerous by-products emitted by stationary and mobile sources in high-temperature combustion processes and constitute well-known atmospheric pollutants that can contribute to the ozone depletion, acids rains, photochemical smog and greenhouse effects. Selective Catalytic Reduction (SCR) is considered a very effective and established technique for the abatement of nitrogen oxides (NO$_x$). It allows converting NO$_x$ into nitrogen (and water) by introducing ammonia (or urea) in the exhausted gases. The current commercial catalysts (e.g. V$_2$O$_5$/TiO$_2$) show high activity and selectivity in the temperature range 300–400 °C. It follows that a further considerable research effort for SCR catalysts efficient at low temperatures is required.

Manganese oxides-based catalysts have been studied in the last years for NO$_x$-SCR because of their versatility, eco-compatibility and the presence of labile oxygen species. They showed excellent low-temperature performance in the SCR of NO$_x$ with ammonia, both unsupported and loaded on different supports [1]. Among the various Mn-supported catalysts, MnO$_x$/TiO$_2$ is the most widely studied system. Several components have been added to Mn-based catalysts in order to improve some lacking features of MnO$_x$/TiO$_2$ catalysts. It was reported that the addition of CeO$_2$ allowed to improve the oxygen mobility and the concentration and distribution of acid sites [2]. Furthermore, the bimetallic system Mn-Fe was proved to significantly enhance the activity [3].

In the present study, bimetallic and trimetalllic Mn-Ce-Fe catalysts were supported on different titanium oxides (micrometric anatase, rutile and nanostructured mixture), since the trimetalllic system as well as different titania supports are an original subject of investigation. The active oxides, for a total amount of 15 wt% of metals, were deposited on TiO$_2$ supports by means of Incipient Wetness Impregnation method and the catalysts were physico-chemically characterized and investigated for low-T SCR.

2. Methods

MnO$_x$, CeO$_2$ and Fe$_2$O$_3$, were deposited on commercial anatase TiO$_2$, commercial rutile TiO$_2$ and nanostructured rutile-containing anatase TiO$_2$, synthesized by a Gel Combustion method [4]. The catalysts were prepared with the Incipient Wetness Impregnation (IWI) method by using Manganese(II) nitrate Mn(NO$_3$)$_2$ tetrahydrate, Cerium(III) nitrate Ce(NO$_3$)$_3$ hexahydrate and Iron(III) nitrate Fe(NO$_3$)$_3$ nonahydrate as precursors. The catalyst powders, after grinding in an agate mortar, were calcined in air at 500 °C for 1h to remove the nitrate ions.

The catalysts were characterized by means of X-ray powder diffraction (XRD), H$_2$ temperature programmed reduction (H$_2$-TPR) and NH$_3$ temperature programmed desorption (NH$_3$-TPD), N$_2$ physisorption at 77 K (BET surface area and pore volume), Field Emission Scanning Electron Microscopy (FESEM), X-ray Photoelectron Spectroscopy (XPS) and Ion Coupled Plasma (ICP-MS). The catalytic activity of the prepared catalysts was analyzed feeding a gas mixture, composed by 500 ppm NO$_x$, 500 ppm NH$_3$, 3% O$_2$ and He to balance, to a catalytic fixed-bed micro reactor. The gas hourly space velocity (GHSV) through the catalytic bed was about 50000 h$^{-1}$. The NO$_x$ concentration was analyzed by means of a NO/NO$_2$ UV Limas gas analyzer, whereas the NH$_3$ and N$_2$O concentrations in a Uras nd-IR gas analyzer. The outlet gas stream
composition was monitored as a function of the bed temperature in isothermal conditions, increasing it from 75 to 350 °C.

3. Results and discussion
The behaviour of the catalytic activity is illustrated in Fig. 1a in terms of NO\textsubscript{x} conversion. As can be noticed, the addition of other metals to manganese allowed to significantly improve the SCR catalytic activity. The bimetallic and trimetallic catalysts showed from sufficient to considerable catalytic activity, with NO\textsubscript{x} conversion varying from 70 to 100% in a wide range of temperature. The most performing catalysts were those containing CeO\textsubscript{2}, in the bimetallic Mn-Ce system supported on all the different kind of TiO\textsubscript{2} (red curves), and in the trimetallic Mn-Ce-Fe system supported on rutile TiO\textsubscript{2}. In particular, the Mn-Ce/ANA and Mn-Ce/NANO catalysts showed NO\textsubscript{x} conversion higher than 95% in a temperature range of 100 °C, from 150 to 250 °C. The rutile phase seemed to improve the catalytic activity at low temperature, with the Mn-Ce/RUT showing almost complete conversion from 125 °C. Due to its mixed composition, the nanostructured TiO\textsubscript{2} support allowed to achieve a very large range of conversion from low to medium temperatures. These catalysts showed sufficiently N\textsubscript{2} selectivity up to 150-200 °C (see Fig. 1b), where the competitive NH\textsubscript{3} oxidation increased the amount of N\textsubscript{2}O produced. In particular, the bimetallic Mn-Ce system supported on nanostructured titania showed a N\textsubscript{2} selectivity higher than 50% for all the range of temperature considered. In the complete work, we have tried to correlate the catalytic activity of such catalysts with their physic-chemical properties, analyzed with the characterization techniques previously described, stressing that the catalytic activity was remarkably improved by the presence of the rutile phase in the TiO\textsubscript{2} support and by the wideness of the specific surface area and pore volume of the support, by its higher reducibility, and higher amount of superficial acid sites and finally by the higher content of Mn\textsuperscript{4+} and Ce\textsuperscript{3+} on the surface.

![Figure 1](image_url) SCR catalytic activity: (a) NO\textsubscript{x} conversion and (b) N\textsubscript{2} selectivity.

4. Conclusions
In conclusion, Mn-Ce-Fe systems supported on different kind of TiO\textsubscript{2} appeared very promising for the SCR catalytic reaction of NO\textsubscript{x} at low temperature. The Mn-Ce bimetallic system seemed to be the most suitable by loading on all the supports, reaching the complete NO\textsubscript{x} conversion in a range of 100 °C from low to medium temperature, and at the same time showing a sufficient level of N\textsubscript{2} selectivity, with values higher than 80% at the point of maximum conversions. The catalytic activity was demonstrated to be affected by TiO\textsubscript{2} phase and specific surface area, reducibility and superficial acid sites and content of Mn\textsuperscript{4+} and Ce\textsuperscript{3+}.

References

Keywords
Selective Catalytic Reduction; Manganese oxide; Low-temperature activity; Cerium oxide.