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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_2O_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 trimetallic Mn-Ce-Fe catalysts were supported on different titanium oxides (micrometric anatase, rutile and nanostructured mixture), since the trimetallic 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_2O_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_2O 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_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_x conversion varying from 70 to 100% in a wide range of temperature. The most performing catalysts were those containing CeO_2, in the bimetallic Mn-Ce system supported on all the different kind of TiO_2 (red curves), and in the trimetallic Mn-Ce-Fe system supported on rutile TiO_2. In particular, the Mn-Ce/ANA and Mn-Ce/NANO catalysts showed NO_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_2 support allowed to achieve a very large range of conversion from low to medium temperatures. These catalysts showed sufficiently N_2 selectivity up to 150-200 °C (see Fig. 1b), where the competitive NH_3 oxidation increased the amount of N_2O produced. In particular, the bimetallic Mn-Ce system supported on nanostructure titania showed a N_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_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^{4+} and Ce^{3+} on the surface.

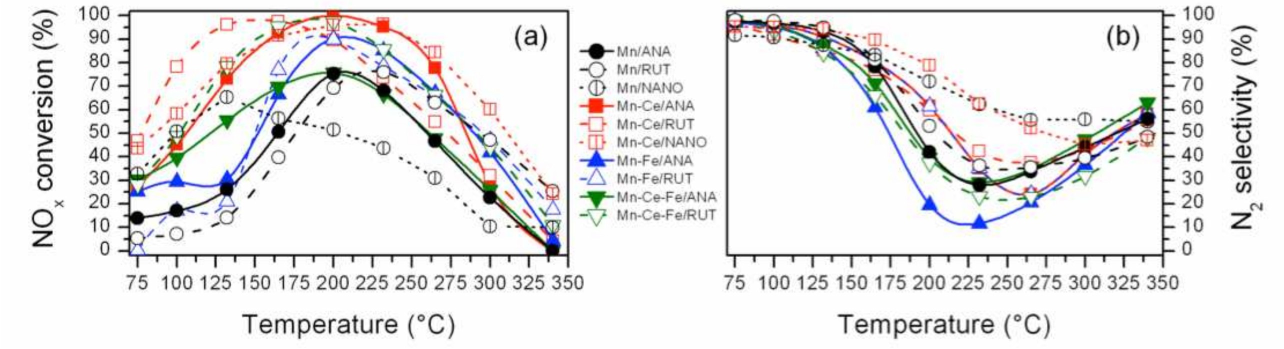

Figure 1 SCR catalytic activity: (a) NO_x conversion and (b) N_2 selectivity.

4. Conclusions

In conclusion, Mn-Ce-Fe systems supported on different kind of TiO_2 appeared very promising for the SCR catalytic reaction of NO_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_x conversion in a range of 100 °C from low to medium temperature, and at the same time showing a sufficient level of N_2 selectivity, with values higher than 80% at the point of maximum conversions. The catalytic activity was demonstrated to be affected by TiO_2 phase and specific surface area, reducibility and superficial acid sites and content of Mn^{4+} and Ce^{3+}.

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