Doped cobalt hydrotalcites as NO$_x$ storage/reduction catalysts

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Introduction

One of the principal environmental concerns in air pollution is the minimization of NO$_x$ emissions coming mainly from mobile sources. Nowadays the tendency is to use engines with better fuel efficiency, as lean-burn gasoline and diesel engines that works with an excess of oxygen over the stoichiometric ratio, i.e. lean conditions. These operation conditions strongly diminish the efficiency of the traditional three way catalysts, for this reason the discovery of an alternative technology which can achieve efficient NO$_x$ reduction at high oxygen concentrations, without increasing fuel consumption, is an imperative need [1]. In the last years a new alternative has appeared that it is attracting much attention, this is the NO$_x$ storage/reduction (NSR) technology. It is based in the selective storage of the NO$_x$ as nitrates under lean (oxidizing) conditions and their non selective reduction under the short, rich (reducing) excursions. NSR catalysts are typically composed of at least one basic compound (alkaline or alkaline-earth oxides) and at least one precious-metal component. One of the most common formulation is Pt and Ba supported on Al$_2$O$_3$ [2-5]. The problem of this material is its fast poisoning by sulphur compounds and its low activity at low temperatures and the price of the noble metals. In this work it is studied the possibility of using other materials, such as cobalt-magnesium-aluminum hydrotalcites, doped with transition (non noble) metals, as the base for an active and stable NSR catalyst.

Materials and Methods

Hydrotalcites were prepared by a standard co-precipitating procedure according to [3]. The hydrotalcites were calcined at 650ºC in air for 3 h before reaction, obtaining a mixed oxide. Some samples were impregnated with salts of other transition metals and calcined at 550ºC for 6 hours. The reaction experiments were carried out in a fixed bed, tubular reactor. In the experiments 1g of catalyst, as particles of 0.25-0.42 mm, was introduced in the reactor and was heated up to 450ºC under nitrogen flow. At this temperature the flow was maintained for 2 hours. After that, the desired reaction temperature was set and the reaction feed admitted. This consists of 650 ml.min-1 of a mixture composed by NO, C$_3$H$_8$, oxygen and balanced with nitrogen. In order to simulate the lean-rich cycles of the engine, during 2 minutes we perform a lean cycle (oxidizing) and during 1 min. a rich cycle (reducing), making a total of 7 cycles at different temperatures in any experiment. The NO$_x$ present in the gas were analyzed continuously by means of a chemiluminescence detector.

Results and Discussion

We have compared the activity for the NO removal of the catalysts based on Mg/Al hydrotalcite containing different cobalt content. The catalysts remove the NO quite efficiently during the lean period, adsorbing the NO$_x$ as nitrates, but the activity falls during the rich period. In all range of the temperatures tested (100, 200, 300 and 450ºC) the best catalyst activity was achieved with the hydrotalcite containing a 15 % wt of cobalt. Nevertheless it is necessary to improve the redox and the acid-base properties of this material. For this reason it was study the possibility of doping this hydrotalcite by adding 1% wt of a transition metal with redox properties, as Pt, Pd, Ru or V on the hydrotalcite. The activity of the material improves two times if compared with the activity of the hydrotalcite only with cobalt. Comparing the activity of the different doped catalysts, we chose the vanadium doped catalyst as the most convenient because the good activity results obtained, the price and the resistance of this metal to potential poisons as sulphur dioxide and water.

Nevertheless in order to improve the activity at low temperatures during the lean cycles, it is necessary to add more basicity to the system, this can be achieved by adding sodium to the hydrotalcite. This material shows a high and stable activity in all the reaction conditions tested, being active even at 100ºC in the presence of H$_2$O and SO$_2$. The catalytic activity of this material was compared with that of a Pt-Ba/Al$_2$O$_3$ reference catalyst, obtaining better results with the doped cobalt hydrotalcite at lower temperatures. This is due to the adequate combination of the cobalt-vanadium redox properties and the magnesium- sodium basic properties, together with the sulphur tolerance of this material. After reaction the material was characterized by infrared, N-elemental analysis and XRD and the results were related with those obtained in the catalytic tests.

The results obtained from this work, suggest that catalysts based in cobalt hydrotalcites are a feasible option as NO$_x$ storage/reduction catalysts, being the most prospective catalysts those based in Mg/Al hydrotalcites containing 15% cobalt in the composition. In order to improve the redox characteristics of these materials is convenient to dope the material with1% wt of a transition metal with redox properties, as vandium and to add sodium to the hydrotalcite for improving its base characteristics.

Significance

This research fits in the topic of catalytic diesel vehicle emission control. The results show the possibilities of using a material with basic properties, as hydrotalcites, doped with a non noble metal with redox properties as an active NSR catalyst. This is very significant because the good results obtained using a low-price material.

References

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