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Investigation of the catalytic performances of supported noble metal based catalysts in the NO + H_2 reaction under lean conditions

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Abstract

This paper compares the catalytic performances of various supported palladium and platinum catalysts on a conventional γ-Al_2O_3, and $LaCoO_3$ perovskite that exhibits peculiar redox properties in the reduction of NO by hydrogen under lean conditions. A particular attention has been paid towards the catalytic behaviour of noble metals at low temperature, mainly below 120 °C. Clearly, their catalytic properties in the selective reduction of NO into N_2 strongly depend on the feed gas composition, and on the nature of the support. In that temperature range, Pt/Al_2O_3 exhibits the better activity, unfortunately undesirable N_2O is predominantly formed. The most prominent results have been obtained on Pd/$LaCoO_3$ because H_2O promotes the reduction of NO without affecting the selectivity behaviour, whereas a strong inhibiting effect on the rate of NO transformation into N_2 is observed on Pd/Al_2O_3. Such differences in the catalytic behaviour of palladium could be related to different interactions between Pd and $LaCoO_3$ generated during the activation thermal treatment under reductive atmosphere.

Keywords: Noble metals; NO reduction; N_2O selectivity; $LaCoO_3$ perovskite

1. Introduction

Presently, the selective reduction of nitric oxides (NO_x) using ammonia as reducing agent is widespread through the world, this technology being the most powerful for reducing selectively NO into N_2 under lean conditions between 200 and 400 °C. On the other hand, at higher temperature, the competitive oxidation of NH_3 usually takes place. Furthermore, restrictive standard regulations on the emissions of atmospheric pollutants should concern an increasing number of industrial plants. Hence, the implementation of these new restrictions should generate significant improvements on the performances of the existing catalytic exhaust systems. The reduction of nitric oxide under lean conditions using ammonia as reducing agent on typical vanadia-titania based catalysts is less efficient for low temperature exhaust gases. In that particular case, the catalytic reduction with hydrogen seems to be a promising technology, although H_2 is usually recognised as none selective. In addition, the formation of undesirable N_2O usually predominates. Recent investigations [1–4] show that supported noble metal based catalysts can profitably be used for reducing more selectively NO into N_2 in the presence of O_2. It is found that the extent of interaction between the metal and the support governs the activity and the selectivity behaviour of noble metals. The most significant results have been obtained on Pt that usually exhibits poorer efficiency than Rh in the dissociation of NO [1].

This paper reports a study on the influence of oxygen and water on the catalytic performances of Pd and Pt supported on $LaCoO_3$ and alumina. This comparison shows that the use of palladium supported catalysts has to be considered, especially when $LaCoO_3$ is used as support.

2. Experimental

$LaCoO_3$ perovskites were prepared using a so-called sol–gel method involving a citrate route [5]. Aqueous solutions of $La(NO_3)_3·6H_2O$ (Fluka) and $Co(NO_3)_2·6H_2O$ (Fluka)

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were mixed with a solution of citric acid (Fluka) with a molar citric acid/(La + Co) ratio of 1. After evaporation the gel thus obtained was dried overnight. Finally, the resulting material was calcined in flowing air at 600 °C for 5 h for obtaining the rhombohedral structure of $LaCoO_3$. The supported noble metal based catalysts were prepared according to a conventional wet impregnation method using palladium nitrate and hexachloroplatinic acid solutions with adjusted concentrations in order to obtain 1 wt.% Pt or Pd. After impregnation on γ-alumina (100 $m^2\ g^{-1}$) and $LaCoO_3$ (20 $m^2\ g^{-1}$), the samples were calcined in air at 400 °C for 2 h, and then reduced at 250 or 500 °C in pure H_2.

The structural properties were studied by XRD on a D5000 diffractometer using Cu Kα (λ = 1.54056 Å) radiation. Temperature-programmed reduction (TPR) was carried out in a Micromeritics Autochem II 2920. Surface compositions were obtained by XPS analyses using a Leybold Heraeus spectrometer. Binding energy levels were referenced to the C 1s binding energy level at 285 eV. Catalytic performances were evaluated from temperature-programmed experiments performed in a fixed-bed flow reactor between 25 and 500 °C with a constant heating rate of 2 °C min^{-1}. Typically, the mass of catalyst was 0.7 g and the global flow rate was adjusted in order to obtain a space velocity of 4000 h^{-1}. The effluents were analysed by a Balzers mass spectrometer and a HP 5890 series II chromatograph fitted with a thermal conductivity detector. Before quantification, products and reactants were separated on a CTR1 column from Alltech.

3. Results and discussion

3.1. *Physico-chemical properties of $LaCoO_3$ before and after subsequent addition of noble metals (Pt and Pd)*

Fig. 1 illustrates structural changes of $LaCoO_3$ during H_2 exposure from room temperature to 800 °C. The X-ray diffraction pattern recorded on $LaCoO_3$ at 20 °C exhibits the characteristic X-ray lines of the typical rhombohedral structure usually stabilised at room temperature with the most intense diffraction lines located at 2θ = 32.9°, 33.3° and 47.5° (see JCPDS data no. 48-0123). No significant contributions related to bulk Co_3O_4 and La_2O_3 phases are detectable. The specific area of 20 $m^2\ g^{-1}$ is approximately one order of magnitude higher than those previously reported on solids obtained via a sol–gel method and calcined at a significant higher temperature of 800 °C [6]. As observed in Fig. 1, $LaCoO_3$ is unstable under reducing atmosphere at high temperature. Such typical modifications have been earlier explained in the literature [7,8]. Below 300 °C, the structural properties of $LaCoO_3$ are preserved. On the other hand, a significant shift in location of the main X-ray lines of $LaCoO_3$ occurs in the range 300–500 °C parallel to appearance of additional contributions at 2θ = 31.5° and 32.5°. Above 500 °C, extensive reduction of $LaCoO_3$, evidenced by the development of X-ray lines characteristic of La_2O_3 at 2θ = 26.2°, 29.2°, 30°, 39.6°, 46.2°, 52.3°, 55.5° and bulk detectable metallic Co crystallites at 2θ = 44.2°, takes place. According to the literature data [8,9], XRD observations suggest that $LaCoO_3$ does not reduce directly to Co and La_2O_3, but probably via the intermediate formation of oxygen-deficient compounds. Also, the formation of La_2CoO_4 cannot strictly be ruled out. Such statements are supported by additional temperature-programmed reduction experiments (Fig. 2). The hydrogen consumption profile of $LaCoO_3$ in Fig. 2(a) exhibits two ranges between 200–500 and 500–730 °C with atomic H/Co ratio of, respectively, 0.98 ± 0.02 and 2.04 ± 0.02 which highlight a two-step reduction process involving the intermediate formation of Co^{2+}. Both information could be explained by the formation of an oxygen-deficient perovskite that could act as intermediate in the overall reduction process, or alternately, by different reaction paths involving the intermediate

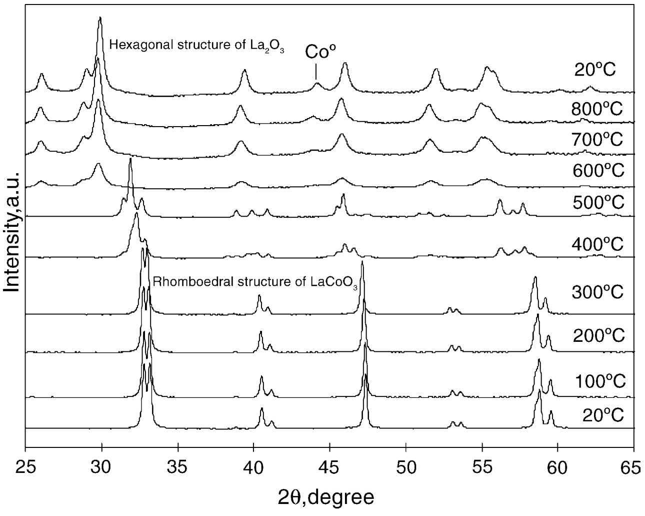

Fig. 1. XRD analysis of $LaCoO_3$ at various temperatures under pure H_2.

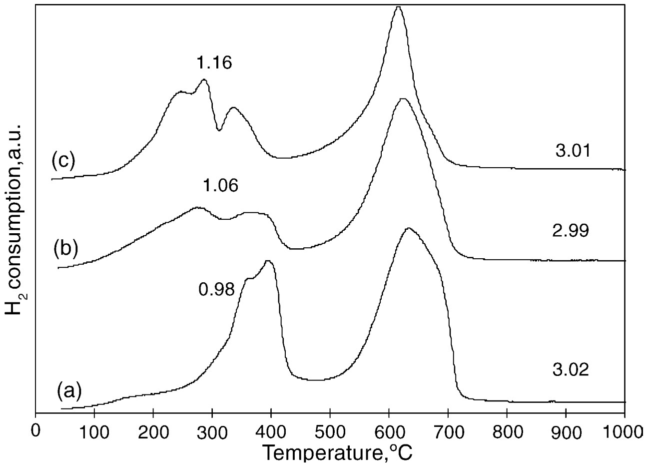

Fig. 2. Temperature-programmed reduction of $LaCoO_3$ (a), Pd/$LaCoO_3$ (b) and Pt/$LaCoO_3$ (c) in 5 vol.% H_2 diluted in He.