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Co and Ni ferrospinels as catalysts for propane total oxidation

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ABSTRACT

Co and Ni ferrospinels were prepared by coprecipitation and by mechano-chemical method, characterized using XRD, N_2 adsorption, EDX and H_2-TPR techniques and tested in the catalytic total oxidation of propane within the temperature range of 250–600 °C. Depending on the ferrospinel composition, the method of preparing it and the reaction conditions, total conversion to CO_2 was observed at temperatures between 400 °C and 500 °C. The best results were obtained with the Co ferrite catalyst prepared by coprecipitation, which gives total conversion at temperatures as low as 400 °C. The ferrospinel catalysts showed a good stability during the catalytic test.

1. Introduction

Volatile organic compounds (VOC) emitted during many industrial processes and transport activities contribute significantly to the atmospheric pollution, they being associated with the increase in photochemical smog, depletion of stratospheric ozone and the production of ground-level ozone [1]. One of the most effective and economically attractive methods of their neutralization is the catalytic total oxidation to carbon dioxide and water [2]. When large gas volumes have to be treated, catalytic total oxidation has to be performed at very high space velocity requiring a very active catalyst. Alkanes are amongst the most prevalent environmental VOC emissions due to their use as transportation fuels as well as being essential feedstocks for chemicals production. Although alkane oxidation leads to CO_2, another greenhouse gas, this can be readily absorbed whereas alkanes cannot. On the other hand, the difficulty in destroying light alkanes by catalytic total oxidation, since they are very difficult to activate, makes them excellent model compounds to test the efficiency of catalysts for VOC combustion, as the catalytic combustion of most organic compounds would be ensured if light alkanes are quantitatively abated.

Seventy-five percent of the catalysts used for VOC destruction are precious metal catalysts, generally supposed to be more active than metal oxide catalysts [3]. Nevertheless they have some disadvantages like high sintering rates, volatility, poisoning in presence of water or sulfur compounds and high price [4]. On the other hand, metal oxides have certain advantages, like price, high thermal stability, higher resistance to poisoning and the easy way of preparation, and they appear to be a promising solution [5]. Moreover, it was recently shown [3] that metal oxides are not necessarily less active than noble metals.

In recent years, many efforts were directed towards the design of catalytic materials based on simple and mixed transition-metal oxides as a replacement for noble metal catalysts. Nevertheless, to our knowledge, there are no studies investigating Ni and Co ferrospinels as catalysts for lower alkanes total oxidation but, on the other hand, Co ferrite based catalysts were shown to be effective for the total oxidation of chlorobenzene [6] and Ni ferrite, for CO oxidation [7,8].

In this paper, we present a study of Co and Ni ferrospinels, prepared by coprecipitation or by mechano-chemical method, used for the first time as catalysts for total oxidation of propane.

2. Experimental

2.1. Catalysts preparation

Two types of methods have been used to prepare the catalysts. The first one (M1) has been applied to the synthesis of both Ni and Co ferrites. It was based by the coprecipitation of metal hydroxides from a stoichiometric mixture of 1 M solution of ferric nitrate and 1 M solution of other nitrates, using 1 M solution of sodium hydroxide as the precipitating agent. The pH of the final slurry was carefully adjusted to 10. The precipitate was kept 72 h in its mother liquor under stirring for ageing with the aim of obtaining a more organized material, and washed free of nitrate ion and alkali. It was then filtered, dried at 60 °C for 72 h and at 80 °C, 100 °C and 120 °C for 1 h at each temperature and calcined at 200 °C,

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300 °C, 400 °C and 500 °C for 1 h at each temperature and at 650 °C for 2 h to achieve transformation into spinel phase.

The second method (M2), known as the mechano-chemical method, has been used for the preparation of $CoFe_2O_4$ only. A stoichiometric mixture of corresponding crystalline metal nitrates, $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$, was grounded in a mechanical mortar until the salts were dissolved in their crystallization water and, after that, crystalline ammonium carbonate was added in the mortar until a paste was formed. Finally it was calcined at 200 °C, 300 °C, 400 °C and 500 °C for 1 h at each temperature and at 650 °C for 2 h.

2.2. Catalysts characterization

The samples' structure, before and after the catalytic test, was investigated by X-ray diffraction (XRD) method. XRD patterns were recorded over the 10–70° angular range with a 0.02° step and an acquisition time of 1 s per point, with a DRON-2 diffractometer equipped with a Cu Kα source ($\lambda = 1.54$ Å).

The chemical composition of the samples was determined by EDX microprobe on a Cambridge Stereoscan 260 apparatus. Accelerating voltage of 20 kV was used.

The textural characterization of the catalysts, before and after the catalytic test, was achieved using conventional nitrogen adsorption/desorption method, with a Micromeritics ASAP 2000 analyzer. Specific surface areas were calculated using the BET method. Prior to nitrogen adsorption, the samples were outgassed for 3 h at 105 °C.

Hydrogen temperature-programmed reduction (TPR) studies were carried out using a Micromeritics Autochem model 2910 instrument. Fresh calcined samples (100 mg), placed in a U-shaped quartz reactor, were pretreated in air at 600 °C before reduction. After cooling down to room temperature and introducing the reduction gas of 3% H_2/Ar, the sample was heated at a rate of 10 °C/min from room temperature to 1000 °C. The hydrogen consumption was estimated from the area under the peak after taking the thermal conductivity detector response into consideration. Calibration of TCD signal has been done with an Ag_2O standard (Merck, reagent grade).

2.3. Catalytic testing

The catalytic total oxidation of propane was carried out in a fixed bed quartz tube down-flow reactor operated at atmospheric pressure. The internal diameter of the reactor tube was 18 mm. The catalyst was supported by quartz wool. The reactor temperature was controlled using a thermocouple attached to the exterior of the reactor. The axial temperature profile was measured using an electronic thermometer placed in a thermowell centered in the catalyst bed. This was the reaction temperature reported in the present paper. Quartz chips were used to fill the dead volumes before and after the catalyst bed to minimize potential gas-phase reactions at higher reaction temperatures. The reaction mixture consisted of 2 vol.% propane in air. Flow rates were controlled by fine needle valves and were measured by capillary flow-meters. Total volume hourly space velocities (VHSV) of 6000 and 11,000 h^{-1} were used, in the temperature range of 250–600 °C. In a typical reaction run, the reactor containing 1 cm^3 of catalyst was heated to the desired temperature in the flow of reactants. The system was allowed to stabilize for about 1 h at the reaction temperature before the first product analysis was made. Each run was carried out over a period of 2–3 h, until two consecutive analyses were identical. The reaction products were analyzed in a Clarus 500 Gas-Chromatograph equipped with a thermal conductivity detector (TCD) using an alumina column and a flame ionization detector (FID) using a CTR I column.

The conversion was calculated as the amount of raw material transformed in reaction divided by the amount that was fed to the reactor. Complete selectivity to CO_2 and H_2O was always observed.

3. Results and discussion

3.1. Catalysts characterization

The X-ray diffraction (XRD) patterns of the three ferrite samples are displayed in Fig. 1. For all the solids, reflections corresponding to crystallized ferrospinel structure were observed: cubic $CoFe_2O_4$ (PDF # 221086) and cubic $NiFe_2O_4$ (PDF # 100325) for Co-ferrite and Ni-ferrite samples, respectively. An additional weak signal observed at ca. 33° (marked with an asterisk), for $CoFe_2O_4$ samples, could be indicative of the presence of a tiny amount of α-Fe_2O_3 phase (PDF # 840309) as already observed by Lavela et al. [9]. It can also be observed that the degree of crystallinity of the Co ferrite-M2 sample was higher than that corresponding to Co ferrite-M1 sample, which was higher than that of the Ni ferrite-M1 sample.

The compositions of the ferrospinel samples were checked by EDX analysis and there was good agreement between the experimental and theoretical values (Table 1).

The physico-chemical characteristics of the catalysts are presented in Table 1. The specific surface areas were relatively high, in particular for the samples prepared using the M1 method, and varied in line with the observed crystallinity of the samples: lower the crystallinity, higher the specific surface area. As expected, the pore volume of the samples also decreased with increasing the crystallinity. All materials displayed type IV nitrogen adsorption/desorption isotherms, according to the BDDT classification [10], with a hysteresis loop of type H3, characteristic of materials with

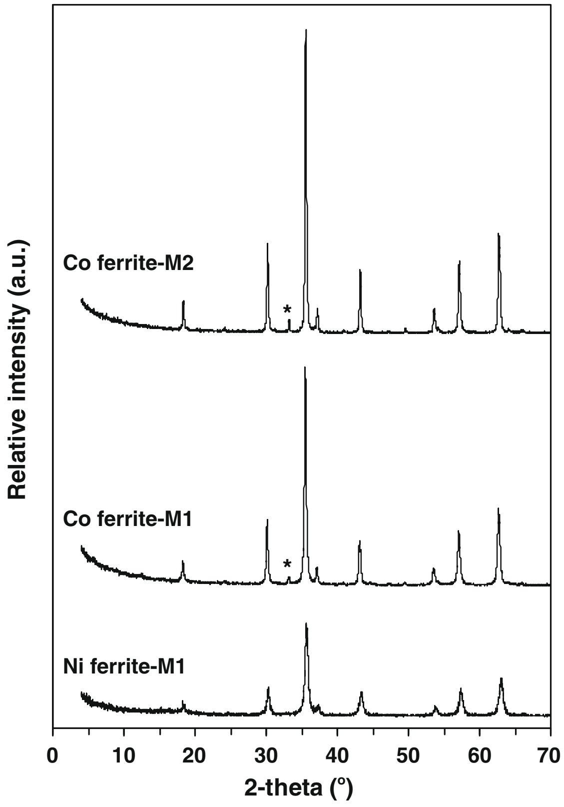

Fig. 1. XRD patterns of the Co and Ni ferrite catalysts (* – α-Fe_2O_3 phase).