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Effect of water vapor over Pd–Co/SZ catalyst for the NO selective reduction by methane

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Abstract

The selective catalytic reduction (SCR) of NO by CH_4 in the presence of excess O_2 has been studied on Pd–Co, Pd and Co catalysts supported on sulfated zirconia (SZ) and activated in reaction mixture at 700 °C. After the addition of Co on Pd/SZ, an promoting effect on the catalytic activity was achieved, especially on 0.2%Pd–2%Co/SZ, which showed the maximum NO conversion higher 60% at 500 °C and 31,000 h^{-1}. The bimetallic catalyst presented practical activity in the presence of water vapor. Stable NO_x conversion was obtained for over 50 h in the presence of 6% water vapor. In order to correlate the catalysts composition with their activity, they were characterized by X-ray diffraction (XRD), diffuse reflectance spectroscopy (DRS) and temperature programmed reduction (TPR) techniques.

Keywords: NO reduction; Methane; Sulfated zirconia; Water tolerance

1. Introduction

The selective reduction of nitrogen oxide with hydrocarbons (HC) is one of the most promising technologies to control NO_x emissions in fixed sources, where it represents an alternative for ammonia used as reducer, as well as in mobile sources that operate with high air/hydrocarbon ratio. Zeolitic catalysts of the Pd/MOR, Pd/ZSM-5, and Co/FER type have been demonstrated to be active for the selective reduction of NO by light hydrocarbons, although they are not stable in the reaction conditions (water vapor, high temperatures, sulfur presence) resulting to be inadequate for practical applications. The activity decrease when water is present in the gas stream, has been attributed to structural modifications of the zeolitic material as well as to the sintering of the metallic phase. In the Pd zeolite catalysts, Ohtsuka and Tabata [1] have determined that the water vapor promotes the Pd agglomeration, thus deactivating the catalyst. There exists evidence [2] that the activity and the selectivity in the SCR of NO are not only a function of the metallic phase but also of the support acidity. Tests of different acid supports in mechanical mixtures with Pd/SiO_2 [3] demonstrated that sulfated zirconia is one of the most effective materials to promote the Pd activity in the SCR of NO by methane. According to the exposed considerations, the Pd catalyst supported on SZ is presented as an important alternative to replace zeolitic catalysts since it shows comparable catalytic properties and higher stability in sulfur presence, although it does not overcome completely the problem of deactivation by water vapor. Inui et al. [4] reported that a protonated Co-contained silicate was effective for NO reduction with methane in 10% water presence

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in the feed. Since Co/zeolite has also shown to be active for the selective reduction of NO by methane [5] and with the intention of stabilizing the Pd, a multimetallic system based on Co and Pd supported on sulfated zirconia (SZ) was prepared to explore its possibilities in the selective reduction of NO_x by hydrocarbons, containing water vapor in the feed.

In this work, the effect of water vapor on the Pd–Co/SZ system was analyzed and compared with the monometallic systems, Pd/SZ and Co/SZ, for the selective reduction of NO by methane in excess oxygen.

2. Experimental

2.1. Preparation of sulfated zirconia

The sulfated zirconia was prepared by the method known as two steps since in a first stage zirconium hydroxide is prepared, $Zr(OH)_4$, and in a second stage sulfate is used for impregnation, thus obtaining the sulfated zirconium, (SZ). The $Zr(OH)_4$ was prepared from zirconium oxychloride [6]. NH_3 was slowly added (28–30%) to a solution of 100 ml 0.4 M of $ZrOCl_2$, under stirring at 32 °C. Then, the solution was settled at rest for 24 h at room temperature, filtered and washed to remove Cl^- ions. It was left for evaporation at room temperature for 48 h, then, it was dried in a furnace at 100 °C for 2 h. The obtained zirconium hydroxide was sulfated by adding a measured volume of 0.5 M H_2SO_4 solution, so as to reach the equivalent to 5 ml of pure H_2SO_4 per gram of zirconium hydroxide. This process was performed under mechanical stirring ("shaker"), and maintained for 1 h. Afterwards, the solid was separated by filtration and dried for 3 h at 70 °C. Then, it was calcined in air at 550 °C for 3 h.

2.2. Preparation of catalysts

The Pd was added to the prepared support ($Sg = 140$ $m^2\,g^{-1}$, $Vp = 0.21$ $cm^3\,g^{-1}$, $rp = 3.3$ nm), using the inorganic salt $(NO_3)_2Pd \cdot 2H_2O$ (Merck) as precursor. For this, an adequate amount of Pd salt was dissolved in 10 cc water, so as to obtain a final metal charge equal to 0.18% wt/wt. This solution was added on the sulfated zirconia by stirring mechanically. The water excess was evaporated maintaining the stirring and was dried at room temperature for 12 h. It was dried at 105 °C, 3 h and calcined in oxygen flow at 500 °C, 1 h.

Co/SZ and Pd–Co/SZ samples were prepared on the SZ and the Pd/SZ calcined at 500 °C, respectively, by impregnation of pore volume at room temperature. An aqueous solution of Co acetate for a suitable metal content (0.5–5 wt%) was used as precursor. Impregnated samples were dried in a furnace and calcined in oxygen at 500 °C for 1 h.

The performance of monometallic and bimetallic solids were tested using various pretreatment procedures prior to reaction. These experiments showed that the samples treated in the reaction mixture at 700 °C after calcination, were the most actives [7]. As a result, all catalysts examined in the current study were pretreated in the reaction mixture at 700 °C prior to any activity testing.

2.3. Characterization of catalysts

Solids prepared were characterized by N_2 adsorption, temperature programmed reduction (TPR), X-ray diffraction (XRD), diffuse reflectance spectroscopy (UV–Vis DRS) and infrared spectroscopy (DRIFT). The catalysts metallic contents were determined by atomic absorption (AA).

The measurements of catalytic activity were performed in a quartz fixed bed reactor containing 0.4 g of catalyst, in a temperature range 200–700 °C and at a space velocity 31,000 h^{-1}. The feed mixture to the reactor was 2000 ppm of methane, 500 ppm of NO, 10% of O_2. The feed and the effluent reactor were analyzed in a "on line" gas chromatograph using a CTR1 column (Altech) at 40 °C, on a thermal conductivity detector and using a He flow of 20 $cm^3\,min^{-1}$ as carrier gas.

The effect of water vapor on the stability of samples was determined by using a feed stream containing 6% water vapor. The scheme of experiments consisted first of measurements of samples in a feed without water, varying the temperature between room temperature and 700° C. Then, the reactor was cooled for 12–15 h, later on, the same sample was measured in feed with water. Finally, it was measured again in a dry feed to observe the activity in water vapor absence.

To compare catalytic activity and selectivity of the mono and bimetallic catalysts the following reactions were considered

$$CH_4 + 4NO \rightarrow 2N_2 + CO_2 + 2H_2O \tag{1}$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \tag{2}$$

The NO conversions to N_2 were calculated in terms of N_2 production

$$X_{N_2}\% = (2N_2/NO^o)100 \tag{3}$$

The conversion of methane combustion was calculated as

$$X_{CH_4}\% = \{[CO_2 - N_2/2]/CH_4^o\}100 \tag{4}$$

The percent selectivities were defined as

$$S(\%) = \{2X_{NO}NO^o/[X_{CH_4}CH_4^o]\}100 \tag{5}$$

Neither N_2O nor CO were detected.