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Oxygen evolution over Ag/$Fe_xAl_{2-x}O_3$ ($0.0 \leq x \leq 2.0$) catalysts via N_2O and H_2O_2 decomposition

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Abstract

In this paper, a comparative study between nitrous oxide and hydrogen peroxide decomposition over a series of catalysts prepared via the combustion of silver, aluminum, and iron nitrates (with different aluminum: iron ratios). Urea was used as a combustion fuel. The calcinations were affected at the 400–700 °C temperature range. The produced catalysts were characterized by using XRD and SEM analyses. The obtained results revealed that silver metal supported on Al_2O_3 and/or Fe_2O_3 represent the major constituents of all the calcinations products, i.e. Ag/$Fe_xAl_{2-x}O_3$. However, two different interfaces are involved in the two test reactions, all the catalysts were able to decompose both reactants yielding oxygen as a joint product. Meanwhile, it was found nitrous oxide destruction activity increases with decreasing both silver particles size and iron content in the catalysts substrate. On the contrary, increasing iron content in the different catalyst was found to enhance hydrogen peroxide decomposition activity. Moreover, a synergic effect was observed for the catalysts having Al:Fe ratio of 0.5:1.5.

Keywords: N_2O decomposition; H_2O_2 decomposition; Silver catalyst; Alumina; Iron oxide

1. Introduction

Man-made nitrous oxide, N_2O, arise as a co-product from some chemical processes, such as the use of circulating fluidized beds for combustion, automotive exhaust emissions and the production of large amounts of adipic acid, which is produced from the HNO_3 oxidation of cyclohexanol–cyclohexanone mixtures, for Nylon 6,6 and 6,12 [1]. Now, it is well known that N_2O contributes to the catalytic stratospheric–ozone destruction, besides it is considered as a strong greenhouse gas [2,3]. According to Kyoto Protocol of the United Nations Convention on Climate Change, N_2O stands as the second non-CO_2 greenhouse gas having a global worming potential of 310 equivalent to CO_2 [4]. Therefore, in the last years, there has been a great worldwide interest in the development of catalysts for N_2O decomposition. Two routs were employed for this purpose, namely direct N_2O decomposition and selective catalytic reduction of N_2O with hydrocarbons. Many catalysts (including supported or unsupported noble metals, pure oxides, mixed oxides, spinels, perovskites, hydrotalcites and zeolites) were tested for N_2O decomposition [5].

Silver-based catalysts are used, industrially, for the partial oxidation of methanol to formaldehyde [6,7] as well as for the oxidation of ethylene-to-ethylene epoxide [8–10]. Concerning its application in the abatement of nitrogen oxides, there are many reports indicating that silver/alumina catalysts exhibited relatively good activity and selectivity for NO reduction to N_2 in the presence of propane/propene [11–14] and methane [15,16] as reducing agents. In these reports, it was demonstrated that the activity of silver/alumina catalysts is influenced by different factors; including silver loading, oxidation state, and particle size. This catalyst, silver/alumina, showed a promising activity also for the $N_2O + CO$ reaction [17]. A synergic effect was observed in this reaction upon the addition of small quantities of rhodium to Ag/Al_2O_3 catalyst [17].

The catalytic decomposition of hydrogen peroxide, H_2O_2, has been studied extensively (see for example references [18–34]). The interest of studying this reaction comes from: (i) it is a useful model reaction for studying the activity of different categories of catalysts, (ii) using a suitable catalysts H_2O_2 might be an efficient source of oxygen, (iii) a mixture of Fe^{2+}

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and H_2O_2, Fenton reagent, represents one of most active systems for the oxidation of organics in water [23–25]. The reactivity of this reagent comes from the in-situ generated hydroxyl radicals according to:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{-}OH + {}^{\bullet}OH \quad (1)$$

Several studies utilized different iron precursors in order to replace the soluble Fe^{2+} in a trail to design heterogeneous Fenton-like catalysts [23–25]. Various catalysts (such as single or supported oxides, mixed oxides, spinels, perovskites, transition metals exchanged molecular sieves and heteropoly compounds) exhibited a promising activity during H_2O_2 decomposition [18–34]. Such catalysts can be classified into two groups: (i) homogeneous and (ii) heterogeneous catalysts.

Combustion method has been employed by many research groups for the preparation of different categories of catalysts [35–40]. This method represents a quick, straightforward preparation process to produce homogeneous, very fine, well-dispersed, nano-size supported catalysts without intermediate decomposition and/or calcinations steps [35,36]. It involves an exothermic, generally very fast and self-sustaining chemical reaction between the desired metal salts and a suitable organic or inorganic fuel, which is ignited at temperatures much lower than the actual phase formation temperature. Urea–nitrate combustion mixture was used in the preparation of catalysts such as $CdCr_2O_4$ [35], CuO–CeO2 [36], and. $Cu_xMn_{3-x}O_4$ [37]. In this paper, Urea–nitrate combustion method was used to prepared silver-aluminum-iron catalysts. The parameters of the preparation were iron:aluminum ratio and the calcinations temperature. The obtained catalysts were characterized by using X-ray diffraction (XRD) and scanning electron microscopy (SEM). Due to the lack of information about the activity of this system towards N_2O as well as H_2O_2 decomposition, the present investigation was devoted to compare between oxygen evolutions via both reactions over the prepared catalysts in a trail to shed some light about the active centers involved in both reactions.

2. Experimental

2.1. Catalysts preparation

The reagents used in the present investigation, $AgNO_3$, $Fe(NO_3)_3{\cdot}9H_2O$, $Al(NO_3)_3{\cdot}9H_2O$, and CH_4N_2O, were analytical grade chemicals. Five mixtures having the general formula $Ag_2O{:}Fe_xAl_{2-x}O_3$ ($x = 0.0, 0.5, 1.0, 1.5$, and 2.0) were prepared using urea as a combustion fuel. The amount of urea was 75% larger than the stoichiometric amount, i.e. the amount corresponding to complete combustion of urea and the nitrate anions in parent mixtures [37]. Prior to the calcination, the appropriate amounts of the reactants, with little added distilled water, were first mixed in a small porcelain crucible, then heated in an oven at 90 °C. Finally, after the solution was converted to a viscous gel it was calcined, for 3 h, in air at 400–700 °C temperature range, and then quenched to room temperature. During the first few minutes of the calcinations process ignition took place with a rapid evolution of a large amounts of gases. Generally, the entire procedure was conducted with minimal exposure to light.

2.2. Catalysts characterization

X-ray diffraction patterns were recorded using a Philips diffractometer (type PW 103/00). The Philips generator, operated at 35 kV and 20 mA, provided a source of CuKα radiation. Average particle sizes were estimated from X-ray line width broadening using the Scherrer equation [41]:

$$\beta = K\lambda / L_w \cos\theta \quad (2)$$

where K is constant taken as 0.94 [42], λ is the X-ray wavelength and β is the corrected peak width. In these experiments, the width is taken as the full width at half maximum intensity of the peaks in the range $2\theta = 37$–40. Scanning electron micrographs were obtained using a JEOL scanning microscope, model JSM-5400 LV. The samples were prepared by the gold sputtering technique.

2.3. Activity measurements

Nitrous oxide decomposition was carried out in an electrically heated quartz tube reactor. The temperature in the reactor was measured using a thermocouple adjacent to the catalyst bed. Prior to each experiment 0.5 g catalyst were treated in N_2 at 500 °C for 1 h. The temperature was measured by a K-type thermocouple inserted in the catalyst bed and was controlled within ±0.2 °C of the desired temperature by a Cole-Parmer temperature controller (model *Digi-Sense* 89000-00). The desired concentration of N_2O was added with the aid of thermal mass flow controllers (AALBORG, DFC2600) using N_2 as a balance gas, the volume flow rate was 200 cm^3/min (NTP). The gases used were all of >99% purity and they are used without further purification. The exit concentrations were monitored by means of a magnetic oxygen analyzer (ABB, AO2020-Magnos 106) and non-dispersive infrared analyzer for the components N_2O, NO (ABB, AO2020-Uras 14). Preliminary experiments for the decomposition of nitrous oxide over all the catalysts showed the absence of NO in the exit gas.

The measurements of the kinetics of catalytic decomposition of hydrogen peroxide have been carried out in a glass volumetric system similar to that described by Dereń et al. [43]. The measurements were conducted at 15–30 °C temperature range. A constant catalyst weight 20 mg was added to a thermostated reaction vessel containing 5 mL of hydrogen peroxide solution (30%, w/v). The analysis of the experimental data has been carried out on the assumption that the decomposition of H_2O_2 is a zero order process. The rates of the reaction have been calculated according to:

$$V = V_o + k_t \quad (3)$$

where V is the volume of oxygen evolved at time t and V_o is the volume of oxygen evolved to the moment at which the measurements started. Silver and iron ions that could be released to