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Catalytic performance of Co_3O_4/CeO_2 and $Co_3O_4/CeO_2–ZrO_2$ composite oxides for methane combustion: Influence of catalyst pretreatment temperature and oxygen concentration in the reaction mixture

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Abstract

The influence of catalyst pre-treatment temperature (650 and 750 °C) and oxygen concentration (λ = 8 and 1) on the light-off temperature of methane combustion has been investigated over two composite oxides, Co_3O_4/CeO_2 and $Co_3O_4/CeO_2–ZrO_2$ containing 30 wt.% of Co_3O_4. The catalytic materials prepared by the co-precipitation method were calcined at 650 °C for 5 h (fresh samples); a portion of them was further treated at 750 °C for 7 h, in a furnace in static air (aged samples).

Tests of methane combustion were carried out on fresh and aged catalysts at two different WHSV values (12 000 and 60 000 mL g^{-1} h^{-1}). The catalytic performance of Co_3O_4/CeO_2 and $Co_3O_4/CeO_2–ZrO_2$ were compared with those of two pure Co_3O_4 oxides, a sample obtained by the precipitation method and a commercial reference. Characterization studies by X-ray diffraction (XRD), BET and temperature-programmed reduction (TPR) show that the catalytic activity is related to the dispersion of crystalline phases, Co_3O_4/CeO_2 and $Co_3O_4/CeO_2–ZrO_2$ as well as to their reducibility. Particular attention was paid to the thermal stability of the Co_3O_4 phase in the temperature range of 750–800 °C, in both static (in a furnace) and dynamic conditions (continuous flow). The results indicate that the thermal stability of the phase Co_3O_4 heated up to 800 °C depends on the size of the cobalt oxide crystallites (fresh or aged samples) and on the oxygen content (excess λ = 8, stoichiometric λ = 1) in the reaction mixture. A stabilizing effect due to the presence of ceria or ceria–zirconia against Co_3O_4 decomposition into CoO was observed.

Moreover, the role of ceria and ceria–zirconia is to maintain a good combustion activity of the cobalt composite oxides by dispersing the active phase Co_3O_4 and by promoting the reduction at low temperature.

Keywords: Cobalt oxide; Ceria; Ceria–zirconia; Methane combustion; Textural properties; Thermal stability

1. Introduction

The challenge of reducing carbon dioxide emission in the energy production and in industrial applications indicate natural gas as a highly desirable fuel. Natural gas, whose main constituent is methane, produces lower emission of carbon dioxide than coal or oil for equivalent energy supply [1,2] and represents an excellent fuel for both light and heavy-duty vehicles. However, the advantages of using natural gas are effective, if the emission of unburned methane, a potent greenhouse gas, is drastically reduced. Therefore, a catalytic after-treatment of exhausts [3,4] must be operative in natural gas vehicles.

The complete oxidation of methane can be performed over either supported noble metals or transition metal oxides [5]. So far, supported noble metal catalysts, especially Pd and Pt, are employed for methane combustion at low temperatures, especially in automotive applications. Besides being expensive, noble metals easily sinter and their deterioration and abrasion can generate even more toxic pollutants [6]. Alternative materials for potential automotive applications, such as hexaaluminates, single and doped transition metal oxides, perovskites show lower catalytic activity than noble metals and in most cases (especially Co_3O_4) even lower thermal stability [7–10].

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The improvement of the catalytic activity and resistance to high temperature of these alternative systems would be desirable in order to use them as co-catalysts and, therefore, reduce the amount of expensive precious metals in conventional catalytic devices. In particular, a good knowledge of the limits of thermal stability of Co_3O_4-based catalysts in the reaction conditions is necessary in order to finally assess their potential in the methane combustion at low temperature.

The purpose of the present work is to evaluate Co_3O_4/CeO_2 and Co_3O_4/CeO_2–ZrO_2 oxides as potential co-catalysts for natural gas emission after-treatment devices. With this aim, we attempted to elucidate the phenomena responsible for the variation of activity in the methane combustion by operating in either lean or stoichiometric conditions. The reaction conditions specific to lean-burn engines include an oxidizing atmosphere [5], whereas bi-fuel engines usually operate in stoichiometric air/fuel ratio [2].

This work represents a fundamental study carried out in order to investigate the behavior of Co_3O_4-based systems and the influence of textural and reduction properties on the methane combustion activity. For this reason, catalytic tests and ageing procedures were performed in conditions of laboratory that obviously are unrealistic for automotive applications. Nevertheless, a basic study is a necessary starting point.

Our recent results on the relationship between methane combustion activity and redox properties of Co_3O_4/CeO_2 and Co_3O_4/CeO_2–ZrO_2 oxides remark the role of the synthetic procedure in order to disperse the active component and to maintain high oxygen mobility [11]. Therefore, in the present paper the interest was focused on the catalytic performance of two Co_3O_4/CeO_2 and Co_3O_4/CeO_2–ZrO_2 oxides prepared with the same method and having the same cobalt loading (30 wt.%). The influence on the methane combustion activity was studied by changing the catalyst pre-treatment temperature (fresh and aged samples) and the oxygen concentration (excess $\lambda = 8$, stoichiometric $\lambda = 1$) in the reaction mixture. Particular attention was paid to the thermal stability of the Co_3O_4 phase, depending on the crystallite sizes and on the oxygen content in the reaction mixture. In this work two samples of pure Co_3O_4 oxide and two different Co_3O_4 (30wt.%)/CeO_2 composite oxides were also studied.

2. Experimental

Two composite oxides Co_3O_4/CeO_2 and Co_3O_4/CeO_2–ZrO_2 containing 30 wt.% Co_3O_4 (labeled as $Co30Ce_{coprcarb}$ and $Co30CeZr_{coprcarb}$) were prepared by a co-precipitation method with sodium carbonate solution (1M) from the calculated amount of $Co(NO_3)_2{\cdot}6H_2O$ (Aldrich 99.0%), $Ce(NO_3)_3{\cdot}6H_2O$ (Aldrich 99.99%), $ZrO(Cl)_2{\cdot}8H_2O$ (Aldrich 98%). The nominal composition of the CeO_2–ZrO_2 solid solution was $Ce_{0.6}$-$Zr_{0.4}O_2$. After addition of sodium carbonate to the precursors dissolved in distilled water, a precipitate was formed. This was aged at room temperature for 3 h, then filtered and washed several times. The dried powders were calcined at 650 °C for 5 h in order to obtain crystalline composite oxides (fresh samples). A portion of each fresh catalyst was further treated at 750 °C for 7 h in a furnace in static air. The resulting samples were labeled as aged.

For comparison reasons, the pure oxides CeO_2 (CeO_{2prec}), CeO_2–ZrO_2 ($CeZr_{copr}$) with nominal composition $Ce_{0.6}$–$Zr_{0.4}O_2$ and Co_3O_4 (Co_3O_{4prec}) were also prepared by precipitation with sodium carbonate. Moreover, a commercial Co_3O_4 powder, purchased from Aldrich, was used as reference.

In order to investigate the influence of the synthetic procedure, a second Co_3O_4(30 wt.%)/CeO_2(70 wt.%) oxide (labeled as $Co30Ce_{coprcitr}$) was prepared by the co-precipitation method in the presence of ammonium citrate at pH 9 as described elsewhere [11]. Calcination treatments at 650 and 750 °C were performed as before in order to obtain the fresh and aged sample.

The weight-based composition of the samples, checked by X-ray fluorescence (S2 Ranger, Bruker) corresponded to the nominal loadings mentioned above within an error of less than 5%. Prior to characterization measurements and catalytic tests, the samples as powder were pressed, crushed and the sieved fraction between 180 and 250 μm was used.

The X-ray diffraction (XRD) measurements were carried out with a Philips (PW 1820) vertical goniometer using Ni-filtered Cu Kα radiation ($\lambda = 1.5418$ Å). A proportional counter and a 0.05° step size in 2θ were used. The assignment of the crystalline phases was based on the ICSD data base (Co_3O_4, no. 24210; CoO, no. 9865; CeO_2, no.28785) [12]. For the sample Co30CeZr due to the visible broadening and tailing of the peaks, the XRD data were analyzed using Rietveld refinement [13,14]. The fitting was performed by the GSAS package program, using Tchebischeff polynomials for the background and Pseudo-Voight functions for the diffraction peaks. The fit goodness was checked by low values of R_p and R_{wp}. By refining the occupancy factors, the stoichiometries of Ce and Zr in the phases were determined, their agreement with the values obtained by the Vegard's law was also controlled [14].

Mean crystallite sizes (d) of different phases were calculated from the line broadening of the most intense reflections using the Scherrer equation [15].

Specific surface area (SSA) measurements were performed using a Sorptomatic 1900 Carlo Erba Instrument, by physical adsorption of N_2 at liquid nitrogen temperature, using the BET equation.

Temperature-programmed reduction (TPR) experiments were carried out with a Micromeritics Autochem 2910 apparatus equipped with a thermal conductivity detector (TCD). In the TPR experiments, a gas mixture H_2 (5 vol.% in Ar, 30 mL/min) was flowed over the sample pre-treated with O_2 (5 vol.% in He) at 550 °C for 30 min, heating from room temperature to 1000 °C (rate 10 °C/min). In order to avoid any influence of mass transfer effects on the shape of the TPR profiles, the absence of inter- and intra-particle mass transfer limitations was accurately checked by employing appropriate K values [16]. TPR experiments were also performed on three selected samples by feeding a mixture of CO (5 vol.%)/He, heating from room temperature up to 1100 °C. The CO conversion and CO_2 formation were monitored by a mass