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Oxidation of residual methane from VNG vehicles over Co_3O_4-based catalysts: Comparison among bulk, Al_2O_3-supported and Ce-doped catalysts

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ABSTRACT

Cobalt oxide based catalysts with three different active phase configurations, namely bulk, alumina supported and cerium-doped Co_3O_4 samples were examined for the complete oxidation of methane under conditions similar to those found in the exhaust of VNG engines. The structural and redox properties of the resulting catalysts were determined by N_2 adsorption-desorption, WDXRF, ICP-AES, X-Ray diffraction, temperature-programmed reactions, UV–vis-NIR DRS, XPS and Raman spectroscopy. Alumina-supported catalysts (10–40%wt. Co) were found to be less active, since the strong interactions between the alumina and the Co_3O_4 active phase were highly detrimental for the redox properties of these catalysts. On the other hand, doping with cerium (10%wt.) led to an increased inherent activity of the Co_3O_4 phase by distorting the spinel lattice, which resulted in improved structural and redox properties and enhanced mobility of the oxygen species within the spinel lattice. These catalysts were also stable over a prolonged period of time under both dry and humid conditions (150 h).

1. Introduction

The use of natural gas as fuel for vehicles (also known as Vehicular Natural Gas or VNG) is considered a reliable alternative, with a well-established technology, that can serve as a transition technology in the way to cleaner H_2-based energy sources. VNG engines are between 10–20% more efficient than gasoline or diesel engines and have a lower environmental impact with limited NO_x and soot emissions [1–4]. Their main technical limitation lies in the release of residual methane, not burned in the engine, which is a powerful greenhouse effect gas.

Catalytic oxidation constitutes an attractive post-treatment strategy to convert methane into CO_2 and water. Unfortunately, it is a noticeably demanding process compared with the oxidation of other hydrocarbons such as propane or butane, due to its high chemical stability. This low reactivity determines the temperature of the process, which should not exceed a temperature threshold of 500 °C, since that is the thermal level of the exhaust gases from the engine. The mostly used catalysts on a commercial scale for VNG vehicles are based on supported noble metals, mainly palladium [5,6]. However, these catalysts, which can contain up to a 4% in weight of palladium, are expensive while their behaviour is negatively influenced by sintering and the presence of water in the reaction stream [7,8]. In this context, finding cheaper, alternative catalysts with an appropriate performance has become an interesting challenge that has the potential to reduce the cost of post-treatment systems for exhaust gases and contribute to increase the attractiveness of VNG engines as well.

Cobalt spinel oxides, like Co_3O_4, have been demonstrated to exhibit a high activity for methane catalytic combustion, and are therefore considered good alternative candidates to noble metal based catalysts, owing to their relatively low cost, high thermal and hydrothermal stability and selectivity to CO_2 [9,10]. However, the specific physico-chemical properties of these catalysts are highly dependent on the specific configuration of the active phase, that is, whether the Co_3O_4 is a bulk phase, supported on a porous media, or mixed with other elements. Pure bulk Co_3O_4 catalysts take advantage of the excellent redox properties of this material, which allow for a good mobility of the oxygen species and reducibility. However, their structural properties are usually very poor when using conventional synthesis methodologies (precipitation or direct calcination), with low specific surface areas and large crystallite sizes [11,12]. Better textural properties can be obtained with solvothermal or hard-template-based routes [13–16]. In a simpler way, an increased available metallic surface area and improved structural properties can be obtained by depositing the Co_3O_4 phase over the surface of a porous media. This strategy has been reported to enhance the inherent catalytic activity of Co_3O_4 in some cases [17,18], but, in other cases, the interactions between cobalt oxide and the support can

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be detrimental owing to their negative impact on the redox properties [19]. For example, when alumina is used as a support the formation of $CoAl_2O_4$ often occurs. This undesired phase fixes a certain amount of cobalt species due to its high stability. Therefore, a fraction of deposited cobalt species is not able to participate in the Co^{3+}/Co^{2+} redox cycle. On the other hand, doping the bulk Co_3O_4 with another metallic element can improve its textural and redox properties [20,21]. The properties of the resultant catalysts strongly depend on various parameters such as the composition or the presence of segregated or undesired phases [22].

Up to now, various cobalt-based catalysts with the described three configurations have been profusely examined for the complete oxidation of methane [9,17,23–28]. However, the different routes employed for catalysts synthesis and the wide range of operation conditions chosen for catalytic evaluation make the comparison of their corresponding performance and properties a particularly difficult task [29]. To the best of our knowledge, no systematic analysis of the three type of catalysts under the same conditions has ever been attempted. Thus, in the present work, these three configurations have been implemented for the design of Co_3O_4 catalysts for methane catalytic oxidation. More specifically, various bulk Co_3O_4 samples were prepared by simple calcination and precipitation. Secondly, a series of Co_3O_4 catalysts supported on alumina with varying cobalt content in the range 10–40%wt. were examined. Lastly, as for doped Co_3O_4 catalysts, several samples modified by cerium, with a content between 5 and 20%wt., were synthesised. Along with a detailed characterisation of the physicochemical properties of these catalysts, by means of a wide number of analytical techniques including BET measurements, XRD, WDXRF, ICP-AES, UV–vis-NIR DRS, Raman spectroscopy, XPS, H_2-TPR and CH_4-TPRe, this work presents kinetic data that were correlated with the key catalytic properties of each type of catalyst. Also, attention has been paid to examining the catalytic stability during a prolonged time interval under both dry and humid conditions.

2. Experimental

2.1. Catalysts preparation

Bulk Co_3O_4 catalysts were prepared following two different routes, already described elsewhere [30]. The first route was a simple calcination in static air of two different cobalt precursors, namely cobalt (II) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$, Sigma-Aldrich) and cobalt (II) hydroxycarbonate ($2CoCO_3{\cdot}3Co(OH)_2{\cdot}xH_2O$, Panreac). The resulting samples were denoted as DC and HC, respectively. The second route consisted of an aqueous basic precipitation of a cobalt precursor, resulting in the formation of cobalt hydroxycarbonate. A solution of Na_2CO_3 1.2 M was added drop-by-drop to 100 ml of $Co(NO_3)_2{\cdot}6H_2O$ 0.5 M, while the temperature was kept constant at 80 °C, until pH 8.5 was attained. The obtained precipitates were collected and washed thoroughly with at least 5 litres of water, to wash off all the sodium ions which are known to be especially detrimental for the activity of oxidation catalysts [31]. The sample was labelled as CC. Finally, a commercial bulk Co_3O_4 sample (Alfa Aesar) was used as reference. This sample was denoted as COM.

Supported Co_3O_4/Al_2O_3 catalysts were prepared by a precipitation route following the same methodology as the CC catalyst, but adding γ-Al_2O_3 (Saint Gobain Norpro SA 6173), previously stabilized at 850 °C for 4 h in static air. The selected metallic Co loadings were 10, 20, 30, 35 and 40 wt%. These samples were denoted as xCo/Al_2O_3 where x stands for the nominal cobalt loading. For comparative purposes, a bulk $CoAl_2O_4$ sample was also obtained by a precipitation route, where a cobalt salt ($Co(NO_3)_2{\cdot}6H_2O$) and an aluminium salt ($Al(NO_3)_3{\cdot}9H_2O$) with stoichiometric proportions were precipitated by the drop-by-drop addition of Na_2CO_3 1.2 M, until pH 9 was achieved.

Cerium-doped bulk Co_3O_4 catalysts were prepared by a precipitation route, similar to the route followed for the synthesis of the CC sample, but starting from adjusted mixtures of $Ce(NO_3)_3{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ to obtain catalysts with nominal cerium loadings of 5, 10, 15 and 20 wt%, which corresponded to Ce/Co molar ratios of 0.03, 0.06, 0.10 and 0.14, respectively. The samples were named as xCe/Co_3O_4 where x is the nominal cerium content. In addition, a sample of pure CeO_2 was prepared using the same route. Again, the obtained precipitates were collected and washed thoroughly with water. All catalyst precursors were dried in static air at 110 °C for 16 h and subjected to calcination in static air to produce the final catalysts. The calcination protocol was defined on the basis of the results obtained from a previous thermogravimetric analysis over the catalyst precursors, and involved three heating steps, separated by 30-minute isotherms: an initial step at 5 °C min^{-1} from room temperature to 125 °C, an intermediate step at 1 °C min^{-1} until 300 °C and a final step at 5 °C min^{-1} until 600 °C, which was then maintained for 4 h. Exceptionally, the bulk $CoAl_2O_4$ sample was also calcined at 850 °C.

2.2. Characterisation techniques

Textural properties of the catalysts were determined from the nitrogen-adsorption isotherms at −196 °C obtained with a Micromeritics TriStar II apparatus. The specific surface of the samples was obtained by the BET method, and the average pore size was calculated using the BJH method. All samples were degassed prior to analysis on a Micromeritics SmartPrep apparatus at 300 °C for 10 h with a N_2 flow.

The composition of the supported Co_3O_4/Al_2O_3 catalysts and the $CoAl_2O_4$ samples was determined by Wavelength Dispersive X-Ray Fluorescence (WDXRF). From each sample in powder form, a boron glass pearl was prepared by fusion in an induction micro-furnace, by mixing the sample with the flux agent Spectromelt A12 (Merck) in an approximate proportion of 20:1. Chemical analysis of each pearl was performed under vacuum, using a PANalytical AXIOS sequential WDXRF spectrometer, equipped with a Rh tube and three different detectors (gas flow, scintillation and Xe sealed). The composition of Ce-doped catalysts was determined by ICP-AES in a Thermo Elemental Iris Intrepid apparatus. The pretreatment involved the acid digestion of 5–10 mg of each sample, followed by dissolution in 100 ml of Milli-Q water.

Structural properties of the catalysts were determined by X-Ray diffraction. XRD analysis were performed on a X'PERT-PRO X-Ray diffractometer using Cu Kα radiation (λ = 1.5406 Å) and a Ni filter. The X-Ray tube was operated at 40 kV and 40 mA of current. The samples were scanned from an initial value of 2θ = 5° to a final value of 2θ = 80°, with a step size of 0.026° and a counting time of 2.0 s for each step. Phase identification was performed by comparison of the obtained diffraction patterns with JCPDS (Joint Committee on Powder Diffraction Standards) database cards. Occasionally, a longer counting time (26.8 s) was applied to perform a detailed XRD analysis over the supported Co_3O_4/Al_2O_3 and Ce-doped catalysts. The cell size of the Co_3O_4 phase was obtained by profile matching of the detailed XRD patterns using FullProf.2k software.

Redox properties and Co species distribution was investigated by means of different techniques. Temperature-programmed reduction with hydrogen (H_2-TPR) was performed on a Micromeritics Autochem 2920 apparatus, using a 5%H_2/Ar mixture as the reducing gas. The analysis protocol involved an initial pre-treatment step with a 5%O_2/He mixture at 300 °C for 30 min. The aim of this step was to remove impurities and/or water that could be retained on the surface of the samples while at the same time fully restoring the oxygen vacancies of the spinel lattice before the analysis of the reducibility. After cooling down to room temperature with flowing He, the TPR experiment was performed, up to 600 °C for the bulk Co_3O_4 catalysts, 950 °C for the supported Co_3O_4/Al_2O_3 catalysts and $CoAl_2O_4$ samples and 900 °C for the Ce-doped Co_3O_4 catalysts. The corresponding final temperature was then maintained for 30 min. The water produced throughout the whole experiment was eliminated using a cold trap, to avoid interference with