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TAP reactor study of the deep oxidation of propane using cobalt oxide and gold-containing cobalt oxide catalysts

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ABSTRACT

A transient reactor study of the oxidation of propane to CO_2 on gold-free and gold-doped CoO_x catalysts has been carried out. It has been demonstrated that the presence of gold markedly promotes the catalytic reactivity of cobalt oxide in the total oxidation of propane. Both catalysts oxidised propane directly to CO_2 via a Mars–Van Krevelen mechanism, and this was confirmed using isotopically labelled oxygen experiments. The increased activity of the gold catalyst is related to the faster reoxidation of the cobalt oxide when gold is present in the catalyst, since the reaction step in which the catalyst is reduced, due to propane oxidation, is similar for both catalysts. The faster reoxidation of the gold catalyst can be linked to the higher concentration of oxygen vacancies in the catalysts, determined by O_2 uptake results obtained from transient studies in the presence of oxygen.

1. Introduction

The release to the atmosphere of volatile organic compounds (VOCs) is directly related to environmental damage. Thus, all hydrocarbon containing compounds presenting appreciable photocatalytic activity are named as VOCs. They are wide ranging in chemical functionality and emission sources. Indeed, VOCs such as light alkanes are organic substances characterised by their high vapour pressure at ambient temperature and their low boiling point [1]. Hence, they are environmentally damaging chemicals that are emitted into air from chemical, petro-chemical and many allied industries. In the atmosphere, they can react with nitrogen oxides to produce low-level ozone, which is highly toxic for the environment and human health [2]. Growing environmental awareness has led to stringent regulations to control VOC emissions and as a result a disposal process with high efficiency, reliability and cost effectiveness is necessary to remove these harmful compounds. Therefore, the elimination of light alkanes, such as propane, is a tough challenge that needs to be dealt with.

Amongst the number of methods employed to remove VOCs, catalytic oxidation is recognised as one of the most efficient, as it provides the potential to destroy pollutants totally to carbon dioxide and water. Currently, the most active catalysts are those based on platinum and palladium, which are dispersed on a high surface area support [3–7]. However, there still remains scope for improved catalysts as more active systems offer considerable economic advantages in terms of operating costs, and the level of environmental protection provided. An alternative to platinum group metal based catalysts is the use of base-metal oxides. Unfortunately, the activity of these catalysts is in most cases lower. For the metal oxides, cobalt oxide has been shown to be one of the most efficient in the total oxidation of VOCs, and higher activities than noble metal catalysts have been reported for the total oxidation of alkanes [8–11]. The use of cobalt oxide offers the advantage of both high reactivity and a relatively low price when compared with precious metals. The main problem of catalysts based on Co_3O_4 is the low stability at reaction temperatures over 400 °C. However, if propane is the substrate to be oxidised completely then these high temperatures are not required [12]. In order to increase the reactivity of cobalt oxide the synthesis of a nanocrystalline Co_3O_4 has been reported to be extremely efficient for propane total oxidation at low temperatures (markedly lower than 300 °C) [12,13]. Also, the addition of gold to Co_3O_4 leads to an improvement in the alkane combustion conversion [14–16].

One of the most appropriate approaches to unravel complex reaction schemes is the use of transient techniques, which involve perturbation of the reacting catalytic system. Most commonly this takes the form of a concentration change by the introduction of

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a gas pulse whilst monitoring the response of reactants and products. One of the most powerful reactor systems for mechanistic determination is the temporal analysis of products (TAP) reactor. TAP studies have been used successfully for the study of total and selective oxidation reaction mechanisms. In particular, they have proved to be useful in the elucidation of the mechanisms of VOC catalytic oxidation using uranium oxide catalysts [17]. However, no specific study has been carried out on the total oxidation of propane in a TAP reactor employing high activity catalysts based on cobalt oxide

This is addressed in the present work, as we report the results of a study of gold-free and gold-doped CoO_x as catalysts for the oxidation of propane using a pulse TAP reactor in order to (i) gain an understanding of the total oxidation mechanism of propane over gold-free and gold-doped CoO_x catalysts and (ii) to establish the role of gold for this enhanced catalytic activity.

2. Experimental

2.1. Catalyst preparation

Au/CoO_x, catalyst was prepared using a coprecipitation method. An aqueous solution of the corresponding Co-nitrate and $HAuCl_4{\cdot}3H_2O$ was stirred at 80 °C. Aqueous sodium carbonate (0.25 M) was added dropwise until a pH of 8.5 was obtained. The slurry obtained was filtered and washed several times with cold and then hot water to ensure the removal of chlorides. After drying in an oven at 120 °C the catalysts were calcined in static air at 425 °C for 3 h. CoO_x was also prepared in the same way but without using the addition of the gold source.

2.2. Catalyst characterisation

Catalysts were characterised by powder X-ray diffraction using an Enraf Nonius PSD120 diffractometer with a monochromatic $CuK_{\alpha 1}$ source operated at 40 keV and 30 mA. Phases were identified by matching experimental patterns to the JCPDS powder diffraction file. The surface areas of the catalysts were determined by multipoint N_2 adsorption at −196 °C, and data were treated in accordance with the BET method from the nitrogen adsorption isotherms.

Brunauer–Emmett–Teller (BET) surface area was determined by N_2 adsorption at 77 K using a Micromeritics ASAP 2000 V2.04 physi/chemisorption unit.

Temperature-programmed reduction was carried out in a Micromeritics Autochem 2910 equipped with a TCD detector. The reducing gas used in all experiments was 10% H_2 in Ar, with a flow rate of 50 ml min^{-1}. The temperature range explored was from room temperature to 700 °C. The heating rate was maintained at 10 °C min^{-1} for all samples whilst the sample mass employed was 20 mg.

Further characterisation of the samples was performed by (TEM), high resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) by using a field emission gun (FEG) TECNAI G2 F20 microscope operated at 200 kV. To prepare TEM samples, after being finely powdered in an Agate mortar, the cerium oxide specimens were treated by sonicating in absolute ethanol for several minutes and a few drops of the resulting suspension were deposited onto a holly-carbon film supported on a copper grid, which was subsequently dried.

2.3. Catalytic tests in a conventional micro-reactor

Catalytic tests for the combustion of propane were carried out at atmospheric pressure in a fixed-bed stainless-steel tubular-flow reactor. The catalyst weight was fixed at 50 mg and the total flow of alkane/air with a molar ratio of 0.5/99.5 was maintained with a total flow rate of 50 ml min^{-1} (GHSV = 46,000 l/(l h)). The reaction temperature was increased from room temperature to 400 °C in incremental steps and the catalyst activity was measured at steady state. Analysis of the reaction products was carried out on-line using gas chromatography. Two different chromatographic columns (Molecular Sieve 5A and Porapak Q) and two different detectors (TCD and FID) were employed.

2.4. Transient studies in a TAP reactor

The TAP reactor employed for this study is the MultiTRACK (multiple time-resolved analysis of catalytic kinetics). The reactor inner diameter 7 mm, bed height 10 mm) is located in an ultra-high-vacuum chamber into which pulses of the order of 10^{15}–10^{17} molecules can be introduced. In our study 2×10^{16} molecules were introduced per pulse. Pulse valve 1 was used for the O_2/Ar and $^{18}O_2$ pulsing and pulse valve 2 for C_3H_8 pulsing.

Samples of CoO_x and Au/CoO_x (5×10^{-3} g) with particle size 212–300 μm were held between SiC plugs. The gases (Hoek Loos Gases) used for experiments were 20 vol.% O_2 in Ar, pure C_3H_8 and $^{18}O_2$. Reactants and products were recorded at the reactor outlet by three PC interfaced Balzers QMA124 quadrupole mass spectrometers (QMS) in line; a fourth mass spectrometer is positioned above the exit point of the reactor to continuously monitor the product stream. Standard fragmentation patterns and sensitivity factors were used to extract the variation in each reactant from the output of the QMS.

One complexity of this study is the fact that propane and CO_2 present the same molecular weight (44) and, therefore, the use of the m/e 44 signal is not indicative of the evolution of both compounds. In order to estimate the amount of propane and CO_2 in the TAP experiments the following protocol was used. Ions at m/e 29 and 44 are characteristic signals of propane, meanwhile only m/e of 44 is characteristic of CO_2. Due to this, and in order to quantify propane, the profiles of m/e 29 are considered. Taking into account the relative intensities of the signals at m/e 44 and 29, when propane is fed alone, the amount of CO_2 can be estimated. Thus the amount of CO_2 can be estimated through m/e 44–k*m/e 29 (where k is the ratio m/e44/m/e29 for pure propane).

3. Results

3.1. Catalyst characterisation

Fig. 1 shows the XRD patterns of the Au/CoO_x catalyst before and after reaction in propane oxidation in a conventional micro-reactor. No appreciable differences could be observed between them. For both catalysts the only cobalt containing crystalline phase is Co_3O_4 (JCDS: 42-1467). No diffractions, related to metallic cobalt or CoO, have been observed. Additionally, two bands of very low intensity at ca. 38.2° (1 1 1) and at ca. 44.4° (2 0 0) related to the presence of metallic gold. Analysis of the X-ray line widths using the Scherrer method gave an average crystallite size for Au° of 6–7 nm. We have to take this data with caution since XRD measurements relate to coherently scattering domains and sometimes these values do not accurately match with the particle size. Moreover, the diffraction peak at 38.2°, the most intense for Au°, is located between two peaks of Co_3O_4 and also the noise of the signal is significant due to the low intensity of the metallic gold diffraction.

Fig. 2 shows HR-TEM images of fresh and used in reaction Au/CoO_x catalyst. No appreciable differences were found between these two samples. It was observed that the samples exhibit a bimodal gold particle size distribution. The smallest and more abundant particles fell into the 2–5 nm size range and to a minor extent particles mainly in the 10–20 nm range. After a mapping of