Journal of Catalysis 284 (2011) 50–59

Contents lists available at SciVerse ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Sulfur promoted low-temperature oxidation of methane over ceria supported platinum catalysts

Lisa Kylhammar, Per-Anders Carlsson *, Magnus Skoglundh

Department of Chemical and Biological Engineering and Competence Centre for Catalysis, Chalmers University of Technology, SE-412 96 Göteborg, Sweden

ARTICLE INFO

Article history:
Received 24 May 2011
Revised 29 August 2011
Accepted 31 August 2011
Available online 29 September 2011

Keywords:
Environmental catalysis
Oxygen excess
Catalytic activity
Methane dissociation
Metal-support interactions
Transient analysis
In situ infrared spectroscopy
Pt/CeO_2

ABSTRACT

The influence of sulfur dioxide on methane oxidation over ceria supported platinum catalysts under lean conditions has been studied by transient flow reactor and in situ Fourier transform infrared spectroscopy experiments. The results show that sulfur dioxide can promote the oxidation of methane, here between 300 and 450 °C, although, as a function of time on stream, the promoting effect diminish and instead the methane oxidation becomes inhibited. We suggest that sulfate formation on ceria creates oxygen vacancies in the ceria that govern oxygen spillover leading to a lowering of detrimental oxygen coverage of platinum and/or decomposition of platinum oxide facilitating the dissociative methane adsorption. Eventually the ceria becomes saturated with sulfates and the oxygen dynamics in the platinum–ceria system settles. As a consequence, the system regresses towards highly oxidized platinum and/or otherwise active sites on the ceria or platinum–ceria boundary become blocked, which may explain the long-term inhibiting effect by SO_2 exposure.

1. Introduction

The efforts to reduce emissions of greenhouse gases necessitates sustainable automotive transports, specifically addressing important areas as alternative fuels and combustion processes for more efficient propulsion. The lean-burn gas engine provides an interesting alternative to conventional diesel or gasoline engines as the benefits of efficient combustion in oxygen excess are combined with superior properties of the fuel, i.e., biogas or natural gas. For example the amounts of formed carbon dioxide per produced quantity of combustion heat is relatively low [1] and the combustion process may be optimized such that negligible formation of soot is achieved without introducing a significant fuel penalty. However, as biogas and natural gas essentially consist of methane, which is a strong greenhouse gas, low levels of CH_4 emissions must be targeted. As engine modifications alone are insufficient to comply with present emission regulations, catalytic exhaust aftertreatment technologies have to be considered. In this connection the main challenge is to find catalysts that are active for total oxidation of methane in the lean and cold exhausts, around 150 °C for significant periods, which is considered representative for future efficient combustion concepts. The situation is further complicated by the presence of sulfur as the derived sulfur species often are poisons in many catalytic aftertreatment systems.

Practically, the most active catalysts for total oxidation of methane are palladium and/or platinum supported on metal oxides, e.g. Al_2O_3, CeO_2, ZrO_2 or combinations of such. Palladium has been widely recognized as the more preferred element to be used under oxygen excess [2–4]. However, Pd based catalysts are sensitive towards sulfur poisoning and even small amounts of sulfur containing species in the exhausts can cause deactivation of the oxidation function through the formation of stable palladium sulfates [3,5]. Contrarily, Pt based catalysts are more sulfur tolerant [3,4] although the activity for methane oxidation is strongly dependent on the stoichiometry of the reactant gas mixture. For example, over Pt/Al_2O_3 the oxidation of methane is inhibited under oxygen excess [2,6–10].

One approach to increase the methane conversion over Pt/Al_2O_3 is to alternate the feed gas between netoxidizing and netreducing composition. By such means, temporarily high activity for methane oxidation closely associated with the changes of the gas composition has been observed [6–9]. Becker et al. [11] showed that the periods with high activity can be prolonged by using oxygen buffering ceria, instead of alumina, as support material for platinum. The high dynamics in the Pt/CeO_2 system may also explain the low light-off temperature (T_{50}) obtained for methane oxidation under continuously lean conditions but particularly active sites in the platinum–ceria boundary were also suggested by Carlsson et al. [12] explaining the difference as compared to Pt/Al_2O_3. Another

---

* Corresponding author.
E-mail address: per-anders.carlsson@chalmers.se (P.-A. Carlsson).

0021-9517/$ - see front matter © 2011 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2011.08.018

approach to circumvent oxygen inhibition is to include in the reactant feed compounds that can be more easily oxidized, for example longer saturated hydrocarbons (HC). Corro et al. [13] reported a decreased light-off temperature for methane oxidation over presulfated Pt/Al_2O_3 by the addition of C_2–C_4 *n*-alkanes. Several authors have also reported on an increased activity for oxidation of short saturated hydrocarbons over Pt/Al_2O_3 catalysts in the presence of sulfur, either through presulfation of the catalyst or by inclusion of low amounts of SO_2 in the feed gas [14–20]. The mechanism for the promotional effect of sulfur on the activity for hydrocarbon oxidation is not fully understood. Wilson et al. [21] reported that the precursor mediated initial sticking probability of propane on a Pt(1 1 1) surface precovered with oxygen is significantly enhanced when SO_2 is added prior to the introduction of propane. For supported catalysts this mechanism is likely of less importance keeping in mind that the degree of promotion has been shown to significantly depend on the type of support material. For example, promotional effects on oxidation of methane and/or propane have been seen for Pt/Al_2O_3 [14–21] and $Pt/Ce_{0.67}Zr_{0.33}O_2$ [22] but not for Pt/SiO_2 [15–17]. The ability of the support to form sulfates is most likely of importance, which explains the difference between SiO_2 and the former two support materials. It is also important which support sites that undergo sulfation. For example, Burch et al. [16] and Hubbard et al. [15] showed that the increase in surface acidity of the support upon SO_2 exposure correlates poorly with the changes in activity for propane oxidation.

In the present study we investigate the promotional effect by sulfur dioxide on methane oxidation over ceria supported platinum catalysts under lean conditions. Here, ceria is chosen as support material for platinum due to the observed higher activity as compared to γ-alumina [11,12] and that SO_2 can be effectively adsorbed via formation of ad-SO_x species on ceria [23,24]. In the latter case we have previously reported the importance of physical contact between platinum and ceria for the SO_2 adsorption [25]. Hence, it is likely that SO_2 can influence the activity for methane oxidation by affecting the chemical state of Pt sites located at the platinum–ceria boundary, which may be especially active for methane oxidation [12].

2. Experimental section

To investigate the activity for methane oxidation of the Pt/ceria samples in the absence and presence of SO_2, flow-reactor experiments with monolith samples were performed. Temperature programmed reaction experiments were performed to gain information of the extinction and ignition characteristics while transient SO_2 exposure experiments were performed to study promotional and poisoning effects induced by sulfur. To gain mechanistic information on the role of SO_2 for the promotional effect, in situ Fourier transformed infrared spectroscopy measurements were performed with powder samples in diffuse reflectance mode (DRIFTS). To facilitate comparisons of different experimental results, the monolith samples were coated with Pt/ceria powder sample from the same batch as the sample used for the DRIFTS experiments. Due to different reactor designs (flow characteristics and sample heating) the observed methane conversion varies somewhat between the flow reactor and DRIFTS experiments. Another important aspect for reliable comparison of results is that fresh monolith samples are used for each flow-reactor experiment. In order to investigate if comparable amount of catalyst and binder adhered to the monolith during coating, the specific surface area of the monolith sample was measured. As all monoliths have the same amount of coating (200 mg) and the binder does not contribute to the high surface area of the samples, it can be assumed that the samples have comparable amounts of catalyst and binder if they also have comparable specific surface area.

2.1. Catalyst preparation and characterization

Ceria powder (99.5 H.S.A. 514, Rhône-Poulenc) was heated in air at 600 °C for 2 h. The Pt/ceria powder catalyst was then prepared by impregnating the ceria powder with a water solution (pH = 12) containing tetraammineplatinum(II)nitrate (4.0 wt% Pt, Alfa Aesar) and ammonia using incipient wetness impregnation. After impregnation, the sample powder was frozen in liquid nitrogen, freeze-dried and calcined in air at 550 °C for 15 min. This temperature was reached using a linear heating ramp rate of 4.4 °C/min starting from room temperature. In order to obtain 4 wt% Pt on ceria, the impregnation procedure was repeated three times. The surface area of the 4 wt% Pt/ceria powder sample was measured with N_2 physisorption at 77 K (Micromeritics Tristar). Using the BET method for $P/P_0 = 0.05$–0.20, the specific surface area was calculated to be 156 m^2/g.

Two types of monolith samples were prepared with the 4 wt% Pt/ceria and pure ceria powder, respectively. Monolith samples ($\varnothing = 13$ mm, length = 15 mm) were cut out from a commercial honeycomb cordierite structure (Corning) with 400 cpsi. The monolith samples were prepared by immersing the monolith body into a water slurry containing a binder (cerium acetate sol, 20 wt% CeO_2 (ACT), 10–20 nm, Nyacol Nano-Technologies) and the Pt/ceria and ceria powder, respectively. The samples were thereafter dried in air at 90 °C for 5 min and then calcined at 550 °C for 2 min also in air. This procedure was repeated until the washcoat loading was 200 mg. All samples were finally calcined in air at 550 °C for 1 h. The specific surface area was measured by N_2 physisorption (Micromeritics ASAP 2010) using a specially designed sample holder suitable for monolith samples. According to the BET method the specific surface area of the Pt/ceria samples was calculated to be 130 m^2/g coating (±3%). The corresponding area of a sample coated with 200 mg of the binder was calculated to be 30 m^2/g coating.

2.2. Catalytic activity studies in continuous gas-flow reactor

The continuous gas-flow reactor consists of a horizontal quartz tube ($\varnothing = 15$ mm, length = 600 mm) surrounded by a metal coil (Kanthal) for resistive heating (effective heating length = 450 mm). The entire coil was insulated with a 20 mm layer of quartz wool (SUPERWOOL 607 HT, Thermal Ceramics) with an outer layer of aluminum foil. The gas temperature 15 mm upstream the sample was measured by a thermocouple (type K, Pentronic) and controlled with a PID regulator (Eurotherm 3508). In order to decrease axial temperature gradients in the sample monolith(s), blank cordierite monoliths functioning as heat radiation shields, were positioned up and downstream the sample. The temperature of both the blank and sample monoliths were measured with individual thermocouples. The feed gas was composed using a set of mass flow controllers (Bronkhorst LOW-ΔP-FLOW) and introduced to the reactor via air actuated high-speed gas valves (Valco, VICI). For analysis of the product stream, the reactor was equipped with a mass spectrometer (Airsense Compact, V&F). The mass to charge ratio (m/z) for appropriate species were followed using chemical ionization with xenon for m/z 64 (SO_2) and electron impact ionization for m/z 2 (H_2), 12 (C), 15 (CH_4), 18 (H_2O), 28 (CO), 32 (O_2 and S), 33 (HS) and 44 (CO_2).

2.2.1. Temperature programmed reaction experiments

Temperature programmed reaction (TPReaction) experiments were performed with two monolith samples. The samples were conditioned in a reaction mixture consisting of 0.05 vol% CH_4 (in