

The oxygen-assisted transformation of propane to CO_x/H₂ through combined oxidation and WGS reactions catalyzed by vanadium oxide-based catalysts

N. Ballarini^{a,1}, A. Battisti^{a,1}, F. Cavani^{a,1,*}, A. Cericola^{a,1}, C. Lucarelli^{a,1},
S. Racioppi^{a,1}, P. Arpentinier^b

^a Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, INSTM, Research Unit of Bologna, 40136 Bologna, Italy

^b Air Liquide, Centre de Recherche Claude Delorme, les Loges en Josas, 78354 Jouy-en-Josas Cedex, France

Available online 11 July 2006

Abstract

This paper reports about the gas-phase oxidation of propane catalyzed by bulk vanadium oxide and by alumina- and silica-supported vanadium oxide. The reaction was studied with the aim of finding conditions at which the formation of H₂ and CO₂ is preferred over that of CO, H₂O and of products of alkane partial oxidation. It was found that with bulk V₂O₅ considerable amounts of H₂ are produced above 400 °C, the temperature at which the limiting reactant, oxygen, is totally consumed. The formation of H₂ derived from the combination of: (i) oxidation reactions, with generation of CO, CO₂, oxygenates (mainly acetic acid), propylene and H₂O, all occurring in the fraction of catalytic bed that operated in the presence of gas-phase oxygen, and (ii) WGS reaction, propane dehydrogenation and coke formation, that instead occurred in the fraction of bed operating under anaerobic conditions. This combination of different reactions in a single catalytic bed was possible because of the reduction of V₂O₅ to V₂O₃ at high temperature, in the absence of gas-phase oxygen. In fact, vanadium sesquioxide was found to be an effective catalyst for the WGS, while V₂O₅ was inactive in this reaction. The same combination of reactions was not possible when vanadium oxide was supported over high-surface area silica or alumina; this was attributed to the fact that in these catalysts vanadium was not reduced below the oxidation state V⁴⁺, even under reaction conditions leading to total oxygen conversion. In consequence, these catalysts produced less H₂ than bulk vanadium oxide. © 2006 Elsevier B.V. All rights reserved.

Keywords: Vanadium oxide; Supported vanadium oxide; Propane oxidation; Hydrogen production; WGS reaction

1. Introduction

The use of oxygen in processes for H₂ production from hydrocarbons transformation is aimed either at directly furnishing the reaction heat from the inside of the reactor, like in autothermal reforming, or at facilitating a specific reaction pathway other than combustion, like in methane (alkanes) partial oxidation [1–12]. For instance, the addition of oxygen to reformers or WGS reactors is a tool to increment the hydrogen concentration and facilitate CO transformation to CO₂. The catalysts employed for these reactions are often based on noble metals, capable of activating less reactive hydro-

carbons and perform the desired transformations. Other approaches include the use of metal oxides (e.g., Fe₂O₃) for the combustion of methane to CO₂ in the absence of gas-phase oxygen, followed by the re-oxidation of Fe with H₂O to produce H₂ (the One-Step-Hydrogen process) [13,14], or the co-production of coke and H₂ from the contact of methane with Ni-based systems or supported noble metal catalysts, followed by coke combustion with O₂ [15].

Very few indications are given in literature concerning the use of vanadium oxide-based catalysts for the transformation of light hydrocarbons into CO₂ and H₂. Vanadium oxide is a key component in the preparation of catalysts for oxidation reactions [16–20]. It is used either as a supported active phase, to increase its surface area, or in combination with other ions to form mixed oxides, in order to obtain a system with modified and enhanced oxo-reductive properties. In the case of alkanes oxidation, catalysts based on supported vanadium

* Corresponding author.

E-mail address: fabrizio.cavani@unibo.it (F. Cavani).

¹ A Partner of Concorde CA and of Idecat NoE (6th FP of the EU).

oxide are often studied for the synthesis of light olefins by means of oxidehydrogenation (ODH) [21–26]. It is believed that the reaction mechanism includes the dehydrogenation of alkanes with co-production of water, while little attention is given to the formation of H₂. Indeed, in most cases ODH is carried out using O₂ as the limiting reactant, since hydrocarbon-rich conditions may lead to a better selectivity to the olefin. This implies that total conversion of oxygen is reached, especially when temperatures higher than 500 °C are used. Under these conditions, a relevant contribution of catalytic dehydrogenation to H₂ formation cannot be excluded. Recent papers confirm that considerable amounts of H₂ are produced with vanadium oxide-based catalysts, under conditions that are typically employed for alkanes ODH [27–32].

In the present work, we report about the investigation on catalytic properties of bulk and supported vanadium oxide catalysts in the oxidation of propane, with the aim of finding whether the active phase properties and the reaction conditions may affect the mechanism in propane oxidation, and the amount of H₂ produced.

2. Experimental

Commercial vanadium pentoxide was supplied by Aldrich (>99.6%). Supported catalysts were prepared with the incipient-wetness technique using γ -alumina powder (AKZO A4) or silica (Sud-Chemie), and an aqueous solution of NH₄VO₃. Samples were calcined in air at 550 °C. Table 1 reports the list of samples prepared, and the corresponding values of surface area. The two supports were chosen so to achieve comparable values of surface areas for the two series of samples.

Catalytic tests were carried out in a quartz, fixed-bed reactor loading 1.8 cm³ of catalyst in powder form (30–40 mesh particles), at atmospheric pressure. Tests of propane oxidation were carried out by feeding a mixture containing 20% propane, 20% oxygen and remainder He. Residence time was equal to 2 s, and was calculated with reference to the entire amount of catalyst (active phase + support, when present). Catalytic tests of WGS reaction were carried out by feeding a mixture containing 9% H₂O, 9% CO and remainder N₂.

Reaction products of propane oxidation were carbon monoxide, carbon dioxide, light hydrocarbons (ethane, ethylene, methane), aromatics, oxygenates (acetaldehyde, propionalde-

hyde, acetone, acrolein, acetic acid, acrylic acid and propionic acid), molecular hydrogen, propylene and water (not analysed). The effluents were analysed by a gas chromatograph equipped with three packed columns: (i) Carbosieve G (TCD) for the analysis of hydrogen, oxygen, carbon monoxide and carbon dioxide; (ii) fused silica Al₂O₃/KCl (FID) for propylene, propane and other hydrocarbons; (iii) Econopak/EC-Wax (FID) for the oxygenated compounds.

Catalysts were characterized by laser Raman spectrometry (Renishaw 1000 instrument, Ar laser at 514 nm, power 25 mW). The amount of residual C content in samples was determined by combustion in pure oxygen at 1300 °C, with detection of the CO₂ formed by infrared analysis (instrument ELTRA 900CS). Thermal-programmed-reduction (TPR) analysis of samples was carried out using a Thermoquest TPDRO1100 instrument. Samples were loaded in a quartz reactor and pre-treated in nitrogen at 150 °C for 30 min to eliminate weakly adsorbed species. After cooling at room temperature, N₂ was replaced by the analyzing gas (5% H₂ in argon) and the temperature was linearly increased up to 650 °C (thermal ramp: 10 °C/min); the samples were finally maintained at 650 °C for 1 h. TPO and TPR-O (re-oxidation after TPR) tests were carried out using a gas mixture of 5% O₂ in He, using the same temperature program as for the reduction.

3. Results and discussion

3.1. The effect of temperature on catalytic performance in propane oxidation of vanadium oxide-based catalysts

Table 1 summarizes the main characteristics of samples; two series of catalysts were prepared by supporting increasing amounts of ammonium vanadate on silica or on alumina. Furthermore, a sample of unsupported bulk V₂O₅ (bulkVO) was used as the reference.

Fig. 1 compares the conversion of propane and of oxygen as functions of temperature, for samples bulkVO, SiV15 and AlV15. Under the conditions employed, oxygen was the

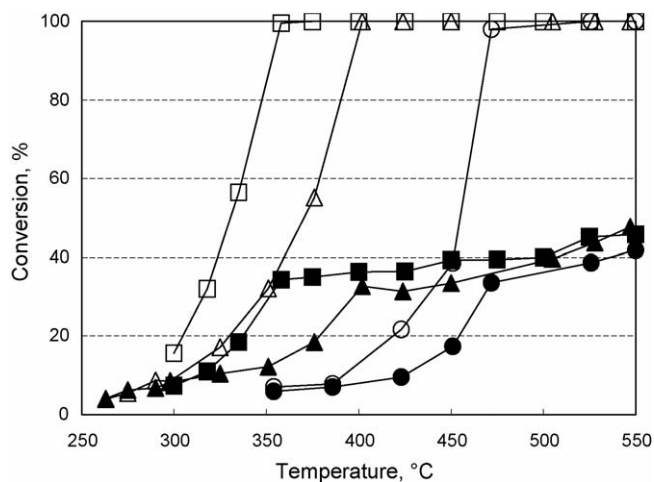


Fig. 1. Conversion of propane (full symbols) and conversion of oxygen (open symbols) as functions of the reaction temperature. Catalysts: SiV15 (●), AlV15 (■) and bulkVO (▲).

Table 1
Catalysts prepared

Sample	V ₂ O ₅ (wt.%)	Support	Surface area (m ² /g)
SiV2	2	SiO ₂	280
SiV7	7	SiO ₂	274
SiV10	10	SiO ₂	259
SiV15	15	SiO ₂	254
AlV2	2	γ -Al ₂ O ₃	234
AlV7	7	γ -Al ₂ O ₃	227
AlV10	10	γ -Al ₂ O ₃	215
AlV15	15	γ -Al ₂ O ₃	191
bulkVO	100	None	8

Download English Version:

<https://daneshyari.com/en/article/58539>

Download Persian Version:

<https://daneshyari.com/article/58539>

[Daneshyari.com](https://daneshyari.com)