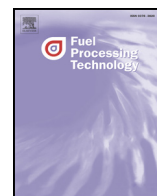




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Insights into the catalytic production of hydrogen from propane in the presence of oxygen: Cooperative presence of vanadium and gold catalysts

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ABSTRACT

H₂ and propylene can be obtained from propane and oxygen in defect using appropriate catalysts. Meanwhile propylene is formed from propane via oxidative or non-oxidative dehydrogenation, molecular hydrogen can be obtained from several reactions such as propane dehydrogenation, coke formation and water gas shift. It has been observed that a gold catalyst hardly activates propane and no H₂ was detected, whereas using vanadium oxide a relatively high concentration of propylene and H₂ was obtained. Interestingly, the simultaneous use of vanadium oxide and gold has meant a higher hydrogen production, higher in a 40% than that of the catalyst containing only vanadium oxide. This performance has been related to the capacity of gold to activate CO in the water gas shift reaction.

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1. Introduction

The oxidative dehydrogenation of propane (ODHP) is an alternative to obtain propylene that presents important advantages over the commercially implemented steam cracking. For example, ODHP is an exothermic process which can operate at temperatures below 500 °C in contrast with steam cracking which needs temperatures over 700 °C [1–3]. Moreover, the catalyst deactivation by coke in the ODHP can be minimized because of the presence of molecular oxygen as an oxidant in the reactor feed. Interestingly, not very high yields to propylene (ca. 30–35%) are estimated to be necessary to compete with the current industrial process, which is much lower than that estimated in the oxidative dehydrogenation of ethane to yield ethylene (65–70%). Unfortunately, yields to propylene reported in the literature are low, due to the large reactivity of the allylic C–H bonds of propylene compared to propane, which leads to an easy overoxidation to CO and CO₂ [4,5]. The low propylene yields achieved up to date are not the only problem since intraparticle pore diffusional limitations are also present in catalytic dehydrogenations [6].

Since propylene cannot be obtained easily from propane in the presence of oxygen due to the large degree of olefin overoxidation, a combined reaction in which, propylene and molecular hydrogen could be significantly obtained from propane, would be highly interesting. The feed would consist of a mixture of propane in excess,

oxygen and inert. Initially at low reaction temperatures (and/or contact times) the oxygen fed has not been consumed and propane reacts to yield mainly propylene and carbon oxides. If the reaction temperature (and/or the contact time) is sufficiently increased, oxygen is completely spent and then two different parts in the catalytic bed can be distinguished: i) a first part in which molecular O₂ is not consumed yet and propane is transformed into propylene and carbon oxides, water being a co-product and ii) a second part of the catalytic bed where the O₂ is absent and many different reactions can take place such as the catalytic dehydrogenation of propane (C₃H₈ → C₃H₆ + H₂), coke formation (C₃H₈ → coke + xH₂), water gas shift (CO + H₂O → CO₂ + H₂) or even the reaction of C, C₃H₈ or C₃H₆ with water to give hydrogen.

This combined process presents a noteworthy advantage over the oxidative dehydrogenation of propane since, apart from propylene, hydrogen is also obtained. On the other hand, the combined process also offers important advantages over the simple dehydrogenation reaction. Firstly, hydrogen is not only formed from propane dehydrogenation but also through WGS reaction and, secondly, the amount of coke formed is expected to be lower as there is some oxygen that initially prevents the formation of coke.

This combined process has been studied by Cavani et al. [7,8] on catalysts based on vanadium. Most efficient catalysts for the oxidative dehydrogenation of propane are based on vanadium oxide [9–14]. Vanadium supported on siliceous materials [9,10] or basic oxides, such as MgO [11,12] or alumina [13] are the most selective catalysts for the oxidative dehydrogenation of propane, which are remarkably more

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selective than bulk vanadium oxide [14]. However, bulk vanadium oxide resulted to be far more efficient than vanadia supported on alumina or silica for hydrogen production in the combined process, as bulk vanadium oxide was remarkably more efficient in the WGS reaction than the supported catalysts. This different result is explained on the basis of the V species formed when the oxygen is completely consumed. Thus, whilst vanadium oxide is detected as V_2O_3 (V^{3+}) in bulk catalysts, V^{4+} and V^{5+} species are observed in the case of supported catalysts, which are less selective to hydrogen [7,8].

In the present article we have tested as catalysts for propane oxidation a bulk vanadium oxide catalyst (fresh present as V_2O_5), a Au/TiO₂ catalyst (1.5 wt.% Au) and a mixture of vanadium oxide and Au/TiO₂ catalyst. As the reaction temperatures to be used are expected to range from 200 to 550 °C, we decided prior to the reaction heat treat all the catalysts at 550 °C. It will be shown that the addition of gold to vanadium oxide highly increases the H₂ production from propane in defect of oxygen. In order to further understand the mechanism of the process, water gas shift and CO oxidation reactions have also been studied over these catalysts.

2. Experimental

2.1. Preparation of the catalysts

The Au/TiO₂ catalyst was prepared by a deposition–precipitation method. TiO₂ P25 from Degussa (which is a mixture of anatase and rutile, mainly anatase) was mixed with distilled water and stirred at room temperature. To this paste, a solution of H₂AuCl₄·3H₂O was added. The mixture was adjusted to pH 9 with an aqueous solution of NaOH, and was then aged for 1 h at this pH with vigorous stirring, filtered and washed with cold and hot water. The catalyst was dried at 120 °C and calcined at 550 °C for 3 h in static air. Chemical analysis by atomic absorption indicated that the gold content was of 1.5 wt.%. This catalyst, Au-1, showed a surface area of 51.4 m²g^{−1}.

V₂O₅, supplied by Sigma-Aldrich and calcined in air at 550 °C, was used as bulk vanadium oxide catalyst. This catalyst, V-1, had a surface area of 4.6 m²g^{−1}.

Finally, the sample named as VAu-1 was prepared by physically mixing vanadium pentoxide with the Au/TiO₂ catalyst in a 1/1 ratio in weight.

2.2. Catalyst characterization

Powder X-ray diffraction was used to identify the crystalline phases present in the catalysts. An Enraf Nonius FR590 sealed tube diffractometer, with a monochromatic CuKα1 source operated at 40 kV and 30 mA was used. XRD patterns were calibrated against a silicon

standard and phases were identified by matching experimental patterns to the JCPDS powder diffraction file.

Catalysts were characterized by N₂ adsorption at −196 °C using a Micromeritics ASAP 2020 apparatus after degasification at 150 °C. The surface area (SBET) was estimated by the Brunauer–Emmet–Teller (BET) method using multipoint data from the relative pressure range of 0.05–0.25.

Morphological and structural characterization of the samples was performed by transmission electron microscopy (TEM), high resolution TEM (HRTEM) and selected area electron diffraction (SAED) by using a FEI Field Emission Gun (FEG) TECNAI G2 F20 STWIN microscope operated at 200 kV. The powder samples were treated by sonicating in absolute ethanol for few minutes, and a drop of the resulting suspension was deposited onto a holey-carbon film supported on a copper grid, which was subsequently dried.

X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos Axis ultra DLD photoelectron spectrometer using a non-monochromatized Mg Ka X-ray source (hm = 1253.6 eV). Analyser pass energy of 50 eV was used for survey scans and 20 eV for detailed scans. Binding energies are referenced to the C1s peak from adventitious carbonaceous contamination, assumed to have a binding energy of 284.5 eV. XPS data were analysed using CasaXPS software. All the peaks of the corrected spectra were fitted with a Gaussian–Lorentzian shape function to peak fit the data. Iterations were performed using the Marquardt method. Relative standard deviations were always lower than 1.5%.

2.3. Catalytic reactions

Catalytic tests for propane oxidation were carried out in a quartz reactor of 12 mm (internal diameter) using 0.5 g of catalyst (pellets from 0.2 to 0.5 mm). The feed consisted of C₃H₈/O₂/He with a molar ratio of 10/10/80 and a total flow of 50 ml/min at atmospheric pressure. These catalysts have been submitted to a ramp temperature and every 25 °C, an analysis was carried out after a stabilization time of 20 min. Blank runs showed no conversion at a reaction temperature of 500 °C and a propane conversion lower than 2% at 550 °C.

Water Gas Shift reaction experiments were conducted in a tubular fixed-bed quartz reactor of 7 mm (internal diameter) using 50 mg of catalyst and a total flow of 75 ml/min. The feed consisted of CO/H₂O/N₂ with a molar ratio of 7.1/32.9/60.04 to give a space velocity of 45,000 h^{−1}. The interval of reaction temperatures studied was 150–500 °C. For some experiments the catalysts were previously submitted to a reduction step in which 25 ml/min of a 10% H₂/N₂ mixture were passed through the reaction system at 300 °C for 2 h. After this time the temperature was decreased to room temperature and then a conventional experiment was carried out.

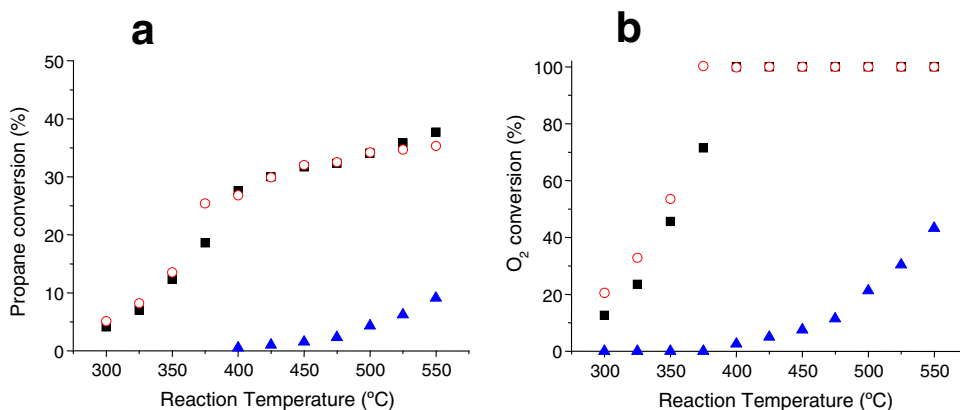


Fig. 1. Evolution of the propane (Fig. 1a) and oxygen (Fig. 1b) conversions with the reaction temperature in the propane oxidation. Symbols: (■) V-1, (○) VAu-1, (▲) Au-1. Note: Propane/O₂/He = 10/10/80 molar ratio. Remaining reaction conditions in text.

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