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, a synergistic effect between gold and vanadium has been observed and the simultaneous use of vanadium oxide and gold has meant a remarkable 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.

**Keywords:** Combined process; propane dehydrogenation; WGS; vanadium oxide; gold; hydrogen.
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].

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. [6-7] on catalysts based on vanadium. Most efficient catalysts for the oxidative dehydrogenation of propane are based on vanadium oxide [8-13]. Vanadium supported on siliceous materials [8, 9] or basic oxides, such as MgO [10, 11] or alumina [12] are the most selective catalysts for the oxidative dehydrogenation of propane, which are remarkably more selective than bulk vanadium oxide [13]. 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 V₂O₃ (V³⁺) in bulk catalysts, V⁴⁺ and V⁵⁺ species are observed in the case of supported catalysts, which are less selective to hydrogen [6, 7].

In the present article we have tested as catalysts for propane oxidation a bulk vanadium oxide catalyst (fresh present as V₂O₅), a Au/titania catalyst (1.5 wt.% Au) and a mixture of vanadium oxide and Au/titania catalyst. As the reaction temperatures to be used are expected to range from 200 to 550 ºC, we decided prior to the reaction heat treat all the
catalysts at 550 ºC. 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 reactions have also been studied over these catalysts.

2. Experimental

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 HAuCl4·3H2O 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 ºC and calcined at 550 ºC for 3 h in static air. Chemical analysis by atomic absorption indicated that the gold content was of 1.5 wt.%. This catalyst, Au-I, showed a surface area of 51.4 m²g⁻¹.

V2O5, supplied by Sigma-Aldrich and calcined in air at 550ºC, 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.

Catalysts characterization

Powder X-ray diffraction was used to identify the crystalline phases present in the catalysts. An Enraf Nonius FR590 sealed tubediffractometer, 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 characterised by N\textsubscript{2} 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 synthesized manganese oxide 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 (hv = 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%.

**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 nm). The feed consisted of C\textsubscript{3}H\textsubscript{8}/O\textsubscript{2}/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 minutes. 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/H_2O/N_2 with a molar ratio of 7.1/32.9/60.04 to give a space velocity of 45000 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%H_2/N_2 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.

CO oxidation experiments were conducted using 50 mg of catalyst into a quartz micro-reactor (inner diameter 7 mm). The gas mixture consisted of CO/O_2/He = 0.5/20/79.5 molar ratio. The total gas flow rate was fixed at 50 ml min⁻¹. Experiments were conducted from room temperature to 100°C and the only reaction product obtained was CO₂.

Reactants and products of all reactions were analyzed by gas chromatography using two packed columns: (i) molecular sieve 5 Å (2.5 m) and (ii) Porapak Q (3 m).

3. Results and discussion

Catalytic experiments for propane oxidation (with a propane/oxygen molar ratio of 1) were conducted on the catalysts synthesized. The main products observed were propylene, CO, CO₂, H₂O and H₂. Low concentrations of C1 and C2 hydrocarbons were identified as well as traces of acrolein, acetaldehyde and acetone. The evolution of both oxygen and propane conversion with the reaction temperature up to 550 °C for Au-1, V-
1 and VAu-1 catalysts are plotted in Figure 1. As can be seen, gold on titania catalyst shows a low catalytic activity which is noticeable after 450°C. Only at 550 °C, propane conversion exceeds 5%. In contrast, catalysts with vanadium (V-1 and VAu-1) have a significant propane conversion in the whole temperature range. In both cases, the oxygen feed is completely consumed, although at slightly lower temperature for VAu-1 catalyst (375 and 400 °C for VAu-1 and V-1, respectively). Therefore, vanadium sites are remarkably more active for propane activation than those of gold.

Figure 2 shows the variation of the selectivity to propylene, CO2 (2a) and CO (2b) with the reaction temperature for Au-1, V-1 and VAu-1 catalysts. For Au-1 the formation of propylene and CO is almost negligible, being CO2 the main reaction product. It must be noted that, due to the low reactivity of this catalyst, the oxygen fed is not consumed in the whole temperature range. On the other hand, propylene is observed for the other two catalysts (V-1 and VAu-1), being especially notorious in the catalyst containing only vanadium. It can be seen that the selectivity to propylene decreases when the reaction temperature increases. This drop in propylene selectivity is related with its high instability and decomposition to carbon oxides. It should be mentioned that this phenomenon takes place in spite of the fact that for a given propane conversion the selectivity to propylene in vanadium catalysts usually increases in the temperature range studied [14]. Fig. 2b shows that the selectivity to CO is the highest for V-1, whereas for VAu-1 is remarkably lower and null for Au-1. Finally, in fig. 2a it can be seen that the selectivity to CO2 is the highest for Au-1, remarkably lower for the catalyst containing both gold and vanadium and the lowest for the sample with only vanadium.

Figure 3 shows the hydrogen production obtained for the different catalysts. Meanwhile no hydrogen is observed for the Au-1 catalyst, a high H2 production is obtained with vanadium containing catalysts. More interestingly, the mixed VAu-1 catalyst shows the
highest hydrogen formation, which is remarkably higher than that obtained with V-1. Therefore, the addition of a gold catalyst to the vanadium catalyst greatly increases the hydrogen formation, although only gold catalyst does not yield hydrogen in the same reaction conditions.

The effect that the addition of a gold catalyst can exert in the hydrogen production from propane is not easy to identify as gold catalysts are active in many reactions involving some compounds present in this combined process. Thus gold catalysts activate CO in different conditions. For example Au nanoparticles on appropriate supports are highly active, even at subambient temperatures, in the oxidation of CO to CO₂ [15]. Therefore, it is expected that in O₂-containing conditions the gold catalyst transforms CO into CO₂. To check this fact, both catalysts were studied in the CO oxidation in the presence of O₂. It was observed that whereas V-1 could not activate carbon monoxide at temperature lower than 100ºC, Au-1 was active even at room temperature. For Au-1 sample, CO conversion at 100ºC reached 45% with a reaction rate of 5.5·10⁻³ mol CO/(gcat·h) in spite of the fact that this catalyst has been activated at 550ºC. These results can explain that CO selectivity observed in the propane oxidation for VAu-1 catalyst is lower than that found for V-1 catalyst.

Additionally gold catalysts are also very effective in the preferential oxidation of CO in the presence of hydrogen (CO-PROX) as transforms CO into CO₂ with high selectivity avoiding a massive oxidation of H₂ [16] [17]. However, the reaction conditions must be controlled in order to prevent undesired reactions. This way, for most catalysts, CO-PROX takes place as the unique reaction until 200 ºC, but at higher reaction temperatures the inverse reactions (reverse water-gas shift and/or CO methanation) also occur to some extent.
More interestingly, Au catalysts are highly efficient in the water gas shift reaction (WGS) [18] with performances which can improve those of the typical industrial CuO/ZnO/Al₂O₃ catalysts [19-20]. In the WGS reaction CO reacts with water to yield H₂ and water as co-product. Therefore, this is the catalytic role of gold that makes it as a highly interesting material to be used for the combined process from propane as a higher H₂ production could be obtained. Besides, as shown above, gold is highly selective in the PROX reaction, so that a low H₂ decomposition is likely to occur. It is important to mention that the choice of the supports is very important as not all the supports for gold lead to efficient WGS results, especially those which are hardly reducible such as alumina or silica [18]. Among the best supports for gold reported in the literature we can find TiO₂ [21] which is the one employed in the present article.

Therefore the superior performance of mixed vanadium-gold catalyst observed in the present work is likely related to the high capacity of gold for water gas shift reaction. In order to corroborate these assumptions water gas shift reactions have been undertaken with these catalysts. Since in the propane reaction the catalysts are reduced throughout the reaction, apart from the fresh catalysts, catalysts pre-reduced in H₂ have also been tested.

Figure 4 shows the evolution of the CO conversion with the reaction temperature in the WGS reaction for fresh and reduced catalysts. If fresh catalysts are compared (Figure 4a) it can be observed that Au-1 catalyst is slightly more active than VAu-1 catalyst whilst V-1 catalyst shows the lowest activity, only being capable to activate CO at temperatures higher than 450ºC. The deficient performance of V-1 catalyst is likely due to the fact that the main vanadium species in the fresh catalyst are V₂O₅ (Fig 5) [6,7]. In fact, if V-1 is reduced in H₂, the catalyst begins to activate CO at only 150ºC (Figure 4b). We assign this behavior to the presence of reduced phases (V₆O₁₃ and V₂O₅) which
have been reported to be efficient phases for WGS [6,7]. It is noteworthy the high activity of mixed VAu-1 considering that it presents half of the gold than Au-1 and half of vanadium than V-1.

If reduced catalysts are compared in the WGS reaction (Figure 4b) different trends can be observed between low and high temperatures. At low temperatures, between 150 and 400ºC, V-1 catalyst presents conversions in the 2-8% range, whereas Au-1 catalyst begins to be active at 250ºC, reaching 10% conversion also at 400ºC. At higher temperature, the CO conversion increases more for the Au-1 catalyst than for the V-1 catalyst. Finally, the catalyst with the two active sites (VAu-1) outlines the best overall catalytic performance. Thus VAu-1 is more active than V-1 at temperatures below 400ºC and more active than Au-1 at higher temperatures.

XRD patterns of the samples are shown in figure 5. In the case of Au-1 the diffractogram hardly shows differences between fresh, reduced and used in propane oxidation, with main peaks corresponding to anatase TiO2 (JCPDS 21-1272) and less intense of rutile TiO2 (JCPDS 21-1276). Metallic gold (JCPDS: 4-784) was also detected with low intensity. Thus, the main peak of Au° at 38º cannot be clearly appreciated as it is overlapped with titania reflections, but a second of low intensity at 44º can be observed. In the case of V-1 important differences can be observed between fresh catalyst and those used in propane oxidation. Thus the fresh catalyst shows the typical diffractions of V2O5, whereas that drawn from the reactor at 425ºC shows mainly V2O5 and V6O13 with some reflections typical of VO2. Finally the sample used up to 475ºC shows diffraction peaks corresponding most of them to V6O13 whereas that used at 550ºC mainly V2O3 peaks. So, higher reaction temperatures in the absence of oxygen leads to more reduced vanadium compounds. In the case of VAu-1 no appreciable differences with the pure V-1 or Au-1 catalysts are observed. Thus the
degree of reduction of vanadium species is very similar compared to the pure V-1 catalyst, showing that the presence of Au/TiO₂ does not affect the reduction of vanadium species.

Figure 6a-f shows the TEM images for Au-1 catalyst in different conditions (fresh, reduced in H₂ or after propane oxidation at 550°C). No appreciable differences were observed among them. TEM and HR-TEM images show TiO₂ particles with sizes between 20-60 nm, with gold crystallites mainly between 4 and 8 nm. Therefore the better results obtained in the WGS by the fresh catalyst compared to the reduced one do not seem to be related to the variation in the size of gold crystallites. In this way Flytzani-Stephanopoulos [22] have reported that cationic Auδ⁺ is the main responsible for WGS reaction in gold catalysts, remarkably more than metallic gold. Then a surface analysis by XPS was conducted on gold (Fig 6g) to see if the different behaviour of fresh and reduced gold catalyst in WGS was related to the surface oxidation state of gold. However, it was observed that in all cases (Au-1 or VAu-1 fresh, used or reduced in H₂) gold is only present as Au⁰ and therefore, the oxidation state of gold neither seems to be the reason for the enhanced WGS reaction of the fresh catalysts containing gold compared to the reduced ones.

**Final remarks**

The addition of gold to a vanadium pentoxide catalyst highly enhances the hydrogen formation of vanadium pentoxide alone utilizing propane and oxygen in defect. Whereas the gold-free vanadium catalyst can produce hydrogen in our reaction conditions, the catalyst with only gold presents low capacity for propane activation and the formation of hydrogen is null. Additionally, the catalyst with only gold if propane and oxygen are fed does not yield CO, only CO₂ with very low amounts of propylene.
Therefore for gold sites to exert the WGS reaction, the previous formation of CO is necessary and this is done by vanadium pentoxide. Thus, when gold and vanadium are present together a remarkably higher hydrogen production is observed. This synergistic effect observed between gold and vanadium is not straightforward to explain as many reactions can take place simultaneously in our work conditions. However we think the improved performance is the result of the presence of different active sites: vanadium sites, mainly oxidised sites, activate propane whereas if reduced are efficient for water gas shift reaction. These two vanadium oxide phases can coexist in the same catalyst as in the first part of the catalytic bed still there is some oxygen with vanadium in an oxidized state then producing propylene, CO$_2$, water and CO; in the second part of the bed already without oxygen vanadium will be present as reduced species, which is relatively efficient for H$_2$ production by water gas shift. On the other hand, gold can hardly activate propane but are highly active in the formation of hydrogen by water gas shift reaction increasing the formation of hydrogen from the CO and water formed in the first part of the catalytic bed.

This study is only preliminary and consequently further experiments are required to fully explain this synergistic effect between gold and vanadium.

**Conclusions**

A catalyst comprising vanadium and gold using titanium oxide as a support yields a high concentration of hydrogen from propane and oxygen in defect, remarkably higher than those obtained by catalysts comprising either only vanadium or only gold (this presenting a low reactivity for this reaction). The excellent performance for the water
gas shift reaction of gold sites and V$_2$O$_3$ complements the capacity of vanadium sites for producing CO from propane, leading to a higher hydrogen formation.

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Figure 1. Evolution of the propane (Fig 1a) and oxygen (Fig. 1b) conversion 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.
Figure 2. Evolution of the Selectivity to propylene and CO₂ (Fig 2a) and CO (Fig. 2b) with the reaction temperature in the propane oxidation. Symbols: (□,■,■) V-1, (○,●,●) VAu-1, (Δ,▲,▲) Au-1. Propylene (□,○,Δ), CO₂ (■,●,▲), CO (●,●,▲). Note: Propane/O₂/He = 10/10/80 molar ratio. Remaining reaction conditions in text. Dotted and continuous arrows indicate the temperature for the oxygen total consumption for VAu-1 and V-1, respectively.
Figure 3. Yield to H$_2$ in the propane oxidation at 425, 475 and 550ºC by V-1 (black bars), VAu-1 (red bars) and Au-1 (white bars). Note: Propane/O$_2$/He = 10/10/80 molar ratio. Remaining reaction conditions in text.
Figure 4. Water Gas Shift reaction on fresh (Fig. 4a) and reduced in H₂ (Fig. 4b) catalysts. **Symbols:** (■) V-1, (○) VAu-1, (▲) Au-1. **Note:** CO/H₂O/N₂ = 7.1/32.9/60.04 molar ratio. Remaining reaction conditions in text.
Figure 5. XRD patterns of V-1, VAu-1 and Au-1 catalysts after different treatments/conditions. Phases: ■ V₂O₅ (JCPDS: 1-359), ○ VO₂ (JCPDS: 72-0514), ● V₆O₁₃ (JCPDS: 27-1318), △ V₂O₃ (JCPDS: 84-317), ▲ Auº (JCPDS: 4-784), ▶ TiO₂-anatase (JCPDS: 21-1272), □ TiO₂-rutile (JCPDS: 21-1276).
Figure 6. Characterization of Au-1 catalyst: A) TEM and HR-TEM images of Au-1 catalyst: fresh (a,d), used in propane oxidation at 550ºC (b,e) and reduced in H₂ (c,f). B) XPS spectra for Au-1 catalyst for fresh, reduced in H₂ and used in propane at 550ºC.