



Total oxidation of propane in vanadia-promoted platinum-alumina catalysts: Influence of the order of impregnation



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ABSTRACT

Differently prepared vanadium promoted Pt/alumina catalysts have been prepared, characterized and tested for propane total oxidation. V-promoted Pt/Al₂O₃ catalysts have shown remarkably higher catalytic activity than V-free Pt/Al₂O₃ catalyst. Among V-promoted Pt catalysts that prepared by coimpregnation gave the highest alkane conversions in the whole range of reaction temperatures studied. Factors such as Pt particle size or the oxidation state of platinum do not seem to be the responsible for the enhanced performance. Modification of the redox properties of the catalyst (i.e. high reducibility of vanadium species) likely provoked by the close contact between platinum particles and vanadium species and the partial introduction of vanadium in the platinum particles can be related to the improved reactivity of the PtV catalysts.

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1. Introduction

Although CO₂ is one of the main responsible for the greenhouse effect, short chain alkanes present a greenhouse effect of more than an order of magnitude greater than CO₂ [1]. In addition, international organizations are imposing increasingly stringent targets for the emissions of volatile organic compounds (VOC's). Therefore, the elimination of these pollutants is becoming a first order priority.

The design and selection of new catalytic systems for complete oxidation of hydrocarbons is an important task of the environmental catalysis. Noble metals based catalysts have been widely studied for the combustion of alkanes due to their high reactivity and their resistance to sulphur poisoning [1], in particular Pd- and Pt-based catalysts. Although noble metal catalysts have been studied by many research groups, there is not a uniform agreement about the active species. Factors such as if short chain alkane combustion is structure-sensitive [2,3] or structure-insensitive [4,5] and the oxidation state of the metal [6–9] are still under discussion.

Modification of noble metal supported catalysts, such as Au, Pd or Pt on Al₂O₃, TiO₂, ZrO₂ or CeO₂, by addition of vanadium

is a subject receiving particularly attention [10–19]. Generally, it has been observed that vanadium promoted catalysts present higher conversions, better selectivity and extended resistance to deactivation than unpromoted catalysts. Although there is not a general agreement in the literature alloying phenomena, modification of the support properties [12], modification of the palladium/platinum particle size [15] and modification of the redox properties [10,11,14,16,17] of the catalysts are considered as the key factors to explain the improvement in the catalytic performance when vanadium is added. The influence of the electronegativity of the additives in Pt-catalyst was also studied for the total oxidation of propane [20]. A decrease in the oxidation state of Pt if the additive presented relatively high electronegativity, as it is the case of vanadium, was associated to the improvement of the catalytic activity.

Although it is generally accepted the promotional effect of vanadium in Pt catalysts for the short chain alkane combustion, there is not any work dealing with the influence of the preparation method of PtV catalysts for the total oxidation of short chain alkanes. The influence of the preparation method in the catalytic performance for Pt–V or Pd–V catalysts has been studied for several catalytic reactions. Barkova and Furman [21,22] studied the effect of the synthesis procedure on Pt–V catalysts for the dehydrogenation and hydrogenolysis of short chain alkanes. They found that the efficiency of Pt–V/Al₂O₃ catalysts can be controlled by varying the conditions of treatment of the modified support or by changing

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the V/Pt atomic ratio. The preparation method of Pd–V catalysts for the reduction of NO in presence of carbon monoxide has also been studied [23].

The present work is devoted to study the influence of the preparation method over the catalytic properties and the physicochemical characteristics of mixed Pt/V/Al₂O₃ catalysts. As most of Pt-catalysts synthesized up to date for the combustion of lower alkanes have been prepared by impregnations methods, these catalysts were synthesized by three different impregnation methods: (i) deposition of vanadium on a Pt/Al₂O₃ catalyst, (ii) deposition of platinum on a V/Al₂O₃ catalyst and (iii) co-impregnation of vanadium and platinum on the alumina support.

2. Experimental

The co-impregnated catalyst was prepared by dissolving H₂Cl₆Pt × H₂O (Aldrich 99.9%) in deionised water at 80 °C. The solution was heated to 80 °C and stirred continuously. An appropriate quantity of ammonium metavanadate (Aldrich 99+%) and oxalic acid (1.59 g, Aldrich 99+%) were added to the solution. Aluminium oxide (Sasol, S_{BET} = 179 m² g⁻¹) was added to the heated solution and stirred at 80 °C to form a paste. The resulting paste was dried at 110 °C for 16 h. The catalyst contained 0.5 wt% Pt and 6.0 wt% V. A similar method was used to prepare Al₂O₃ based materials with vanadium, 6.0 wt% V/Al₂O₃ and with noble metal, 0.5 wt% Pt/Al₂O₃. These based materials were used as supports by the two steps impregnated catalysts. Pt was impregnated on the 6.0%V/Al₂O₃ catalysts and V was impregnated on the 0.5%Pt/Al₂O₃ catalysts, following the above explained method. Final catalysts were prepared by calcination in static air at 550 °C for 6 h.

Catalytic activity was determined using a fixed bed laboratory micro reactor. Catalysts were tested in powdered form using a 1/4" o.d. stainless steel reactor tube. The reaction feed consisted of 5000 vppm hydrocarbon in air. A total flow rate of 50 ml min⁻¹ was used and catalysts were packed to a constant volume to give a gas hourly space velocity of 45,000 h⁻¹ for all studies. At each temperature three analyses were made and the value plotted corresponds to the average of them. The relative standard deviation of the repeated activity values was ca. 3%. Prior to the first analysis at a given temperature the system was left for 60 min stabilizing.

Stabilization tests on selected catalysts (data not shown in this article) were carried out overnight at different reaction temperatures depending on the catalyst. Thus, the reaction temperature for the stabilization experiments was fixed to give a propane conversion between 60 and 80%. No deactivation was observed for all the catalysts tested.

Analysis was performed by an on-line gas chromatograph with thermal conductivity and flame ionization detectors. Catalytic activity was measured over the range 100–550 °C and temperatures were measured by a thermocouple placed in the catalyst bed. Conversion data were calculated by the difference between inlet and outlet concentrations and all carbon balances were in the range 100 ± 10%.

Catalyst surface areas were determined by multi point N₂ adsorption at 77 K, and data were treated in accordance with the BET method. The CO uptake of platinum catalyst was measured by pulse-adsorption of CO at 35 °C using an Argon flow of 20 ml min⁻¹ and pulses of 0.2 ml of 10% CO in Argon. Prior to CO uptake determination all samples were treated under flowing hydrogen (50 ml min⁻¹) at 400 °C and then flushed by Ar at 400 °C (20 ml min⁻¹) for 60 min.

Temperature-programmed reduction (TPR) was carried out in a Micromeritics Autochem 2910 equipped with a TCD detector. The reducing gas used in all experiments was 10% H₂ in Ar, with a flow rate of 50 ml min⁻¹. The temperature range explored was

from room temperature to 650 °C. The heating rate was maintained at 10 °C min⁻¹ for all samples whilst the sample mass was varied depending on the sample under study. Details of specific conditions are given with the TPR profiles.

X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra-DLD photoelectron spectrometer employing monochromatic Al K α radiation (12 mA, 12 kV), utilizing the hybrid spectroscopy mode, incorporating both electrostatic and magnetic lenses for increased sensitivity, in this mode the analysis area is approximately 300 × 700 μ m. Charge compensation was achieved using the Kratos immersion lens and subsequently setting the C(1s) peak attributed to adventitious carbon to 284.8 eV. Spectra were processed using CasaXPS v2.3.16 using sensitivity factors provided by the manufacturer. All binding energies quoted are \pm 0.2 eV.

Diffuse reflectance UV–vis spectra were recorded on a Cary 5 equipped with a Praying Mantis attachment from Harric. The sample cell was equipped with a reaction chamber that allows “in situ” experiments under controlled environment. In particular our samples were dehydrated in dry air at 673 K for 30 min. The spectra were collected upon cooling down to room temperature flowing dry air through the sample to avoid re-hydration processes.

Morphological, compositional and structural analysis of samples were performed by high resolution transmission electron microscopy (HRTEM) with a field emission gun TECNAI G2 F20 microscope operated at 200 kV, having the capabilities of selected area electron diffraction (SAED) and energy dispersive X-ray spectroscopy (EDX). The samples were also used to determine the elemental composition and distribution of platinum and vanadium in alumina matrix by using EDX-mapping. The composition of samples was determined by energy dispersive X-rays spectroscopy (EDX) measuring 6 different extended areas of about 200 nm × 200 nm areas for all catalysts. As the areas analyzed are large the distribution was found to be very uniform. In order to prepare the TEM samples, the Pt–V/Al₂O₃ powder samples were treated by sonicating in absolute ethanol for several minutes, and a drop of the resulting suspension was deposited onto a holey-carbon film supported on a copper grid, which was subsequently dried.

3. Results and discussion

Fig. 1 shows the evolution of the propane conversion with the reaction temperature for V, Pt and mixed Pt/V catalysts. Only CO₂ was detected as product in Pt and Pt/V catalysts, whereas in V-catalyst CO₂ was the main product and propene was also

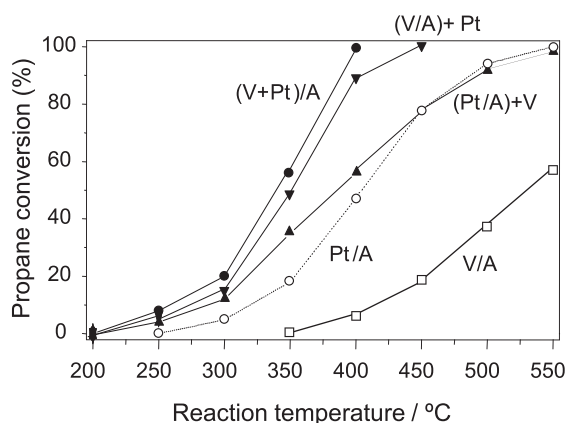


Fig. 1. Evolution of the propane conversion with the reaction temperature for V/A (□), Pt/A (○), (Pt/A)+V (▼), (V/A)+Pt (▲) and (V+Pt)/A (●). Reaction conditions in text.

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