



Supported, bulk and bulk-supported vanadium oxide catalysts: A short review with an historical perspective



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This paper is dedicated to Prof. Israel E. Wachs on the occasion of his three decades in academia.

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ABSTRACT

The beginning is a very delicate time for understanding. Concepts are better understood when the student knows the historic perspective. Their minds apprehend the evolution of knowledge and, to some extent, share fundamental discoveries. Students will not understand, for example, the actual model of the structure of an atom if they do not understand first the models proposed by Thomson and Bohr. However, due to the high number of research papers that are nowadays published, sometimes researchers forget to review some of the old papers in which the basis of knowledge were established, and those bases allow to build new achievements, allow to understand where are we, and where are we going. In this context, the main objective of the this article is to present the basis of knowledge regarding supported vanadium oxide catalysts, with an historical point of view. It presents how the main achievements were described in this field, and to do that, the literature century has been reviewed, and especially the progress in the 1980s and 1990s, since the influence of synthesis method and oxide support, the structure of the active phases, and the concept of monolayer were established in those years. The final part of this paper briefly presents the evolution of knowledge that has taken place during the past decade in this field, and some future trends are anticipated.

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1. Bulk and supported vanadium oxide catalysts: once upon a time a hundred years ago

Vanadium oxides are fascinating materials that are well-known for their catalytic properties. Nowadays, these materials find several industrial applications such as gas sensors, electrochemical and, optical switching devices, reversible cathode materials for Li batteries, and as catalysts. For developing such applications, these materials have been extensively studied during the past 100 years; it is the aim of present paper to present a brief review about how the knowledge that we have about vanadium oxide catalysts, specially about supported vanadium oxide, and how it has been evolving during the last century.

In 1922, Taylor published a nice review entitled “Catalysis and Catalytic Agents in Chemical Processes” [1] in which V₂O₅ and other oxides, such as MoO₃ and WO₃, appeared as catalytic agents for oxidation of hydrocarbons reactions. Taylor pointed out the reason of the catalytic activity of such oxides in that paper: “The oxides of well-defined stability are conspicuously absent (it refers to the list of known catalysts). The oxides of the alkali metals, to a less

extent those of the alkaline earths, definite irreducible oxides such as magnesium oxide and aluminium oxide are not frequently to be found among the oxide catalysts of oxidation. On the other hand, the labile oxides such as those of iron, copper, manganese, silver, vanadium, tungsten, molybdenum, uranium, chromium, cobalt and cerium are frequently to be noted in a systematic study of such oxide catalysts of oxidation. In view of what has been said with regard to the catalyst as promoter of electronic instability in the reacting molecules, it is interesting to observe that this large class of catalytic agents is made up of compounds of elements which all show a ready tendency to modify the configuration of electrons surrounding their positive nuclei. In the older nomenclature they are the oxides of polyvalent metals. It is undoubtedly due to this variability of electronic configuration that their oxidation activity is due. In this paper we find a nice introduction to the catalysis of V₂O₅ and other oxides and to the advantages of the use of a catalytic support: ‘... the loss of catalytic activity can be largely suppressed if the active material is spread upon an inert support’. Thus, catalytic supports, such as asbestos fibers, magnesium sulphate, glass wool or silica, have been used for more than one hundred years for improving mechanical resistance of the solid catalysts, for achieving active sites isolation, and to reduce the amount of active phase required for preparing an active catalyst. The question is, what is a supported catalyst? When is a simple mixture of two oxides consid-

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ered a supported catalyst? Where is the composition limit between a supported catalyst (a small amount of a certain active phase such as V_2O_5 on the surface of another material that normally is another oxide) and a simple mixture of oxides?

During the following decades, more efforts were done understand the relationships between the structure of vanadium oxides and their catalytic properties; for example, in 1957 [2], a paper by Berets et al. discusses about the electronic properties and the structure defects, and their relationship with the catalytic activity. It is also well known that in the fifties, Mars and van Krevelen investigated the reaction mechanism involved in the oxidation reactions carried out by V_2O_5 catalysts, and they postulated that a lattice oxygen of the oxide catalysts was incorporated to the oxidation product [3], then, such reduced site would be oxidized by the molecular O_2 reactant, recovering the original catalysts structure. The experimental evidences of such mechanism have been found for different oxidation reactions and several oxide catalysts [4]. In 1979, it was described [5] that the catalytic properties of doped V_2O_5 were improved with respect to those of undoped bulk V_2O_5 , this fact was related with the possibility of having oxygen ion vacancies in the doped sample. Several kinetic studies of reaction catalyzed by V_2O_5 catalysts were performed during 1960's and 1970's [6–10], but the problem at that time was that the characterization techniques were not able to give an idea about the real structure of catalysts. So, it was not possible to perform studies about the relationships between structure and activity of catalysts. In addition, most of these studies were performed by chemical engineers, and were more focused on the reaction conditions and reactor properties than in the structure of catalysts, although it is also necessary to understand which the structure of catalysts is in order to understand the catalytic process. Some studies also focused on supported V_2O_5 catalysts [11], since up to that moment the major part of the studies about supported catalysts focused on noble metals. Although XRD was available, in those days it was difficult to characterize V_2O_5 catalysts. Some efforts were still necessary to develop the adequate techniques for characterization of the surface of solids under different conditions.

2. First steps on the discovery of the structure of supported vanadium oxide catalysts

Around 1970, the catalysis researchers started to think that it was important to characterize the structure of the catalysts in order to identify the active phases and to establish relationships between the structure and the activity of catalysts; this would allow the design of more active and selective catalysts. One of the first papers that tried to describe the characterization of supported V_2O_5 catalysts was published in 1969 by Takahashi and coworkers [12]. In this paper they prepared two supported V_2O_5 catalysts using two different supports, both around 5 wt% of V_2O_5 , without considering the surface area of aluminas and Neobead-Alundum. Both supported catalysts were characterized by ESR, the spectrum of one of the samples was found to be similar to that of bulk V_2O_5 , whereas the other was completely different. This finding was very important since it demonstrated that the structure of the V_2O_5 oxide changes when it is supported. They did not take into consideration the surface area of both supports, thus, it is likely that these two samples had very different amounts of VOx units per nm^2 , and this could be the reason of such differences in the ESR spectra. One year later [11], a paper was published in which the concept of effective surface area was considered since it was found an optimum amount of the active component (V_2O_5) supported on the support (SiO_2 in this case). They assumed that the effective surface area is proportional to the amount of the active component supported on the carrier,

and interpreted the dependence of the rate constant on the amount of the supported active component.

During the 1970s, spectroscopy techniques such as FTIR (earlier) and Raman (later) started to be applied for the characterization of solids, and the spectra of the series of oxides were described and catalogued. The catalysis researchers started to apply those characterization techniques to supported catalysts and; in the case of oxides, they discovered that Raman spectroscopy was a very informative technique. Brown et al. published two papers in 1977 [13,14] that can be considered the first rigorous study of characterization of supported metal oxide catalysts with Raman spectroscopy. They focused in supported MoOx catalysts, using alumina and silica-alumina as supports. They pointed out that, in contrast to the IR spectra, the Raman spectra are almost free for a contribution of the oxide support, permitting the study of the vibrations associated with the supported oxide active phases. They determined that depending on the amount of MoOx incorporated, bulk MoO_3 was detected or not, thus, they propose that each support has a limit of MoOx units that can be incorporated resulting in a “saturation” of the surface. They calculated a limit of approximately 20% MoO_3 in this study, assuming a surface area of $200\text{ m}^2/\text{g}$ for the support. Thus, this could be considered as the first definition of what a supported metal oxide catalyst is, establishing a limit of active phase that can be incorporated to the support without the presence of crystalline oxide structures. Below this limit, they could not identify completely the nature of the supported MoOx phase, described as tetrahedral MoO_4^{2-} , $Al_2(MoO_4)_2$, and “other interaction products”. They also detected a Raman band near 950 cm^{-1} , whose exact nature could not be described at that moment.

By 1985, Wachs published a seminal paper [15] that gave a step ahead in this field, introducing the modern concept of monolayer coverage. Both XRD and LRS were used to characterize supported VOx/ TiO_2 catalysts employed for o-xylene oxidation to phthalic anhydride. In this paper two different types of VOx species on the TiO_2 support were described. Below monolayer coverage, surface vanadia species coordinated to the TiO_2 support are described and characterized by a very broad Raman band, around 1000 cm^{-1} , that was described to belong to disordered surface phase of vanadium oxide (Fig. 1). For coverages higher than monolayer, crystallites of V_2O_5 were found. It was demonstrated that the dispersed surface vanadia species were the active phase for the oxidation reaction, and subsequently, the catalysts with coverage close to the monolayer were found to be the most active and selective. It was described that the V_2O_5 crystallites were detrimental for the catalytic activity. In this paper, it was pointed out that the coordination of the surface vanadia species could not be assigned by the Raman data, and it was presented a XANES study by Kozłowski et al. [49] that described the vanadia species supported on titania with two terminal bonds (Fig. 2). Wachs suggestion that monolayer coverage catalysts were more active was confirmed one year later, by the group of Ross [16], which described as the most active and selective for the NOx reduction with ammonia the supported vanadium catalysts with coverage close to monolayer. They found these supported catalysts with coverage close to monolayer as more active and selective than commercial bulk catalysts, giving an important step ahead in the design of catalysts with commercial applications. In this line, several papers were published by 1986. Two papers by Bond et al. [17,18], that described the characterization by XPS and LRS of supported vanadium oxides on titania. They described three types of VOx species and made an estimation of monolayer capacities. The monolayer was defined in this study as $0.10\text{ wt}\% V_2O_5/nm^2$, and they described the appearance of V_2O_5 crystals for coverages up to 4 monolayers, establishing three types of VOx species. Below one monolayer they described VOx species as oxo-hydroxy species bonded to two surface oxygens. Between one and four as “layers of amorphous V_2O_5 ” and for contents up to 4 mono-

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