Catalytic activity in partial oxidation of methane and physico-chemical characterization of a VPO system obtained from boiler ash

Luis J. Alemany*, María A. Larrubia, José M. Blasco
Departamento de Ingeniería Química, Facultad de Ciencias, Campus de Teatinos s/n, Universidad de Málaga, E-29071 Malaga, Spain

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Abstract

Bottom ash from the combustion of fossil fuels contain a higher amount of vanadium. The recovery and the precipitation could be an attractive route for the synthesis of a catalytic system (VPO). The morphology and structure of the precursor and the final systems, calcined at different temperatures, obtained using bottom ash as raw material, have been assessed using different techniques. Both VPO-bulk system and supported on different silicas have been tested in the partial methane oxidation. The experimental results are comparable to those reported for catalyst systems and performed in similar conditions. The reactivity appears to be essentially related with the exposed sites and the contribution of catalyst surface. © 1998 Elsevier Science B.V.

Keywords: Ash; Waste recovery; Chemical synthesis; VPO catalyst; Methane oxidation

1. Introduction

Catalytic oxidation is a very important technology in modern chemical industry. The best-known oxidation of a lower alkane is the selective oxidation of \textit{n}\textendash{}butane to maleic anhydride on vanadium\textendash{}phosphorus oxides (VPO) [1\textendash{}3], this represents one of the few highly selective processes available for the utilization of an alkane. VPO catalysts can also be selective in the oxidation of ethane and propane, but only when very mild conditions are used, at which the products can be saved from consecutive unselective degradation [4\textendash{}6].

The VPO are a fascinating and complex system; various distinct compounds can be formed whose structural, redox, catalytic and topological interrelationships have been extensively discussed due to its wide applications, especially in the \textit{n}\textendash{}butane oxidation. In a previous research, exclusive attention has been paid to catalysts formed from the catalyst precursor \textit{VOHPO}_{4}0.5 \textit{H}_{2}\text{O} leading to a final catalyst comprising mainly \textit{(VO)}_{2}\text{P}_{2}\text{O}_{7}, which is the active/selective phase for the commercial production of maleic anhydride by gas-phase catalytic oxidation of \textit{n}\textendash{}butane [7,8], but there are no clear and unequivocal data that demonstrate this belief [9]. The catalysts surface, the composition and structure under reaction are studied because these remain unresolved not only due to the difficulty to characterize the catalyst, but also because of the particular conditions of preparation of the VPO precursor. Moreover, some recently published data seem to indicate that the active phase is
an amorphous vanadium phosphate of P/V ratio around two supported on vanadyl pyrophosphate [10]. Recently, the catalytic role of VO(H2PO4)2, the precursor of VO(PO3)2 phase has been studied for n-butane oxidation. The final catalyst derived from VO(H2PO4)2 has a low specific activity on the basis of n-butane conversion per unit mass, but the intrinsic activity is found to be higher than that of (VO)2P2O7 [11], thus the preparation of catalysts based on the phosphorus-rich VO(H2PO4)2 should be of great significance for industry.

Oil-fired furnaces produce two grades of waste ashes. One is produced directly in the furnace and deposited in the ash pit beneath the flame zone or outside the boiler tubes (boiler ash), it is known to be rich in elements such as vanadium and nickel [12]. The second is collected in the electrostatic precipitators (fly ash) and its vanadium content is lower. Resource recovery of ashes generated from power plant is one of the most important issues of power plant waste management.

In this work, a possible new potential use of this waste has been identified by synthesizing widely sought VPO from the bottom ash as one of the starting raw materials. We propose an attractive route synthesis of VPO systems from boiler ash which is relatively inexpensive and environment-friendly. Their catalytic behavior has been testified in the partial methane oxidation (POM), because this reaction has attracted the attention of many research groups over the last years. The activity for the methane conversion has been reported to be related with dispersed surface metal oxides on silica-supported Mo and V oxides. Besides, the addition of various promoters have resulted in an increase of the yield. Thus, P atoms have been described as promoters for the oxygenated yield when added to metal oxide systems. As VPO phases are good partial oxidation catalysts, it was deemed interesting to explore its behavior during methane oxidation.

2. Experimental

The bottom ash used in this study was collected from a conventional fuel-oil power plant (Puertollano-Spain). The chemical composition of this material has been determined and is given in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>(ppm) or (%w/w)</th>
<th>Element</th>
<th>(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>180 000</td>
<td>V</td>
<td>123 700</td>
</tr>
<tr>
<td>Ni</td>
<td>85 000</td>
<td>Ni</td>
<td>25 700</td>
</tr>
<tr>
<td>Co</td>
<td>500</td>
<td>Co</td>
<td>—</td>
</tr>
<tr>
<td>Cr</td>
<td>35 000</td>
<td>Cr</td>
<td>—</td>
</tr>
<tr>
<td>Cu</td>
<td>2 000</td>
<td>Cu</td>
<td>—</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>17.15</td>
<td>Fe</td>
<td>11 800</td>
</tr>
<tr>
<td>SiO2</td>
<td>14.08</td>
<td>Si</td>
<td>—</td>
</tr>
<tr>
<td>Al2O3</td>
<td>11.19</td>
<td>Al</td>
<td>6 800</td>
</tr>
<tr>
<td>MgO</td>
<td>1.08</td>
<td>Mg</td>
<td>800</td>
</tr>
<tr>
<td>CaO</td>
<td>0.73</td>
<td>Ca</td>
<td>2 000</td>
</tr>
<tr>
<td>NaO</td>
<td>3.69</td>
<td>Na</td>
<td>25 500</td>
</tr>
<tr>
<td>K2O</td>
<td>0.18</td>
<td>K</td>
<td>—</td>
</tr>
<tr>
<td>P</td>
<td>nd*</td>
<td>P</td>
<td>205 000</td>
</tr>
</tbody>
</table>

* Not determined.

2.1. Preparation of bulk system

A sample of ash was leached with hydrochloric acid solution (37%) for recovery of vanadium at room temperature whereas weight ratio of ash/reagent (HCl) was 1/4. The leachate was filtered and partially evaporated. At this point 2-propanol and a phosphoric acid solution (85%) were added (2/1 vol. ratio) and the mixture was refluxed for 2 h. The precipitated solid was obtained by mild evaporation, and it was washed repeatedly with acetone and dried in air at 333 K overnight. This product is identified as VPO-RT (at room temperature). The VPO-RT was calcined in air at 773, 1023 and 1173 K for 4 h. These are labeled as VPO-LT (low temperature), VPO-MT (medium temperature) and VPO-HT (high temperature), respectively.

2.2. Preparation of supported systems

Supported VPO samples (denoted as VPO/A and VPO/D, where A is associated to silica from Aldrich and D to Aerosil from Degussa) have been prepared so as to contain an amount proportional to the support surface area. The amount loaded was calculated to be similar to that needed to cover all the support surface in the case of a homogeneous dispersion. They were prepared by a conventional impregnation technique using VPO-RT water solutions and calcined at 673 K for 4 h.
2.3. Characterization techniques and catalytic test

Chemical analysis by ICP (Inductive Coupling Plasma) measurements were performed in a Perkin–Elmer Emission Spectrometer Plasma 40 instrument. The specific surface areas were measured according to the BET method, using N$_2$ at 77 K in a Carlo Erba 1800 Serie instruments. The resulting phosphorus and vanadium contents were evaluated by EDX with a Philips CM-200 apparatus. Thermal analysis (TG and DTA) was carried out on a Rigaku Termoflex instrument with a heating rate of 15 K/min, in air. X-Ray powder diffraction patterns were obtained with a Siemens D-501 automated diffractometer using graphite monochromatic CuK$_\alpha$ radiation. For each sample, Bragg’s angles between 5 and 50° (2θ) were scanned at a rate of 1°/min. Raman spectra were obtained with a Brucker FT-Raman instrument using the 1064 nm exciting line. Samples were placed in stationary sample holders and kept in the ambient environment. The power was fixed to the range 20–40 mW in order to avoid sample vaporization. Infrared spectra were recorded with a Perkin–Elmer 1760 X Fourier Transform infrared spectrometer. The samples were prepared by dilution in KBr (1%).

Steady-state reaction was carried out at atmospheric pressure in a 9 mm I.D. quartz fixed-bed reactor. The reactor was designed so that very low dead volume was present downstream of the catalyst bed to prevent further decomposition of partial oxidation products. The reactor effluent was analyzed by an on-line Hewlett–Packard HP-5890-II gas chromatograph (GC) fitted with thermal conductivity detector. Chromosorb 107 and 5A molecular sieves packed columns were used with a column isolation analysis system. All the lines from the reactor to the GC were heated above 373 K to avoid water and formaldehyde (FA) condensation. The catalytic runs were performed with 0.2 g of catalyst pretreated for 2 h in O$_2$ at 1023 K before starting the flow of methane in the system, CH$_4$/O$_2$ = 2, W/F = 2 gh/mol.

3. Results and discussion

3.1. Characterization

The ash consists of a relatively insoluble alumino-silicate core with a surface of more soluble trace elements with a minimal specific surface area (< 4 m$^2$/g) and a significant content of transition elements such as vanadium, nickel and chromium.

The obtained precursor (VPO-RT) is a blue–green solid, highly soluble in water with low specific surface area (< 2 m$^2$/g). The chemical analysis shows that this system is formed by an important weight of vanadium and phosphorus. It is important to note that what is to be added in the preparation, besides phosphorous so that the chemical composition of VPO-RT obtained further differs from that of boiler ash. However, it also showed an amount of some elements, mainly Ni, Fe and Na. Because the leaching with strong acid solution is not a selective method (Table 1).

The phosphorus and vanadium contents for VPO-RT and VPO-MT were obtained by EDX analysis and the results show a good consistence with those obtained by chemical analysis (ICP). The results are given in Table 2.

Thermal evolution of VPO-RT system was evaluated by TG-DTA run, and TG and DTA are shown in Fig. 1. As can be seen, mainly three regions can be delimited in the TG curve. For temperatures below 573 K, a gradual loss of weight is observed (c.a. 14%) which probably corresponds to the loss of non-structural water/solvent molecules due to both the precursor system, as well as the excess decomposition of superficial H$_3$PO$_4$ and two associated endothermic peaks centered at 373 and 413 K, respectively. In the 573–953 K range, a strong loss weight (c.a. 11.6%) is measured. An endothermic peak close to 673 K might be associated with the precursor (VPO-RT) decomposition. Apparently, the thermal decomposition of the precursor occurs in a single transition. A slight loss of weight (c.a. 2%) can be observed at higher temperatures and the consequent endothermic peak c.a. 1023 K is may be due to further structural changes and/or partial fusion and sublimation.

<table>
<thead>
<tr>
<th>System</th>
<th>P/V</th>
<th>$S_{\text{BET}}$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VPO-RT</td>
<td>1.43</td>
<td>≈ 2</td>
</tr>
<tr>
<td>VPO-MT</td>
<td>1.18</td>
<td>≈ 2</td>
</tr>
<tr>
<td>VPO/A</td>
<td>1.38</td>
<td>4</td>
</tr>
<tr>
<td>VPO/D</td>
<td>1.33</td>
<td>19</td>
</tr>
</tbody>
</table>
The X-ray diffraction pattern of the four obtained systems (VPO-RT, VPO-LT, VPO-MT and VPO-HT) are shown in Fig. 2. The VPO-RT pattern was found to contain the VO(H₂PO₄)₂ phase [13,14], demonstrating that this phase has been successfully synthesized, but it contain a small phase non identified possibly related to a mixture phosphate phase (Ni, Fe, Na) in accordance with the chemical analysis where an important amount of these elements can be seen. This fact might be responsible for a lower temperature in the precursor decomposition (673 K versus 693 K) than that for another obtained systems [15].

The dehydrated product at 1023 K was identified as VO(PO₃)₂ phase, according to the literature [1,8,11,14]. However, this phase was also evident at 873 K. The transformation occurs through an amorphous phase as can be seen for the VPO-LT in the X-ray diffraction pattern (Fig. 2). It must be noted that, no evidence was observed in the powder X-ray diffraction pattern for the formation of a new crystalline phase at high temperature (VPO-HT). The VPO-MT and VPO-HT X-ray patterns are similar for these systems. The diffraction patterns of the VPO-MT and, to a lesser extent, of VPO-HT indicated the presence of VO(PO₃)₂ phase.

At the highest temperature for sample treatment superimposed to the aforementioned features, a broad amorphous contribution can be detected. This fact can be related to a partial fusion with a minimal sublimation, (associated with a strong endothermic peak detected at 1023 K, see. Fig. 1) and, subsequently, a decreasing in the XRD intensities.

Besides, as previously reported, the endothermic peak in the 633–703 K range is associated with VO(H₂PO₄)₂ decomposition [16]. During this transformation, a rearrangement occurs due to loss of water. Possibly, the transformation involves only breaking of V-OH₂ and/or P-(OH)...H bonds and leaves the V–O–P ones intact. The single transition can be explained with the help of a different structure of VO(H₂PO₄)₂. According to Bordes [14], O–V–O–P–O chains are diagonally formed, each equatorial oxygen of the VO₆ octahedron being shared with one of a tetrahedron O₃P(OH)₂, and four tetrahedra are hydrogen-bonded by means of the two hydroxyl groups. In the perpendicular direction, the O=V...V=O chains are parallel to the square channels drawn by the hydrogen bonds between the chains of...
O$_2$P(OH)$_2$. As a consequence of this structure, the decomposition of VO(H$_2$PO$_4$)$_2$ affects two hydroxyl groups of the same phosphorus unit and, thus, explains the transformation as a single step.

FT-Raman characterization studies of these materials are scarce in literature. Sananes et al. [11] have studied the precursor structure using LRS (Laser Raman Spectroscopy) and the reported results are the first for this phase. Fig. 3 presents FT-Raman spectra recorded at room temperature in the 800–1200 cm$^{-1}$ range, related to the stretching modes of the P–O and V–O bonds. The precursor VO(H$_2$PO$_4$)$_2$ presents an intense band close to 932 cm$^{-1}$. The VPO-LT presents a poor spectra, typical of a lower crystallinity, in concordance with the X-ray diffraction for the amorphous phase showed at this temperature. When the precursor is calcined at 1023 K (VPO-MT) a major characteristic band is visible at 971 cm$^{-1}$, in accordance with the literature.

It is noteworthy that the bottom ash can be used as a starting raw material for the vanadium recovery and precipitation as a VPO catalytic system.

Partial oxidation of methane (POM) to C$_1$-oxyg enates (formaldehyde and methanol) in a single catalytic step appears to be one of the most attractive routes to convert natural gas into chemicals [17,18]. Among the best catalysts reported to selectively oxidize methane to C$_1$-oxyg enates are MoO$_3$/SiO$_2$ and V$_2$O$_5$/SiO$_2$ [19–22]. High formaldehyde selectivity is only obtained at low methane conversions, whereas at higher conversions the total oxidation products (CO and CO$_2$) become predominant. The contribution of the catalyst surface area and the addition of various promoters to the aforementioned catalysts have resulted in an increase of the formaldehyde yield. Thus, P atoms have been described as promoters for the formaldehyde yield when added to metal oxides systems [23,24]. As vanadyl phosphate phases are good partial oxidation catalysts for the conversion reaction of butane to maleic anhydride, it was deemed interesting to explore its behavior during methane oxidation. Consequently, we analyze the activity behavior of VPO synthesized system and VPO-supported ones, on the POM.

Two different supported materials have been synthesized using two different types of silica. The specific surface area of VPO/A and VPO/D are 4 and 19 m$^2$/g, respectively.

Fig. 4(A and B) show the X-ray diffraction patterns of the supported systems and the silica substrates. XRD pattern of the silica Aldrich shows sharp diffraction peaks, they are identified as quartz phase, while Aerosil-Degussa presents an amorphous phase. As can be seen, the supported systems obtained are well dispersed. In the case of VPO-RT/D, due to the lower intensity recorded, the XRD pattern was magnified (seven times). The silica-support contribution signal was also magnified. Only two sharp and weak peaks (VPO-RT/D) have been detected. As can be seen the intensities corresponding to the unknown structure are very weak and, possibly, partially shielded by the silica signal. Subsequently, it is not feasible to index with two lines alone. The FT-IR confirm this result (Fig. 5(A and B)), it detects only the characteristics of the Si–O–Si modes of silica and a small disturbance in the 900–1000 cm$^{-1}$ range, which can be related to νV=O modes. The non existence of a different crystalline phase on the silica support, obtained by FT-IR measurements, is clear evidence of the higher sensivity of this technique for small and
dispersed aggregates. Only a weak shoulder can be detected in the 960–980 cm\(^{-1}\) region, thus providing information regarding the vibration modes associated with dispersed structures. EDX analysis, which is confined to surface region in the order of 1 \(\mu\)m, revealed the presence of V and P, although no crystalline species appears to be developed on the surface on to the silica surface. The EDX analysis indicates that vanadium and phosphorus are present in the same ratio for VPO-RT system (Table 2).

3.2. Activity

Axial temperature profile was found to be essentially isothermal above the bed of the catalyst. An adequately designed reactors remove the diffusion control [25] and SiO\(_2\) samples showed a very small activity in the actual conditions.

Fig. 6 shows the percent of methane conversion as function of the temperature for the systems tested (VPO-MT bulk, VPO/A and VPO/D). Fig. 7(A, B and C) show \(C_1\)-oxyg enates, \(C_2\)-hydrocarbons and \(CO_x\) selectivities as a function of methane conversion, respectively. The distribution of products in \(C_1\)-oxyg enates, \(C_2\)-hydrocarbons and \(CO_x\) are related to the formaldehyde/methanol, saturates/unsaturates and \(CO/CO_2\) ratios, respectively. The trend observed for the three tested catalysts are almost similar. The product distribution for methane oxidation over VPO-MT was similar to the literature reports for
another traditional VPO catalyst and tested in similar conditions [26]. However, in this work, a considerable amount of C₂ hydrocarbons were formed. Moreover, the results show that an increase in the reaction temperature or surface area lead to higher methane conversion. The production of C₁-oxygenates products decreases when methane conversion increases and, for a specific methane conversion the production of C₁-oxygenates decreases on increasing the specific surface area for supported systems.

The VPO-MT system shows a similar behavior to that of VPO/A. These materials have a similar specific surface area (Table 2). The production of C₂-hydrocarbons exhibits an increase with either higher methane conversion for low conversions or minimal specific surface area. For a higher conversion, the selectivity of C₂-hydrocarbons remain stable. The formation of non-selective oxidation products (COₓ) appear to be significantly affected by the high specific surface area.

The production of C₁-oxygenates is higher at low temperatures; any increase in the reaction temperature has a negative effect on the production of C₁-oxyge-
nates. Decreasing the specific surface area, the C$_1$-oxygenates and C$_2$-hydrocarbons yields are appreciable.

The presence of mixed volume above the bed of catalyst allows activation of methane with oxygen in the gas phase formed at a lower temperature. Methylperoxy radical species are predominant due to the homogeneous initiation and, consequently, yield C$_1$-oxygenates [25,27]. The equilibrium between methyl and methylperoxy radicals is very sensitive to changes in reaction temperature, hence the methylperoxy radicals dominate at lower temperatures and atmospheric pressure [28]. The reactivity of these radicals appears to be essentially related with exposed vanadium sites which may then react with an oxygen containing product or decompose into methyl radicals again, in a manner similar to the paths proposed by Sinev et al. for methylperoxy radicals on phosphate catalysts [29]. The contribution of the catalyst surface area is critical, because the non-selective degradation processes leading to CO$_x$ becomes dominant at the expense of C$_1$-oxygenates and C$_2$-hydrocarbon species on high surface area catalysts by increasing their contact with the catalyst [30]. On the contrary, the very low surface area catalyst system inhibits degradation reactions C$_1$-oxygenates and C$_2$ hydrocarbons at the catalyst surface. Traditionally, catalytic reactions are promoted by high surface area supports, (activation and exposure). However, it is now evident that these reactions not only promotes methane activation, but also the degradation of intermediates.

The use of different supported oxides has shown that better selectivities are achieved in case of less reactive systems.

The heterogeneous–homogeneous nature of POM permit us to avoid the problem of surface area. The use of a catalytic system combining gas-phase activation with a low surface area catalyst lowers the heterogeneous activation in case of methane, and further oxidation of the intermediates is hindered.

4. Conclusions

The results for the synthesis of a VPO system from boiler ash, show that, in principle, VO(H$_2$PO$_4$)$_2$ has been successfully synthesized by the vanadium recovery and precipitated as an attractive catalytic system. The techniques used to characterize the solids obtained have provided a good and complementary information according to the reports of other authors using a traditional synthesis.

The catalytic test (POM) shows that the experimental results are comparable to that catalysts reported in literature and tested in similar conditions. The use of a catalytic system combining gas-phase activation with a very low surface area catalyst shows a lowering of heterogeneous activation for methane, but at the same time, further oxidation is minimized.

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References