

A NEW AND HIGHLY SELECTIVE VANADIUM CARBON-BASED CATALYSTS

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Introduction

Direct synthesis of acrylic acid from propane is an attractive approach since it is a very useful chemical commonly used as raw material for various synthetic resins, paints, fibbers etc. Acrylic acid is currently produced from propylene by a two-step gas phase oxidation in the scale of several million tons per year in the world. Thus, the replacement of propylene feeds with a lower-cost feedstock such as propane is being an important challenge today. There are three groups of catalysts that seem to be promising for this process and that have been extensively studied during the last years (1): i) vanadium phosphate type; ii) heteropoly acids and salts and iii) multi-compound mixed metal oxides (2-4). Despite all these efforts, this process is not commercially viable at the moment (5) and improvement of the catalytic behaviour of such catalysts or the development of new catalytic system is needed.

VPO catalytic system seems to be attractive for partial propane oxidation since it has been successfully used in the industrial process of n-butane oxidation to maleic anhydride. The use of supported VPO catalysts have many advantages since the use of the support (6-7) improves the mechanical strength, poison resistance, and heat transfer with a larger surface area to volume ratio of active component. The nature of the support presents a significant influence on the catalyst performance. In this sense, carbon materials are attractive as catalyst support since they can satisfy most of the desirable properties required for a suitable support: high surface area, chemical stability in both highly acidic and based media and, in addition, the chemistry of the carbon surface can be modulated. However, carbon supports have not been used for oxidation reaction since they would become gasified to yield CO₂ (or CO) in the presence of oxygen at relatively low temperatures. A previous work (8) showed that it is possible to prepare carbon materials with a high oxidation resistance by chemical activation of lignocellulosic materials with phosphoric acid, since stable C-O-PO₃, C-PO₃ and C-P groups during activation that act as a physical barrier, blocking the active carbon sites for the oxidation reaction.

In the present study, several vanadium carbon supported catalysts have been obtained by impregnation of an oxidation resistant activated carbon with vanadium solution.

By this manner carbon-supported VPO catalysts are obtained. Different raw materials including biomass residues can be used for the preparation of activated carbons [9]. This derives to a revalorization of the waste in a high valuable product, such as an activated carbon useful for catalytic applications.

Experimental

Orange skin harvested from Guadalhorce Valley (Málaga, Spain) was used raw material for the activated carbon preparation. The carbon precursor was impregnated by incipient wetting with 85% (w/w) aqueous H₃PO₄ at room temperature and dried for 24h at 60° C, with an impregnation H₃PO₄ to orange skin weight ratio of 3. The impregnated citrus skin was thermally treated under continuous N₂ flow at 500 °C for 2 h. The activated sample was washed with distilled water at 60° C until neutral pH and negative phosphate analysis in the eluate. This activated carbon was impregnated with an oxalic acid solution of NH₄VO₃ (Sigma-Aldrich). The water excess was removed in a rotatory evaporator at 80°C and at a reduced pressure of 10-40 mmHg. The resulting solid was dried at 120°C for 24 h and then calcined at 250°C for 2 h in air. Two samples were prepared with different coverages, 0.5 and 1 V/ACP, referring to 0.5 and 1 atoms per nm² of carbon support, respectively.

The porous structure of the activated carbons was evaluated by N₂ adsorption-desorption at -196 °C. The surface chemistry of the samples was analyzed by temperature-programmed desorption profiles and X-ray photoelectron spectroscopy. Oxidation resistance of the different catalysts and carbon were obtained by non-isothermal thermogravimetric analyses, carried out in a gravimetric thermobalance system, CI electronics, with a heating rate of 10 °C/min. Activity measurements were performed using a conventional microreactor with no void volume. The feed stream and effluents of the reactor were analyzed by an on-line gas-chromatograph equipped with flame ionization and thermal-conductivity detectors. The accuracy of the analytical determinations was checked for each test by verification that the carbon balance (based on the propane converted) was within the cumulative mean error of the determinations (±10%). The catalytic tests were made using 0.2 g of powder sample with particle dimensions in the 0.25-0.125 mm range. The axial temperature profile was monitored at 375°C by a thermocouple sliding inside a quartz tube inserted into the catalytic bed. Tests were made using the following reaction feed composition (% volume): 20.4 % O₂, 12.5% propane and 15.9% steam in helium. The total flow rate was 40 ml/min, corresponding to 4800 h⁻¹ gas hourly-space velocity (GHSV). The quantity of catalyst and total flow were determined in order to avoid internal and external diffusion limitations. Yields and selectivities in products were determined on the basis of the moles of propane feed and products, considering the number of carbon atoms in each molecule.

Results and Discussion

Table 1 shows the structural parameters obtained for the carbon support and the carbon supported vanadium catalysts. As expected, both BET and external surface area values decrease as the vanadium coverage is increased, in any case, the carbon-supported VPO catalysts present high surface area values. The decrease of the external surface area, observed after vanadium loading, is related to the formation of wider micropores. Atomic concentrations have been obtained by XPS and are shown in Table 2. The V2p3/2 binding energies for the vanadium catalysts are 516.5 and 516.7 for 0.5V/ACP and 1V/ACP, respectively; such values are associated with V⁴⁺ species; indicative that the amount of reduced vanadium species is higher when the carbon material is used as support. Thus, the carbon support is able to stabilize reduced vanadium sites, which have been described as active during partial oxidation reactions (10-11) since V⁴⁺ species are involved in the O-insertion to form acrylic acid. Such reduced vanadium sites are present as M2 phase, responsible for acrylic acid formation in the multicomponent Mo-V-Nb-Te-O catalytic system (11).

Table 1. Structural parameters obtained for carbon support (ACP) and V-supported catalysts

	ABET (m ² /g)	At (m ² /g)	Vt (cm ³ /g)	ADR (m ² /g)
ACP	1013	833	0.075	439
0.5V/ACP	701	595	0.041	342
1V/ACP	667	524	0.061	320

Table 2. Atomic concentration obtained from XPS for carbon support (ACP) and V-supported catalysts

	C1s	N1s	O1s	P2p	V2p	P/V
ACP	88.53	0.82	9.16	1.5	0	-
0.5V/ACP	80.81	1.36	16.07	1.27	0.49	2.59
1V/ACP	84.93	1.92	11.31	1.09	0.75	1.45

Thermogravimetric analyses obtained in air (not show) indicate that both the carbon support as well as the vanadium catalysts are resistant to oxidation in air atmosphere until ca. 400°C. The conversion of propane and the selectivities to different reaction products are shown in Figure 1. In line with the thermogravimetric analysis, the carbon balance obtained during the oxidation experiments indicated that the catalysts are stable under reaction conditions. The selectivity to acrylic acid for 1V/ACP catalysts is close to 100% with a propane conversion of 15.2%, being the yield to acrylic acid close to 15%, quite high, compared with literature.

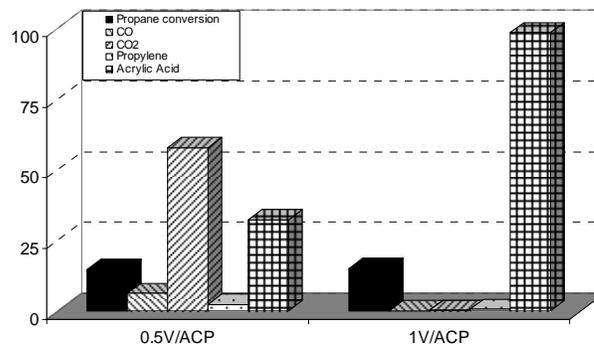


Fig. 1 Activity Results during propane oxidation reaction.

Conclusions

It has been possible to obtain an activated carbon material resistant under oxidizing conditions until 400°C. Such carbon material is a non-expensive material obtained by revalorization of a biomass residue. When such activated carbon is impregnated with vanadium, a carbon supported VPO catalyst is obtained. The activity results showed a very high selectivity to acrylic acid. As far as we known, we are reporting for the first time the use of a carbon material as catalysts support during partial propane oxidation reaction.

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