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Significant catalytic recovery of spent industrial DuPont catalysts by surface deposition of an amorphous vanadium-phosphorus oxide phase

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ABSTRACT

DuPont's vanadium phosphorous oxide catalyst (VPO) deactivated with time-on-stream in a commercial butane to maleic anhydride reactor. Coincidentally, V^{5+} phases formed on the surface (based on XPS) – principally β-$VOPO_4$ but also V_2O_5. This catalyst was reactivated by introducing a small amount of a VPO (theoretical P/V atomic ratio = 0.86) phase. The maleic anhydride production rate of the reactivated catalyst was higher by about 60% compared to the used catalyst. *n*-Butane conversion increased by about 50% and the selectivity to maleic anhydride improved by 15%. The analyses of the modified catalyst by X-ray diffraction, Raman spectroscopy and X-ray photoelectron spectroscopy showed that the V_2O_5 and β-$VOPO_4$ phases disappeared and suggested that an amorphous phase formed on the surface. The treatment resulted in a lower V^{5+}/V^{4+} and P/V ratios on the used catalyst surface.

1. Introduction

Some efforts have been made to study the deactivation and/or the regeneration of VPO catalysts during the last 40 years. Attempts have been made to protect VPO catalysts against deactivation by using metal promoters [1]. The kinetics of reoxidation of the selective vanadyl pyrophosphate (VPP) phase have also been studied, but no catalytic performance after such a treatment have been reported [2]. The deactivation of doped or supported VPO catalysts during the oxidation of *n*-butane to maleic anhydride has been attributed to modifications of their properties depending on the process conditions (pressure, temperature, molar concentrations of *n*-butane and air and type of reactor). The deactivation mechanisms may include the crystallization of amorphous phase(s), the accumulation of carbonaceous species on the surface, the over-reduction (V^{4+} into V^{3+} sites) or over-oxidation (V^{4+} into V^{5+} sites) of vanadium, the loss of phosphorus and the agglomeration or sintering of the catalyst surface during relatively long oxidation periods [3–6]. A proper combination of the oxidation states of the surface vanadium species, or an optimal V^{4+}/V^{5+} ratio, were related to high activity and selectivity, as well as a P/V atomic ratio slightly higher than 1.0. Another determining factor in VPO catalyst activity is the P/V ratio on the catalyst surface, which is related to the mean oxidation state of vanadium, the higher the value the lower the trend for VPP over-oxidation [7–9]. An excessive oxidation and/or high temperature (as in hot spots typical of fixed bed reactors) could also result in catalyst deactivation by means of the gradual transformation of surface amorphous layers into crystalline $VOPO_4$ phases [10,11]. Typically, the P/V = 1.02 in the DuPont catalyst was chosen to avoid over-reduction in the recirculating solid riser reactor [12,4].

The following bases were considered for the strategy to study the reactivation of VPO spent catalyst. (i) *The dynamics of VPO catalysts.* The oxidation state of vanadium as well as the structure of catalyst surface adapt to the prevailing red/ox C_4/O_2 conditions [13–18]. The catalytic properties of the fresh catalyst are thus modified during the "equilibration" period [8], which may take weeks in industrial reactors [16], before the actual steady state is reached. During that period, the bulk composition and/or structure may be modified accordingly. (ii) *The multiphase composition of the catalysts.* It is well known from the literature, that besides crystalline $(VO)_2P_2O_7$, which is the major phase, a variety of $VOPO_4$ (α, δ, γ) phases have been observed. (iii) *The VPO location.* The VPO active sites are, seemingly, displayed as a thin amorphous layer on the top of $(VO)_2P_2O_7$ [13–15]. (iv) *The oxidation state of vanadium.* On the surface, the two oxidation states, V^{5+} and V^{4+}, of vanadium were associated with high catalytic performance, V^{5+} species being necessary to oxidize the intermediates to MA, besides V^{4+} species for activation of *n*-butane as well as of dioxygen. (v) *The exact nature*

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of the active sites, considered to be made of dispersed V^{5+} on the surface of $(VO)_2P_2O_7$, or of $VOPO_4$ microdomains coexisting with $(VO)_2P_2O_7$. (vi) *A synergetic effect due to the cooperation between VPO phases*. Coherent interfaces between $VOPO_4$ and $(VO)_2P_2O_7$ owing to their low crystallographic misfit [5,8,9] and surface oxygen migration [19] were proposed. Higher catalytic performance was observed when two catalysts containing different P/V atomic ratio were brought into physical contact [19]. Finally, the surface and bulk reactivities of the catalyst, as well as its crystal morphology to which they are related, depend primarily on the "sample history" (nature of raw materials, method of preparation, heat treatment, activation, etc.) determined by the method of preparation [3,20,21], This is even the raison why there are so many discrepancies in the literature.

In this work, we rejuvenated spent DuPont VPO catalyst by a treatment resulting in the loading of two monolayers of a VPO phase on its surface. The main properties of this catalyst modified by impregnation with a small amount of a VPO phase were compared to those of deactivated VPO catalyst and their catalytic performance was studied.

Indeed, the deactivation was assumed to be due to the transformation of V^{5+} containing phase(s) during the long time-on-stream exposure (more than 2 years) in the reaction conditions of DuPont's Circulating Fluidized Bed reactor. It was expected that the surface would be restructured, either by regenerating a VPO phase, or by reaching a more appropriate V^{5+}/V^{4+} ratio and P/V ratio.

2. Experimental

2.1. Preparation of catalysts

2.1.1. The DuPont catalysts

The DuPont VPO precursor was prepared on a commercial scale in an organic medium with isobutanol and benzyl alcohol. This step was followed by micronization to 1–2 μm, then spray drying with polysilicic acid to form microspheres resulting in VPO encapsulated in a porous silica shell [22,23].

Two samples were investigated: (i) the precursor, $VOHPO_4{\cdot}0.5H_2O$, denoted as VPO-P catalyst, and (ii) the spent catalyst (8 $m^2\,g^{-1}$) used in DuPont's commercial circulating fluidized bed reactor. This catalyst is denoted as VPO-S. The nominal silica content in VPO-S was 10%.

2.1.2. Phosphorus-vanadium catalyst prepared in isobutanol (VPO-2M)

40 g of V_2O_5 (PANREAC, ref. 17524) was first dissolved in 500 ml of isobutanol (ALFA AESAR, ref. 36643) under reflux and stirred (900 rpm) during 16 h; the resulting suspension was then filtered. In the second step, the filtrate (containing 27.2 wt.% of V) was refluxed and stirred (900 rpm) with H_3PO_4 85% aqueous solution (PANREAC, ref. 18067) during 16 h. The precipitate obtained was filtered and then dried in an oven at 150 °C for 20 h [19]. This catalyst is denoted as VPO-2M. The value of P/V atomic ratio was 0.86 as determined by chemical analysis.

2.1.3. VPO-S catalyst modified by 2 monolayers of VPO

A modified spent VPO DuPont catalyst was obtained by suspending its particles in the same type of mixture as the one used to prepare VPO-2M, with an amount corresponding to two theoretical monolayers of VPO-2M (P/V = 0.86). The amount of VPO necessary to form a monolayer was calculated from the specific surface area of VPO-S (8 $m^2\,g^{-1}$) and the area covered by 'a molecule' of (100) layer of $(VO)_2P_2O_7$, assuming that the surface occupied by this molecule is the same as one occupied by a molecule of V_2O_5 (11 Å^2) [24]. The following procedure was adopted. The filtrate, obtained after filtering a suspension containing 40 g of V_2O_5 dissolved in 500 mL isobutanol in the same conditions as previously detailed (27.2 wt.% of V), was diluted in 1000 mL isobutanol under stirring. VPO-S particles (20 g) were suspended in a solution containing the amount of vanadium prepared as above to which H_3PO_4 necessary to achieve a P/V ratio = 0.86 was added. The resulting suspension was refluxed and stirred (900 rpm) during 16 h. The solvent was then evaporated under vacuum and the solid was dried in an open oven at 150 °C for 20 h. The modified solid is denoted as VPO-S + 2M.

2.1.4. Blank samples

To ensure that the step in isobutanol was not modifying the DuPont sample properties, blank samples were prepared by suspending the VPO precursor (VPO-P) or the spent VPO catalyst (VPO-S) in 20 ml of isobutanol under reflux and stirring (900 rpm) during 16 h. The solvent was evaporated under vacuum and the solid thus obtained was dried in an oven at 150 °C for 20 h. Samples are denoted as VPO-P-b and VPO-S-b, respectively. The denotation of all catalytically tested samples is extended by "*t*".

2.2. Characterization methods

The VPO-S sample was analysed by X-ray diffraction (XRD) using a Huber diffractometer (CuKα radiation, $\lambda = 0.15418$ nm), in the range $2\theta = 10–80°$ at room temperature. Lines were attributed using the DIFFRACPlus software (Bruker). All the other samples were characterized using a Siemens D5000 diffractometer (CuKα radiation, $\lambda = 0.15418$ nm).

XPS analyses were performed using a Kratos Axis Ultra spectrometer (Kratos Analytical, UK), equipped with a monochromatized aluminium X-ray source (powered at 10 mA and 15 kV). Charge stabilization was achieved by using the Kratos Axis device. Analyses were performed in the hybrid lens mode with the slot aperture and the iris drive position set at 0.5 inch; the resulting analysed area was 700 μm × 300 μm. The pass energy of the hemispherical analyser was set at 160 eV for the wide scan and 40 eV for narrow scans. In the latter conditions, the full width at half maximum (FWHM) of the Ag 3d5/2 peak of clean silver reference sample was about 0.9 eV. The sample powders were pressed into small stainless steel troughs mounted on a multi-specimen holder. The pressure in the analysis chamber was 10^{-6} Pa. The photoelectron collection angle θ between the normal to the sample surface and the electrostatic lens axis was 0°. The following sequence of spectra were recorded: survey spectrum, C 1s, O 1s, V 2p, P 2p, Si 2p, N 1s and C 1s again to check for charge stability as a function of time and the absence of sample degradation. The C-(C,H) component of the C 1s peak of carbon was fixed to 284.8 eV to set the binding energy scale. The data was analysed with the Casa XPS software (Casa Software Ltd., UK). The peaks were decomposed using a linear baseline, and a component shape defined by the product of a Gauss and Lorentz function, in a 70:30 ratio, respectively. Molar concentration ratios were calculated using peak areas normalized according to the acquisition parameters and the relative sensitivity factors and transmission function provided by the manufacturer.

Laser Raman spectra (LSR) of all samples were recorded using a Labram Infinity Laser Raman Spectrometer (JY-DILOR) equipped with an optical microscope. The laser intensity (Ar^+, 514.5 nm) was reduced by various filters (<1 mW), and the data were treated by Labspec software. The spectral resolution and the accuracy of the Raman shifts were evaluated at 2 cm^{-1}.

2.3. Catalytic activity

The catalytic properties were measured in a fixed bed microreactor; 400 mg of catalyst were loaded to a 7 mm quartz tube and a reactant mixture was fed at a rate of 40 mL/min (STP). The catalytic