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Behavior of vanadium–phosphorus-oxides catalyst for butane oxidation to maleic anhydride in a single-tube packed bed reactor

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Abstract

Vanadium–phosphorus-oxides catalysts for butane oxidation to maleic anhydride were prepared in an organic medium in pilot-scale equipment and were tested in a single-tube packed bed reactor. To avoid reactor thermal runaway, a nonuniform catalyst loading was adopted to moderate the reactor temperature. The precursors and catalysts were characterized by average oxidation states of vanadium, P/V atomic ratios, X-ray diffraction and pore size distribution. $VOHPO_4\cdot 0.5H_2O$ and $(VO)_2P_2O_7\cdot 9H_2O$ in precursors, $(VO)_2P_2O_7$ and α-$VOPO_4$ in catalysts were observed in the present work.

After completion of a long run catalytic test, the used catalysts were carefully sectioned and removed from the reactor for characterization. The axial profiles of average oxidation states of vanadium and P/V atomic ratios were obtained. The average oxidation states of vanadium were between 4.0 and 4.3 for the used catalysts and were related to the axial profiles of temperature obtained during the test. The P/V ratios of the used catalysts were in the range of 1.07–1.08, almost the same as that of the precursor. No phosphorus loss was observed after a long-run test and this enabled the catalyst to maintain a long useful life. The long-run catalytic test results showed that the catalyst was of high activity and good selectivity for butane oxidation to maleic anhydride.

Keywords: Vanadium–phosphorus-oxides catalyst; Butane oxidation; Maleic anhydride; Nonuniform catalyst loading; Single-tube packed bed reactor

1. Introduction

The selective oxidation of butane has been a dominant route for maleic anhydride (MA) production since the mid-1970s [1]. Vanadium–phosphorus-oxides (VPO) catalysts are well known for this process [2]. The catalytic activity has been associated with many factors. The most important factors which determine the final performance of VPO catalysts are: (1) the method of preparation of the precursor; (2) the P/V ratio; (3) the activation procedure [1].

The VPO catalysts are usually prepared in an aqueous or organic medium. The catalysts prepared in an organic medium are characterized by high values of surface area and by high activity and selectivity in the oxidation of butane to maleic anhydride [3]. The suitable P/V atomic ratio of the catalyst is close to 1.1:1. The role of phosphorus present in excess of 1:1

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ratio is as yet unclear, but it is known that one of the causes of the catalyst deactivation can be attributed to the phosphorus loss. It is possible that excess phosphorus helps to stabilize vanadium in the 4^+ oxidation state [4]. However, the mechanism of stabilization is not understood [5,6].

A variety of well-defined compounds and phases for the precursor and catalyst have been reported [7–10]. To date most work has been concentrated on the preparation of catalysts using $VOHPO_4{\cdot}0.5H_2O$ as the precursor, which is claimed as the optimal precursor to obtain active and selective catalyst for the oxidation of butane to maleic anhydride. Very often, the VPO catalyst and its precursor are a mixture of two or more compounds or phases [3]. The catalyst using $VOHPO_4{\cdot}0.5H_2O$ and $(VO)_2P_2O_7{\cdot}9H_2O$ as precursor has proved suitable for the oxidation of butane to maleic anhydride in our work. Under certain activation and reaction conditions, $VOHPO_4{\cdot}0.5H_2O$ topotactically transforms to $(VO)_2P_2O_7$ [11,12] and $(VO)_2P_2O_7{\cdot}9H_2O$ leads to α-$VOPO_4$ [13]. As the transformation of $VOHPO_4{\cdot}0.5H_2O$ is topotactic, it follows that the morphology of the catalyst precursor will control the morphology of the final catalyst. Hence, careful control of the precursor preparation procedure is of immense importance [14].

The loading pattern of catalyst in a reactor is vital for the control of fast exothermic reactions, such as butane oxidation. Uniform loading of catalyst may lead to a large axial temperature gradient, even in a wall-cooled reactor with a medium for heat transfer because of the poor heat conductivity of catalyst. A high hot spot temperature may easily damage the catalyst and lead to reactor thermal runaway occurring.

Catalyst dilution with inert materials is widely utilized in industry. The dilution pattern has a significant effect within the reactor performance. The optimal distribution of catalyst for butane oxidation in a packed bed reactor has been investigated by Buchanan and Sundaresan [15]. The knowledge of optimal distribution of catalyst in reactor is useful in establishing the best performance possible, but is difficult to apply in industry. The significance of the study is of help in the selection of suboptimal approximations to be implemented in practice. The aim of this work is mainly to describe and discuss the performance of the catalyst in a single-tube packed bed reactor.

2. Experimental

2.1. *Catalyst preparation*

V_2O_5 (90 kg) was suspended in isobutyl alcohol (180 l). The suspension was refluxed with stirring for 4 h, then O-H_3PO_4 (P/V=1.3) was added to the slurry of reduced vanadium. The mixture was again refluxed for 12 h and then cooled to room temperature and the precipitate was isolated by filtration. The precipitate obtained was dried in air (100°C, 4 h), yielding a blue powder. The powder was moistened with water and mixed with 1.5%, by weight adhesive and then shaped into $\phi 2\times 5$ (diameter 2 mm; height 5 mm) cylinders. After drying at 150°C for 8 h, the precursor was obtained. After activating under reaction conditions, the final catalyst was obtained.

2.2. *Catalytic test*

The catalytic test was performed in a single-tube packed bed reactor ($\phi 25\times 2200$ mm) with a diameter and length equal to those of a commercial reactor. A thermocouple for the indication and control of axial temperature was inserted in a longitudinal tube ($\phi 3$ mm). Molten salt was used as a medium for heat transfer in the wall-cooled reactor.

According to the previous data obtained in laboratory-scale reactor and consideration for industrialization, a nonuniform loading of catalyst precursor was adopted. The single-tube reactor was divided into four zones (zone 1–4 from reactor inlet to outlet). Zone 1 and 4 were loaded with inerts, zone 2, mixtures of inerts and catalyst precursor. Zone 3 was loaded with catalyst precursor only.

The catalytic test conditions were as follows:

- Reaction temperature: 380–440°C (hot spot).
- Space velocity: 1500–2500 h^{-1}
- Feedstock: 1.5% (volume) butane in air.

The feedstock and noncondensable effluent gases were analyzed by an on-line gas chromatograph system. The condensable products were analyzed by volumetric titration.

2.3. Characterization of precursors and catalysts

The average oxidation state of vanadium (AV) was determined by a redox titration procedure as reported by Nakamura et al. [5]. About 0.1 g of catalyst or precursor was dissolved in 17 ml of 12 M H_3PO_4 and boiled until a clear solution was obtained. This solution was added to a mixture of 10 ml of H_2SO_4 in 250 ml water. Vanadium ions were oxidized to V^{5+} by titration with 0.05 N $KMnO_4$ solution. The pentavalent ions were then reduced to V^{4+} by using a 0.05 N $Fe(NH_4)_2(SO_4)_2$ solution, with diphenylamine as an indicator. The average oxidation of vanadium was calculated as

$$\mathrm{AV} = 5 - \frac{\text{Volume of KMnO4}}{\text{Volume of Fe(NH}_4)_2(\text{SO}_4)_2}.$$

Phosphorus analysis was carried out gravimetrically with quinoline molybdate in acetone and citric acid. X-ray powder diffraction patterns were obtained by a Rigaku D/max-B diffractometer using Cu K_α radiation with a graphite monochromator.

The pore size distributions were determined using a Micrometrics Autopore II mercury porosimeter. After completion of catalytic test, the reactor was rapidly cooled to room temperature and the used catalysts were sectioned and removed from the reactor. The catalyst bed of 2 m length was divided into 20 cm segments, each segment was characterized.

3. Results and discussion

3.1. Phases of precursor and catalyst

Fig. 1 shows the X-ray diffraction (XRD) patterns of the precursor, for which the P/V atomic ratio is 1.07 and average oxidation state of vanadium is 4.0. The precursor was found to possess X-ray diffraction lines at 5.72, 4.53, 3.68, 3.30, 3.11, 2.94, 2.80 and 2.66 Å. These lines were assigned to the vanadyl hydrogen phosphate hydrate $VOHPO_4{\cdot}0.5H_2O$ [11]. Besides $VOHPO_4{\cdot}0.5H_2O$, there existed another compound, $(VO)_2P_2O_7{\cdot}9H_2O$ [4], in precursor. It was characterized by the following principal diffraction lines: d=7.48, 6.56, 4.21, 4.04, 3.20, 2.90 and 2.80 Å. Fig. 2 shows the X-ray diffraction patterns of the catalyst, for which the P/V atomic ratio is 1.07 and average oxidation state of vanadium is 4.13. The XRD analysis revealed the presence of $(VO)_2P_2O_7$ [8] (d=7.24, 3.86, 3.14, 3.00 Å) and α-$VOPO_4$ (d=3.57, 3.07, 3.01 Å) in the catalyst.

$VOHPO_4{\cdot}0.5H_2O$ is the optimal precursor for obtaining the catalyst for butane oxidation to maleic anhydride. However, we consider that it should be the dominant but not the only compound in the precursor. In present work, the precursor consisted of $VOHPO_4{\cdot}0.5H_2O$ and $(VO)_2P_2O_7{\cdot}9H_2O$. Activated in the reaction atmosphere, $VOHPO_4{\cdot}0.5H_2O$ was topotactically transformed to $(VO)_2P_2O_7$ and $(VO)_2P_2O_7$

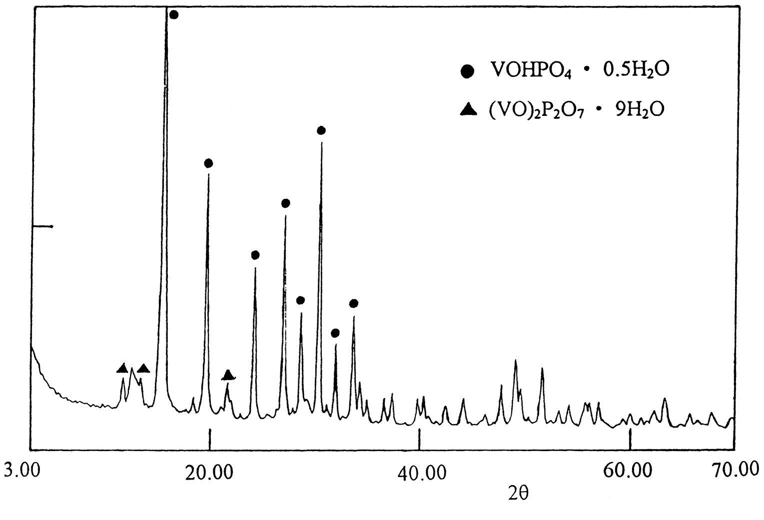

Fig. 1. X-ray diffraction patterns of the precursor (P/V=1.07, AV=4.0).

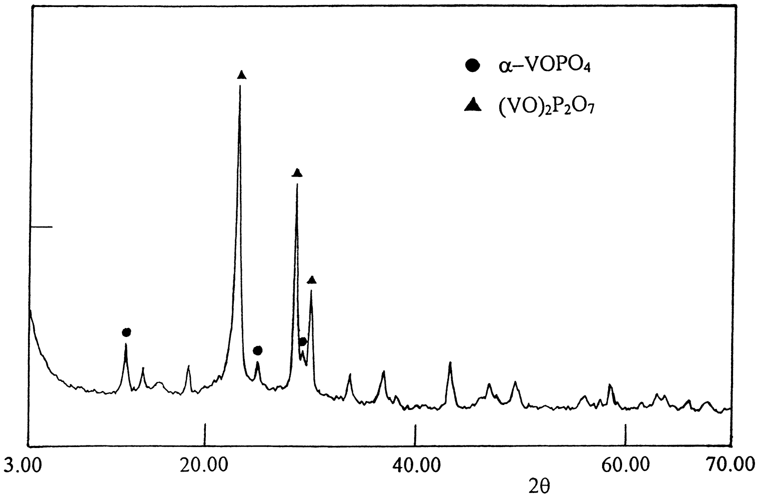

Fig. 2. X-ray diffraction patterns of the catalyst (P/V=1.07, AV=4.13).

$\cdot 9H_2O$ transformed to α-$VOPO_4$, another necessary phase in catalyst. The topotactic mechanism of dehydration of $VOHPO_4 \cdot 0.5H_2O$ was reported by Bordes et al. [12].

The reaction of butane oxidation to maleic anhydride is possibly carried out on two active sites including V^{4+} and V^{5+} of catalyst. There is a $V^{4+} \leftrightarrow V^{5+}$ redox equilibrium under reaction conditions. The compounds with V^{4+} and V^{5+} should exist in the catalyst. According to the Mars and Van Krevelen mechanism [8], the redox system 2 $VOPO_4$/$(VO)_2P_2O_7$ is involved in the reaction.

There is an optimal ratio of $(VO)_2P_2O_7/VOPO_4$, which can be characterized by the value of AV of the catalyst.

3.2. *Pore structures of precursor and catalyst*

The pore size distributions of precursor and catalyst are shown in Fig. 3. The precursor and catalyst almost

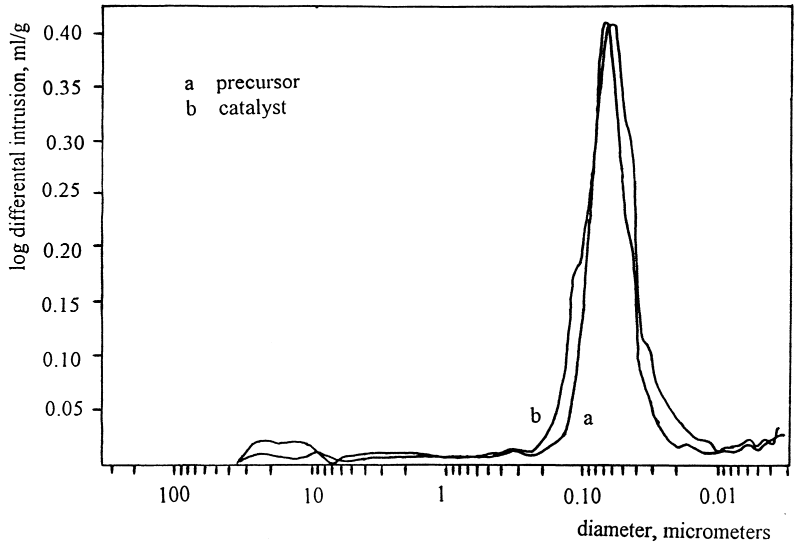

Fig. 3. Pore structures of precursor and catalyst: (a) precursor; (b) catalyst.

possess the same pore patterns and diameter ranges, although the total and partial pore volume in some diameter ranges indicate some differences. It shows that the pore structure of catalyst mainly depends on its precursor, further on the preparation method of the precursor. In order to obtain a catalyst with certain pore structure, a certain precursor must be obtained firstly.

3.3. *Axial profiles of temperature*

The axial profiles of temperature under different reaction conditions are shown in Fig. 4. During the initial period (0–100 h) of the oxidation reaction, there existed only one hot spot, which was in nondilution zone. The profile of temperature in dilution zone was fairly plain, except the reactor inlet. With increasing reaction time (~300 h), another hot spot was presented in dilution zone and the hot spot in nondilution zone shifted upwards slightly (Fig. 4(A)). After 300 h, the space velocity was increased from 1500 to 2000 h^{-1} and the bath temperature was raised to 380°C. It could be noted that hot spots were all higher than those in Fig. 4(A) (Fig. 4(B)). After 800 h, the space velocity was increased from 2000 to 2500 h^{-1} and bath temperature was raised to 400°C. The temperature profile was shown in Fig. 4(C).

It can be seen that the axial profiles of temperature are variable and dependent on the catalyst properties, the catalyst loading and the reaction conditions.

3.4. *Axial profiles of AV and P/V ratios*

Fig. 5 shows axial profiles of AV and P/V ratios. The AV values of used catalysts were all higher than 4.0, but not constant in different zones of the reactor. Two lower values were presented in the AV profile, whose positions in reactor corresponded with those of the hot spots, since the reaction in hot spots was extensive and the amount of butane consumed was more than other zones. This made $V^{4+} \leftrightarrow V^{5+}$ balance to shift to V^{4+}.

The AV values of the used catalysts near reactor inlet and outlet were all higher than their nearby zones. The former was 4.13 and the later 4.24. At reactor inlet, the oxidation reaction was at a marginally lower temperature, so the properties of catalyst were almost the same as that of catalyst just activated. At reactor outlet, there was a relatively higher temperature and more butane-deficient (oxygen-rich) atmosphere, which made $V^{4+} \leftrightarrow V^{5+}$ balance to shift to V^{5+}, leading to a higher AV value.

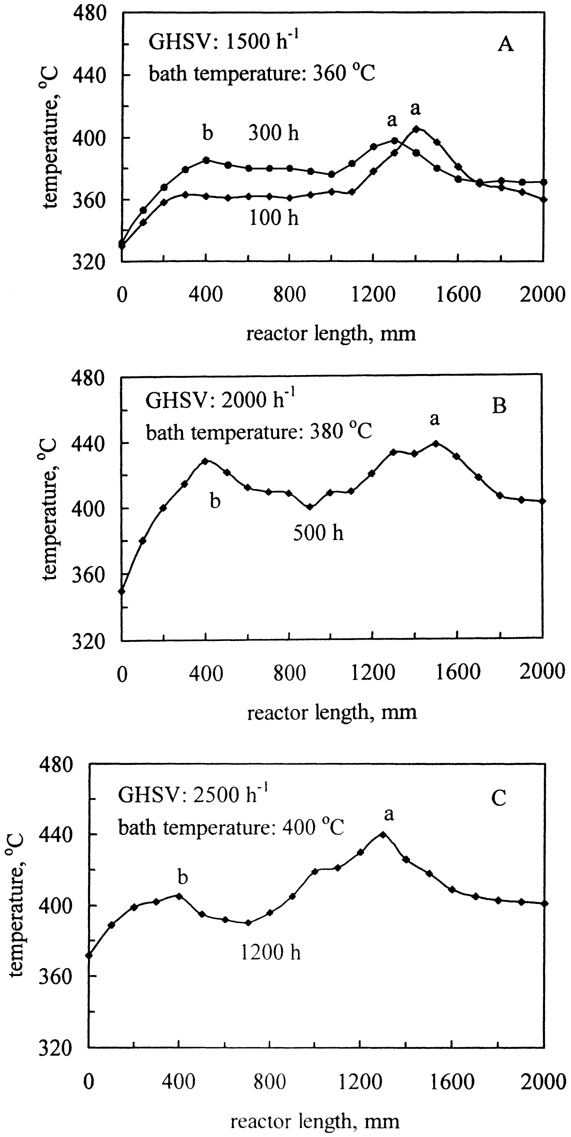

Fig. 4. Axial profiles of temperature: (a) hot spot in nondilution zone; (b) hot spot in dilution zone.

The P/V ratios of the used catalysts coming from different zones in reactor were almost the same as those of catalyst just after activation and precursor.

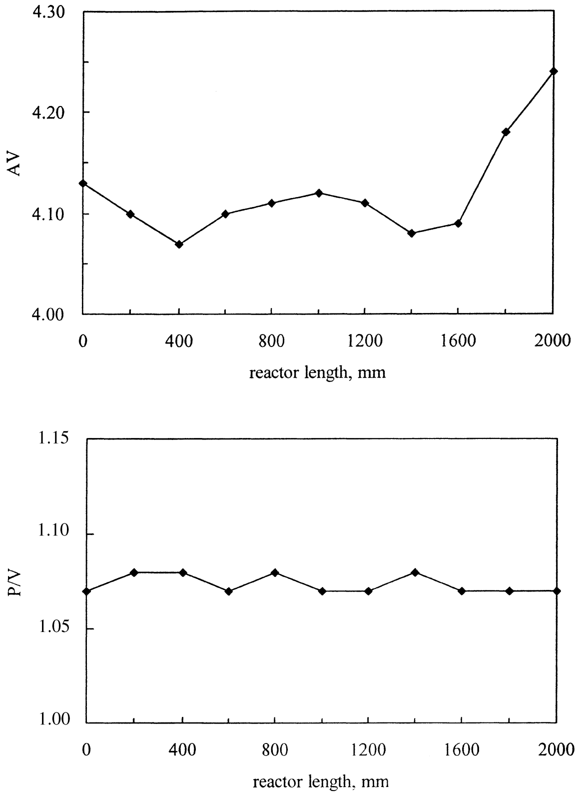

Fig. 5. Axial profiles of AV and P/V of the used catalysts from the reactor.

This showed that phosphorus in catalyst was stable and no loss occurred under different temperature and atmospheres after a long-run test. It is favorable for catalyst to maintain a long useful life.

3.5. The phases of used catalysts from different zones in the reactor

Fig. 6 shows the XRD patterns of the used catalysts from different zones of the reactor. The four samples were of typical in the single-tube reactor.

It can be noted in Fig. 6 that $(VO)_2P_2O_7$ and α-$VOPO_4$ exists in all used catalyst samples, but the relative amount of those compounds are different from each other. At reactor inlet and outlet, the amount of the α-$VOPO_4$ phase was higher than that of catalysts in other zones. At hot spots, this phase was less than that of catalyst in nearby zones. This trend corresponds with the AV profile. From all the above, it can be noted that α-$VOPO_4$ and $(VO)_2P_2O_7$ phases are possibly in redox equilibrium and can be transferred to each other in reaction conditions. The reaction may be expressed as follows:

$$2VOPO_4 \leftrightarrow (VO)_2P_2O_7 + 0.5O_2$$

The equilibrium shift is influenced by reaction temperature and atmosphere.

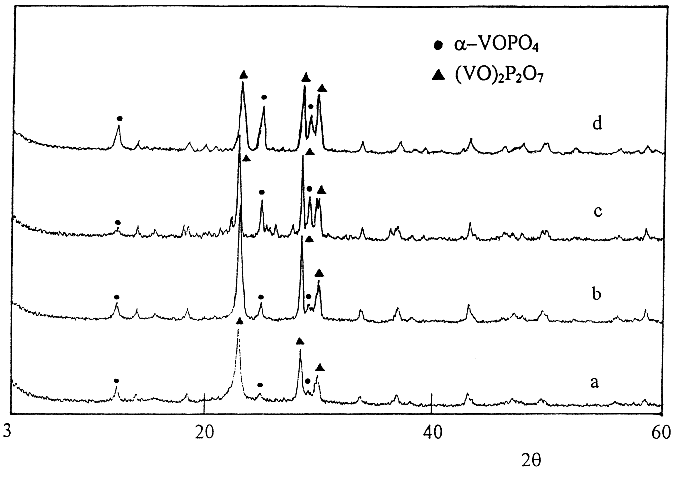

Fig. 6. X-ray diffraction patterns of the used catalysts from the reactor: (a) catalyst in hot spot of dilution zone; (b) catalyst in hot spot of nondilution zone; (c) catalyst near the inlet of reactor; (d) catalyst near the outlet of reactor.

Table 1
Catalytic test data in single-tube reactor

Time (h)	Hot spot (°C)		Space velocity (h^{-1})	Conversion (%)	Yield (wt%)	Selectivity (mol%)	Space–time yield (g/l h)
	Zone 2	Zone 3					
50	–	400	1500	55.0	67.0	72.1	38.2
100	–	405	1500	56.1	68.6	72.4	39.4
200	382	401	1500	71.3	80.9	67.1	47.1
500	428	438	2000	80.5	97.1	71.4	83.1
800	418	435	2000	79.4	96.4	71.8	80.7
1200	405	440	2500	72.9	90.4	73.4	87.3
1400	407	438	2500	74.8	92.7	73.3	91.9
1500	404	442	2500	75.6	93.1	72.9	92.4

3.6. *Catalytic test data*

Table 1 summarizes the catalytic test data under different conditions. The selectivity for maleic anhydride was found to be unaffected by changes in the experimental conditions. The space–time yield of catalyst was observed to increase with increasing temperature and space velocity.

4. Conclusions

The precursor preparation method is of a vital role in the formation of catalyst, which determines catalyst properties, such as P/V, morphology and pore structure. $VOHPO_4{\cdot}0.5H_2O$ and $(VO)_2P_2O_7{\cdot}9H_2O$ are observed in the precursor in the present work. After activation, the obtained catalyst consists of $(VO)_2P_2O_7$ and α-$VOPO_4$ phase, on which butane oxidation reaction is carried out. The AV profile of the used catalysts from the single-tube reactor is associated with the temperature profile of the reactor in correspondence with evidence provided from the XRD patterns. In the position of hot spots, lower values of AV and less amount of α-$VOPO_4$ are observed (i.e. the catalyst is more reduced). The P/V ratios of used catalysts from different zones of the reactor are almost constant and the same as that of precursor. It means that no phosphorus loss after activation and a long-run test, occurred, a feature which is favorable for the catalyst to maintain a long useful life. The axial temperature profile of the reactor has been observed to change with experimental conditions. A long-run catalytic test shows that the catalyst used in the present work displays excellent catalytic behavior.

Acknowledgements

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