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Synthesis of 2,6-dichlorobenzonitrile from 2,6-dichlorotoluene by gas phase ammoxidation over VPO catalysts

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ABSTRACT

Ammoxidation of 2,6-dichlorotoluene to 2,6-dichlorobenzonitrile is indeed an industrially important reaction for producing various commercially useful chemicals. In this contribution, differences in the catalytic performance of bulk, supported and promoted VPO samples are described. The choice of P/V ratio is found to play a key role on the catalytic properties of the catalysts. Activity is observed to decrease with increase in P/V ratio of the catalysts. About 55% yield of DCBN and ca. 95% conversion of DCT is obtained over bulk VPO solids having low P/V ratios (≤ 1). However, the catalytic performance of these bulk VPO solids is considerably improved when they are supported on γ-Al_2O_3 (Y-DCBN = 70% and X-DCT = >90%). In the direction of further enhancing the yield of DCBN, some selected transitional metal ions (Cr, Fe, Co and Mo) are also used as promoters for the present VPO solids. These promoted catalysts displayed superior performance compared to bulk and supported VPO catalysts. Amazingly, the yield of DCBN is significantly enhanced from 55% (on bulk VPO solids) to ca. 80% on the promoted VPOs, which is indeed a remarkable outcome of this study. This increase in the catalytic performance can be attributed to the surface enrichment of phosphorus in the supported and promoted catalysts compared to their corresponding bulk VPOs. Additionally, the influence of calcination temperature on the distribution of oxidation states of vanadium is presented.

1. Introduction

Ammoxidation of alkyl aromatics and heteroaromatics to their corresponding nitriles has been the subject of great interest in recent times, because the nitriles are very useful organic intermediates to prepare a good number of industrially important chemicals [e.g. 1]. Ammoxidation of 2,6-dichlorotoluene (DCT) to 2,6-dichlorobenzonitrile (DCBN) by means of gas phase ammoxidation is of particular importance due to the high industrial importance of target product (DCBN) for manufacturing a series of commercially useful chemicals.

DCBN is basically a kind of herbicide but also valuable intermediate for preparing a series of high efficient pesticides (e.g. 2,6-difluoro benzamide, a fluorinated derivative of DCBN, is used to synthesize benzyl urea like pesticides). Many other agricultural chemicals such as chlorfluazuron, flufenoxuron, flucycloxuron, hexaflumuron, diflubenzuron, teflubenzuron, etc. [2] are also prepared from DCBN. Furthermore, it acts as a hormone type pesticide. This means it interferes with the precipitation of cytoplasm of the pests and destroys the formation of their new skin due to failure of normal disintegration, which ultimately leads to the death of pests. In addition, DCBN is used to prepare “polyphenyl ether hydrocyanic ester” which is one of the best kinds of special engineering plastics with the most outstanding features in today’s world. This kind of plastics bears high heat resistant properties among all other thermoplastics. After being reinforced by glass fibres or carbon fibres, its thermal distortion temperature can also be enhanced to >300 °C [2]. Thus, the prospect of 2,6-DCBN is bright and expected to be promising for the future of its marketing value. Literature survey reveals [2–5] that only a few research groups were engaged on the direct conversion of DCT to DCBN in the last three decades. Since the 1980s mainly the Japanese companies [e.g. 3] and a Chinese research group from Wuhan University [2] claim the synthesis of DCBN through gas phase ammoxidation of DCT in various patents. Despite such high industrial importance, this particular ammoxidation reaction is somehow ignored by scientific community and hence the available data on this reaction is very much limited [6–9].

Moreover, the ammoxidation of DCT to DCBN is somewhat difficult reaction because of the location of methyl group in DCT between the two bulky chlorine atoms on both the ortho positions of the ring. Due to this, the methyl group to be oxidised has a

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restricted accessibility, which in turn makes it relatively less active. Therefore, the selective insertion of nitrogen into such an alkyl group is constrained to a greater extent because of the steric hindrance caused by the bulky chlorine atoms. Regardless of such difficulty, the present investigation focuses on the direct conversion of DCT to DCBN at atmospheric pressure and in a fixed bed reactor.

Generally, the catalytic systems like V/Ti, V/Mo, V/Fe, V/Sb, V/Sn, Fe/Sb oxides promoted by further transition metals and also some zeolite-based catalysts are reported to be active and selective for various ammoxidation reactions [e.g. 10–13]. Vanadium phosphorous oxides (VPOs) are another class of catalysts that are widely used for oxidation of butane to maleic anhydride [e.g. 14]. Academic and patent literature [1,15,16] reveals that the VPO catalysts are not only used for partial oxidation reactions but also applied for different ammoxidation reactions. The catalytic properties of these solids are however dependent on various factors such as (i) method of preparation, (ii) type of reducing agent, (iii) P/V ratio, (iv) activation conditions, (v) use of support, (vi) nature of promoter (doping elements), etc. Furthermore, iron phosphates are also used as catalysts for ammoxidation reactions in recent times [17,18].

With this background, the present study is aimed at investigating the performance of different bulk VPO solids (with varying P/V ratios), supported and promoted VPOs. The primary objective of this study is to develop highly active and selective catalysts with a special emphasis devoted to enhance the yield of DCBN as well as the conversion of DCT.

2. Experimental

2.1. Catalyst preparation

Different VPO precursors with varying P/V ratios (P/V = 0.5–2) were prepared through an organic route using benzyl alcohol and 2-butanol as reducing agents. Required amount of V_2O_5 is suspended in a mixture of benzyl alcohol and 2-butanol at room temperature and the suspension was stirred continuously under reflux for 3 h, then cooled to room temperature and kept under stirring at room temperature for overnight. Then, the 85% o-H_3PO_4 in desired amounts was slowly added; the solution was again heated and maintained under reflux with constant stirring for another 2 h. The resulting slurry was filtered, washed with ethanol and dried in oven at 120 °C for 24 h. The precursor phase is $VOHPO_4{\cdot}0.5H_2O$, which after calcination (450 °C/3 h/N_2) gave mainly $(VO)_2P_2O_7$ phase.

In the present study, three types of catalysts were prepared such as bulk, supported and promoted VPOs. The preparation of these supported and promoted catalysts involve three steps. The first step deals with the preparation of bulk VPO solid as described above. Second step involves the preparation of bulk promoted VPO solids using some selected transition metal ions (Cr, Fe, Co and Mo) as described below. Requisite amount of promoter source (Cr as nitrate, Fe and Co as acetate, and Mo as ammonium heptamolybdate) was dissolved in ca. 40 ml of ethanol or H_2O depending upon the solubility of precursor. The solution was warmed up on a water bath for some minutes and then impregnated on to the precursor compound $VOHPO_4{\cdot}0.5H_2O$ being present in powder form. The resulting slurry was evaporated to dryness on a water bath followed by oven drying at 120 °C for 16 h. In the last step, the bulk promoted solid thus obtained was further used to prepare supported catalysts by solid–solid wetting method. In this method, both the bulk promoted VPO solid and the carrier (γ-Al_2O_3) were taken in powder form in desired amounts and mixed together in a porcelain mortar for about 15 min, i.e. until the colour of the mixture became perfectly uniform. After such thorough mixing, the powder material was pressed into tablets, crushed to desired particle size (1–1.25 mm size) and then calcined at the desired temperature. In case of supported catalysts (i.e. 25%VPO/γ-Al_2O_3 with three different P/V ratios), similar procedure as described above is used. In this case, the powders of bulk VPO precursors (P/V = 0.5–0.95) and γ-Al_2O_3 powders were mixed separately. In the final catalysts after these three steps of preparation, the atomic ratio of transition metal to vanadium is kept constant at 0.05, P/V = 0.95 and the loading of VPO at 25 wt%. More details on the preparation of all these samples are described elsewhere [16].

2.2. Catalyst characterisation

BET surface areas and pore volume measurements of the catalysts were carried out by N_2 adsorption method at −196 °C using Micromeritics, Gemini-2375, instrument, by taking 300–500 mg of sample.

Oxidation states of vanadium in the catalysts were determined by potentiometric titration method on Schott Geräte instrument, Germany. About 20 mg of the sample is dissolved in 70 ml of 1:1 H_2SO_4, heated at 140 °C for 20 min. Cooled and diluted the solution to 150 ml, and then the estimation of oxidation states were carried out by potentiometric titrations [19].

XRD patterns were obtained on X-ray diffractometer STADI-P (Stoe) using Ni-filtered Cu Kα radiation (λ = 1.5418 Å). The powder samples were placed on a quartz mono crystal sample holder (Stoe). The crystalline phases were identified by referring to ASTM data files.

FTIR spectra of the catalysts were recorded on Mattson-Galaxy 5020, FTIR spectrometer. Self-supporting discs were prepared with KBr and catalysts by applying pressure. These discs were used for recording FTIR spectra.

XPS measurements were done with an ESCALAB 220iXL instrument. Al Kα radiation was used to obtain the XP spectra. The binding energy scale was calibrated with pure and clean Cu, Ag and Au samples. For quantitative analysis after Shirley background subtraction the peaks were fitted with Gaussian–Lorentz curves. The obtained peak areas were divided by the element-specific Scofield-factor and the analyser-specific transmission function to get the composition in the near-surface region.

2.3. Catalytic tests

Ammoxidation runs were carried out in a fixed bed tubular glass reactor. Air, NH_3 and N_2 supplied were commercially available gases from compressed gas cylinders. The flow rates of these gases were measured using mass flow controllers. The organic feed (DCT) and water were dosed by means of HPLC pumps (LC-9A HPLC, Shimadzu) and were vaporised in a preheating zone. 5 g of the catalyst particles (1.0–1.25 mm size) mixed with corundum were loaded in the reactor and the reaction was performed. The product stream was collected for every half-an-hour and analysed off-line by gas chromatography (GC 17A, Shimadzu, Japan) equipped with FID module. The carbon oxides were measured on-line by infrared analyser (i.e. Infralyt 40 E, Germany).

3. Results and discussion

3.1. Influence of calcination temperature on BET surface areas and pore volumes of 0.95 P/V

After preparing different VPO precursors with varying P/V ratios, it was intended to establish suitable calcination conditions to obtain desired active phase with reasonably good surface area and vanadium valence. In view of this, a VPO solid with a P/V ratio of 0.95 was selected as a model catalyst and subjected to different calcination temperatures over a wide range from 350 to 970 °C in nitrogen atmosphere. This particular sample was selected because of its P/V ratio, which is close to the stoichiometric P/V ratio of vanadyl pyrophosphate (VPP), the desired active phase.

It has been observed that the sample exhibited almost unchanged surface areas (ca. 40 m^2/g) and pore volumes (ca. 0.11 cm^3/g) in the temperature range from 400 to 600 °C. The surface areas were decrease significantly when calcined at and above 700 °C. On the other hand, the sample calcined at 350 °C is also transformed into $(VO)_2P_2O_7$, however, its surface area and pore volumes were not increased considerably as in the case of the samples calcined from 400 to 600 °C. It appears that even though the phase transformation to $(VO)_2P_2O_7$ is occurring at 350 °C, the dehydration process of the precursor seems to be not completed and also the trapped alcohols in the layers of precursor are not expelled completely, which is also evidenced by thermo-gravimetric analysis. Based on these results, a temperature of 450 °C has been selected as a suitable calcination temperature, which is also higher than the reaction temperature. After fixing this parameter, all other samples of this study are calcined at this temperature.

3.2. Influence of calcination temperature on the oxidation states of vanadium in 0.95 P/V solid

The results presented in Table 1 illustrate the influence of calcination temperature on the bulk distribution of oxidation states of vanadium in the VPO solid (P/V = 0.95). It is obvious that all the samples contain V^{4+} as their major oxidation state with a small amount of V^{3+}. However, the content of V^{3+} in the catalysts is gradually increasing at the expense of V^{4+} with rise in temperature. The average oxidation state of vanadium (AV) is observed to decrease from 3.96 to 3.83 with rise in calcination temperature. It should be noted that these solids have layered structures and were prepared though an organic route. Thus, it is reasonable to assume that certain amounts of alcohols get trapped in the layers of these precursors, which on evolution at high temperatures causes further reduction in the catalysts and thereby enhance the concentration of V^{3+} species in the catalysts. Due to problem of solubility with the last two samples calcined at 772 and 970 °C, precise estimation of oxidation states could not be possible (Table 1).

3.3. Influence of P/V ratio on the surface areas and pore volumes

After finding 450 °C as a suitable calcination temperature, all the samples with varying P/V ratios were calcined at this temperature, estimated the influence of P/V ratio on the surface areas and depicted in Table 2. BET-surface areas and pore volumes are observed to increase up to 0.95 P/V ratio (i.e. close to stoichiometric P/V ratio of VPP phase), and then decreased continuously with further increase in P/V ratio. In other words, the catalysts with higher P/V ratios (>1) exhibited low surface areas and pore volumes compared to the ones with low P/V ratios. This increase in surface area can be attributed to the complete dehydration of precursors and also due to release of trapped alcohols from the layers of precursors during such heat treatment. Large reactant P/V ratios also produce larger and well-defined vanadyl hydrogen phosphate crystals, which after topotactic transformation lead to equally large and well-formed vanadyl pyrophosphate crystals. The most probable cause for the formation of larger and better defined crystals with increasing reactant P/V ratio appears to be higher solubility of crystalline product in the synthesis medium due to increased acidity as a result of addition of larger amounts of o-H_3PO_4 during the synthesis of especially higher P/V solids. Similar such tendency of increase up to 0.95 P/V ratio is also commonly observed in the precursor samples. From these results, the catalyst with 0.95 P/V ratio appears to be optimum for exhibiting higher surface area (40 m^2/g) and pore volume (0.11 cm^3/g) compared to others. All calcined samples except 0.5 P/V solid exhibited exclusively VPP phase, while the 0.5 P/V sample showed some traces of $VOPO_4$ in addition to the major VPP phase. It is also clear from Table 2 that the surface P/V ratios (XPS) are somewhat higher than their corresponding bulk phases particularly up to 0.95 P/V and then there is a slight decrease compared to their bulk P/V ratios. This increase in surface P/V reveals that there is a surface enrichment of phosphorus but only up to stoichiometric P/V ratio of VPP phase.

Table 1
Effect of thermal treatment on the distribution of oxidation states of vanadium in bulk VPO solid (P/V = 0.95).

T (°C)	V^{3+} (%)	V^{4+} (%)	V^{5+} (%)	V_{total} (%)	AV
350	1.81	30.03	0	31.21	3.96
400	2.68	29.69	0	32.37	3.92
450	3.58	28.83	0	32.41	3.89
500	4.45	27.67	0	32.12	3.86
600	4.9	27.76	0	32.45	3.86
700	5.36	26.43	0	31.79	3.83
772[a]	3.48	24.45	0	27.93	3.88
970[a]	0.69	6.72	0	7.41	3.91

[a] Solubility problem for analysis; AV = average oxidation state of vanadium.

Table 2
BET surface areas, pore volumes and surface P/V ratios in bulk VPO solids.[a]

P/V ratio	BET-SA (m^2/g)	Pore volume (cm^3/g)	Surface P/V ratio (XPS)
0.5	14.6	0.035	0.60
0.7	17.1	0.043	0.83
0.95	40.0	0.113	1.28
1.2	28.2	0.049	1.08
1.5	6.6	0.013	1.02
2.0	–	–	0.59

[a] Calcined at 450 °C/3 h/N_2.

3.4. XRD patterns of different VPO solids with varying P/V ratios

It is evident from Fig. 1 that all the samples except the one with the lowest P/V ratio (0.5 P/V) have exhibited monophasic XRD patterns, that all reflections correspond well to $(VO)_2P_2O_7$ phase with principal *d*-spacings at 3.87, 3.13, 2.98 and 2.08 that correspond to crystal faces (0 2 0), (2 0 4), (2 2 1) and (0 0 8). However, the sample with 0.5 P/V has shown traces of γ-$VOPO_4$ phase in addition to major $(VO)_2P_2O_7$ phase. The γ-$VOPO_4$ phase corresponds to *d*-spacings at 4.15, 3.50 and 3.21, which belong to crystal planes (0 0 4), (2 3 0) and (2 2 3). Almost all the samples calcined in N_2 atmosphere are found to exhibit bad crystallinity and appear to be almost amorphous in nature compared to the XRD patterns of the oven dried precursors. As mentioned above, all the precursors were prepared in organic medium using alcohols as reducing agents. Therefore the presence of these organic alcohols trapped between the layers of precursor is believed to modify the mechanism of the phase transformation from precursor into an active vanadyl pyrophosphate phase during calcination. When the samples are calcined under anaerobic conditions (i.e. in N_2 atmosphere), the removal of trapped alcohols as CO_2 occurs probably due to consumption of lattice oxygen from the catalyst structure, which in turn makes the sample amorphous in nature.

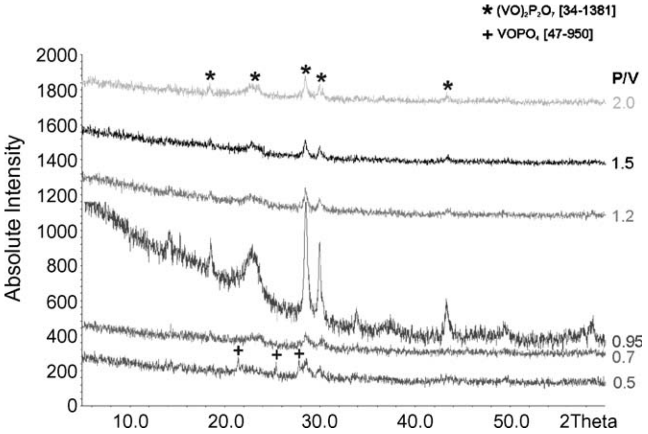

Fig. 1. XRD patterns of bulk VPO solids with different P/V ratios.

According to this interpretation, the process of alcohol release in the absence of gaseous oxygen seems to be very slow process and hence causes further reduction in the catalysts during the course of release of alcohols with simultaneous phase transformation. This also results in the reduction of the average oxidation state of vanadium that can be seen in the following sections.

3.5. FTIR spectra of different VPO solids with varying P/V ratios

Fig. 2 depicts that the spectral characteristics of VPO solids calcined in N_2 at 450 °C/3 h particularly in the region from 900 to 1300 cm^{-1} where skeletal vibrations of VPOs fall. Careful examination of the intensity of the band at 972 cm^{-1}, which can be attributed to stretching vibrations of $V^{4+}{=}O$, is observed to increase with increase in P/V ratio of the catalysts. This is due to the fact the catalysts with higher P/V ratio contain higher amounts of reduced vanadium species. This observation is also evidenced from the estimation of oxidation states of vanadium shown below in Table 3. It is interesting to note that the bands at 850 and 1024 cm^{-1} which can be assigned to V–O–V deformations and $V^{5+}{=}O$ stretching vibrations of V_2O_5 were observed only in the lowest P/V ratio solid (i.e. 0.5 P/V) indicating the presence of traces of V^{5+} phase. The presence of $VOPO_4$ phase in this solid is also evidenced from XRD studies (see Fig. 1). The bands at 634 and 744 cm^{-1} are due to δ-OPO and ν_s P–O–P vibrations while the bands appeared at 1142 and 1242 cm^{-1} are attributed to asymmetric stretching frequency of PO_3 groups.

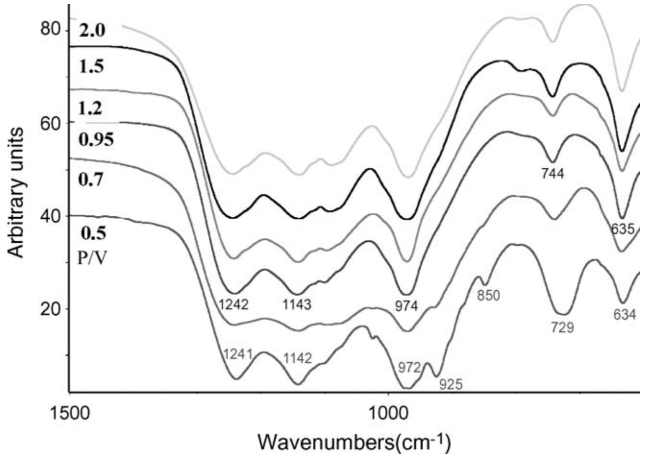

Fig. 2. FTIR spectra of bulk VPO solids with different P/V ratios.

Table 3
Distribution of oxidation states of vanadium in bulk VPO catalysts with different P/V ratios.

P/V	V^{3+} (%)	V^{4+} (%)	V^{5+} (%)	V_{total} (%)	AV
0.5	0	36.69	3.26	39.96	4.08
0.7	1.81	32.15	0	33.95	3.95
0.95	3.58	28.83	0	32.41	3.89
1.2	6.32	23.75	0	30.07	3.79
2.0	4.63	25.45	0	30.08	3.85

3.6. Influence of P/V ratio on the distribution of oxidation states of vanadium in VPO solids

Influence of P/V ratio on the oxidation states of VPO solids with varying P/V ratios is shown in Table 3. All these catalysts except the one with the lowest P/V ratio (i.e. 0.5 P/V) exhibit certain amounts of V^{3+} species in addition to major V^{4+} species. In addition, the concentration of V^{3+} species is also found to increase with increase in P/V ratio. As a result, the average oxidation state of vanadium (AV) is decreased with rise in P/V ratio of the solids. All samples except 0.5 P/V are totally devoid of V^{5+} species. The common feature in these catalysts is that they all contain V^{4+} as their major oxidation state. Another interesting observation is that the catalyst with the lowest P/V ratio (0.5 P/V) contains higher content of total vanadium (i.e. 39.6%), while the other catalysts contain low and comparable amounts of $\%V_{total}$, which is varied between 30 and 34%. This fact shows that the lowest P/V catalyst (0.5 P/V) might contain some additional phases in which vanadium can present in higher oxidation state. XRD and FTIR also gave supporting evidence for the presence of $VOPO_4$ phase in this particular sample. AV is reduced from 4.08 to 3.85 with increase in P/V ratio from 0.5 to 2.

3.7. Surface areas, pore volumes and average oxidation state of vanadium in supported and promoted VPO catalysts

Surface areas and pore volumes of supported and promoted catalysts are presented in Table 4. It is evident that the surface areas of these samples are much higher than the bulk VPO compounds. Both the AV and surface areas are found to vary with varying promoter element. The surface areas and pore volumes of these samples are varied in the range from 69 to 83 m^2/g and 0.16 to 0.2 cm^3/g, respectively. The highest surface area and pore volume was exhibited by pure γ-Al_2O_3 support, as expected.

In addition, pore size distribution of these supported and promoted samples is illustrated in Fig. 3. It is clear that bulk VPO exhibited uni-modal pore volume distribution with a dominant pore diameter around 35 Å. However, the pure support (γ-Al_2O_3) displayed bi-modal distribution with a very narrow distribution around 35 Å and a broad and prominent distribution in the range from 40 to ca. 100 Å. All supported and promoted catalysts showed similar distribution like the pure support but with marginal

Table 4
Surface areas, pore volumes and average oxidation state of vanadium of bulk, supported and promoted VPO catalysts (P/V = 0.95; M/V = 0.05).

Catalyst	BET-SA (m^2/g)	P.V. (cm^3/g)	AV
0.95 P/V (bulk)	40.0	0.113	3.89
25 wt%VPO/γ-Al_2O_3	69.3	0.166	4.53
25 wt%VPCrO/γ-Al_2O_3	73.6	0.197	4.37
25 wt%VPFeO/γ-Al_2O_3	82.6	0.199	4.21
25 wt%VPCoO/γ-Al_2O_3	78.2	0.186	4.19
25 wt%VPMoO/γ-Al_2O_3	77.4	0.198	4.30
Pure γ-Al_2O_3	102.8	0.230	–

P.V. = pore volume; AV = average oxidation state of vanadium.

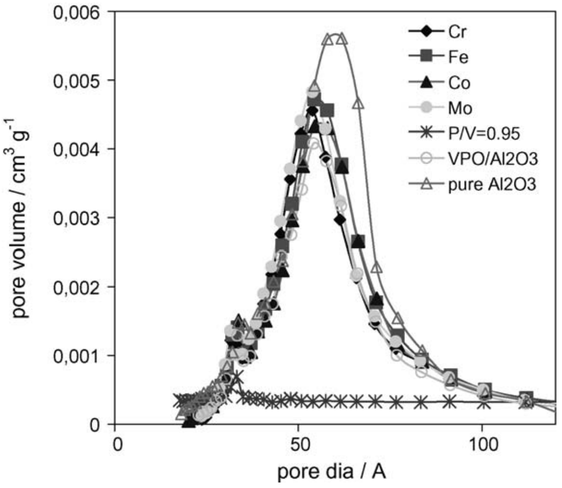

Fig. 3. Influence of promoter on the pore size distribution of bulk and Al_2O_3-supported VPO catalysts.

variations in their intensities due to varying pore volumes as well as surface areas.

3.8. Comparison of surface P/V ratios in different fresh and spent VPO catalysts

Fig. 4 demonstrates that there is a clear and significant enrichment of phosphor in the near-surface region of supported and promoted VPO catalysts compared to their bulk VPO (P/V = 0.95) phase (see Table 2). The surface P/V ratio in some cases has become more than doubled of bulk VPO solid. This result gives indications that the enhancement in the selectivity of DCBN from the promoted VPO catalysts might be due to enrichment of phosphorus at the surface. However, such surface enrichment of phosphorus appears to have no considerable influence on the conversion of DCT. If we compare the surface P/V ratios between fresh and spent solids (Fig. 4), it appears that the P/V ratio is slightly decreasing in most of the spent samples compared to their fresh ones. Interestingly, the surface P/V ratios even after such decrease in the spent samples, they are still much higher than their bulk values. In case of Co and Mo as promoters, the P/V ratio is increased in the spent samples, which is somewhat unexpected tendency and is not yet understood properly. After careful examination of the surface P/V ratios and their comparison with the unsupported bulk VPOs, it can be deduced that the surface enrichment of phosphor in the near-surface region seems to be the most probable reason for the observed enhancement in the selectivity of DCBN.

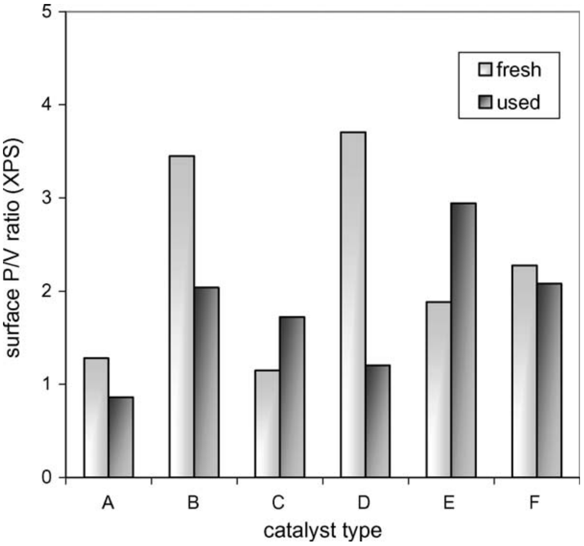

Fig. 4. Comparison of surface P/V ratios in different fresh and spent VPO catalysts (A = bulk VPO (0.95 P/V); B = 25VPO/γ-Al_2O_3; C = 25VPCoO/γ-Al_2O_3; D = 25VPFeO/γ-Al_2O_3; E = 25VPMoO/γ-Al_2O_3; F = 25VPCrO/γ-Al_2O_3).

3.9. Catalytic results

3.9.1. Influence of P/V ratio on the catalytic performance of bulk VPO solids

Fig. 5 clearly demonstrates that the P/V ratio has a strong influence on the catalytic performance. The reaction was carried out at 440 °C and at a mole ratio of DCT:H_2O:NH_3:air = 1:15:6:50. DCBN is the desired product while CO and CO_2 are the major by-products. Additionally, formation of trace amounts of dichlorobenzene and NH_4Cl is also observed in the products. The VPO solid having the lowest P/V ratio (0.5) displayed the highest conversion of DCT (ca. 98%) whereas the selectivity of DCBN (57%) is relatively low. The DCT conversion is observed to decrease at a slower rate up to a P/V ratio of 0.95 and then decreases significantly, while the nitrile selectivity is increased over a small range with rise in P/V ratio. The increase in P/V ratio of the catalysts has shown a detrimental effect on the conversion of DCT, which is decreased remarkably from 98 to 43%, while the nitrile selectivity has been increased over a narrow range from 57 to 70%. The non-selective nature of low P/V solid (0.5) might be due to the fact that it contains the excess of highly active lattice oxygen owing to higher vanadium concentration in it. On the whole, it can be stated that the catalysts with low P/V ratios (≤ 1) are found to display comparable and better performance. In view of this, in the next step, all these three solids are further supported on γ-Al_2O_3 and tested their performance. These results will be discussed below.

The choice of P/V ratio plays a major role on the catalytic properties of VPO catalysts in several ways. It mainly influences the redox properties of the catalysts, which means that the reducibility of the catalysts by hydrocarbon and the oxidisability by oxygen are affected to a greater extent with change in P/V ratio. This is more likely because the role of phosphorus is mainly to stabilise the reduced vanadium species in these catalysts. The rise in P/V ratio beyond 1 causes extra stabilisation of reduced vanadium species and hence excess phosphorus inhibit the re-oxidation of the bulk, which in turn leads to a considerable decrease in the activity as seen in the present study. Excess phosphorus also affects both the rate of hydrocarbon activation and the rates of formation of nitrile

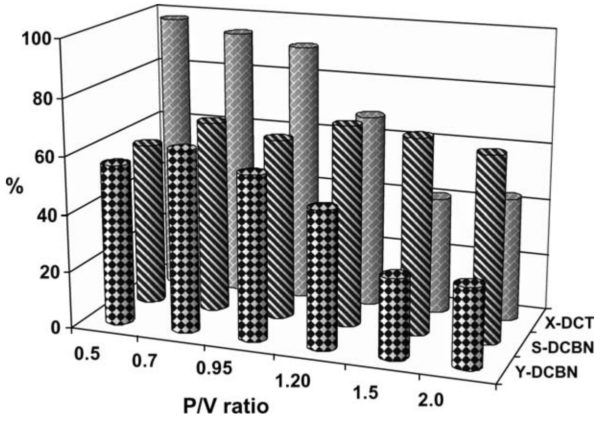

Fig. 5. Influence of P/V ratio in bulk VPO solids with different P/V ratios (T = 440 °C; DCT:H_2O:NH_3:air = 1:15:6:50).

and carbon oxides. In addition, the morphology of the catalysts is also believed to change with change in P/V ratio, which is also expected to have its own impact on the catalytic properties. Another reason for such decrease in catalytic activity might also be due to dilution of active vanadium sites in presence of excess phosphorus. The results showed that all these factors collectively influence the overall performance and decrease the activity of the catalysts with increase in phosphorus content.

3.9.2. Influence of γ-Al_2O_3 support on the catalytic performance of VPO solids

After investigating the influence of P/V ratio on the catalytic performance, we have reached respectable yields of DCBN close to 55% and the conversion of DCT over 90%. Both the conversion of DCT and the yields of DCBN obtained on the low P/V catalysts (P/V = 0.5–0.95) are somewhat comparable and hence they are considered as the best bulk VPO catalysts. After obtaining such an amazing influence of P/V ratio on the performance, in the next step, these three best VPO solids (P/V = 0.5, 0.7 and 0.95) were further used to prepare their corresponding supported catalysts using γ-Al_2O_3 as a support. Subsequently, the γ-Al_2O_3-supported catalysts were also tested for the title reaction and the results obtained on the influence of support are given in Table 5. The reaction was performed at a temperature of 400–420 °C, with a mole ratio of DCT:H_2O:NH_3:air = 1:15:4.6:23, GHSV = 700–976 h^{-1} and τ = 3.7–5.1 s. It is notable that these supported catalysts gave better performance even at low reaction temperatures (400–420 °C) compared to the bulk VPO solids (440 °C). Though the reaction on all these catalysts was performed under similar conditions with the constant weight of catalyst particles (5 g), the GHSV and residence times are considerably varied due to the differences in their catalyst volumes.

It is also interesting to see that all γ-Al_2O_3-supported VPO catalysts irrespective of P/V ratio exhibited superior performance compared to their corresponding parent bulk VPO samples (Table 5). Even though, there is no significant improvement in the conversion levels, the selectivity of DCBN is appreciably improved over these supported catalysts. The catalytic performance of the bulk VPO solids is largely increased when supported on γ-Al_2O_3 giving a DCBN yield of nearly 70% (against 55% yields on bulk VPOs) at comparable DCT conversion (over 90%). This means the selectivity of DCBN is improved appreciably. It is also known from the literature [20–22] that the γ-Al_2O_3 as a catalyst carrier can be used even for other ammoxidation reactions (e.g. propane to acrylonitrile). Guerrero-Pérez et al. [20] reported that alumina-supported $VSbO_4$ catalysts exhibit stable behaviour during time-on-stream studies and the addition of $VSbO_4$ phase to alumina decreases the total oxidation. In another study [21], the same authors claim that at a dispersion limit loading of Sb + V on alumina, the catalysts show an increase in the conversion values during the first 5 h due to decrease in the yield of CO and a concomitant increase mainly in the yields of propylene and acrylonitrile. Nilsson et al. [22] have also investigated the performance of bulk and supported $SbVO_4$ for the ammoxidation of propane to acrylonitrile. The authors reported that the pure $SbVO_4$ is unselective towards acrylonitrile formation and additionally enhances both undesired total oxidation and ammonia combustion. However, the addition of alumina improves the yield of both propylene (intermediate product in the ammoxidation of propane) and acrylonitrile while simultaneously reduces the ammonia combustion. It is also mentioned that alumina not only acts as a support but also becomes a part of an important element of the active phase. In fact, Al–$SbVO_4$ presents a trirutile-type super lattice, which is claimed to be the most selective phase towards the formation of acrylonitrile. All these reports indicate that supported catalysts particularly (e.g. alumina as a support) exhibit better catalytic performance compared to their bulk samples. Our results on the influence of alumina as a suitable support are in good agreement with those reported above.

Table 5
Influence of support on ammoxidation activity of different VPO and V_2O_5 catalysts.

P/V ratio	Catalyst	X-DCT (%)	Y-DCBN (%)	S-DCBN (%)
0.5	25%VPO/γAl_2O_3	99.1	71.3	71.9
0.7	25%VPO/γAl_2O_3	98.6	71.2	72.2
0.95	25%VPO/γAl_2O_3	96.4	68.5	71.1

DCT:H_2O:NH_3:air = 1:15:4.6:23; *T* = 400–420 °C; catalyst wt.: 5 g.

3.9.3. Influence of promoters on the catalytic performance of VPO catalysts

After a detailed study on the influence of P/V ratio and after restricting our initial choice to γ-Al_2O_3 as a suitable support, we further explored the influence of addition of different promoters (Cr, Fe, Co and Mo) on the catalytic performance. The intention is again to enhance further the yield of DCBN. Influence of promoters on the activity and selectivity behaviour of γ-Al_2O_3-supported catalysts are portrayed in Fig. 6. Interestingly, the performance of the supported catalysts is further enhanced by the addition of promoters and obtained a maximum DCBN yield of 80.8% at almost total conversion. In general, the DCBN selectivities obtained on all these promoted VPO catalysts are found to vary over a small range from 75 to 81% at DCT conversions ca. 90 to almost 100%. The by-products identified were only total oxidation products (i.e. CO and CO_2) and the sum of the selectivities of total oxidation products are varied in the range from 15 to 20%. Carbon balances are found to be good on all the catalysts (≥95%). Another notable difference is that these promoted catalysts displayed better performance at relatively low reaction temperatures (*T* = 400 °C) compared to supported and bulk VPO solids (*T* = 440 °C). Among all promoters, cobalt promoted catalyst is found to display the best performance giving a DCBN yield of 80.8% at almost total conversion (99.3%) of DCT, followed by iron, which gave a conversion of 97.4% and a DCBN yield of 77.7%. Interestingly, the selectivity of desired product, DCBN, is significantly improved from bulk VPOs to supported ones and then further to promoted VPOs. Based on these results, it can be stated that more pronounced differences between the catalytic behaviour of bulk, supported and promoted catalysts are clearly noticed. Finally, it is worth-mentioning that the yield of DCBN has been increased significantly from ca. 55% (bulk VPOs) to ≥80% with the addition of promoters. However, the precise role of

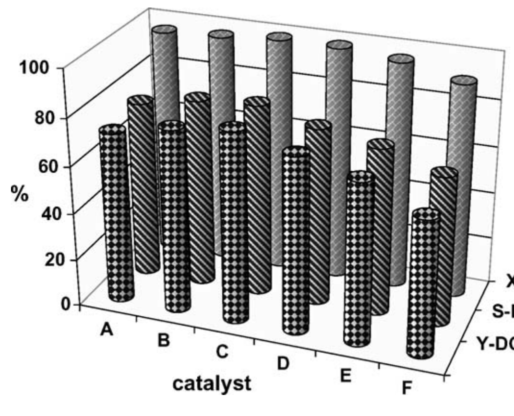

Fig. 6. Comparison of catalytic performance of bulk, γ-Al_2O_3-supported and promoted VPO catalysts (A = 25%VPCrO/γ-Al_2O_3; B = 25%VPFeO/γ-Al_2O_3; C = 25%VPCoO/γ-Al_2O_3; D = 25%VPMoO/γ-Al_2O_3; E = 25%VPO/γ-Al_2O_3; F = bulk VPO (0.95 P/V); *T* = 400 °C; DCT:H_2O:NH_3:air = 1:15:4:21; GHSV = 654–746 h^{-1}; τ = 4.8–5.5 s).

promoter in enhancing the performance could not be identified. Further studies are necessary to develop new insights on such enhancement. Neither XRD nor FTIR could provide clues on their location due to their presence in smaller amounts.

4. Conclusions

P/V ratio in VPO solids showed strong influence on the catalytic performance and low P/V ratio (≤ 1) solids exhibit better performance compared to higher ones under the conditions applied in the present study. γ-Al_2O_3-supported VPOs showed better performance compared to their parent bulk VPO solids. Oxidation state of vanadium and phase composition of VPO is also found to show an influence on the performance of catalysts. Results revealed strong evidences that the nature of promoter has an appreciable influence on the performance. Promoted VPOs displayed much superior performance compared to bulk and supported VPO catalysts. Such enhanced performance is attributed to the surface enrichment of phosphorus in the supported and promoted catalysts compared to their corresponding bulk VPOs. A maximum DCBN yield of 80% could be attained at a conversion degree of DCT ca. 99%. This is indeed a good achievement and remarkable outcome of this study.

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