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Mono-, Bi-, and Tri-Metallic DES Are Prepared from Nb, Zr, and Mo for n-Butane Selective Oxidation via VPO Catalyst

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Abstract: In recent work, deep eutectic solvents (DESs) as ionic liquid analogues have been abundantly used in catalysis. Herein, vanadium phosphorus oxide (VPO) catalysts were synthesized from mono-, bi-, and tri-metallic DES of Nb, Zr, and Mo metal dopants as structure-directing agents and electronic promoters for n-butane selective oxidation towards maleic anhydride. Higher MA selectivity and larger n-butane conversion was successfully obtained using the newly developed catalysts, while oxidation by-product CO and (CO, CO₂) was minimized. Characterization techniques including FTIR, DSC, XRD, TEM, SEM, EDS, Raman spectroscopy, TGA, XPS, and NH₃-TPD were employed to fully characterize the DESs, precursors and catalysts. This work led to an increase of 7.8% in MA mass yield with 16% more n-butane conversion as compared to an unpromoted VPO catalyst. Moreover, the utilization of a low-carbon alkane brought in a green impact on the chemical plant as well as the environment.

Keywords: deep eutectic solvent; vanadium phosphorus oxide; n-butane selective oxidation; structure directing agent; electronic promoter

1. Introduction

Vanadium phosphorus oxide (VPO) catalysts are extensively used in selective oxidation of light alkanes, especially n-butane, for producing maleic anhydride (MA) [1–3], which is considered a potential candidate for the industrial production of many useful chemicals such as pesticides, coatings, unsaturated resins, medicines, etc. [4]. In 2023, expected production capacity for MA will be almost 3.43 million metric tons; approximately 70% of MA is produced from n-butane oxidation, while the remaining capacity is obtained from benzene synthesis [5]. The trend has moved towards n-butane oxidation from benzene synthesis as this reduces the amount of toxic byproducts and associated environmental issues. Researchers have reported that the VPO catalyst shows good industrial prospects for n-butane selectivity. It has been found that the VPO catalyst is produced after topochemical transformation of the VPO precursor. The VPO precursor phase (VOHPO₄·0.5H₂O) transforms into the active phase (VO₂P₂O₆) of the VPO catalyst after reaching the activation condition. The VPO complex exists in fifteen different phases, including the α₋, α₊, β₋, γ₋, and δ-VOPO₄ phases [6]. The complex catalytic reaction involves insertion of three oxygen atoms and transfer of fourteen electrons with parallel and consecutive reactions [7,8]. Therefore, it has been hard to achieve the optimum MA yield in existing experiments [9–11].
It has been commonly found that efficient VPO catalysts exhibit adequate surface characteristics such as surface area, structure morphology, active sites, V\textsuperscript{4+}/V\textsuperscript{5+} ratio, P/V ratio, valence state of vanadium, and surface and lattice oxygen [12]. In addition to these physiochemical properties, the electronic characteristics also affect the catalytic performance. Various synthesis techniques such as ultrasound [13], microwave [14], ball milling [15], hydrothermal [16], electrospinning [17], and barothermal [18] have been introduced to explore the physiochemical properties of efficient VPO catalysts. The purely crystalline catalysts and precursors prepared via the above-mentioned process found in literature usually adopt a smooth lamellar structure. In other words, these techniques facilitate crystallinity, which has been linked to the catalyst performance. Interestingly, metal dopant added to VPO synthesis not only acts as a structure-directing agent but also an electronic promoting agent. Various metal dopants such as Ce, Nb, Al, Zr, Mo, Cu, Cr, Fe, Co, Ni, Bi, Mg, Ag, Zn, etc., from metal salts have already been tested, with results finding limited active sites along with poor crystallinity, impeding the catalytic performance [8,19–24]. Ultimately, the introduced metal dopants simultaneously increase the production cost of the VPO catalyst and exhibit metal draining. Additionally, these dopants have a bad effect on the environment. Therefore, we prepared a eutectic solvent from various metal dopants for a VPO catalyst [25–27]. The issues of poor crystallinity and limited active sites were solved by organic modifications and template strategies.

Ionic liquids (ILs) as emerging energetic solvents have been utilized for different chemical syntheses [28–30]. Herein, we considered deep eutectic solvents (DESs) as IL analogues for VPO synthesis [31]. A DES is easy to prepare at room temperature and possesses amazing properties such as low melting point, low flammability, and low vapor pressure [1,32]. These valuable features of the eutectic solvent significantly affect VPO synthesis and regulate its intrinsic characteristics. The inexpensive, nontoxic, and biodegradable qualities of DESs further enhances their importance [1]. Interestingly, as a green promoter, DES use did not result in environmental pollution.

He Bin et al. synthesized a VPO catalyst from choline chloride/oxalic acid (ChCl/OA) DES. They found that the active sites of the VPO catalyst were responsible for enhancing the catalytic performance [25]. Further, the addition of ChCl into glucose (Glu) (ChCl/Glu) DES also improved the selective MA yield via the development of a crystalline and porous VPO catalyst [26]. Moreover, the polyols-based DES acted as a structure-directing agent in VPO synthesis [27]. Importantly, the electronic properties of the VPO catalyst could be improved via iron-based ionic liquids (Fe-ILs) such as VPO-OMIMFeCl\textsubscript{4} and VPO-BMIMFeCl\textsubscript{4} [12]. All of these findings provoked us to prepare a novel and green modifier for the VPO catalyst, which could potentially act as structure-directing agent and electronic promoter.

In the current study, initially we prepared the DES from a eutectic mixture containing a hydrogen bond acceptor (ChCl) and hydrogen bond donors of mono-, bi- and tri-metallic salts of niobium, molybdenum and zircon; then VPO was synthesized from the as-prepared DES. A fixed-bed reactor was used to evaluate the catalytic performance (Scheme 1). Finally, we characterized the DES, precursor and catalyst using different techniques such as FTIR, DSC, XRD, Raman spectroscopy, SEM, EDS, TEM, TGA, XPS, and NH\textsubscript{3}-TPD.
2. Materials and Methods

2.1. Reagents and Solutions

Vanadium pentoxide ($\text{V}_2\text{O}_5$) was purchased from Nanyang Handing High-tech Materials Co., Ltd., Nanyang, China. Choline chloride (ChCl), Ammonium heptamolybdate ($\text{NH}_4\text{MoO}\text{$_2$}_4\cdot 4\text{H}_2\text{O}$), Zirconium(IV) nitrate pentahydrate ($\text{Zr(NO}_3\text{)}_4\cdot 5\text{H}_2\text{O}$), Niobium oxalate ($\text{C}_{10}\text{H}_5\text{NbO}_20$), Benzyl alcohols ($\text{C}_7\text{H}_8\text{O}$), Phosphoric acid ($\text{H}_3\text{PO}_4$), and Isobutanol ($\text{CH}_3\text{CHCH}_2\text{OH}$) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., Shanghai, China. All analytical grade chemicals were used as received without further purification.

2.2. Synthesis of DES

Initially, the eutectic mixture of the hydrogen bond acceptor (ChCl) and hydrogen bond donors (Zr-, Nb-, and Mo salt) was utilized to form DES at 90−135 °C for 2−3 h with a 1:0.5 molar ratio, with constant magnetic stirring until a liquid solution was formed. Bi- and tri-metallic DES was formed by using two- and three-hydrogen bond donors with similar hydrogen bond acceptors.

2.3. Catalyst Preparation

The PVPO precursor ($\text{VOHPO}_4\cdot 0.5\text{H}_2\text{O}$) was produced using the organic phase method. $\text{V}_2\text{O}_5$ (10 g), isobutanol (80 mL), benzyl alcohol (20 mL) and DES (1 mL) were mixed together inside a three-neck distilling flask (250 mL) at 140 °C with mechanical stirring (350 rpm/min) under 3 h reflux. The solution was cooled to 70 °C after which $\text{H}_3\text{PO}_4$ (7.53 mL) was added drop-wise (P/V ratio = 1.04). After that, the reaction temperature was returned to 140 °C for 16 h with the same reflux. The obtained slurry was cooled to room temperature and then extracted via filtration and washed with water and ethanol at least three times. The slurry solution was dried in an oven (120 °C, 4 h) to obtain the precursor (DES-PVPO). An unpromoted precursor (Blank-PVPO) was also produced via the same procedure without adding the DESs.

2.4. Characterization

The as-obtained DES, precursor and catalyst were analyzed via various characterization techniques. Transition temperature of DES was analyzed using differential scanning calorimetry (DSC, Mettler-Toledo, Greifensee, Switzerland). The sample was heated from −100 °C to 400 °C at 10 °C/min in a nitrogen atmosphere. The FT-IR spectra of all
samples was obtained using a Fourier transform infrared spectrometer (FTIR, Thermo Electron Corp., Waltham, MA, USA). The crystalline behavior of each precursor and catalyst was analyzed using an X-ray powder diffractometer (XRD, Rigaku Corporation, Tokyo, Japan) employing Cu Kα radiation (λ = 0.15406 nm, P = 9 kW, Scanning rate = 15°·min⁻¹) and the crystallite size was assessed with the Scherrer formula. The active phase of the VPO catalyst was further confirmed through Raman spectroscopy (Raman, Horiba Jobin Yvon, Palaiseau, France) via excitation light (source = argon ion laser, λ = 633 nm, range = 200–2000 cm⁻¹). The structural morphology and elemental composition was evaluated using scanning electron microscopy (SEM, Hitachi, Tokyo, Japan) with 5 KV accelerating potential and 8 mm working distance. The SEM was equipped with a JEOL JSM-6010/LA microscope, which was also used for energy dispersive spectrometry (EDS) (accelerating potential = 20 KV, working distance 15 mm). The effect of transition temperature on precursor phase was determined from differential thermal analysis (DTA), and quantification of weight loss upon temperature via thermogravimetric analysis (TG) (temperature = 35–850 °C, rate = 10 °C/min, atmosphere = N₂). The electronic properties of the VPO catalyst were measured through X-ray photoelectron spectroscopy (XPS, Thermo Fisher Scientific, Waltham, MA, USA) (C 1s binding energies~284.5 eV). The acidic content present at the catalyst surface was calculated using thermal programmed desorption of ammonia (NH₃-TPD Micrometrics, Norcross, GA, USA); initially the sample under observation (~40 mg) was heated to 250 °C (10 °C min⁻¹, 1 h, N₂ environment) and then cooled to ambient temperature. Afterwards, NH₃ gas (He~10% w/w) was used as a probe molecule to record the TCD signal of the desorption curve, while the sample was again heated to 650 °C at 10 °C min⁻¹ rate in He flow.

2.5. Catalyst Activity Tests

The main active phase of the VPO catalyst (i.e., vanadyl pyrophosphate phase (VO)₂P₂O₇) was produced after the activation of the precursor. Initially, the as-obtained precursor was meshed into small pellets with a mesh size of 20~40 (381–864 μm). After that, 2.7 g (3 mL) of precursor was placed inside the fixed-bed reactor tube at the isothermal zone. Subsequently, reactant gas (air/n-butane mixture= 1.34 vol. %) was supplied at 2000 h⁻¹ GHSV (gas hourly space velocity). Afterwards, the temperature was gradually increased to 430 °C for 12 h at a 2 °C·min⁻¹ heating rate. These procedures enabled the activation process to complete its transformation of the precursor into catalyst, which was denoted the VPO catalyst. The catalytic performance of the developed catalyst was assessed via on-stream gas chromatography (GC, Shimadzu, Duisburg, Germany) using the “two valves and three columns” system; exhaust gaseous product COₓ (CO and CO₂) and n-butane were analyzed using the thermal conductivity detector signal (GC-TCD) and flame ionization detector (GC-FID) respectively.

2.6. Catalysts Evaluation

The catalytic performance of activated precursors (VPO catalyst) was examined in a fixed-bed micro-reactor (l = 80 cm, dinternal = 10 mm) at 420 °C, while other reaction parameters were identical with the activation process. On-line output gas was evaluated. Catalytic performance was investigated in terms of n-butane conversion, MA selectivity, and MA yield, stated as follows [8]:

\[ \text{C}_4\text{H}_{10} \text{Con.} = \frac{X_{\text{in}} - X_{\text{out}}}{X_{\text{in}}} \times 100\% \]  

\[ \text{MA Sel.} = \frac{\text{MA out, mol}}{X_{\text{in}} - X_{\text{out}}} \times 100\% \]  

\[ \text{MA yield} = \text{C}_4\text{H}_{10} \text{Con.} \times \text{MA Sel.} \times 100\% \]  

\[ X_{\text{in}} = \text{C}_4\text{H}_{10 \text{ in, mol}}, \ X_{\text{out}} = \text{C}_4\text{H}_{10 \text{ out, mol}} \]
3. Results and Discussion

3.1. Characterization of DES

Different mono-, bi- and tri-metals were used to synthesize the DES using ChCl as hydrogen bond acceptor and zirconium (Zr(NO$_3$)$_4$·5H$_2$O), molybdenum (NH$_4$)$_6$MoO$_{24}$·4H$_2$O), and niobium (C$_{10}$H$_5$NbO$_{20}$) metal salts as hydrogen bond donors at a molar ratio of 1:0.5. FT-IR spectroscopy of DES was utilized to characterize the hydrogen bonding. Figure 1a represents the FTIR spectrum of the hydrogen bond acceptor (ChCl) and hydrogen bond donors (Zr, Nb, and Mo metal salts). Stretching of the –OH bond can be observed at the associated characteristic peaks. The stretching vibration of the –OH bond of the as-prepared DES was found close to 3400 cm$^{-1}$ (Figure 1b). Surprisingly, the –OH bond stretching of the hydrogen bond acceptor (ChCl) was blue-shifted compared to that of the hydrogen bond donors (metal salts).

Figure 1. FTIR spectra of the hydrogen bond acceptor (ChCl) and hydrogen bond donors (Zr(NO$_3$)$_4$·5H$_2$O, (NH$_4$)$_6$MoO$_{24}$·4H$_2$O, and C$_{10}$H$_5$NbO$_{20}$) (a), and a eutectic mixture of hydrogen bond acceptor and hydrogen bond donor at a molar ratio of 1:0.5 (b).

Differential scanning calorimetry was utilized to observe the nature of the eutectic solvent. The hydrogen bond acceptor and hydrogen bond donors of the eutectic solvent had unique characteristics as compared to the DES. For instance, the DSC curve of ChCl, Zr(NO$_3$)$_4$·5H$_2$O and ChCl/Zr(NO$_3$)$_4$·5H$_2$O = 1:0.5 depicted melting points of 87 °C, 137 °C, and 300 °C respectively (Figure 2). As a result, we can conclude that the DES possessed the characteristics of low vapor pressure, low melting point and low viscosity. Additionally, DESs are easy to synthesize. Therefore, our as-prepared DES displayed all of the properties of a eutectic solvent. As such, it can be hypothesized that introduction of DES into VPO synthesis is a good opportunity to obtain an optimum selective oxidation yield.
Figure 2. The DSC curve of the hydrogen bond acceptor (ChCl), a hydrogen bond donor (Zr(NO$_3$)$_4$·5H$_2$O) and a eutectic mixture with the molar ratio of 1:0.5.

In the DES, the intrinsic characteristics of each hydrogen bond donor and acceptor were changed. A thermogravimetric analyzer (TG-DTA) was utilized to analyze the transition temperature and vaporized content of the mono-metallic Zr-DES sample. Characterization proceeded via heating to 800 °C at a rate of 10 °C/min in a N$_2$ atmosphere. TG-DTA temperature profiles of the hydrogen bond acceptor (ChCl), the hydrogen bond donor (Zr-metal salt) and the DES (ChCl:Zr = 1:0.5) were categorized into three stages: primary (below 200 °C), secondary (200~400 °C) and tertiary (above 400 °C), according to their different temperature zones (Figure 3). In the primary stage almost 35% weight loss was observed, but in the secondary stage complete weight loss was recorded. The transition temperature profile (DTA) describes the transition phase. The maximum peaks of the DTA curve for the hydrogen bond acceptor and donor were observed at 330 °C and 239 °C respectively. Interestingly, maximum DTA peaks for the DES were observed at 280 °C and 146 °C, which is lower than the corresponding DTA peaks of the hydrogen bond donor and acceptor individually. Therefore, we can conclude that the DES possessed low vapor pressure and a low melting point. The utility of the DES lies in its ease of modulating the physicochemical properties of VPO analogues.

3.1.1. Characterization of Precursors and Catalysts

XRD was performed to determine the main phases of the precursors and catalysts. The crystallinity of precursors and catalysts is based on these main phases. The main phase in the precursor was vanadyl hydrogen phosphate hemihydrate (VOHPO$_4$·0.5H$_2$O), which was easily assessed from XRD spectra (Figure 4). The crystalline planes of the precursor were found at 20 = 15.552° (001), 19.638°(101), 24.220° (021), 27.073° (121) and 30.415° (130) (JCPDS #84-0761). Interestingly, irrelevant phases were not developed during VPO synthesis. The crystallite sizes of mono-, bi- and tri-metallic precursors were larger than that of the un-doped precursor (Blank-PVPO). Their respective integral intensities appeared with their full width and half maximum (FWHM) values (Table 1). We observed that the ratios of integral intensity $I_{(001)}/I_{(130)}$ of the mono-, bi- and tri-metallic precursors were larger than that of the unpromoted precursor (Blank-PVPO). This resulted in an expanded crystalline plane. It can be concluded that this expanded crystalline plane is very crucial for C-H bond activation, which is required for initiating the catalyzed reaction.
Researchers believe that the (001) plane in the precursor generates the (020) plane in the catalyst after precursor activation [12,33]. Thus, the main precursor phase (VOHPO$_4$·0.5H$_2$O) is topologically transformed into the main active phase (VO)$_2$P$_2$O$_7$ (Figure 5); herein, the relative integral intensity $I_{(020)}/I_{(204)}$ ratio was used to evaluate the crystallinity of the VPO catalyst. XRD characterization data shows that crystalline planes (021), (120), (002), (200), (013) and (023) were observed at $\theta = 14.115^\circ$, 15.647$^\circ$, 18.497$^\circ$, 22.962$^\circ$, 28.418$^\circ$ and 29.943$^\circ$ respectively (JCPDS #50-0380). The ratios of relative integral intensity $I_{(020)}/I_{(204)}$ in the mono-, bi- and tri- metallic catalysts were smaller, but crystallite sizes were larger than that of the unpromoted catalyst (Blank-VPO). The visual crystallite size of each precursor and catalyst was clearly seen in the SEM micrograph.
Processes 2021, 9, 1487

Figure 4. XRD spectra of mono- (a), and bi- and tri-metallic precursors (PVPO) (b) for identifying the main precursor phase VOHPO$_4$·0.5H$_2$O.

Figure 5. XRD spectra of mono- (a), and bi- and tri-metallic catalysts (VPO) (b) used to observe the main active phase (VO)$_2$P$_2$O$_7$ of the catalysts.

Table 1. The crystallite size and relative integral intensity of precursors ($I_{(001)}/I_{(130)}$) and catalysts ($I_{(200)}/I_{(013)}$) are described below.

| Sample            | PVPO  | PVPO  | PVPO  | VPO   | VPO   | VPO   |
|-------------------|-------|-------|-------|-------|-------|-------|
|                   | $I_{(001)}/I_{(130)}$ | FWHM/nm | Crystallite size/nm | $I_{(200)}/I_{(013)}$ | FWHM/nm | Crystallite size/nm |
| Blank             | 52.4  | 0.0456| 18.1  | 78.4  | 0.0456| 14.5  |
| DES-Nb (1:0.5)    | 61.3  | 0.0397| 20.9  | 40.5  | 0.0268| 18.4  |
| DES-Mo (1:0.5)    | 82.6  | 0.0268| 32.2  | 62.4  | 0.0506| 16.4  |
| DES-Zr (1:0.5)    | 84.5  | 0.0276| 31.2  | 57.4  | 0.0558| 14.8  |
| DES-Zr-Mo (1:0.5) | 90.2  | 0.0260| 33.4  | 55.3  | 0.0494| 16.8  |
| DES-Zr-Nb (1:0.5) | 82.1  | 0.0249| 35.2  | 53.3  | 0.0470| 21.9  |
| DES-Zr-Mo-Nb (1:0.5) | 95.1  | 0.0226| 39.5  | 31.5  | 0.0360| 23.4  |

The presence of active domains on the precursor and catalyst surfaces was further assured from FT-IR characterization. Figure 6 shows the FT-IR spectra of mono-, bi- and tri-metallic precursors in the range of 900~1300 cm$^{-1}$ [12]. After the FT-IR spectra were obtained, the precursor phases were compared with the unpromoted precursor (Blank-PVPO) with the following results: V $\nu$(P-(OH)) and V $\nu$(V=O) emerged at 927 cm$^{-1}$ and 979 cm$^{-1}$ respectively, while asymmetric PO$_3$ absorption peaks appeared at 1203 cm$^{-1}$, 1105 cm$^{-1}$ and 1045 cm$^{-1}$. Interestingly, we found that the characteristic peak of the promoted precursor had similarity with that of the Blank-PVPO. Thus we can assume that the mono-, bi- and tri-metallic DESs suitably regulated themselves during VPO synthesis.
The as-prepared precursors were activated at higher temperatures in order to produce the catalyst. The as-produced catalysts were analyzed using FT-IR spectra (Figure 7). All relevant characteristic peaks appeared in the range of 600–1600 cm$^{-1}$. The asymmetric PO$_3$ vibration band was stretched at 943 cm$^{-1}$, 1025 cm$^{-1}$ and 1159 cm$^{-1}$. Additionally, symmetrical P-O-P stretching was observed at 738 cm$^{-1}$, and the V-P (V=O) bond emerged at a 796 cm$^{-1}$ vibration band. The newly prepared catalysts from mono-, bi- and tri-metallic DESs were compared with unpromoted catalyst (Blank-VPO). Characteristic results revealed that DES easily became a part of VPO conjugates.

The presence of the active phase (VO)$_2$P$_2$O$_7$ in the VPO catalysts was further confirmed with Raman spectroscopy. We found important phases in the range of 500–1500 cm$^{-1}$ characteristic peaks. Figure 8 shows the associated phases of each characteristic peak. Both 931 cm$^{-1}$ and 995 m$^{-1}$ characteristic peaks represent the active phase (VO)$_2$P$_2$O$_7$. Other phases such as $\alpha_{II}$-VOPO$_4$, $\gamma$-VOPO$_4$, and $\beta$-VOPO$_4$ are also highlighted. The role of these specific phases in selective oxidation has yet to be determined, but the role of (VO)$_2$P$_2$O$_7$ in selective oxidation is well understood and addressed. Other phases, especially $\beta$-VOPO$_4$, are considered important for n-butane conversion. $\alpha_{II}$-VOPO$_4$ and $\gamma$-VOPO$_4$ phases do not have a leading role in selective oxidation but we cannot ignore their presence regarding C-H bond activation and optimizing reaction conditions.
Figure 8. Raman spectra of mono- (a), and bi- and tri-metallic catalysts (VPO) (b) to explore the reactive phases in the catalysts, especially \((\text{VO})_2\text{P}_2\text{O}_7\) and \(\beta\)-VOPO₄.

The addition of \(\text{H}_3\text{PO}_4\) into the \(\text{V}_2\text{O}_5\) generated precursor (\(\text{VOHPO}_4\cdot0.5\text{H}_2\text{O}\)) phase was due to the reduction mechanism. The alcoholic solvents, i.e., isobutyl alcohol and isobutanol, played a vital role in the crystal development of the precursor. The blank-PVPO exhibited a nano-sliced structure with 0.01 \(\mu\)m thickness and about 0.5 \(\mu\)m diameter (Figure 9a). Weihao Weng et al. found that this type of sliced structure was inappropriate for \((001)\) and \((130)\) crystallographic plane induction, and its relative integral intensity ratio \(I_{(001)}/I_{(130)}\) was lesser, as evaluated from XRD characterization [34]. The addition of DES into VPO synthesis regulated the structural morphology of the crystal because DESs have enriched hydrogen bond networks as green promoters, which regulate the chemical state and viscosity of the precursor’s solvent. DESs could disturb the structural morphology, usually by producing layered-type thin slices (Figure 9b–g). Surprisingly, DES addition changed the lamellar thickness, and thus we can conclude that DES performed the role of a structural directing agent. All three types of DES examined—mono-, bi- and tri-metallic—successfully changed the shape memory. Therefore, we can expect better catalytic performance, but also the drawback of the structural directing group only assisting in improving catalytic surfaces and initiating C-H bond activation. Although we know catalyzed reactions are overly dependent on surface, topotactic transformation and generating the active phase \((\text{VO})_2\text{P}_2\text{O}_7\) is very crucial for overall catalytic performance. For better understanding of the catalytic performance, we examined the electronic properties as well.

Structural morphology helped us to understand the reactive area for chemical reaction. SEM micrographs were observed to evaluate the particle shape, size and distribution at the surface. Lamellar thickness was assessed from SEM imaging. The lamellar thickness of the mono-metallic DES precursor was 0.09 \(\mu\)m, which was three times thicker than that of the unpromoted precursor at 0.03 \(\mu\)m (Blank-PVPO) (Figure 9(a₁,d₁)). The bi-metallic precursor (PVPO-DES-Zr-Mo) also showed the same behavior (Figure 9(e₁)). Surprisingly, the lamellar thickness of the trimetallic DES precursor was the same as that of the Blank-PVPO. Reduced lamellar thickness is not suitable for selective oxidation [27]. We can conclude that structural morphology of the as-prepared precursor is responsible for carrying out the catalyzed reactions.
Figure 9. SEM imaging was obtained to observe the structural morphology of the unpromoted precursor (Blank-PVPO) (a), and promoted precursors prepared from DES-Nb (b), DES-Mo (c), DES-Zr (d), DES-Zr-Mo (e), DES-Zr-Nb (f), DES-Zr-Mo-Nb (g). The lamellar thickness of the unpromoted precursor (Blank-PVPO) (a₁), and promoted precursors prepared from monometallic DES-Zr (d₁), bi-metallic DES-Zr-Mo (e₁), and trimetallic DES-Zr-Mo-Nb (g₁).

The activation process removed the precursor water content and generated the active phase. As water content was removed, crystal structure was affected, losing its structural binding. Unpromoted (Blank-VPO) and promoted (mono-, bi- and tri-metallic) catalysts were transformed into micron particles and debris structure appeared (Figure 10). Selective oxidation catalytic performance is based on the catalyst’s crystalline structure. Only the Zr-DES catalyst was completely transformed into particle structure and its catalytic performance was better than that of other mono-, bi- and tri-metallic catalysts. We can conclude that the best precursors have large lamellar thickness and are fully transformed into the smallest particles after activation.

Figure 10. SEM imaging was obtained to observe the structural morphology of unpromoted catalyst (Blank-VPO) (a), and promoted catalysts prepared from DES-Nb (b), DES-Mo (c), DES-Zr (d), DES-Zr-Mo (e), DES-Zr-Nb (f), DES-Zr-Mo-Nb (g).
VPO synthesis directs the catalytic performance. Metal-based DES regulated the structural morphology. The metals present in the DES became part of the VPO conjugates after synthesis. Energy dispersive spectroscopy (EDS) was performed to confirm the presence of newly introduced metal. Figures 11a and 12a show the spectra of monometallic Zr-DES precursor and catalyst. We observed zirconium peaks in both total spectrum diagrams. Therefore, we can conclude that zirconium as metal dopant became part of the VPO precursor and catalyst. In overall catalytic performance zirconium definitely contributed, because the catalyzed reaction mostly occurred at the catalyst surface, which was only responsible for C-H bond activation and initiating the reaction mechanism.

Figure 11. The total EDS spectrum of the monometallic Zr-DES precursor reveals the spectrum peaks of V, P, O and Zr (a). EDS maps illustrate the distribution of phosphorus (b), vanadium (c), zirconium (d), and all elements (e).

Figure 12. The total EDS spectrum of the monometallic Zr-DES catalyst (a). EDS maps show the distribution of phosphorus (b), vanadium (c), zirconium (d), and all elements (e).

TEM spectroscopic techniques confirmed the presence of interlayer spacing, which could easily be calculated numerically. Specifically, we evaluated the interlayer spacing of the active domain in the unpromoted catalyst (Blank-VPO; $d_{013} \sim 0.78$ nm) (Figure 13a–c), which was larger than that of the promoted catalyst prepared from mono-metallic Zr-DES-VPO ($d_{013} \sim 0.57$ nm) (Figure 13e–g). The as-obtained TEM results are clearly consistent with XRD results. Notably, the involvement of DES in VPO synthesis was similar to the behavior of polyethylene glycols (PEGs) when employed as electronic promoters and surface modifiers [35].

Using TEM micrographs, we evaluated the distributed particles at the catalyst surface. Herein, we evaluated the particle threshold via TEM microscopic graph (Figure 13d,h). It revealed that after activation, the promoted catalyst exhibited smaller crystallite size as compared to the unpromoted catalyst. Smaller crystallite size produced a large specific area and favored selective oxidation due to easy initiation of the C-H bond activation.
Thermogravimetric analyzer (TG-DTA) techniques were utilized to observe the transition state and weight loss of the precursor at higher temperatures. Herein, the temperature of the sample was raised from room temperature 25 °C to 800 °C under a nitrogen (N₂) environment at a rate of 10 °C/min. TG/DTA curve were obtained to analyze the decomposition temperature and weight loss. Figure 14a shows the TG-DTA profile of the unpromoted precursor (Blank-PVPO) and promoted precursors prepared from monometallic (b), bimetallic (c), and trimetallic (d) DES. The TG-DTA temperature profiles were classified into three different stages, i.e., primary, secondary and tertiary, with respect to their different temperature zones as below 220 °C, between 220~460 °C and above 460 °C respectively. In the primary stage we observed that desorbed water and alcoholic solvent were removed, and in the secondary stage we observed the topotactic transformation of precursors to produce the catalyst crystal; in the tertiary stage a dehydration process with a slight decrease in weight loss was observed. In Figure 14b–d we observe that the DTA curve of promoted precursors (mono-, bi-, tri-metallic DES) was shifted towards the right as compared to the unpromoted precursor, while the TG curve of weight loss was shifted towards the left. We observe that initial stage weight loss was greater in the unpromoted precursor than in the promoted precursors because DES affected the binding energies of the latter, but in second stage promoted precursors lost more weight than the unpromoted precursor due to the decomposition of DES. Therefore, we can conclude that the eutectic mixture of a hydrogen bond acceptor (ChCl) and hydrogen bond donors (metal salts) was actively involved in VPO synthesis and responsible for the higher exothermic signal in the TG-DTA profile.

In the literature, it has been reported that VPO catalyst surface exhibits important redox characteristics such as valence surface, surface acidity, and surface basicity that are based on surface element distribution, and control the overall catalytic performance. Characterization techniques such as NH₃-TPD and XPS were performed to analyze the VPO catalysts’ surface characteristics prepared from a mixture of hydrogen bond acceptor (ChCl) and hydrogen bond donors (metal salts). The acidic behavior of the catalyst surface was quantified using the NH₃-TPD technique in which ammonia (NH₃) probe molecules were used to evaluate the thermal desorption curve (Figure 15). The as-obtained desorption curve was classified into three acidic sites: weak (α ≤ 200 °C), medium (β = 200~500 °C) and strong (λ ≥ 500 °C), according to their different temperature zones. The strength of the acidic sites was measured using the desorption peak, which appears at each temperature zone at a specific temperature. Interestingly, it was found that the promoted (monometallic Zr-DES-VPO) catalysts possessed more acidic sites as compared to the unpromoted catalyst.
(Blank-VPO), in which the strong acid site (λ) was not observed. The unpromoted catalyst had total acidic strength of nearly 5.88446 mmol/g at 120 °C (α) and 450 °C (β), which was nearly half that of the promoted (monometallic Zr-DES-VPO) catalyst (10.620 mmol/g) (Table 2). More acidic sites easily accommodate the incoming carbonyl bond for selective oxidation, which is convenient for desorbing and preventing excessive oxidation from the catalyst surface. More acidic sites and higher acidic strength assists the selective oxidation yield.

![Figure 14](image_url)

**Figure 14.** TG-DTA analysis of the unpromoted precursor (Blank-PVPO) (a), and promoted precursors prepared from monometallic (b), bimetallic (c), and trimetallic (d) DES.

**Table 2.** NH₃-TPD results describing the acidic sites and their acidic strength for activated Ce-DES-VPO catalysts under different activation streams.

| Catalyst | Acid Sites Distribution, n(NH₃)/(mmol/g) | Weak (α) | Medium (β) | Strong (λ) | Total |
|----------|----------------------------------------|----------|------------|------------|-------|
| Blank    |                                        | 1.40191  | 4.48255    | –          | 5.88446 |
| VPO-DES-Zr |                                     | 1.26426  | 4.53262    | 4.82319    | 10.620 |
Figure 15. The desorption curve obtained from NH$_3$-TPD analysis of unpromoted (Blank-VPO) and promoted (monometallic Zr-DES-VPO) catalysts, classified into weak ($\alpha$), medium ($\beta$) and strong ($\lambda$) acidic sites.

The surface chemical behavior of O and V species with their composition content was measured using XPS characterization. Herein, peaks were determined using Avantage software and the curve was fitted via Gaussian function. In literature exhibiting the binding energies associated with vanadium, characteristic peaks (V2p$_{3/2}$) are reported repeatedly (Figure 16a) [26,27]. The V2p$_{3/2}$ characteristic results obtained from the fitted curve correspond to the whole catalyst vanadium species V$^{5+}$(VOPO$_4$) and V$^{4+}$((VO)$_2$P$_2$O$_7$). All catalyst particles were obtained at the catalyst surface. Moreover, surface oxygen (Sur-O) and lattice oxygen (Lat-O) were also quantified from XPS characteristic peaks and their associated binding energy curves examined under the range of O1s at 528~534.5 eV (Figure 16b). Table 3 shows the calculated values of the phosphorus/vanadium (P/V) ratio and the average valence state of vanadium (Vox). Selectivity towards MA is highly dependent on the V$^{5+}$ phase, which is required for C-H bond activation. The least active sites of the (VO)$_2$P$_2$O$_7$ phase and the VOPO$_4$ phases are not suitable for optimum selective oxidation. It is commonly understood that the catalyst surface possesses a vanadium oxidation state of approximately +4.00~+4.40 [36]. The appropriate distribution of V$^{5+}$ and V$^{4+}$ species at the catalyst surface is considered to play an active role in selective oxidation, which can be corroborated with Raman characterization [37,38]. Hutchings et al. proposed that the different valence state of vanadium V$^{5+}$/V$^{4+}$ be recognized as a catalyst active site, as it achieves the optimal relative strength within VPO catalysts considered to have the most effective catalytic activity [39]. The activity of VPO catalysts is manipulated by the P/V ratio. Herein, the monometallic Zr-DES based catalyst showed the optimum surface charge distribution of V$^{5+}$ and V$^{4+}$, and thus its P/V ratio was reduced and conventionally its surface/lattice oxygen was also optimal (4.113), not lower as in the blank-VPO (3.790) nor higher as in the bimetallic Zr-Nb-DES-VPO (6.588). The oxidation state of vanadium at 4.150 was close to the blank-VPO. Apart from the surface morphology, the electronic effects of the catalyst in comparison are important parameters for evaluating the catalytic performance. Therefore, C-H bonds were activated at appropriate chemical states of the surface, which was analyzed using XPS characterization.
Figure 16. The V2p$_{3/2}$ fitting curve (a) and O1s fitting curve (b) of VPO catalysts prepared from monometallic, bimetallic and trimetallic DES.

Table 3. The XPS characterization data of V2p$_{3/2}$ and O1s of Zr-, Nb-, Mo- DES-VPO catalyst are described as follows.

| Catalyst       | V2p$_{3/2}$ | O1s  | Peak Area of Lat-O (a) | Peak Area of Sur-O (a) | Lat-O/Sur-O | V$_{ox}$ (b) | P/V   |
|----------------|-------------|------|------------------------|------------------------|-------------|-------------|-------|
| Blank-VPO      | 517.45      | 531.67 | 10035.1 eV              | 8903.108 eV            | 533.2 eV    | 3.79        | 4.150 | 1.561 |
| VPO-DES-Nb     | 517.02      | 531.26 | 22507.8 eV              | 15029.52               | 533.2 eV    | 5.07        | 4.136 | 1.552 |
| VPO-DES-Mo     | 516.57      | 530.81 | 19957.3 eV              | 15750.58               | 533.2 eV    | 4.40        | 4.136 | 1.545 |
| VPO-DES-Zr     | 517.40      | 531.62 | 11653.5 eV              | 9694.215               | 533.2 eV    | 4.11        | 4.150 | 1.545 |
| VPO-DES-Zr-Mo  | 517.37      | 531.61 | 19168.9                 | 16500.02               | 533.2 eV    | 3.90        | 4.136 | 1.552 |
| VPO-DES-Zr-Nb  | 517.05      | 531.2  | 22665.2                 | 22665.29               | 533.2 eV    | 6.58        | 4.198 | 1.584 |
| VPO-DES-Zr-Mo-Nb | 517.4      | 531.7  | 17999.6                 | 15427.97               | 533.2 eV    | 4.62        | 4.096 | 1.573 |

Note: (a) XPS-Peak41 software; Lorentzian-Gaussian: 20%; Shirley background; (b) V$_{ox}$ = 13.82 − 0.68[O1s–V2p$_{3/2}$].

3.1.2. Performance of Promoted Catalysts

Figure 17a shows the catalytic performance of promoted catalysts prepared from mono-, bi- and tri-metallic DESs. We observed that the catalytic yield of MA was significantly changed due to the addition of DES as compared with unpromoted VPO catalyst (Blank-VPO) (Figure 17). Herein, we found that different metal promoters (i.e., Nb, Mo, and Zr) regulated the selective oxidation product. The catalytic performance of the VPO catalysts was evaluated in terms of n-butane conversion, MA selectivity and MA yield. The n-butane conversion of the monometallic VPO catalysts (Nb: 79.28%, Mo: 93.01%, and Zr: 96.53%) was higher than that of the bimetallic (Zr-Mo: 74.77%, Zr-Nb: 84.13%) and trimetallic (Zr-Mo-Nb: 82.39%) VPO catalysts. Furthermore, we noted that the MA selectivity of the trimetallic VPO catalyst (Zr-Mo-Nb: 40.02%) was lower than that of the bimetallic (Zr-Mo: 49.94%, Zr-Nb: 53.56%) and monometallic (Nb: 47.45%, Mo: 51.03%, and Zr: 53.48%) VPO catalysts. Interestingly, the n-butane conversion and MA selectivity of monometallic Zr-DES-VPO catalyst was greater than that of not only the other monometallic (Nb, Mo) but also the bimetallic (Zr-Mo, Zr-Nb) and trimetallic (Zr-Mo-Nb) DES-VPO catalysts. Similarly, the opposite trend was observed for CO$_x$ (CO and CO$_2$) selectivity. Moreover, the MA yield of the monometallic Zr-DES-VPO catalyst (51.63%) was much higher than that
of the unpromoted (43.92%), monometallic (Nb: 37.62%, and Mo: 47.46%), bimetallic (Zr-Mo: 37.34%, Zr-Nb: 47.46%), and trimetallic (Zr-Mo-Nb: 32.97%) VPO catalysts. Overall catalytic performance is determined from the catalytic yield of the selected product.

Figure 17. The catalytic performance of mono- (a), and bi- and tri-metallic DES-VPO catalysts (b) as compared with the unpromoted (Blank-VPO) catalyst.

Increased conversion will definitely produce increased oxidation byproducts but selectivity will limit the final yield. Higher n-butane conversion produces higher MA selectivity and thus higher utilization of low carbon alkanes, which indicates a green impact on the environment. The MA selectivity of VPO catalysts prepared from monometallic conjugates showed that increased n-butane conversion resulted in higher MA selectivity. A similar trend was seen with the bimetallic VPO catalyst. We can determine that catalytic performance of the VPO catalyst was improved significantly due to the addition of Zr-DES and controlling the “trade off” attribute. A lower ratio of CO/CO$_2$ is very crucial for chemical plants. We observed that Nb-DES-VPO had the smallest CO/CO$_2$ ratio, but unfortunately, overall CO$_x$ oxidation product (51.23%) was very high compared to Zr-DES-VPO (45.55%). In addition, the trimetallic VPO catalyst also displayed the smallest CO/CO$_2$ ratio with maximum CO$_x$ selectivity (58.53%).

3.2. Discussion

In general, the catalytic performance of a VPO catalyst is first determined by its structural morphology and the presence of active sites. The structural morphology was observed using SEM. Herein, we observed that different metal dopants had an influence on structural morphology and acted as templates or structure-directing agents. In particular, the monometallic Zr-DES precursor elicited horizontal sliced structures as compared to the cluster-type structure of the blank precursor. Interestingly, after applying the activation condition, the structure of the Zr-DES precursor was totally transformed into very fine nano-particles. Thus, the specific surface area increased rapidly and extended the exploitable surface area. The as-obtained pulverized particles were characterized using XRD and Raman techniques to evaluate their precursor main phase and active phase after the activation process. Selective MA yield is based on smaller crystallite size of the VPO catalyst as compared to the VPO precursor (Figure 18a). The crystallite size of Zr-DES-VPO was the smallest, so its catalytic performance exceeded that of other produced catalysts. The relative integral intensity ratio ($I_{(200)}/I_{(013)}$) of the VPO catalysts was presented with respect to their n-butane conversion (Figure 18b). TG-DTA analysis elaborated the transition temperature profile and weight loss when applying the higher temperature. It illustrated
that transition temperature affected the crystalline phase and helped elucidate the C-H bond activation of n-butane, which can be confirmed from Tables 2 and 3.

It is believed that physicochemical characteristics dominate the catalytic performance of VPO catalysts (Figure 19). We conclude that n-butane conversion (Figure 19a), CO/CO$_2$ ratio (Figure 19b), Lat-O/Sur-O ratio (Figure 19e), and $V_{ox}$ (Figure 19f) are positively correlated with MA selectivity. However, the selective catalytic yield of MA negatively corresponds with the crystallite size of VPO catalysts (Figure 19c). In addition, we examined the effect of P/V ratio on MA selectivity and found a positive response for all catalysts except the monometallic Zr-DES-VPO catalyst (Figure 19d). A greater Lat-O/Sur-O ratio is required for MA selectivity because surface oxygen drives the reaction towards over-oxidation and produces a greater by-product yield. The addition of DES into VPO synthesis reduced the CO/CO$_2$ ratio, indicating suitability for chemical plant efficiency and controlling industrial pollution. Moreover, we observed more acidic sites and greater total acidic content in the monometallic Zr-DES-VPO catalyst as compared to the unpromoted (Blank-VPO) catalyst, which assists the adsorption ability of MA, reduces over-oxidation, and supports the enrichment of P at catalyst active sites. Therefore, it evolves a selective yield due to reorganization of the existing variant energies of $V=O$ and $P=O$ (Figure 19). The above discussion confirms the role of the newly developed catalyst as an electronic promoter and structure-directing agent cooperatively participating in catalytic performance.

**Figure 18.** The crystallite size and relative integral intensity ratio of VPO precursors ($I_{(001)}/I_{(130)}$) and catalysts ($I_{(200)}/I_{(013)}$) is depicted using XRD characterization results (a); we correlate the relative integral intensity ratio of the VPO catalysts ($I_{(200)}/I_{(013)}$) with their n-butane conversion (b).

**Figure 19.** MA selectivity is dependent on n-butane conversion (a), the molar ratio of CO/CO$_2$ (b), crystallite size of the VPO catalyst (c), the P/V ratio (d), the lattice to surface oxygen ratio (Lat-O/Sur-O) (e), and the oxidation state of vanadium ($V_{ox}$) (f).
4. Conclusions

In this study, for the first time, mono-, bi-, and tri-metallic deep eutectic solvents (ChCl : metal – salt = 1 : 0.5) were prepared and then used to synthesize VPO catalysts as structure-directing agents and electronic promoters for n-butane selective oxidation towards MA. The evolution of catalytic performance showed that themonometallic Zr-DES-VPO catalyst exhibited the maximum MA yield (51.63%), which was 7.71% more than the unpromoted catalyst (Blank-VPO) under the same reaction parameters. Investigation of the surface morphology confirms that the addition of DES fully supported the generation of active phase (VO)\(_2\)P\(_2\)O\(_7\) and ignored pollutant phases such as γ-VOPO\(_4\). The structural morphology of Zr-DES-VPO showed horizontal slices with improved thickness. This resulted in a more extended surface area than that of the Blank-VPO. This might be due to the presence of hydrogen bonding in the DES, which encourages the nucleation and growth process of crystallite. Therefore, DES played the role of structure-directing agent in VPO synthesis. Additionally, as electronic promoter DES modulated the physicochemical properties such as surface P/V ratio, V\(^{+4}/V^{+5}\) ratio, Sur-O/Lat-O ratio, acid base redox properties, and reducible capability of V\(^{+4}/V^{+5}\) species. All these characteristics were well addressed with the help of various characterization techniques and explained in respect to the catalytic performance of VPO catalysts.

Author Contributions: Conceptualization, R.L. and M.F.; methodology, F.D.; software, N.M. and H.L.; validation, F.D., R.Z. and R.L.; formal analysis, M.F. and R.Z.; investigation, F.D.; resources, S.Z.; data curation, H.N.; writing—original draft preparation, M.F.; writing—review and editing, K.U.K.N.; visualization, H.L.; supervision, R.L.; project administration, F.D.; funding acquisition, S.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the National Key Research and Development Program of China (2017YFA0206803), the National Nature Science Foundation of China (21808223), the Key Programs of the Chinese Academy of Sciences (KFZD-SW-413), the Key Programs of Fujian Institute of Innovation, CAS (FJCXY18020203), Chinese Academy of Sciences, and the One Hundred Talent Program of CAS.

Acknowledgments: The authors are grateful for the assistance from teachers Julie Jin, Wu Hui, Wang Ling and Zhou Na of Analysis and Test Center, Institution of Process Engineering, Chinese Academy of Sciences, Beijing.

Conflicts of Interest: There are no conflict to declare.

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