Selective Oxidation of Bimetallic Gd-Ce Doped Vanadyl Pyrophosphate Catalysts

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Abstract : VPOs catalysts doped with varying fraction of bi-metallic Gd and Ce dopants were investigated. XRD diffractogram of undoped and Gd-Ce doped VPOs catalysts showed diffraction patterns of $(VO)_2P_2O_7$ phase. Two peaks attributable to α_{II}-$VOPO_4$ species emerged for all Gd-Ce doped VPOs catalysts with gradual agglomeration of thin platelets into distinctive rosette-shaped clusters as shown in SEM micrographs. TPR in H_2 profile showed two peak maxima corresponding to the removal of V^{5+}-O^{2-} and V^{4+}-O^-. The enhancement of the catalytic performances has suggested that pairing of rare earth dopants could induce positive synergistic effect on VPOs catalysts.

Keywords : Vanadyl pyrophosphate catalysts, *n*-butane oxidation, maleic anhydride

1. Introduction

In recent years, the increase in unsaturated polyester resins (UPR) production is observed due to high demand. Raw material for UPR production, maleic anhydride is synthesised from *n*-butane using vanadium phosphorus oxide (VPO) catalyst, resulting in greater need for highly active and selective catalyst to alleviate the industry. Research showed that vanadyl pyrophosphate compound, $(VO)_2P_2O_7$ is the active phase for selective oxidation of *n*-butane to maleic anhydride [1]. Dopants have been incorporated to induce morphological and activity promotion to enhance VPO performance [2]. In this study, the physico-chemical properties, reactivity and catalytic performances of undoped and Gd-Ce doped VPOs will be investigated.

2. Experimental

The catalysts were synthesised via sesquihydrate route. Vanadium oxide, V_2O_5 (15.0 g, Merck) was suspended in *ortho*-phosphoric acid, *o*-H_3PO_4 (90 ml, 85%, Merck) and deionised water (24 mlg^{-1} solid). The suspension was refluxed under continuous stirring at 393 K for 24 h. The resultant yellow solids ($VOPO_4 \cdot 2H_2O$) were centrifuged and oven-dried at 373 K for 48 h. Then, 10.0 g of $VOPO_4 \cdot 2H_2O$ solids were suspended in 1-butanol (150 ml, Merck), Gadolinium Nitrate, $Gd(NO_3)_3$ (1 mol%, Alfa Aesar) and Cerium Nitrate, $Ce(NO_3)_3$ (1, 3 and 5 mol%, Alfa Aesar). The mixtures were refluxed under continuous stirring at 393 K for 8 h. The resultant light blue solid precursors ($VOHPO_4 \cdot 1.5H_2O$) were centrifuged and oven-dried at 373 K for 24 h. Undoped precursor was prepared using the same method and reflux condition as above without adding Gd and Ce dopants. The dried precursors were then calcined in a reaction flow of 0.75% *n*-butane/air mixture at 733 K for 24 h. The activated undoped and Gd-Ce doped VPOs catalysts were denoted as Bulk, Gd1Ce1, Gd1Ce3 and Gd1Ce5, respectively. The synthesised catalysts were characterised using XRD, BET surface area, SEM-EDX, ICP-OES, redox titration, TPR in H_2/Ar and catalytic performances.

3. Results and discussion

XRD diffractogram of undoped and Gd-Ce doped VPOs catalysts (Fig. 1) showed similar diffraction patterns with major peaks at $2\theta = 22.8^o$, 28.4^o and 29.8^o, signified the existence of crystallised $(VO)_2P_2O_7$ phase at (020), (204) and (221) planes, respectively. Two additional peaks were emerged at $2\theta = 24.9^o$ and

29.2° (α_{II}-$VOPO_4$) were found in all Gd-Ce doped VPOs catalysts, which led to higher oxidation state of vanadium. Undoped catalyst exhibited the highest specific surface area, i.e. 23.2 m^2g^{-1}. As Gd (1 mol%) and Ce (1 to 5 mol%) were incorporated into VPOs catalyst system (denoted as Gd1Ce1, Gd1Ce3 and Gd1Ce5), the specific surface area has increased from 13.9 m^2g^{-1} to17.1 m^2g^{-1}. Surface morphologies from SEM micrographs (Fig. 2) showed small and thin platelets that were agglomerated into distinctive rosette-shaped clusters in undoped catalyst. However, the presence of Gd and Ce has produced VPOs catalysts with larger and thicker crystal platelets. This effect could have contributed to the decrease in specific surface area of the Gd-Ce doped VPOs catalysts as found in the BET surface area measurements. Reduction by H_2 (Fig. 3) profiled two significant peak maxima at temperature regions of 774-799 K and 993-1014 K, which were corresponded to the removal of V^{5+}-O^{2-} and V^{4+}-O^{-}, respectively [3]. The catalytic performances of *n*-butane to maleic anhydride was found to be increased, which was due to more prominent formation of desired V^{5+} phase (Tab. 1).

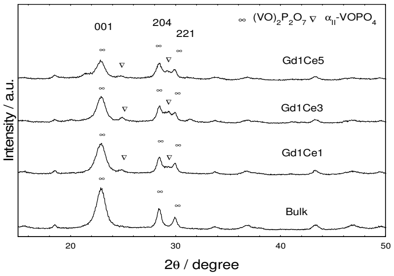

Figure 1. XRD profiles of Bulk and Gd-Ce Doped VPOs catalysts

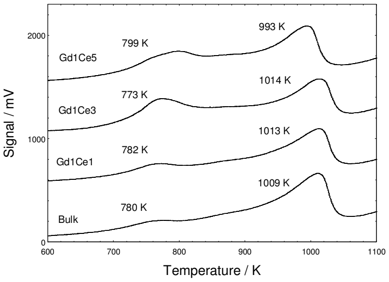

Figure 3. TPR in H_2/Ar profiles of Bulk and Gd-Ce Doped VPOs catalysts

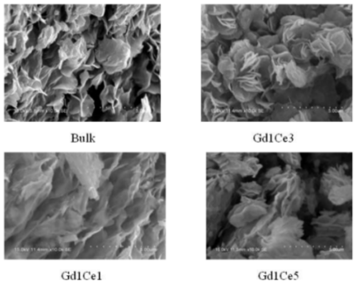

Figure 2. SEM micrographs of Bulk and Gd-Ce Doped VPOs catalysts

Table 1. Catalytic performances of Bulk and Gd-Ce doped VPOs catalysts

Sample	*n*-Butane Conversion (%)	Product Selectivity (%)	
		MA	Carbon Oxides
Bulk	33	53	47
Gd1Ce1	35	68	32
Gd1Ce3	40	70	30
Gd1Ce5	42	74	26

4. Conclusions

$(VO)_2P_2O_7$ active phase was found in undoped Bulk and Gd-Ce-doped catalysts. Additional V^{5+} phase (α_{II}-$VOPO_4$) was observed in all Gd-Ce doped VPOs catalysts. This has contributed to higher catalytic performances of *n*-butane to maleic anhydride within the range of study.

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References

1. G.Centi, Catal. Today, 1993, 16, 1-5.
2. G.J. Hutchings, Appl. Catal., 1991, 72, 1.
3. M.Abon, J.M. Hermann, J.C. Volta, Catal. Today, 2001, 71, 121.