Experimental evidence for the significance of the well-dispersed V^{5+} species in VPO catalyst for the partial oxidation of *n*-butane to mealic anhydride

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Introduction

Partial oxidation of *n*-butane to maleic anhydride is the only commercialized process for the catalytic conversion of light alkanes. The VPO catalysts are most effective for this reaction, although it has been recognized that $(VO)_2P_2O_7$ is the major active phase [1], controversies are still existed on the function of the V^{5+} species in these catalysts [2-5]. Reported in this paper are our characterization and catalytic evaluation results on a series of samples prepared by carefully adjusting their V^{5+} content and maintaining other major characteristics, e.g., surface area, phase composition and surface P/V ratio, of the catalysts basically unchanged, with the hope that the role of the V^{5+} species in these catalysts can be reliably clarified. In short, the catalyst precursors were prepared in iso-butanol/benzoic alcohol mixtures and by adding appropriate additives, e.g., PEG, gelatin, amylum and citric acid, the content of V^{5+} species in the final catalysts can be intentionally adjusted and the additives are completely removed upon calcination carried out under the reaction atmosphere [6]. The additive-free catalysts were characterized by XRD, XPS, IR, LRS and TPR and their catalytic properties were evaluated by a micro-reactor with an on-line GC.

Results and Discussion

Characterizations on a series of samples with various V^{5+} contents (0-25 atom%) are made to explore the role of the V^{5+} species on the catalytic properties of the catalysts. Raman and quantitative TPR results revealed that there is a large portion of V^{5+} species (ca. 25 atom%) in catalyst P1 consisting of $(VO)_2P_2O_7$ and $\alpha-VOPO_4$ prepared without additive. The V^{5+} species in P1 can not be detected by XRD but visualized by LRS might exist in the form of $\alpha-VOPO_4$ domains, which have also been reported in literature [7]. By adding various additives during preparation, the catalysts (P2-P8) with essential features of the $(VO)_2P_2O_7$ phase but containing less V^{5+} species, i.e., ca. 0-10 atom%, are obtained. Different from the bulk $\alpha-VOPO_4$ and the “domains” described above, the V^{5+} species in these low V^{5+}containting samples are highly dispersed on the surface of $(VO)_2P_2O_7$ and closely contacted with it. The reaction data indicated that the surface area is not a key factor responsible for the performance of the catalysts, as the P5 and P7 samples prepared by adding PEG and amylum respectively have very similar surface areas (56 m^2/g vs. 54 m^2/g) but rather big difference in their activities shown in Table 1. As a matter of fact, most physico-chemical features of these two samples, namely, the phase composition of the $(VO)_2P_2O_7$, the crystallinity and morphology as well as the surface P/V ratio are essentially the same, their difference in activity should be attributed to the presence of the well-dispersed V^{5+} species (ca. 10 atom%) in the P5 catalyst while the P7 sample is almost V^{5+} free. The results suggested that the presence of an appropriate amount and well-dispersed V^{5+} species is crucial for the catalytic activity of the sample. P1 catalyst has an apparently lower activity than that of P5 indicating the fact that too much V^{5+} present in the sample has an negative effect attributing to the aggregation of the V^{5+} species resulting in the formation of the bulk-like species. Our results are in support of the assumption made by Volta et al., i.e., a well-balanced V^{4+}/V^{5+} ratio is important for the catalytic activity of the catalysts [8].

It is suggested that the coupling of V^{4+}-V^{5+} species has a favorable synergistic effect on the catalytic performance of the catalysts, and the dispersion state hence the structural feature of the V^{5+} species is the key factor needed to be concerned for optimizing the effect. Our results have shown that the presence of well-dispersed V^{5+} species in the catalysts favors the initial activation of butane, leading to a higher conversion with a similar MA selectivity. To verify the above discussion on the role of V^{5+} species, two V^{5+}-free VPO catalysts prepared by other experimental methods have also been characterized, although their catalytic performances could be slightly modified by changing experimental conditions, they are always lower than that of the V^{5+}-containing catalysts.

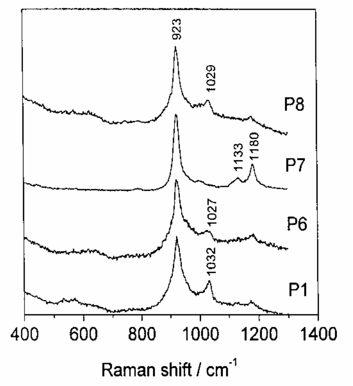

Fig. 1. The Raman Spectra of the catalysts. P1: without additive, P6-P8: derived with gelatin, amylum and citric acid respectively.

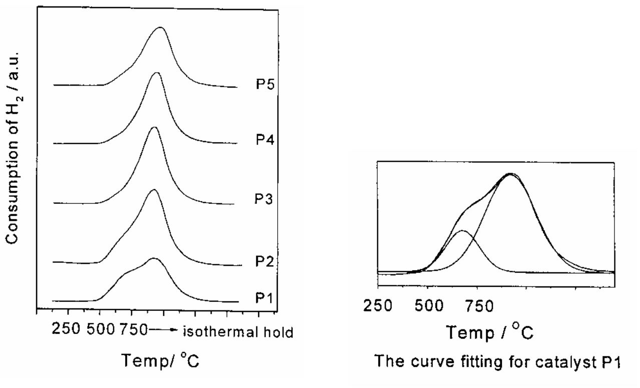

Fig. 2. The TPR profiles of the catalysts (left) and the curve fitting analysis of P1 (right). P1: without additive, P2-P5: with the PEGs of different molecular weights.

Table 1. The characteristics and the reaction performances of the P1 and P5-P7 catalysts

Catalyst	Main Phase	Surface Area (m^2/g)	Surface P/V Ratio	V^{5+}/V_{total}	MA Yield (mol%, 658K)
P1	$(VO)_2P_2O_7$	19	1.5	25	50
P5	$(VO)_2P_2O_7$	56	1.5	10	68
P6	$(VO)_2P_2O_7$	34	1.4	8	64
P7	$(VO)_2P_2O_7$	54	1.5	~0	38

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