



# Samarium-modified vanadium phosphate catalyst for the selective oxidation of *n*-butane to maleic anhydride



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## ABSTRACT

A series of samarium-modified vanadium phosphate catalysts were prepared and studied in selective oxidation of *n*-butane to maleic anhydride. The catalytic evaluation showed that Sm modification significantly increased the overall *n*-butane conversion and intrinsic activity. N<sub>2</sub>-adsorption, XRD, SEM, Raman, XPS, EPR and H<sub>2</sub>-TPR techniques were used to investigate the intrinsic difference among these catalysts. The results revealed that the addition of Sm to VPO catalyst can increase the surface area of the catalyst, lead to a significant change in catalyst morphology from plate-like structure into rosette-shape clusters, and largely promote the formation of (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. All of these were related to the different catalytic performance of Sm-doped and undoped VPO catalysts. The roles of the different VOPO<sub>4</sub> phases and the influence of Sm were also described and discussed.

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## 1. Introduction

Vanadium phosphorus oxide (VPO) is used as the most effective catalyst for partial oxidation of *n*-butane to maleic anhydride (MA), which is the only successful industrial process in the oxidation of utilizing alkanes [1,2]. Typically, the final catalyst is usually composed by a complex mixture of vanadium (IV) and (V) phosphates [3–5], such as vanadyl pyrophosphate ((VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub>), vanadium polyphosphate (VO(PO<sub>3</sub>)<sub>2</sub>) and vanadyl orthophosphates (α<sub>1</sub>-, α<sub>II</sub>-, β-, δ- and γ-VOPO<sub>4</sub>). Much effort has been made employing spectroscopic and diffraction characterizations to reveal the role of the above-mentioned phases, especially the intrinsic different role of vanadyl pyrophosphate and vanadyl orthophosphates in this 14-electrons-transferring process [5–7]. It is generally accepted that the major active component of the catalyst is (VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> which is originating from the topotactic transformation of the precursor VOHPO<sub>4</sub>·0.5H<sub>2</sub>O [1,5]. However, there is still a matter of controversy on the role of VOPO<sub>4</sub> in the literatures [5–9].

Metal cations (Mo, Co, Fe, Nb) are usually used to enhance the catalytic performance of the VPO catalysts for this reaction [10–12]. To date, a wide kind of cations has been studied and reported in both

patents and literatures such as Co, Cd, Zn, Bi, Li, Ni, Cr, Zr, Mg, Nb, Fe, Al and Sn [11–14]. Generally, the effects of the promoters could be classified into two types [11]. The first type of the promoters produced structural effects on the catalysts and led to the increase of surface areas. In this case, the promoters were used to remove excess phosphorus and hinder the formation of deleterious phases. The second type of the promoters introduced electronic changes. Herein, the metal cations could replace V<sup>4+</sup> and form the solid solutions of the type [(VO)<sub>1-x</sub>M<sub>x</sub>]<sub>2</sub>P<sub>2</sub>O<sub>7</sub>. Despite the location and the role of the promoters in the catalysts have been investigated, there is still a lack of agreement on the functions of the promoters in controlling the morphology, phase composition and redox properties of VPO catalysts, which have a significant influence on their catalytic behaviors [15].

In addition, up to now, few studies are reported employing rare earth as the modifier in VPO catalyst, though the use of rare earth in the catalyst is attractive, especially in oxidation reaction [16]. Barbero et al. [17] evaluated the catalytic performance of V<sub>2</sub>O<sub>5</sub>–SmVO<sub>4</sub> catalysts in the oxidative dehydrogenation of propane and a synergistic effect at low reaction temperature was observed. Patel et al. [18] found that SmVO<sub>4</sub> was an active and selective catalyst for the oxidative dehydrogenation of butane and its selectivity for butene was the same as that of Mg<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> and V–Mg–O. Recently, Rownaghi et al. [19] had experimentally shown that the use of Ce and La promoters could lead to substantial improvement of VPO catalyst performance in selective oxidation of *n*-butane to maleic

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anhydride. However, the effects of various phases on the catalytic behavior were discussed in less detail. Furthermore, the influence of Sm promoter on this catalyst has not been reported so far to our best knowledge.

In this paper, we modified VPO catalyst with Sm and explored the physicochemical characteristics and catalytic performance changes deduced by the introduction of Sm to VPO catalyst. Besides, the relationships between catalytic reactivity and the surface morphologies, the phase composition and the redox properties were also described and discussed.

## 2. Experimental

### 2.1. Precursor synthesis

The undoped precursor was prepared in the following way:  $V_2O_5$  (2.95 g) was refluxed in a mixture of *iso*-butanol (33 mL) and benzyl alcohol (33 mL) for 6 h, then orthophosphoric acid (85%) was added dropwise to reach a P/V atomic ratio of 1.2 and the mixture was refluxed for a further 6 h. The light blue solid was filtered after refluxing and washed with *iso*-butanol and ethanol, then dried in air at 383 K. For the Sm-doped precursors, the preparation method is the same as the undoped precursor, with the required amount of  $Sm(NO_3)_3 \cdot 6H_2O$  (Sm/V atomic ratio = 0.01, 0.03, 0.05, 0.1) added to the  $V_2O_5$ /alcohol mixture at beginning. The resulted undoped and Sm-doped samples are denoted as VPO and xSm-VPO, respectively, where x refers to the Sm/V atomic ratio.

### 2.2. Catalyst characterization

The X-ray diffraction analyses were carried out using a Panalytical X'pert PRO employing  $CuK\alpha$  radiation to generate diffraction patterns from power crystalline samples at ambient temperature. The Raman spectra were recorded Renishaw UV-Vis Raman 1000 System equipped with a CCD detector and a Leica DMLM microscope. The line at 532 nm of an  $Ar^+$  laser was used for excitation.  $N_2$  adsorption/desorption isotherms were recorded at 77 K on an automated micromeritics Tri-Star 3000 apparatus. Surface areas were calculated using the multipoint BET equation.  $H_2$ -TPR experiments were performed by a TCD detector, using 5%  $H_2/Ar$  mixture flowing at 20 mL/min. The heating rate was 10 K/min. Surface morphologies of the catalysts were observed under a scanning electron microscope (SEM), using a S-4800 operated at accelerating voltages of 10 kV. The surface compositions of the catalysts were determined by X-ray photoelectron spectroscopy (XPS), which was performed using a VG ESCALAB/Auger. All binding energies were corrected with reference to the C1s signal located at 284.6 eV. Electronic paramagnetic resonance (EPR) spectra were recorded at 100 K using a Bruker ER 200D-SRC spectrometer. The microwave power was set at 20 mW with a resonance frequency of ca. 9.46 GHz and 100 kHz modulation.

### 2.3. Catalytic reaction

Catalytic tests were carried out in a fixed-bed flow microreactor containing a standard mass of catalyst precursor (0.6 g). A mixture of 1.5% *n*-butane in air was fed with a gas hourly space velocity (GHSV) of  $3000 h^{-1}$ . Reactants and reaction products were analyzed on-line by gas chromatography. Carbon mass balances were typically better than 95%.

The precursor, pressed into pellets and sieved to 40–60 mesh, was activated *in situ* before the catalytic test. It was heated in a mixture of 1.5% *n*-butane in air (GHSV =  $3000 h^{-1}$ ) from room temperature to 693 K at a rate of 2 K/min, leaving it at this temperature

for 16 h. After such an activation procedure, the precursor was transformed into the final catalyst.

## 3. Results

### 3.1. Catalyst characterization

The specific surface areas of various samples are listed in Table 1. For all the activated samples, except 1%Sm-VPO, the addition of Sm leads to an enhancement of surface area and the surface area increases with increasing Sm content.

The XRD patterns of the undoped and Sm-doped precursors are shown in Fig. 1(A). All the patterns are characteristic of vanadyl (IV) hydrogen phosphate hemihydrate ( $VOHPO_4 \cdot 0.5H_2O$ ) phase with the main reflections appearing at  $2\theta = 15.5^\circ, 19.5^\circ, 24.2^\circ, 27.0^\circ$  and  $30.3^\circ$  which correspond to (001), (101), (021), (121) and (220) planes, respectively. For Sm-doped samples, no reflections of Sm-containing phases are detected. However, the addition of small amount of Sm leads to a significant increase in the relative peak intensity ratio of  $I_{(001)}/I_{(220)}$ , especially for the sample doped with 1%Sm. It seems likely that Sm addition can effectively control the morphology of the catalyst precursor. The similar effect was also reported for Fe-doped hemihydrates [20], but the addition of Fe led to a decrease in the value of  $I_{(001)}/I_{(220)}$ , contrasting with the influence of Sm-doping observed in this work. It has been known that the (001) plane of the  $VOHPO_4 \cdot 0.5H_2O$  phase transforms to the topologically similar (200) plane of  $(VO)_2P_2O_7$ , which is believed to be responsible for the catalytic activity for *n*-butane oxidation [1,15,21].

Fig. 1(B) shows the XRD patterns of the precursors after being activated. All the patterns indicates the presence of  $(VO)_2P_2O_7$  phase (JCDs File No. 01-089-8338), with the main peaks appearing at  $2\theta = 23.0^\circ, 28.4^\circ$  and  $29.7^\circ$  related to (200), (024) and (032) reflections, respectively. However, the relative intensity and the peak broadening of the main reflections are quite different for the catalysts with different composition. The Sm-doped samples show the peaks with a higher intensity than the undoped sample and the intensities of the peaks increase with the increase of Sm content. This indicates an increment of the amount of  $(VO)_2P_2O_7$  introduced by the addition of Sm. Table 1 also summarizes the  $I_{(200)}/I_{(024)}$ , full width at half maximum (FWHM) and crystallite size of the (200) and (024) plane results calculated by using Debye-Scherrer equation. It can be seen that compared with the undoped sample, the Sm-containing catalysts show higher FWHM values and consequently smaller crystallite sizes along the (200) and (024) planes. Furthermore, the addition of a small amount of Sm leads to a significant increase in the ratio of  $I_{(200)}/I_{(024)}$ , indicating an enhancement of the exposure of (200) plane which contains the vanadyl group [22].

The surface morphologies of undoped and Sm-doped catalysts characterized by SEM are shown in Fig. 2. The undoped catalyst

**Table 1**  
Surface areas and XRD data of the various activated catalysts.

Sample	Surface area (m <sup>2</sup> /g)	$I_{(200)}/I_{(024)}^a$	FWHM <sup>b</sup> (°)		Crystallite size <sup>c</sup> (nm)	
			(200)	(024)	(200)	(024)
VPO	13.9	0.53	0.46	0.40	20.8	24.1
1%Sm-VPO	13.2	0.93	1.14	0.60	7.5	13.9
3%Sm-VPO	15.8	0.70	0.82	0.55	10.7	16.7
5%Sm-VPO	17.1	0.60	0.65	0.48	13.7	19.3
10%Sm-VPO	20.0	0.52	0.50	0.41	18.4	23.2

<sup>a</sup> Ratios of relative peak intensities.

<sup>b</sup> Full width at half maximum.

<sup>c</sup> Calculated by the Scherrer Formula.

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