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Enhancing catalytic performance of phosphorus-modified ceria supported VPO catalysts for *n*-butane oxidation

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ABSTRACT

Vanadium phosphorus oxide (VPO) catalysts supported on CeO_2 and P-modified CeO_2 (P-CeO_2) have been firstly synthesized for selective oxidation of *n*-butane to maleic anhydride (MA). The catalysts supported on P-CeO_2 showed higher catalytic performance, especially higher MA selectivity than catalysts on pure ceria, and their specific activities (normalized to per unit mass of VPO loading) were also superior to that of bulk VPO. TG, TEM, XRD, Raman, H_2-TPR and XPS results revealed that the structure and property of VPO are largely affected by the support. The loaded VPO existed almost wholly as $VOPO_4$ phases on pure ceria, while mainly in the form of $(VO)_2P_2O_7$ with small amount of $VOPO_4$ phases on phosphorus-modified ceria. Both VPO/P-CeO_2 and bulk VPO catalysts have the similar VPO phase structure, but the former showed the enhanced reducibility of V^{4+} phase. These differences in structure and properties of the catalysts were discussed and related to their different catalytic performances.

1. Introduction

The 14-electron partial oxidation of *n*-butane to maleic anhydride (MA) is the most successful sample for the commercial application of light paraffin conversion [1]. The most effective catalyst for this reaction is vanadium–phosphorus-oxide with vanadyl pyrophosphate ($(VO)_2P_2O_7$) as the main component [2,3]. So far, great effort has been devoted to getting insight into the peculiar properties of the catalyst, while questions still exist as to the form of the active phase (amorphous versus crystallized) and the nature of the active components [4–8].

Definitely, supported VPO catalysts have several superiorities compared with bulk VPO catalysts, such as larger surface area to volume ratio of active component, more active sites available for per unit mass of catalyst and better mechanical strength. In recent years, several groups have reported their investigations on VPO catalysts supported on SiO_2, TiO_2, SiC, Al-containing MCM-41, SBA-15, ZrO_2, RGO and ZrP [9–16]. Notably, the preparation methods have great influences on phase compositions and the catalytic performance of the VPO catalysts [9,10,13,17]. The results of plenty of literature have reached the agreement that VPO catalysts synthesized in an organic medium have better performance than those synthesized in an aqueous solution [18–20]. Generally, in organic synthesis, a mixture of *iso*-butyl/benzyl alcohols is adopted for producing VPO catalysts and the use of an organic medium yields an increase in surface area of the precursor and enhances the activity of the catalyst [19–22]. Nevertheless, as reported previously [23–25], supported VPO catalysts, especially for those prepared in aqueous medium, usually had a certain amount of $VOPO_4$ such as α-$VOPO_4$ and γ-$VOPO_4$. The existences of a massive amount of α-$VOPO_4$ and γ -$VOPO_4$ were harmful to the catalytic performance of supported VPO catalysts. Besides, it is found that the nature of the support also affects phase compositions and catalytic performance of the VPO catalysts [12,26]. Nie et al. [12] modified MCM-41 with certain amount of aluminum and concluded that the incorporated Al^{3+} in the framework of MCM-41 support might have an impact on MA selectivity. Buena et al. [26] adopted hydrophobic and hydrophilic

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silica as the supports and found that $(VO)_2P_2O_7$ could be formed easily on the former support.

Ceria is usually used as catalyst support or catalyst in various applications such as CO oxidation, three-way catalysts (TWCs), selective oxidation and the water–gas shift [27–30]. It has attracted widely attention for its distinctive properties, including high lattice oxygen mobility, high oxygen-storage capacity and ease of exchange of surface lattice oxygen with gas-phase oxygen [31,32]. Due to these properties, supporting VPO catalysts on ceria perhaps contains fascinating information. However, so far few reports have been made on the employment of ceria as support for VPO catalyst. Wachs et al. [33] investigated the oxidation of *n*-butane to maleic anhydride over a series of model-supported vanadia catalysts and observed that the MA selectivity closely followed the lewis acid strength of the oxide support cations, Al > Nb > Ti > Si > Zr > Ce. Herron et al. [34] employed ceria-supported VPO catalyst in *n*-butane oxidation and found that the catalyst exhibited low *n*-butane conversion and especially low MA selectivity. No detailed studies have been done to understand the effect of this support on the structure and properties of VPO catalysts. Especially, no any attempt has been made to modify ceria and thus improve the catalytic performance of ceria-supported VPO catalysts for the reaction.

It has been reported that the addition of phosphorus to some of the catalysts can enhance their catalytic performance in ODH of light alkanes [14,29,35,36]. For chromium oxide supported on phosphorus-loaded alumina, the addition of phosphorus influenced the nature of the Cr oxide species and thus heightened the selectivity to propylene [35]. For P-containing ceria, the phosphorus decreased the lattice oxygen mobility through the formation of Ce—O—P bonds and increased the propylene selectivity [29]. In case of VPO catalysts supported on H_3PO_4-treated ZrO_2, the way of H_3PO_4 treatment conducted on ZrO_2 had a great influence on the state and structure of the VPO component loaded on it [14]. In case of phosphorus-modified silica supported vanadium catalysts, phosphorus modification improved the yield of MA in the selective oxidation of *n*-butane [36].

The present study is the first to adopt phosphorus-modified ceria as a support material for VPO catalysts and to investigate the influence of the support on the structure and nature of supported VPO species. The physicochemical properties of the VPO catalysts supported on ceria and on phosphorus-modified ceria were systematically examined by XRD, TEM, Raman, XPS and H_2-TPR techniques.

2. Experimental details

2.1. Materials and preparation

2.1.1. Synthesis of pure ceria

Ceria was fabricated according to the method described elsewhere [37]. Briefly, a solution of $(NH_4)_2CO_3$ (0.9 mol L^{-1}, 50 mL) was added dropwise to the cerium nitrate solution (0.3 mol L^{-1}, 50 mL) and white powders were produced immediately. After vigorous stirring for 30 min, the mixture was transferred to a reflux device and heated at 100 °C for 12 h. The powder obtained after filtration was washed with water and ethanol. Subsequently, it was dried at 80 °C for 12 h and then calcined at 500 °C for 4 h.

2.1.2. Synthesis of P-modified CeO_2

To achieve phosphorus-modified ceria, the as-prepared ceria powder (1 g) was added to solutions of $NH_4H_2PO_4$ (10 mL) at concentrations of 1, 1.5 and 2 mol L^{-1}. The above suspension was stirred at room temperature for 6 h and then filtered by Buchner funnel. The obtained solid was dried at 80 °C for 12 h and calcined at 500 °C for 4 h. The phosphorus-modified samples were marked as 1P-CeO_2, 1.5P-CeO_2 and 2P-CeO_2, respectively.

2.1.3. Synthesis of supported VPO catalysts

Typically, supported VPO precursor was prepared in the following way: V_2O_5 (0.6 g, 3.3 mmol) was added to a mixture of *iso*-butanol and benzyl alcohol (26 mL, volume ratio of 1/1) and refluxed at 135 °C for 5 h, then a suitable amount of support materials was introduced. After one hour, phosphoric acid (0.6 mL, 85%) was added dropwise to reach a P/V atomic ratio of 1.2. After refluxing for another 6 h, the suspension was filtered, and the solid was washed with *iso*-butanol and ethanol, and then dried in air at 110 °C for 12 h. The catalysts are denoted as *x*VPO/CeO_2 or *x*VPO/P-CeO_2, where x = 9, 14, 18 and 23%, which refer to the vanadium content of 9, 14, 18 and 23 wt%, respectively.

The precursor, previously pressed into pellets and sieved to 40–60 mesh, was activated under the reaction conditions (1.5% *n*-butane in air, GHSV = 1500 h^{-1}) from ambient temperature to 400 °C at a rate of 2 °C min^{-1}, holding it at this temperature for 16 h. After that, the precursor was transformed into the final catalyst.

2.2. Catalyst characterization

The structural properties of the catalysts were characterized by using the Rigaku Ultima IV X-ray diffractometer with monochromatized CuKα radiation. Raman spectra were recorded by using Renishaw UV–vis Raman 1000 system equipped with a CCD detector and a Leica DMLM microscope. The line at 532 nm of Ar^+ laser was used for excitation. H_2-TPR experiments were carried out in a quartz tube of 4 mm diameter with 50 mg sample by raising the temperature from 100 to 800 °C at a rate of 10 °C min^{-1} under a 5%H_2/Ar mixture flowing at 30 mL min^{-1}. The thermogravimetric (TG) analysis was conducted on a TG209F1 thermal analyzer. The surface compositions of the samples were obtained from X-ray photoelectron spectroscopy (XPS) using a VG ESCALAB/Auger. All binding energies were corrected with reference to the C1s signal located at 284.6 eV. The morphologies of the samples were investigated by TECNAI F-30 FEG transmission electron microscope.

2.3. Catalytic reaction

The selective oxidation of *n*-butane was executed in a fixed-bed flow microreacter using 0.5 g of catalyst with a gas hourly space velocity (GHSV) of 1500 mL g^{-1} h^{-1}. The reaction mixture (1.5% *n*-butane in air) was fed into the reactor via calibrated mass flow controller. The test temperature was in the range of 340–440 °C. The outlet effluents were analyzed with an on-line gas chromatography and the carbon balance was usually >95%.

3. Results

3.1. Catalyst characterization

Shown in Fig. 1 are the results of thermogravimetric (TG) analysis and differential thermogravimetry (DTG) analysis on the thermal decomposition of bulk VPO and 18%VPO/1.5P-CeO_2. Three distinct stages in weight loss curve are observed for both catalysts. The first weight loss step occurring below 200 °C originates from the desorption of physically adsorbed water, the second step from 200 to 430 °C arises from the conversion of $VOHPO_4$ to $(VO)_2P_2O_7$ and from the removal of alcohols trapped in the layers of precursor, while further weight loss above 430 °C may be due to the progressive dehydration and to the formation of crystal defects [38,39]. The results show that the catalysts have similar thermal decomposition process, except the second stage where the central decomposition temperature of the 18%VPO/1.5P-CeO_2 is 342 °C,