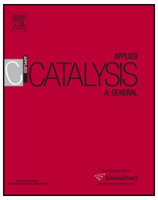
Applied Catalysis A: General 482 (2014) 189–197

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Vanadium phosphorus oxide catalyst promoted by cobalt doping for mild oxidation of benzyl alcohol to benzaldehyde in the liquid phase

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ARTICLE INFO

Article history:
Received 20 November 2013
Received in revised form 29 April 2014
Accepted 2 June 2014
Available online 9 June 2014

Keywords:
Vanadylpyrophosphate
Promoter
Co
Benzyl alcohol oxidation

ABSTRACT

A series of cobalt-doped vanadium phosphorus oxides (VPO-Co) catalysts, as well as unpromoted sample (VPO) were prepared using classical organic method *via* $VOHPO_4{\cdot}0.5H_2O$ precursor followed by calcinations in *n*-butane/air environment at 400 °C for 24 h. Techniques such as XRD, BET surface area, chemical titration, SEM, TPR and FT-IR were used for characterization of the catalysts. The results showed that promoted and unpromoted VPO catalyst were contained crystalline form of V^{4+} (vanadyl pyrophosphate, $(VO)_2P_2O_7$) and also a small amount of V^{5+} (β-$VOPO_4$ phase). However, Co promoted VPO contained poorer crystallinity compared to the unpromoted catalysts. $CoPO_4$ phase also observed in the VPO-Co series and the intensities of the X-ray lines of $CoPO_4$ increased with the increase of the Co/V molar ratio. In addition, the promotion of Co resulted in larger amount of V^{5+} species. Co was found to increase the average oxidation number of vanadium from 4.28 to 4.35 due to an addition of V^{5+} oxidation state from 28% to 35%.

Oxidation of benzyl alcohol, for the first time, was studied in the liquid phase over VPO and VPO-Co catalysts, using tert-butylhydroperoxide (TBHP) as an oxidant. The catalytic tests showed that cobalt doping significantly increased the overall activity for the oxidation of benzyl alcohol. At 90 °C, the obtained activities were 0.662 and 1.014 $g_{pro}\,g^{-1}{}_{VPO}\,h^{-1}$ over the VPO and VPO-Co (molar ratio Co/V = 0.01) catalysts, respectively. The effects of reaction temperature, amount of the catalyst, solvents, and catalyst recycling of VPO-Co in liquid phase were also investigated.

1. Introduction

Vanadium phosphorus oxide (VPO) catalysts have long been recognized as the most fascinating catalyst in achieving high conversion with good selectivity in *n*-butane partial oxidation to maleic anhydride [1]. It is the most complex reaction as compared to other industrially practiced hydrocarbon oxidations and represents the only industrially practicable selective oxidation reaction involving an alkane [2]. It is generally accepted that VPO catalysts composed mainly of vanadyl pyrophosphate ($(VO)_2P_2O_7$) are effective for the oxidation of *n*-butane to maleic anhydride (MA) [2–5]. One of the effective means of improving the catalytic properties is the introduction of metal ions into the lattice [6–8]. The effect of the dopant is to change the structure characteristics of catalyst phases [7,9]. It also plays a role in having an effect on the adsorption of oxygen and its diffusion within the lattice, by which a non-selective route of butane oxidation is suppressed [10].

One of the most studied metal dopant introduced in VPO catalysts is cobalt. Kladekova et al. [11] found that the catalyst modified by Co increased the specific rate of butane oxidation and maleic anhydride formation three times compared to the unmodified catalyst. Abdelouahab et al. [12] observed an enhancement in the $VOPO_4/(VO)_2P_2O_7$ dispersion at the surface of the Co doped VPO catalyst prepared by the normal organic route. However, the same catalyst prepared *via* $VOPO_4{\cdot}2H_2O$ precursor [13] gave a better catalytic performance. Cornaglia et al. [14,15] prepared a series of Co-promoted VPO ranging from 1 to 6 wt.% Co and found that the addition of Co significantly increased the overall activity while decreasing the selectivity slightly in *n*-butane partial oxidation to maleic anhydride. They concluded that the non-equilibrated unpromoted and promoted VPO catalysts with a small percentage of Co showed V(V) phases present in low proportions, which after several hundred hours on stream showed only the V(IV) vanadyl pyrophosphate phase. Recently, Sajip et al. [16] reported that the Co significantly enhanced the selectivity and the intrinsic activity to maleic anhydride. They proposed that the origin of the promotional

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http://dx.doi.org/10.1016/j.apcata.2014.06.003
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effect of Co is associated with its interaction with the disordered VPO phases.

Selective catalytic oxidation of benzyl alcohol to benzaldehyde is one of the most important chemical transformations in industrial chemistry. Benzaldehyde has been widely applied in the manufacture of odorants, flavors, aniline dyes, plastic additives and pharmaceutical intermediates as an important raw material [17].

Several studies have been reported on the catalytic oxidation of benzyl alcohol to benzaldehyde with different catalysts and oxidants [18–27]. The increasing needs of efficient and selective catalysts as well as the fundamental investigations are continuously the driving forces for synthesis of new catalysts.

VPO has been applied as a heterogeneous catalyst in gas phase oxidation reactions and its application is very limited in liquid phase reactions. Recently, a VPO catalyst has been used for the synthesis of aldehydes and ketones from alcohols in the presence of hydrogen peroxide [28]. We have recently reported the oxidation of alcohols with TBHP using VPO/HMS catalyst [29]. In present study for the first time, we developed the use of cobalt-doped VPO catalyst (VPO-Co) for the oxidation of alcohols with tert-butylhydroperoxide (TBHP) in the liquid phase.

2. Experimental

2.1. Materials

All materials were of commercial reagent grade. All the alcohol substrates and V_2O_5 were obtained from Aldrich. H_3PO_4 (85%) and tert-butylhydroperoxide (TBHP) 70% solution in water were purchased from Merck chemical company. All of the solvents acetonitrile, toluene, p-dioxane, chloroform and ethanol used were of the highest commercial quality supplied from Merck Company and used without further purification.

2.2. Preparation of unpromoted and Co-promoted VPO catalysts

The unpromoted $VOHPO_4{\cdot}0.5H_2O$ precursor was prepared by adding V_2O_5 (15.0 g) to a mixture of isobutanol (90 mL) and benzyl alcohol (60 mL). The vanadium oxide–alcohol mixture was refluxed for 4 h at 105 °C with continuous stirring. The mixture was then cooled to room temperature and aged at this temperature overnight. *Ortho*-phosphoric acid (11 mL, 85%) was added to obtain the P:V atomic ratio of 1. The resulting solution was then heated again to 120 °C and maintained under reflux with constant stirring for 4 h. The precipitate was removed by filtration, washed thoroughly and dried at 150 °C overnight.

For the preparation of Co-doped catalyst precursor, V_2O_5 (15.0 g) and the cobalt promoter in the nitrate or acetylacetonate form was suspended by rapid stirring into a mixture of isobutyl alcohol (90 mL) and benzyl alcohol (60 mL). The amount of cobalt nitrate/acetylacetonate was adjusted to obtain 0.01–1.0 molar ratio of Co/V. The vanadium oxide–cobalt nitrate/acetylacetonate–alcohol mixture was refluxed for 7 h at 110 °C with continuous stirring. The mixture was then cooled to room temperature and aged at this temperature overnight. *Ortho*-phosphoric acid (11 mL, 85%) was added in such a quantity as to obtain P:V atomic ratio of 1.0. The resulting solution was then heated again to 120 °C and maintained under reflux with constant stirring for 4 h. The precipitate was removed by filtration, washed thoroughly with water and dried at 150 °C overnight.

Both unpromoted and promoted precursors were heated from room temperature to 400 °C at a rate of 5 °C/min in the air flow (30 mL/min) and kept at this temperature for at least 24 h. The contents of cobalt and vanadium were determined by atomic absorption spectroscopy (AAS) using a Perkin-Elmer Analyst instrument, after dissolving of samples in H_2SO_4 (2 M). Cobalt-containing VPO catalysts prepared from nitrate are designated as VPO-Co-n(x), while the materials obtained from acetylacetonate are represented as VPO-Co-a(x), x being the Co/V molar ratio. These samples with grain size of 200–230 mesh were separated and in the next step, were used in liquid phase to catalyze the oxidation of benzyl alcohol by TBHP.

2.3. Catalysts characterization

The total surface areas of the catalysts were measured by the BET (Brunauer–Emmer–Teller) method using nitrogen adsorption at 77 K. This was done by the Micromeritics ASAP 2000 nitrogen adsorption/desorption analyzer.

The average oxidation states of vanadium in the catalysts were determined by redox titration following the method of Niwa and Murakami [30]. About 0.1 g of each catalyst was dissolved in 100 mL of 2 M H_2SO_4 at 80 °C. The vanadium(IV or III) content was determined by titration with a solution of $KMnO_4$ (0.01 N). The vanadium(V) content was determined by titration with a solution of a Mohr-salt ($FeSO_4{\cdot}(NH_4)_2SO_4{\cdot}6H_2O$, 0.01 N) using diphenylamine as an indicator.

The structure of the catalysts was studied by X-ray diffraction (XRD) experiments. A diffractometer Philips model PW 1800 instrument with Cu Kα radiation and Ni filter was used to collect the X-ray data. The SEM image was obtained with a Philips XL30 instrument.

The infrared spectra of the catalysts were taken as KBr pellets on a Galaxy-5000 Fourier transform infrared (FT-IR) spectrometer. Temperature-programmed reduction in H_2(H_2-TPR) was carried out in order to observe the reducibility of the VPO catalyst by using a Thermo Finnigan TPDRO 1110 apparatus utilizing a thermal conductivity detector (TCD). H_2-TPR experiment was performed using a quartz reactor tube (4 mm i.d.), in which a 40 mg sample was mounted on loosely packed quartz wool. Prior to H_2-TPR measurement, a catalyst was pretreated in N_2 at 473 K (heating rate of 10 K min^{-1} and hold time 30 min), then cooled down under He. The reduction gas was composed of 5 vol% H_2 in Ar. The reaction temperature was programmed to rise at a constant rate of 10 K min^{-1}. A thermocouple in contact with the catalyst allowed the control of the temperature. The amount of H_2 uptake during the reduction was measured by a thermal conductivity detector (TCD). The effluent H_2O formed during H_2-TPR was adsorbed by a 5A molecular sieve adsorbent.

2.4. Oxidation of alcohols

In a typical procedure, a mixture of 0.1 g catalyst (VPO or VPO-Co), with a grain size of 200–230 mesh 15 mL acetonitrile and 10 mmol of alcohol was stirred in a three-necked flask under nitrogen atmosphere at 50 °C for 30 min. The stirring rate of the solution was set at 750 cycle/min. Then 10 mmol of the oxidant (TBHP) was added and the mixture was refluxed at 90 °C for 8 h under nitrogen atmosphere. After filtration, the solid was washed with ethanol and the reaction mixture was analyzed by GC. A GC (Perkin Elmer Model 8500) equipped with a flame ionization detector (FID) connected to a 3% OV-17 column with a length of 2.5 m and diameter of 1/8 in. was used for product analysis.

3. Results and discussion

3.1. Characterization of the catalysts

3.1.1. X-ray diffraction (XRD)

Fig. 1 shows the XRD patterns of unpromoted and Co-promoted VPO catalysts with different Co/V molar ratio. XRD patterns showed well crystalline materials. The appearance of lines at $2\theta = 22.8, 28.3,$