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Synthesis, characterization of VPO catalyst dispersed on mesoporous silica surface and catalytic activity for cyclohexane oxidation reaction

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ABSTRACT

A precipitation-deposition method in an organic medium was used to prepare vanadium phosphorus oxide (VPO) catalysts supported on SBA-15 and TUD-1. Oxidation of cyclohexane has been examined over mesoporous silica supported VPO catalyst. The supported VPO catalyst has been characterized by XRD, N_2 physisorption, SEM, HRTEM, H_2-TPR and NH_3-TPD techniques. The characteristic X-ray diffraction patterns of bulk VPO catalyst and VPO catalysts supported on mesoporous SBA-15 and TUD-1 showed that each of them are having well-crystallized vanadyl pyrophosphate $[(VO)_2P_2O_7]$ phase. The vanadium redox centers were easily accessible for supported VPO catalyst. The TUD-1 supported VPO catalyst had higher acidity as found in NH_3-TPD studies. The conversion of cyclohexane increased in the case of VPO dispersed on TUD-1 mesoporous material. From SEM and HRTEM results it is found that the nature of the support and VPO loading had a profound influence on the crystallinity, morphology and chemical property of the dispersed VPO phase. The changes in all the property had a prominent role on its catalytic activity for the oxidation of the cyclohexane.

1. Introduction

The selective oxidation of hydrocarbons is an area of great interest both academically and industrially. This is due to the utility of partially oxidized hydrocarbons as industrial raw materials and the scientific challenge of getting partially oxidised products in good yields. The products of cyclohexane oxidation, both cyclohexanol and cyclohexanone are important intermediates in the manufacture of nylon-6 and -66 polymers [1]. In general, both cyclohexanol and cyclohexanone are produced on an industrial scale by the oxidation of cyclohexane or hydrogenation of phenol [2]. Vanadium phosphorus oxide (VPO) catalyst with vanadyl pyrophosphate $[(VO)_2P_2O_7]$ as the major component are very well known for industrial production of n-butane oxidation to maleic anhydride [3], partial oxidation of propane [4], ammoxidation of picoline [5] etc. Apart from being environmentally friendly and less expensive VPO catalysts are also efficient towards selective oxidation process [6]. Mostly VPO catalysts contain two phases i.e. $[(VO)_2P_2O_7]$ and $VOPO_4$. Centi et al. [7] suggested that the presence of V^{5+} species in excess (>5%) could lead to oxidation of n-butane to carbon oxides whereas Chen et al. [8] reported that the average oxidation state of vanadium in VPO catalyst was 4.00–4.03 for selective oxidation reaction [9].

The use of VPO phases as catalysts for liquid phase oxidation reactions is very limited. Potentially, supported VPO catalysts have advantages over unsupported ones, e.g. better heat transfer character, higher mechanical strength, controllable textures of catalyst and large surface area to volume ratio of active component [10]. However type and nature of support and preparation method also exhibited significant influence on catalyst performance [11,12]. VPO catalysts prepared in an organic medium are known to perform better than those prepared in an aqueous solution. Iso-butanol and benzyl alcohol have been adopted for generating VPO catalysts in an organic medium [13]. Among silica-based mesoporous materials SBA-15, MCM-41 have well-ordered hexagonal porosities with high thermal stability and surface area. Nie and co-workers found that VPO dispersed on Al-containing MCM-41 could produce maleic anhydride with high selectivity [14]. It is found that V_2O_5–TiO_2 [15],

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amorphous microporous vanadium oxides mixed with silica [16], V-MCM-41, V-MCM-48 [17], metal complexes anchored on other materials [18–20] etc. have been reported as catalysts for the oxidation of cyclohexane.

In the present study we have investigated the physicochemical property of VPO catalyst dispersed on two different mesoporous silica e.g. SBA-15 and TUD-1 catalytic activity for cyclohexane oxidation reaction. The catalysts have been characterized by XRD, N_2-adsorption–desorption, SEM, HRTEM, FT-IR, H_2-TPR and NH_3-TPD techniques. The catalytic activity was evaluated for cyclohexane oxidation reaction using hydrogen peroxide as an oxidant. The several parameters like VPO loading, temperature, oxidant to substrate ratio have been varied for correlating the characterization result with catalytic activity. The results are highly rewarding as it focus the change in catalytic activity due to the presence of two different mesoporous silica having different morphology.

2. Experimental

2.1. Catalyst preparation

The VPO was synthesized in an organic medium according to the literature procedure [21]. In a typical synthesis, 1 g V_2O_5 (Sigma Aldrich) was added in a 1:1 (V/V) mixture of benzyl alcohol and n-butanol at room temperature and the suspension was stirred continuously under reflux condition (140 °C) for 5 h. The instance orange colour was changed to greenish and finally turned to deep green colour is obtained. Then 1.27 mL of H_3PO_4 (85%, Sigma Aldrich) was added drop wise. Then colour changed to bluish green from dark green. The stirring was continued at 140 °C temperature for 6 h. Finally blue particles of vanadyl pyrophosphate formed. The suspension was decanted and centrifuged followed by washing with 1:1 n-butanol/acetone solution. The sample was then dried in the oven at 120 °C for 24 h and it was calcined at 400 °C with 2 °C/min increments for 22 h. Finally the deep greenish VPO catalyst was obtained after calcinations.

Ordered mesoporous SBA-15 was synthesized in acidic condition as reported in literature [22]. In this method pluronic P123 (Aldrich) (4 g) was dissolved in 150 mL distilled water and 7–8 g 35% HCl (Merck) by continuous stirring. After 4 h of stirring a clear solution was obtained and then 4 g n-butanol (Merck) was added to this solution with continuous stirring for 1 h. Finally tetraethyl orthosilicate (8.4 g) (TEOS, Acros) was added drop wise to the solution. The mixture was stirred for 24 h at room temperature and then it was transferred into a closed polypropylene bottle for ageing at 100 °C for another 24 h. After cooling to room temperature, the solid product was washed with deionised water and dried in air at 100 °C overnight. For decomposing the templates, the as-synthesized material was calcined in air at 550 °C with 1 °C/min increment for 5 h.

The TUD-1 was prepared according to literature report by several groups [23]. In brief 14.9 g triethanolamine was added drop wise to 10.4 g tetraethyl orthosilicate. Then deionised water was added drop wise in the mixture followed by addition of 7.35 g tetraethyl ammonium hydroxide with vigorous stirring. The whole mixture in the ratio of $TEOS:TEA:H_2O:TEAOH = 1:2:11:1$ was stirred for 24 h at room temperature. Then the mixture was placed in an oven at 110 °C for 24 h. The product was calcinated in air at 700 °C with a rate of 1 °C/min for 10 h.

The preparation of the VPO precursor supported on the mesoporous SBA-15/TUD-1 material was performed as reported in literature [13]. Typically 0.18 g V_2O_5 was refluxed at 140 °C for 5 h in a mixture of isobutanol and benzyl alcohol (10 mL each) to obtain VPO-loading of 20 wt%. Then, 0.175 g of PEG-6000 (Sigma Aldrich) and 0.90 g of SBA-15/TUD-1 material were added to the mixture. After 1 h stirring, 0.274 g of phosphoric acid (Sigma Aldrich, 85%) was added drop wise to the mixture. The mixture was allowed to reflux for 6 h. The suspension was filtered and washed with isobutanol as well as acetone. The solid was dried in air at 120 °C for 24 h. Then the solid was calcined at 400 °C for 15 h with heating rate 2 °C/min. The phosphorus to vanadium ratios of the synthesized 20 wt% VPO-SBA-15 or 20 wt% VPO-TUD-1 materials was 1.09 as calculated theoretically.

2.2. Catalyst characterization

2.2.1. X-ray diffraction (XRD)

The XRD patterns are recorded at room temperature using Rigaku Ultima IV system using CuK_α radiation as X-ray source. The catalysts are ground to fine powder prior to measurement. The scans are recorded in the 2θ range between 10 and 75° using step size of 0.02° and scan speed of 2 s/step. Peaks are identified by search match technique using X'Pert Highscore software with reference to the JCPDS database.

2.2.2. BET surface area and porosity measurement

The nitrogen adsorption–desorption isotherm of the sample were measured at liquid nitrogen temperature with a Quantachrome NOVA 3200 at −196 °C. Degassing of the samples was done at 200 °C for 6 h under high vacuum. The surface area was determined by Brunauer–Emmett–Teller (BET) equation. Pore size distributions were calculated using BJH (Barrett, Joyner and Halenda) method.

2.2.3. Scanning electron microscope (SEM)

The SEM was obtained from Leo Seris 1430 VP. The powder sample was supported on aluminium stubs and then coated with gold by plasma prior to measurement.

2.2.4. High resolution transmission electron microscope (HRTEM)

The HR-TEM investigation was done on JEOL JEM 2100 microscope operated at 200 KV acceleration voltage using lacey carbon coated Cu grid of 300 mess size.

2.2.5. Fourier transform infrared spectroscopy (FTIR)

The FT-IR measurements were carried out by using Perkin Elmer GX spectrophotometer. The spectra were recorded in the range 400–4000 cm^{-1} using KBR pellet.

2.2.6. Temperature programmed reduction (TPR)

TPR profiles of the samples were recorded with ChemiSorb 2720 (Micrometrics, USA) equipped with a TCD detector. The TPR profiles were obtained by reducing the catalyst samples by a gas mixture of 10% H_2 in Ar with a flow rate of 20 mL/min while the temperature was increased from ambient to 700 °C at a rate of 10 °C/min.

2.2.7. Temperature programmed desorption (TPD)

TPD profiles of the samples were recorded with ChemiSorb 2720 (Micrometrics, USA) equipped with a TCD detector. The TPD was carried out by first heating under He flow from room temperature to 350 °C for 30 min. The dried catalysts were cooled to ambient temperature. The NH_3 uptake on the catalyst surface took place when the gas flow was changed to 4% NH_3 in He. The NH_3-TPD profile was obtained by a temperature programme under He with a flow rate of 20 mL/min from ambient temperature to 1000 °C at a rate of 10 °C/min. The amounts of NH_3 desorbed in the TPD peak area was evaluated by pulses of NH_3 in a flow of He.