



Heterogeneous catalysis

Influence of cesium and vanadium contents on the oxidation functionalities of heteropoly molybdate catalysts

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ABSTRACT

Keggin-type heteropoly molybdates with different cesium and vanadium contents were synthesized and characterized by X-ray diffraction, FT-infrared, *in situ* Laser Raman, X-ray photo electron spectroscopy and temperature programmed desorption of NH₃ techniques. The catalytic functionalities were evaluated for vapor phase aerobic oxidation of benzyl alcohol. Raman spectral studies suggest the partial destabilization of Keggin structure of the catalyst with more than two vanadium atoms per one Keggin unit in the primary structure. The conversion of benzyl alcohol and selectivity to benzaldehyde was influenced by both Cs and V contents. The correlation between catalytic activity and physico-chemical properties of the catalysts suggested that the acidity and redox nature of the catalysts have an important role in the oxidation of benzyl alcohol and these properties are influenced by the amounts of Cs and V, respectively, in heteropoly molybdates. A plausible mechanism for Cs_xMPAV_y/TiO₂ catalyzed oxidation of benzyl alcohol has been proposed.

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1. Introduction

Selective oxidation of alcohols to aldehydes is an important reaction in both fundamental research and industrial manufacturing point of view [1]. The world-wide annual production of carbonyl compounds is over 10⁷ tons and most of these compounds are produced from oxidation of alcohols [2]. This functional group transformation can be accomplished by a number of diverse methods. However, many of the processes in practise are hazardous as they produce toxic waste in stoichiometric amounts. Traditionally, these transformations have been performed with stoichiometric inorganic oxidants, notably chromium(VI) and manganese(VII) reagents [3]. Growing environmental restrictions are forcing the shutdown of such hazardous processes. Over the years, constant innovations in catalyst and process design have resulted in a number of new developments for improving economics and eco-friendliness. In this context, many of the researchers have been focusing on the use of environmentally benign heterogeneous catalysts, such as, supported noble metals [4,5], complexes of transition metals [6,7], and solid acids [8,9]. The application of solid

catalysts for the oxidation of alcohol was reviewed in detail by Mallat and Baiker [10]. Among the different available solid acid catalysts, heteropoly acids (HPAs) have attracted considerable attention in recent times [11,12].

Heteropoly acids with Keggin structure have been intensively studied as green oxidation catalysts for both heterogeneous and homogeneous processes due to their unique acidic and redox properties [13–15]. The main advantage of these heteropolyacids is that their acid and redox properties can be tuned in a systematic way by changing their molecular composition. However, due to low thermal stability, surface area and high solubility in polar solvents, HPAs cannot be used as heterogeneous catalysts in their pure form. In order to make these heterogeneous, three kinds of modifications can be done which are *viz.*, (i) exchanging the protons present in secondary structure with large cations, such as Cs⁺, NH₄⁺, *etc.*, (ii) incorporating redox atoms, such as V, Nb into the primary structure in place of addenda atoms, (iii) dispersing HPAs on stable supports. The acidity of HPAs can be customized by secondary structure modification while redox nature can be altered by primary structure modification. Partial alkali exchanged HPAs exhibit dramatic changes in surface area, pore size, acidity and thermal stability. Salts with large monovalent ions, such as Cs⁺, NH₄⁺, Rb⁺ and Ag⁺ are practically insoluble in water or other polar solvents and possess high surface areas [15,16]. Incorporation of V, Nb, *etc.*, in place of addenda atom enhances redox nature of the catalysts.

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The role of Cs and V atoms present in heteropoly molybdate catalysts have reported for the oxidative dehydrogenation of propane [17]. The oxidation activity decreased significantly with increasing cesium content (2–4) over $Cs_xH_{3-x}PMo_{12}O_{40}$ and $Cs_xH_{4-x}PVMo_{11}O_{40}$ catalysts with different cesium contents. Lee et al. [18] studied the catalysts with fixed Cs^+ and variables (0, 1, 2) vanadium contents for the reaction of oxidative dehydrogenation of isobutyric acid to methacrylic acid and reported that acidity and redox nature of the catalysts are essential for the better performance of the catalysts. The influence of Cs and V contents in heteropoly molybdates toward oxidation of methacrolein to methacrylic acid was studied and highlighted the drawbacks of these catalysts [19]. It has also been reported that the introduction of vanadium at the primary structure of Keggin anion of molybdophosphates can enhance the catalytic activity and a small fraction of vanadium can be segregated in the form of $(VO)^{2+}$ during the reaction [20]. The addition of vanadium species to the secondary structure can result in a much more active and selective catalyst for acrylic acid production during partial oxidation of propane. Majority of these reports deals with bulk catalysts and further studies are needed to shed light on the role of Cs and V contents on oxidation properties of supported cesium salts of vanado molybdophosphate catalyst systems.

In the present study, heteropoly molybdates are modified by exchanging its protons with Cs^+ ions, incorporating V atoms in place of Mo and dispersing them on TiO_2 support. The oxidation functionalities of these catalysts were tested for vapor phase oxidation of benzyl alcohol using air as oxidant. The influence of Cs, V present in the primary and secondary structures of heteropoly molybdates, respectively, for their oxidation activity is explored. A plausible mechanism for Cs_xMPAV_y/TiO_2 catalyzed oxidation of benzyl alcohol has been proposed. The catalytic activities were correlated with the textural properties obtained from different characterization results.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of $H_{3+y}PMo_{12-y}V_yO_{40}/TiO_2$ catalyst

Vanadium incorporated molybdophosphoric acid catalysts $H_{3+y}PMo_{12-y}V_yO_{40}$ ($y = 1, 2, 3$) were prepared according to the reported procedure [21]. The detailed method of $H_4PMo_{11}V_1O_{40}$ (MPAV₁) preparation was explained elsewhere [22]. Preparation of $H_5PMo_{10}V_2O_{40}$ (MPAV₂) and $H_6PMo_9V_3O_{40}$ (MPAV₃) catalysts is also similar to that of MPAV₁ except by taking the required amount of sodium metavanadate and sodium molybdate. Titania (Loba Chemie, India) supported catalysts were prepared by impregnation method. The required quantity of MPAV_y ($y = 1, 2, 3$) was dissolved in minimum amount of water, and this solution was added to support with constant stirring. The excess water was removed using water bath and the catalyst masses were dried in an air oven at 120 °C for 12 h. These catalysts were denoted as MPAV_y/TiO₂ ($y = 1, 2, 3$). The samples used for activity studies are calcined at 350 °C for 4 h in air. The active component content on TiO₂ was kept constant at 20 wt% for all the catalysts.

2.1.2. Preparation of $Cs_xH_{3+y-x}PMo_{12-y}V_yO_{40}/TiO_2$ catalyst

The protons present in the above prepared catalysts were exchanged with cesium by using cesium nitrate ($CsNO_3$) as precursor. The required quantity of $CsNO_3$ dissolved in water was added drop wise to MPAV_y/TiO₂ to exchange the protons of MPAV_y with Cs. The excess water was removed on water bath and the final catalysts were obtained by calcining at 350 °C for 4 h. The content of Cs was varied from 1 to 3 moles to replace equivalent protons in

MPAV_y. The catalysts are denoted as Cs_xMPAV_y/TiO_2 , where the x indicates the number of Cs ions substituted for proton and y indicates number of V atoms substituted for Mo.

2.2. Catalysts characterization

Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer using Cu K α radiation (1.5406 Å) at 40 kV and 30 mA and secondary graphite monochromatic. The measurements were obtained in steps of 0.045° with a count time of 0.5 s and in the 2θ range of 10–80 degrees.

Raman spectra were recorded at room temperature in the range of 200–1200 cm^{-1} using a Horiba Jobin-Yvon Lab Ram HR spectrometer of a 17 mW internal He–Ne (Helium–Neon) Laser source with excitation wavelength of 632.8 nm. The catalyst samples in powder form (about 5–10 mg) were loosely spread on a glass slide below the confocal microscope for Raman measurements. *In situ* Raman spectra of the catalyst were recorded by the same Raman spectrometer equipped with high-temperature catalyst cell reactor (Linkam CCP 1000) using 50X long working distance objective. The catalyst sample, typically consisting between 10 and 15 mg of loose powder, was placed in an environmentally controlled high-temperature cell reactor containing a quartz window. The temperature of the reactor cell was controlled by programmable temperature controller.

Temperature programmed desorption of ammonia (TPD) was carried out on a laboratory-built apparatus equipped with a gas chromatograph using thermal conductivity detector. In a typical experiment, about 0.1 g of the oven dried sample was taken in a quartz tube and treated at 300 °C for 1 h by passing pure helium (99.9%, 50 ml/min). After pretreatment, the sample was saturated with anhydrous ammonia (10% NH₃ balanced with He) with a flow of 50 mL/min at 100 °C for 1 h and was subsequently flushed with He at the same temperature to remove physisorbed ammonia. The process was continued until a stabilized base line was obtained in the gas chromatograph. Then the TPD analysis was carried out by programming the temperature from 100 to 600 °C at a heating rate of 10 °C/min.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a KRATOS AXIS 165 with a DUAL anode (Mg and Al) apparatus using Mg K α anode. The non-monochromatized Al K α X-ray source ($h\nu = 1486.6$ eV) was operated at 12.5 kV and 16 mA. Before acquisition of the data, each sample was out-gassed for about 3 h at 100 °C under vacuum of 1.0×10^{-7} T to minimize surface contamination. The XPS instrument was calibrated using Au as standard. For energy calibration, the carbon 1s photoelectron line was used. The carbon 1s binding energy was taken as 285 eV. Charge neutralization of 2 eV was used to balance the charge up of the sample. The spectra were deconvoluted using Sun Solaris Vision-2 curve resolver. The location and the full width at half maximum (FWHM) value for the species were first determined using the spectrum of a pure sample. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible within ± 0.1 eV.

³¹P nuclear magnetic resonance (NMR) spectra of solids were recorded in a 400 MHz Bruker spectrometer. A 4.5 μ s pulse (90°) was used with repetition time of 5 s between pulses in order to avoid saturation effects. Spinning rate was 5 kHz. All the measurements were carried out at room temperature using 85% H₃PO₄ as standard reference.

2.3. Catalyst activity measurements

Aerobic oxidation of benzyl alcohol was carried out in a fixed bed vertical glass reactor ($h = 350$ mm, $d = 12$ mm) under atmospheric pressure. In a typical experiment, about 0.5 g of catalyst (crushed to

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