



The role of niobia location on the acidic and catalytic functionalities of heteropoly tungstate

Ch. Ramesh Kumar^a, S. Gatla^b, O. Mathon^b, S. Pascarelli^b, N. Lingaiah^{a,*}

^a Catalysis Laboratory, Inorganic & Physical Chemistry Division, CSIR–Indian Institute of Chemical Technology, Hyderabad, Telangana 500 007, India

^b Electronic Structure and Magnetism (ESM) Group, European Synchrotron Radiation Facility (ESRF) 71, Avenue des Martyrs, 38000 Grenoble, France

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ABSTRACT

12-Tungstophosphoric acid (TPA) was modified systematically by incorporating niobium into its primary and secondary structure. TPA supported on niobia catalyst was also prepared by impregnation method. These catalysts were characterized by FT-infra red, X-ray diffraction, Laser Raman, X-ray photo electron spectroscopy, X-ray absorption spectroscopy, UV–vis diffuse reflectance spectroscopy, solid state ³¹P nuclear magnetic resonance spectroscopy, temperature programmed desorption of ammonia and pyridine adsorbed FT-IR spectroscopy. Characterization results suggest the presence of intact Keggin structure after modification of parent TPA. Incorporation of Nb into the secondary structure results in generation of Lewis acidic sites. Nb containing TPA catalysts exhibited high acidity compared to the TPA supported on niobia catalyst. The activity of the catalysts was evaluated for benzylation of anisole with benzyl alcohol. Catalyst activity depended on the location of niobium ion in the heteropoly tungstate.

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1. Introduction

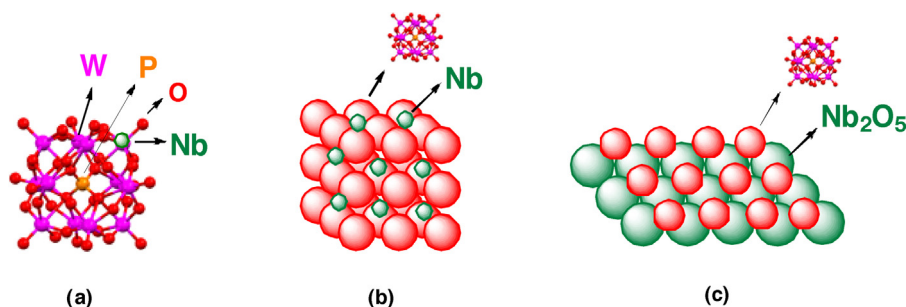
Polyoxometalates (POMs) are composed of early transition-metals of group V and VI in their highest oxidation states [1]. POMs are classified into two categories, namely isopolyoxometalates and heteropolyoxometalates. Among the heteropolyoxometalates, Keggin type are the most frequently used in catalysis, represented by the formula $[XM_{12}O_{40}]^{n-}$. The Keggin anion is made of an assembly of twelve MO_6 octahedrons sharing their corners or edges with a central XO_4 tetrahedron, where X is a hetero atom (P^{5+} , Si^{4+}), n is the oxidation state and M is the addenda atom (Mo^{6+} , W^{6+} , V^{5+}). The metal oxide cluster molecule $[XM_{12}O_{40}]^{n-}$ is called as primary structure. Secondary structure is a regular arrangement of poly anions counter cations and also some polar molecule such as water [2]. The catalytic properties of heteropoly acids (HPAs) can be tuned in a systematic way by exchanging counter-cations and hetero atoms [3–6]. Park et al. studied the acidic and oxidation properties of HPA catalysts by exchanging the identity of addenda atom with group-V metal ions such as V^{5+} , Nb^{5+} and Ta^{5+} [7–9].

The acidic and redox properties of the modified HPA catalysts depend on the nature of metal ion and its location in Keggin ion. HPAs with incorporation of V into its primary structure were reported [7,10]. This modification resulted in the increase of the redox nature of HPAs particularly heteropoly molybdate for different oxidation reactions [11–13]. The modification of HPAs by incorporating different metal ions in their primary and secondary structures will totally provide new catalytic functionalities. It is anticipated that by modifying the heteropoly tungstate which is the strongest acid among the HPAs by different metal ions such as Nb will result in much stronger acidic catalysts. Niobia is known for its acidic behavior and expected to modify the acidity and stability of HPA to a great extent.

In the present work, the role of niobium in the heteropoly tungstate is investigated by preparing (i) incorporation of niobium in the primary structure of Keggin ion of heteropoly tungstate ($TPANb_1$), (ii) incorporation of niobium in the secondary structure i.e., substitution of counter cations (H^+) of TPA with niobium ($Nb_{0.6}TPA$) and (iii) TPA supported on Nb_2O_5 (25% TPA/Nb_2O_5) as illustrated in Scheme 1. These catalysts are characterized by different techniques to derive their surface, structural and acidic properties. The catalysts were evaluated for their catalytic activity by taking benzylation of anisole with benzyl alcohol as a

* Corresponding author. Fax: +91 40 27160921.

E-mail address: nakkalingaiah@iict.res.in (N. Lingaiah).



Scheme 1. Structure of (a) niobium incorporated Keggin ion (TPANb₁ or [PW₁₁Nb₁O₄₀]⁴⁻), (b) niobium salt of tungstophosphoric acid (Nb_{0.6}TPA or Nb_{0.6}PW₁₂O₄₀), and (c) tungstophosphoric acid supported on niobia (25% TPA/Nb₂O₅ or 25% H₃PW₁₂O₄₀/Nb₂O₅).

model reaction. The influence of different benzylating agents is also studied.

2. Experimental

2.1. Catalyst preparation

Nb_{0.6}TPA catalyst was prepared as following. 5 g of TPA was dissolved in distilled water and 0.56 g of niobium oxalate dissolved in 0.1 M oxalic acid solution was added to aqueous solution of TPA with continuous stirring. The resultant mixture was stirred for 3 h. Excess water was evaporated on a water bath and the dried catalyst mass was kept for further drying in an air oven for overnight. Finally the sample was calcined at 300 °C for 2 h.

TPANb₁ catalyst was prepared according to the procedure reported in the literature [7]. In a typical procedure, 10 g of niobium oxalate was dissolved in 100 ml of 0.1 M oxalic acid solution and 6 g of Na₂HPO₄ was dissolved in 100 ml of distilled water. These two solutions were mixed together. 100 g of Na₂WO₄·2H₂O was dissolved in 150 ml of distilled water, and subsequently added to the solution containing niobium and phosphorous precursors with vigorous stirring. After heating the resulting solution to 80 °C, 60 ml of H₂SO₄ was slowly added to it. The solution was further kept for reflux at 80 °C for 8 h. After cooling the solution to room temperature, the formed TPANb₁ was extracted with diethyl ether. The resulting etherate was maintained at 50 °C to obtain solid product, dried in an oven and calcined at 300 °C for 2 h.

TPA supported niobium oxide catalyst was prepared by impregnation method. In a typical procedure, required amount of TPA was dissolved in water and this solution was added to niobium oxide with continuous stirring. The resultant mixture was allowed to stand for 3 h and excess water was evaporated on a water bath. The catalyst was kept overnight for drying in an air oven at 120 °C and finally calcined at 300 °C for 2 h. The TPA content on niobia is kept as 25 wt%. The catalyst is denoted as 25% TPA/Nb₂O₅.

2.2. Characterization of catalysts

The FT-IR spectra were recorded on a Bio-Rad Excalibur series spectrometer using the KBr disc method.

The nature of the acid sites (Bronsted and Lewis) of the catalyst samples was determined by FT-IR spectroscopy with chemisorbed pyridine. The pyridine adsorption studies were carried out in the diffuse reflectance infrared Fourier transform (DRIFT) mode. Prior to the pyridine adsorption catalysts samples were degassed under vacuum at 200 °C for 3 h and exposed to dry pyridine. Then, the excess pyridine was removed by heating the sample at 120 °C. After cooling the sample to room temperature, FT-IR spectra of the pyridine-adsorbed samples were recorded. X-ray powder 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 count times of 0.5 s, in the 2θ range of 2–80°.

Confocal micro-Raman spectra were recorded at room temperature in the range of 200–1200 cm⁻¹ using a Horiba Jobin-Yvon Lab Ram HR spectrometer with a 17 mW internal He-Ne (Helium-Neon) laser source of excitation wavelength of 632.8 nm. The catalyst samples in powder form (about 5–10 mg) were loosely spread onto a glass slide below the confocal microscope for measurements.

The acidity of the catalysts was measured by temperature programmed desorption (TPD) of ammonia. In a typical experiment, 0.1 g of catalyst was loaded and pre-treated in He gas at 300 °C for 2 h. After pre-treatment the temperature was brought to 100 °C and the adsorption of NH₃ was carried out by passing a mixture of 10% NH₃ balanced He gas over the catalyst for 1 h. The catalyst surface was flushed with helium gas at the same temperature for 2 h to flush off the physisorbed NH₃. TPD of NH₃ was carried with a temperature ramp of 10 °C/min and the desorbed ammonia was monitored using thermal conductivity detector (TCD) of a gas chromatograph.

X-ray photo electron 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.

The X-ray absorptions (XAS) experiments were performed at the Nb K edge (18.986 KeV) at the BM23 beam line at the European Synchrotron Radiation Facility (ESRF, Grenoble). Monochromatic X-ray beam was obtained from the white beam by using Si(1 1 1) double crystal; a harmonic rejection has been performed using Si coated mirrors. Both the incident (I_0) and transmitted (I_1) monochromatic beam intensities were measured by using ionic chambers filled with 0.65 bar Ar and 2.1 bar Ar, respectively, and eventually I_0 filled up to 2 bar with He. The photon energy was calibrated with the edge energy obtained from the maxima first derivative of the Nb K-edge in the Nb foil (18.986 KeV). The reference samples (Nb foil, NbO₂) were measured in transmission mode. Nb₂O₅ is according to <http://ixs.iit.edu/database> For the TPANb₁, Nb_{0.6}TPA and 25% TPA/Nb₂O₅ samples measurements were done in fluorescence mode with a 13-element Ge detector (Canberra Industries). The extraction of the

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