



Niobium oxide and phosphoric acid impregnated silica–titania as oxidative-acidic bifunctional catalyst



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ABSTRACT

Silica–titania modified by impregnation of niobium oxide and phosphoric acid (P/Nb/Ti–Si) possesses both oxidative active site and Brønsted acid. Results of the catalytic evaluation in consecutive transformation of 1-octene to 1,2-octanediol through formation of 1,2-epoxyoctane suggested that Nb₂O₅ was a more important oxidative active site compared to tetrahedral Ti species. Besides, co-existence of Nb₂O₅ and PO₄³⁻ modifiers was crucial for Brønsted acidity formation. However, the amount of Brønsted acid created was strongly dependent on the synthesis method that was greatly influenced by the interfacial interaction between Nb₂O₅ and PO₄³⁻ in the material to produce Nb–O–PO₄³⁻–H⁺ bonding. It has been demonstrated that the P/Nb/Ti–Si was an excellent oxidative-acidic bifunctional catalyst to produce 1,2-octanediol.

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1. Introduction

Since the last decade, development of catalysts consisting two different active sites has attracted attention of researchers. These catalysts, so-called bifunctional catalyst, are applicable for a consecutive reaction, for example, formation of diol from alkene through transformation of epoxy. In fact, diols are important feedstocks in fine chemical industry and also the main intermediates in the manufacture of pharmaceutical, fragrance and pesticide [1,2]. In industry, however, diols are currently produced via a two-step process involving of epoxidation of an olefin with presence of oxidative catalyst, followed by hydrolysis of the resulting epoxides using another catalyst possessing Brønsted acidity. The manufacture process is not only time consuming, but also costly due to involvement of two different reactions in two separate reactors. Therefore, design of an effective bifunctional catalyst is highly desired for a speedy and cheaper production.

In our previous study, it had been demonstrated that vanadium-phosphate impregnated silica–titania aerogel was a promising bifunctional oxidative and acidic catalyst [3]. Both tetrahedrally coordinated Ti species and V acted as oxidative sites in the catalyst. Besides, we had also proved that the interaction between V and PO₄³⁻ was essential for Brønsted acidity formation, contributing to high yield of diol. Similarly, phosphate treatment on

MCM-41 increased amount of Brønsted acid site in the material [4]. However, no any oxidative site was available in the MCM-41 materials. It is widely accepted that a support is important to provide high surface area for more effective reaction and well dispersion of TiO₂ as catalyst. Nevertheless, the usage of PO₄³⁻ tended to collapse the pores and subsequently destroyed the mesoporous structure of the support including the SiO₂ aerogel, resulting in low surface area in the synthesized catalysts [3]. Since the production of SiO₂ aerogel is considerably complicated and costly, replacement of alternative low cost SiO₂ support which is able to provide high surface area for good distribution of TiO₂ as well as its modifiers in the bifunctional catalyst design is desired.

Due to high acidic properties of Nb₂O₅, there is an increasing interest for its utilization in heterogeneous catalysis [5–8]. Its catalytic behavior in various reactions was summarized by Ziolek [9], Tanabe and Okazaki [10]. In fact, the catalytic activity of Nb₂O₅ was greatly affected by its form. The highly distorted surface of NbO₆ octahedral contributed to generation of Lewis acidity; while the slightly distorted NbO₆, NbO₇ and NbO₈ groups associated with Brønsted acidity creation [11]. It was reported that more Lewis acidity which is the important active site for many chemical reactions was formed when Nb₂O₅ was supported on various oxides [12,13]. Interestingly, Brønsted acid sites were only found in Al₂O₃ or SiO₂ supported Nb₂O₅ [14]. It was claimed that the existence of Nb compound in Nb impregnated TS-1 catalyst promoted generation of Brønsted acidity, leading to sufficient production of diol [15].

Owing to the similar chemical properties of V and Nb in group 5, it is definitely worthy to explore role of Nb as oxidative site in epoxidation reaction as well as its contact with phosphate group

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in Brønsted acidity formation. It was documented that niobium phosphate possessed higher acidic strength than niobic acid [16]. Therefore, in this work, an attempt was made to synthesize Nb₂O₅ and phosphoric acid impregnated TiO₂–SiO₂. The bifunctional catalytic activity of the materials was evaluated in consecutive transformation of 1-octene to 1,2-octanediol through formation of 1,2-epoxyoctane using aqueous H₂O₂. Since it is impossible to produce diols directly from alkenes by involving only one type of active site, the existence of both oxidative and Brønsted acid in the material could be easily confirmed with formation of 1,2-octanediol from 1-octene in the catalyzed reaction. The role of each element in creating oxidative and acidic active sites in the material was discussed.

2. Experimental

2.1. Synthesis of bifunctional catalysts

Synthesis of TiO₂–SiO₂ was carried out via sol gel method as described elsewhere [17]. A mixture of tetraethylorthosilicate (TEOS, Aldrich, 99.8%), ethanol (EtOH), H₂O and HNO₃ (mol ratio = 1: 1: 4: 0.6) was stirred at room temperature for 30 min. Later, a yellowish mixture of titanium(IV) isopropoxide (TTIP, Aldrich, 97%), EtOH and acetylacetone (mol ratio = 1: 100: 0.5) was added into the previously prepared solution and stirred for 30 min at room temperature, followed by drying at 353 K for 1 h until clear gel was obtained. The wet gel was then dried at 383 K overnight and calcined at 773 K for 5 h to yield TiO₂–SiO₂ powder.

Nb₂O₅ was loaded onto TiO₂–SiO₂ via wet impregnation method. In this work, 1 wt% of Nb was prepared by dissolving sufficient amount of niobium(V) ethoxide Nb(OC₂H₅)₅ (Aldrich, 99.95%) in 10 mL of *n*-hexane. The process was continued with stirring process at room temperature for 1 h, followed by drying at 383 K for overnight. The resulted solid material was ground and calcined at 773 K for 5 h. Finally, the material was treated using 0.2 M H₃PO₄ via impregnation method following the same procedure as used for Nb₂O₅ loading. The material was denoted as P/Nb/Ti–Si.

For comparison purpose, different preparation methods were applied in synthesis of other materials. In order to create dissimilar interaction among the elements, TiO₂ was impregnated onto fume silica (SiO₂) which was prepared via sol–gel method by using TEOS as SiO₂ source [18]. In brief, the mixture of TEOS, EtOH, H₂O and HNO₃ was heated and stirred at 351 K to obtain white sol through hydrolysis. Later, H₂O was added drop wise into the mixture until gelation process occurred at 373 K. Finally, the wet gel was dried at 393 K, followed by grinding and calcination at 773 K for 5 h to produce the amorphous SiO₂ powder. Impregnation of TiO₂ onto the prepared SiO₂ powder was carried out by adding 1.8 g SiO₂ into TTIP containing 1-propanol solution. The mixture was stirred vigorously at room temperature for 1 h before drying overnight at 383 K. The dry powder TiO₂/SiO₂ was obtained after calcination at 773 K for 5 h. Later, Nb₂O₅ and phosphoric acid were loaded separately onto via TiO₂/SiO₂ wet impregnation method. The resulted material was labeled as P/Nb/Ti/Si. Another material of P/(Nb + Ti)/Si was prepared by adding precursors of both Nb and Ti simultaneously onto SiO₂ via impregnation method, followed by phosphoric acid treatment.

2.2. Characterizations

Powder X-ray diffraction (XRD) was used to examine crystalline phase of the catalysts. The XRD analysis was carried out using a Bruker Advance D8 using Siemens 5000 diffractometer with the Cu K_α ($\lambda = 1.5405 \text{ \AA}$) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. The spectra were scanned in the range 2θ range

between 2° and 60° at a step 0.030° and step time 1 s. Diffused reflectance UV spectra were collected in order to identify the Ti and Nb species formed in the samples. The analysis was done under ambient condition using a Perkin Elmer Lambda 900 DRUV/VIS spectrometer over range from 190 to 800 nm.

All the samples were characterized by means of BET N₂ adsorption using Micromeritics ASAP2010 surface area analyzer to determine the surface area of samples. The analyzer was calibrated using Al₂O₃ as the standard material prior to analysis. On the other hand, infrared measurements were performed on a Perkin Elmer Spectrum One FT-IR spectrometer, with a spectral resolution of 2 cm⁻¹, scan time of 10 s using the KBr pellet technique. The framework spectra were recorded in the region of 400–4000 cm⁻¹. The type of acidity created in synthesized samples was determined via FTIR technique using pyridine as a probe molecule. In the measurement of FTIR spectra, a self-supported wafer was placed in an in situ stainless steel IR cell with CaF₂ windows. Prior to the analysis, the samples were heated at 573 K in vacuum conditions for 1 h to get rid of the possible moisture and organic impurities on the surface of the samples. After that, 10 torr of pyridine was adsorbed on activated samples at 423 K for 15 min, followed by outgassing at 573 K. The IR spectra of the samples were taken at room temperature in the hydroxyl region of 3000–4000 cm⁻¹ and pyridine vibration region at 1400–1600 cm⁻¹ using Perkin-Elmer Spectrum GX FT-IR Spectrometer.

2.3. Catalytic testing

The bifunctional catalytic performance of the prepared materials was evaluated through the consecutive reaction of formation of 1,2-octanediol through transformation of 1,2-epoxyoctane from 1-octene. The reaction mixture consisting of 15 mmol of 1-octene (Aldrich, 98%), 30 mmol of H₂O₂ in H₂O (Qrec, 30%) in 10 mL acetonitrile (Merck, 99.8%) as solvent and 250 μ L of cyclooctane (Fluka, 99%) as an internal standard was placed in a round bottom flask equipped with a magnetic stirrer and condenser. Later, 0.05 g catalyst was added into the solution. The reaction was carried out in oil bath at 343 K for 24 h under stirring condition. The products of the reaction were analyzed on a HP Agilent 6890 N gas chromatograph using Ultra-1 column.

3. Results and discussion

3.1. Physical properties

The samples of P/Nb/Ti/Si, P/(Nb + Ti)/Si and P/Nb/Ti–Si were light and fluffy powder even after calcination at 773 K for 5 h. XRD patterns indicated amorphous structure in the P/(Nb + Ti)/Si and P/Nb/Ti–Si. This implied the introduced elements were well distributed on the surface of SiO₂ or TiO₂ was incorporated into the SiO₂ framework in both of these samples. Alternatively, the presence of small amount of PO₄³⁻ and Nb₂O₅ in the samples was beyond the detection limit of the XRD instrument used. On the other hand, an identified peak of TiO₂ oxide at $2\theta = 25.3^\circ$ was observed in P/Nb/Ti/Si. Apparently, the addition of solely TiO₂ onto SiO₂ via impregnation method did not facilitate a well dispersion of TiO₂ on the surface on the SiO₂. The results clearly showed that different synthesis methods affected the dispersion of metal on the SiO₂ support.

Fig. 1 shows the UV–vis spectra of the samples. As observed, P/Nb/Ti/Si exhibited a weak shoulder at 210 nm which was attributed to ligand-to-metal charge transfer associated with isolated Ti⁴⁺ framework sites (between O²⁻ and the central Ti(IV) atoms) in tetrahedral coordination [19] (Fig. 1(a)). The band at 240 was assigned to octahedral Nb species [20]. Meanwhile, the

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