



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



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ARTICLE INFO

Article history:

Received 9 July 2013

Received in revised form

25 November 2013

Accepted 28 November 2013

Available online 5 December 2013

Keywords:

Bifunctional catalyst

Oxidative

Brønsted acidity

Niobium

Phosphoric acid

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 Nb_2O_5 and phosphoric acid impregnated $\text{TiO}_2\text{-SiO}_2$. 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 H_2O_2 . 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 $\text{TiO}_2\text{-SiO}_2$ was carried out via sol gel method as described elsewhere [17]. A mixture of tetraethylorthosilicate (TEOS, Aldrich, 99.8%), ethanol (EtOH), H_2O and HNO_3 (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 $\text{TiO}_2\text{-SiO}_2$ powder.

Nb_2O_5 was loaded onto $\text{TiO}_2\text{-SiO}_2$ via wet impregnation method. In this work, 1 wt% of Nb was prepared by dissolving sufficient amount of niobium(V) ethoxide $\text{Nb}(\text{OC}_2\text{H}_5)_5$ (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 H_3PO_4 via impregnation method following the same procedure as used for Nb_2O_5 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, TiO_2 was impregnated onto fume silica (SiO_2) which was prepared via sol-gel method by using TEOS as SiO_2 source [18]. In brief, the mixture of TEOS, EtOH, H_2O and HNO_3 was heated and stirred at 351 K to obtain white sol through hydrolysis. Later, H_2O 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 SiO_2 powder. Impregnation of TiO_2 onto the prepared SiO_2 powder was carried out by adding 1.8 g SiO_2 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 $\text{TiO}_2/\text{SiO}_2$ was obtained after calcination at 773 K for 5 h. Later, Nb_2O_5 and phosphoric acid were loaded separately onto via $\text{TiO}_2/\text{SiO}_2$ 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 SiO_2 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 $\text{Cu K}\alpha$ ($\lambda = 1.5405 \text{ \AA}$) 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 N_2 adsorption using Micromeritics ASAP2010 surface area analyzer to determine the surface area of samples. The analyzer was calibrated using Al_2O_3 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 $400\text{--}4000 \text{ cm}^{-1}$. 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 CaF_2 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 $3000\text{--}4000 \text{ cm}^{-1}$ and pyridine vibration region at $1400\text{--}1600 \text{ cm}^{-1}$ 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 H_2O_2 in H_2O (Qrec, 30%) in 10 mL acetonitrile (Merck, 99.8%) as solvent and 250 μL 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 SiO_2 or TiO_2 was incorporated into the SiO_2 framework in both of these samples. Alternatively, the presence of small amount of PO_4^{3-} and Nb_2O_5 in the samples was beyond the detection limit of the XRD instrument used. On the other hand, an identified peak of TiO_2 oxide at $2\theta = 25.3^\circ$ was observed in P/Nb/Ti/Si. Apparently, the addition of solely TiO_2 onto SiO_2 via impregnation method did not facilitate a well dispersion of TiO_2 on the surface on the SiO_2 . The results clearly showed that different synthesis methods affected the dispersion of metal on the SiO_2 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 Ti^{4+} framework sites (between O^{2-} 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

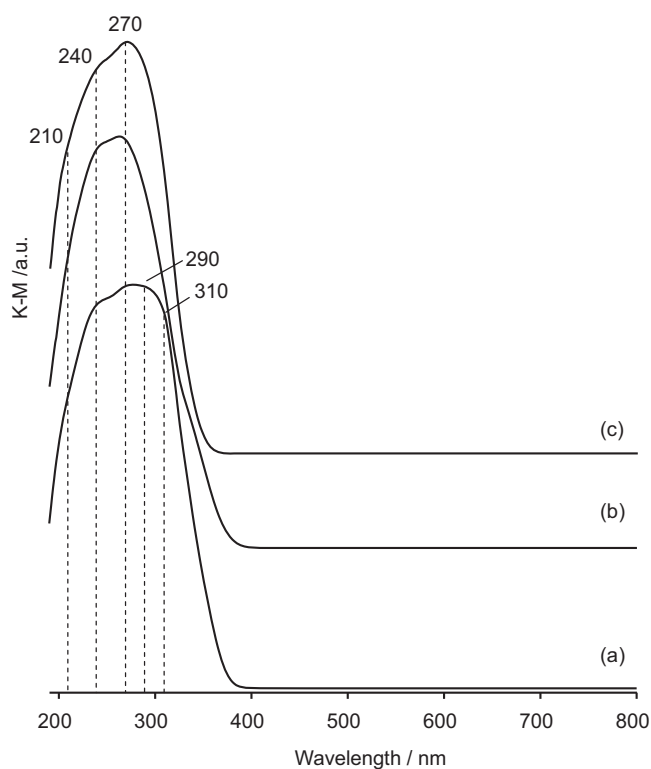


Fig. 1. UV-vis spectra of (a) P/Nb/Ti-Si, (b) P/(Nb+Ti)/Si and (c) P/Nb/Ti-Si.

detected broad band ranged 270–320 nm was due to presence of tetrahedral Ti, octahedral or polymeric Ti and Nb^{5+} species in the sample. In fact, the band at 270 nm was associated with tetrahedral Ti species that is widely recognized as the most important Ti species to provide active site for oxidation reaction. This electronic transition was assigned to a charge transfer of tetrahedral Ti sites between O^{2-} and the central Ti(IV) atom. Meanwhile, the creation of octahedral or polymeric Ti observed at around 290 nm could be due to the transformation of some tetrahedral Ti framework to octahedral structure during the attachment of SiO_2 . The band at 310 nm was an indicative of charge transfer transitions O^{2-} to Nb^{5+} , which was associated to the energy gap between O 2p-valence band and Nb 4d-conductance band [19]. As can be seen in Fig. 1(b), only octahedral Nb and tetrahedrally coordinated Ti were found in P/(Nb+Ti)/Si.

The spectrum of P/Nb/Ti-Si exhibits two bands at around 240 and 270 nm (Fig. 1(c)). Apparently, the tetrahedral Ti species at 270 nm appeared as the predominant species in this sample. Besides, a weak shoulder at 210 nm corresponding to isolated tetrahedral Ti species was observed. The UV-vis results strongly suggested that synthesis methods gave great impact on the type of Ti and Nb species generated in the samples.

The fumed silica possessing high surface area ($572 \text{ m}^2 \text{ g}^{-1}$) was used as catalyst support. As expected, both surface area and pore volume of the materials decreased remarkably after addition of TiO_2 , Nb_2O_5 and PO_4^{3-} (Table 1). It was reported that the treatment using PO_4^{3-} group would lead to coalescence process during calcinations, bringing to destruction of the SiO_2 structure [21,22]. Among these samples, P/Nb/Ti-Si has the highest surface area of $38 \text{ m}^2 \text{ g}^{-1}$, followed by P/(Nb+Ti)/Si and P/Nb/Ti-Si. It is believed that sol-gel method has contributed to stronger SiO_2 structure by loading of TiO_2 into the SiO_2 matrix which was evidenced by detection of isolated tetrahedrally coordinated Ti species in P/Nb/Ti-Si (see Fig. 1). Unlike impregnation method, the introduced elements are always located on the surface of a solid material [23].

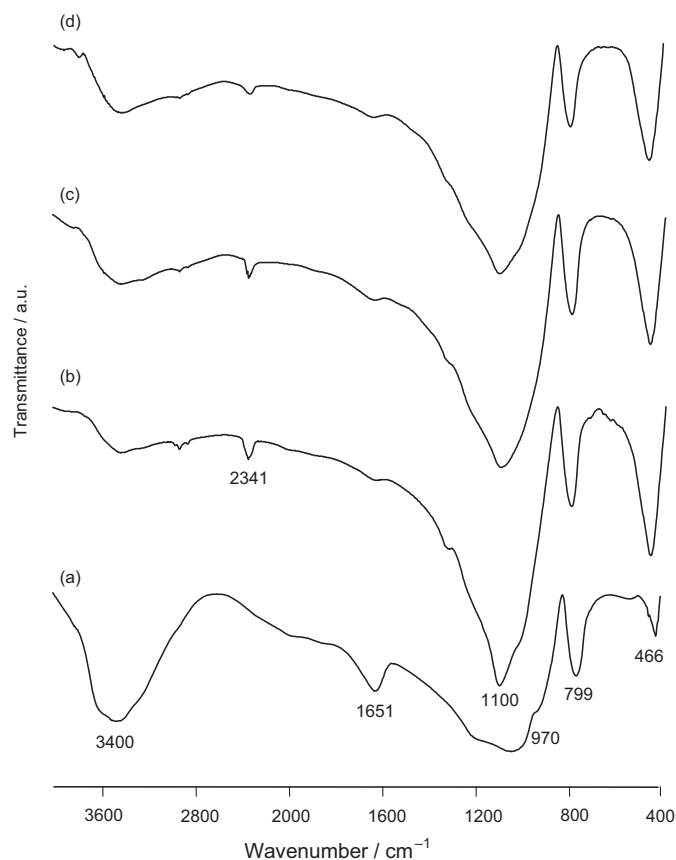


Fig. 2. FTIR spectra of (a) SiO_2 , (b) P/Nb/Ti-Si, (c) P/(Nb+Ti)/Si and (d) P/Nb/Ti-Si.

FTIR spectra of samples show typical silicate absorptions at 466 and 1100 cm^{-1} which were attributed to Si–O–Si bending and stretching vibrations, respectively [24,25] (Fig. 2). The band at 799 cm^{-1} was associated with absorptions of Si–O–Ti or Si–O–Nb bond, which also correspond to tetrahedral Ti and Nb. Meanwhile, the small band at 2341 cm^{-1} was due to presence of Nb. The band at $\sim 970 \text{ cm}^{-1}$ appeared as a weak shoulder in the samples, implying the Si–O–Si bonding decreased dramatically after treatment of phosphoric acid [20]. This observation well agreed with the significant loss in surface area in these samples. In fact, similar finding was reported in sulphated silica–titania aerogel, another oxidative-acidic bifunctional catalyst from our previous work [24]. Besides, a broad band at 3400 cm^{-1} was attributed to the hydroxyl (OH) groups on the amorphous surface [26].

3.2. Acidity

The hydroxyl group and acidity measurement of the samples were monitored via infrared spectroscopy technique. Fig. 3(A) illustrates the infrared spectra of the Nb_2O_5 , PO_4^{3-} and TiO_2 supported on SiO_2 samples after evacuation at 573 K for 1 h under vacuum. Both P/(Nb+Ti)/Si and P/Nb/Ti-Si samples showed a peak at 3740 cm^{-1} in the region of OH group, which was assigned to silanol hydroxyl groups. However, this band was not noticeable in P/Nb/Ti-Si, indicating the introduced PO_4^{3-} groups were located at the sites that previously occupied by silanol groups [13]. The significant decrease of silanol group in this sample was supported with the FTIR results that showed a less intense band of OH group at 3400 cm^{-1} as compared to P/(Nb+Ti)/Si and P/Nb/Ti-Si. Besides, a small peak at 3670 cm^{-1} due to OH stretching mode of free Nb–O–H group was observed only in P/Nb/Ti-Si. Although the

Table 1
The physical and acidity properties of samples.

Sample	Notation	Surface area ($\text{m}^2 \text{g}^{-1}$)	Pore volume ($\text{cm}^3 \text{g}^{-1}$)	Acidity ($\mu\text{mol g}^{-1}$)	
				Lewis	Brønsted
$\text{PO}_4^{3-}/\text{Nb}_2\text{O}_5/\text{TiO}_2/\text{SiO}_2$	P/Nb/Ti/Si	8	0.03	2.3	0.7
$\text{PO}_4^{3-}/(\text{Nb}_2\text{O}_5 + \text{TiO}_2)/\text{SiO}_2$	P/(Nb+Ti)/Si	16	0.05	2.0	1.2
$\text{PO}_4^{3-}/\text{Nb}_2\text{O}_5/\text{TiO}_2-\text{SiO}_2$	P/Nb/Ti-Si	38	0.12	14.6	2.4

P/(Nb+Ti)/Si and P/Nb/Ti/Si contained also Nb, different loading approaches had produced dissimilar Nb species in the samples.

The type and amount of acidity in the samples was monitored by FTIR using pyridine as a probe molecule. Fig. 3(B) shows that the infrared spectra of the samples in the pyridine region after pyridine adsorption and evacuation at 423 K for 15 min. All the spectra show an adsorption peaks at 1445 and 1545 cm^{-1} which are the indication of presence of Lewis and Brønsted acid sites, respectively [27,28]. Meanwhile, the peak at 1490 cm^{-1} is assigned to pyridine associated with both Lewis and Brønsted acid sites [29].

The amount of Lewis and Brønsted acid sites existed in the samples was calculated on the basis of peak area at ca. 1445 and 1545 cm^{-1} , respectively. As shown in Table 1, P/Nb/Ti-Si has the highest amount of Brønsted acid sites, followed by P/(Nb+Ti)/Si and P/Nb/Ti/Si. It is expected that synthesis method used in preparation of P/Nb/Ti-Si has aided the effective interaction between

PO_4^{3-} and Nb_2O_5 as TiO_2 were dominantly in the framework of SiO_2 support, hence contributing to formation of more Brønsted acidity in this sample. Meanwhile, the competition between Nb_2O_5 and Ti to react with PO_4^{3-} in P/(Nb+Ti)/Si and P/Nb/Ti/Si had restricted the Brønsted acid sites generation.

P/Nb/Ti-Si possessed the highest amount of Lewis acid sites (Table 1). It was suggested that Nb species probably reacted with tetrahedral Ti species or directly with Si–O–Si on the SiO_2 , leading to creation of more Lewis acidic sites in this samples. The statement was further supported with UV–vis DRS results (see Fig. 1(c)), which indicated presence of more tetrahedrally coordinated Ti species in the sample.

3.3. Catalytic performance

The catalytic performance of the samples was tested through consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane using aqueous hydrogen peroxide at 343 K for 24 h. As depicted in Fig. 4(a), negligible 1,2-epoxyoctane was detected without presence of any prepared samples in the reactor. Meanwhile, trace of 1,2-epoxyoctane was observed in $\text{TiO}_2-\text{SiO}_2$ catalyzed reactions (Fig. 4(b)), implying Ti species acted as weak oxidative site for the epoxy formation. This sample was inactive in 1,2-octanediol production since it has no Brønsted acidity [29].

After loading of Nb_2O_5 and phosphoric acid, both P/Nb/Ti/Si and P/(Nb+Ti)/Si have remarkably enhanced catalytic activity in oxidation reaction to form 1,2-epoxyoctane (Fig. 4(c) and (d)). Since the tetrahedral Ti^{4+} is widely recognized as the active site for epoxidation, the excellent oxidative catalytic activity of the sample could be closely associated to the existence of Ti^{4+} species as evidenced in UV–vis DRS results. Besides, these samples were also promising acidic catalysts to generate 1,2-octanediol.

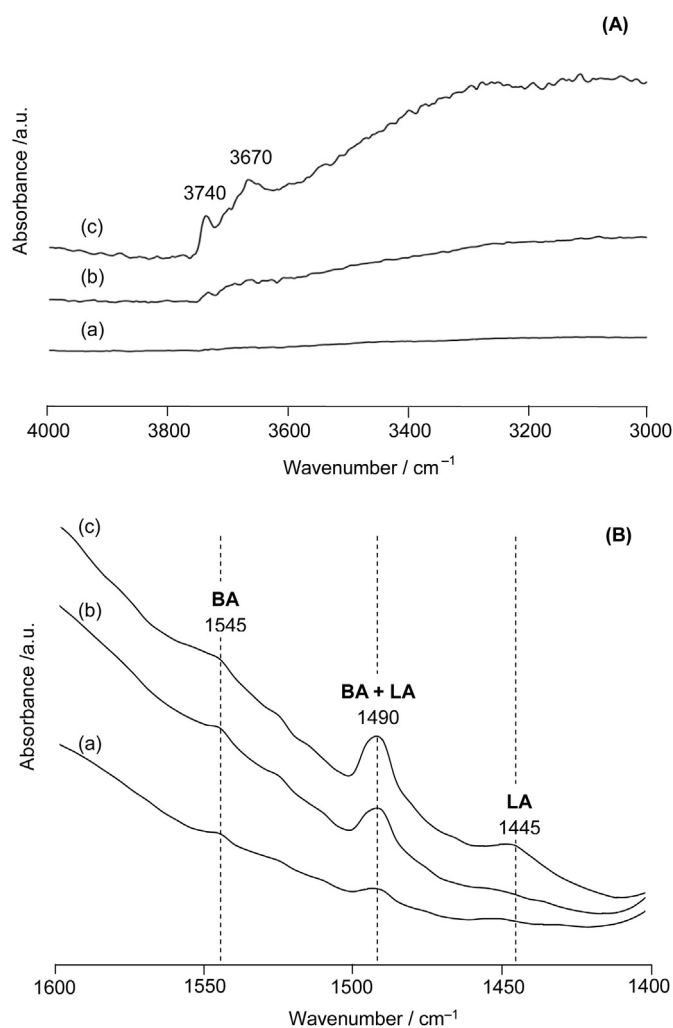


Fig. 3. The FTIR spectra of (a) P/Nb/Ti/Si, (b) P/(Nb+Ti)/Si and (c) P/Nb/Ti-Si (A) after evacuation at 573 K for 1 h, (B) after pyridine adsorption and evacuation at 423 K for 15 min (LA = Lewis acidity, BA = Brønsted acidity).

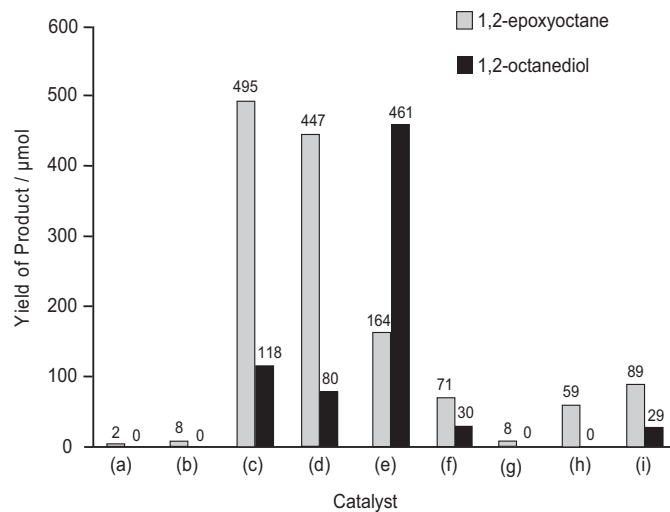


Fig. 4. The product yields of (a) catalyst free, (b) Ti-Si, (c) P/Nb/Ti/Si, (d) P/(Nb+Ti)/Si, (e) P/Nb/Ti-Si, (f) Nb/Ti-Si, (g) P/Ti-Si (h) Nb/Ti-Si and (i) P/Nb/Ti in transformation of 1-octene to 1,2-octanediol through formation of 1,2-epoxyoctane at 343 K for 24 h.

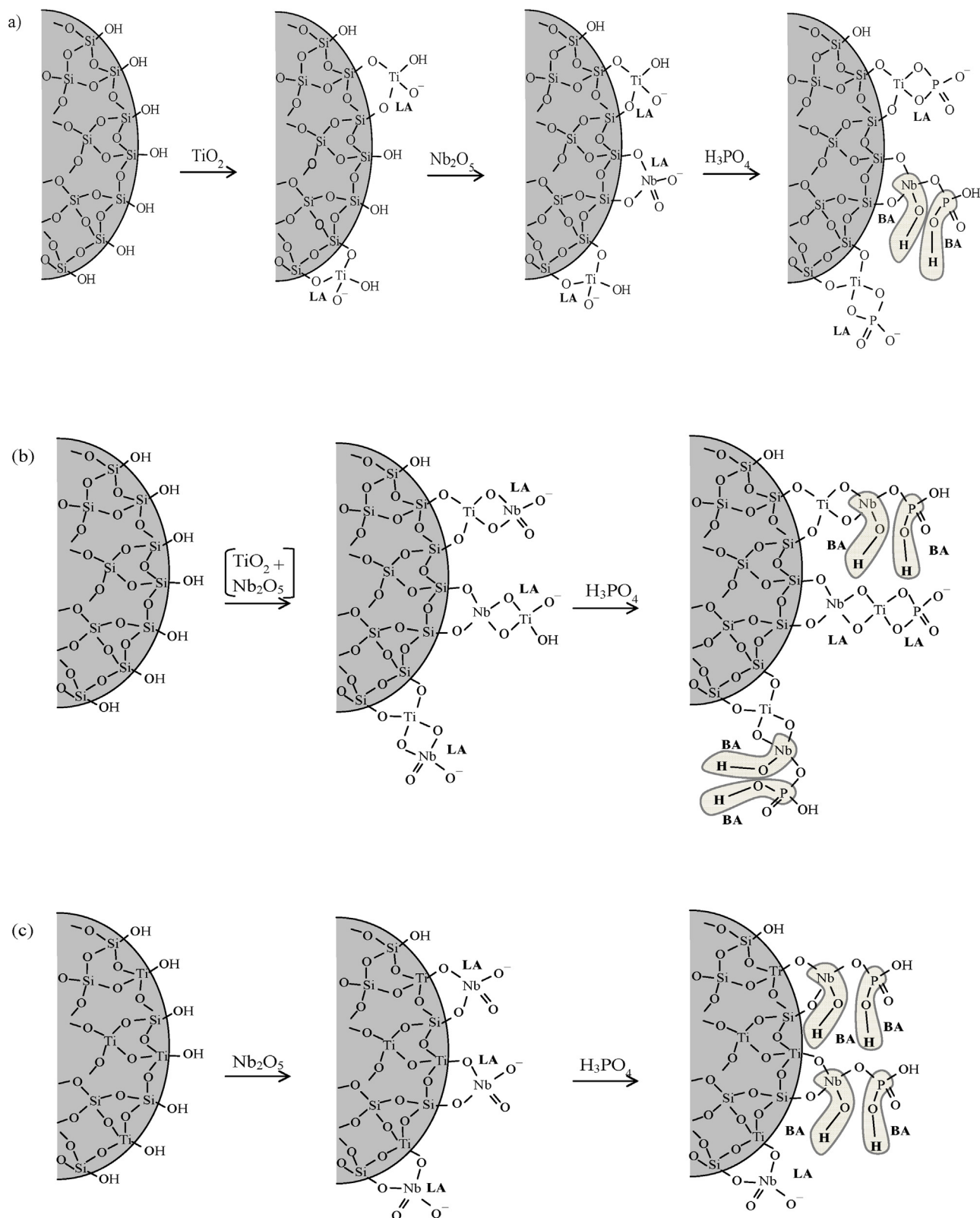


Fig. 5. Proposed model of (a) P/Nb/Ti/Si (b) P/(Nb+Ti)/Si and (c) P/Nb/Ti-Si showing the formation of Lewis acid (LA) and Brønsted acid (BA) sites.

Even though P/Nb/Ti/Si has lesser amount of Brønsted acid sites than that of P/(Nb+Ti)/Si, it produced more 1,2-octanediol. It could be explained by the high yield of 1,2-epoxyoctane using P/Nb/Ti/Si that has assisted formation of 1,2-octanediol in the end of reaction.

P/Nb/Ti-Si was also active in the consecutive reaction (Fig. 4(e)). As compared to P/Nb/Ti/Si and P/(Nb+Ti)/Si, this sample yielded lower amount of 1,2-epoxyoctane but higher amount of 1,2-octanediol. This could be attributed to availability of more Brønsted acid sites for the transformation of diol in the sample. One

should realize that the relatively low yield of 1,2-epoxyoctane using P/Nb/Ti–Si was most probably due to the presence of strong acidic active site in the sample, hence leading to effective conversion of 1,2-epoxyoctane to 1,2-octanediol. Besides, the higher surface area in P/Nb/Ti–Si may have provided more active sites for the reaction, subsequently contributing to its excellent catalytic performance. Obviously, different synthesis procedures have produced samples of varied physical–chemical properties and subsequently resulted in diverse catalytic activities. The proposed structure of Lewis and Brønsted acid sites in the samples is illustrated in Fig. 5.

Since 15 mmol of 1-octene was used in the reaction, the theoretical maximum activity was 15 mmol 1,2-octanediol of yield. This can be achieved only if conversion of 1-octene was 100% and selectivity of the catalyst toward 1,2-octanediol was 100%. In the present work, the conversion of 1-octene by using P/Nb/Ti–Si was 50%. The conversion value could be even lower as some of the 1-octene may have adsorbed onto the SiO₂ supported catalyst. The selectivity of 1,2-epoxyoctane and 1,2-octanediol was approximately 25 and 75%, respectively, with detection of trace of some byproducts. If the presence of byproducts is ignored, the theoretical maximum activity was 5.6 mmol 1,2-octanediol of yield. As evidenced from pyridine adsorption analysis, amount of Brønsted acidity in P/Nb/Ti–Si was 2.4 μmol g⁻¹. Thus, there was only 0.12 μmol Brønsted acidity in 0.05 g of the catalyst used in the reaction. Since the formation of 1,2-octanediol strongly depends on amount of Brønsted acidity available in the catalyst, only 461 μmol 1,2-octanediol was yielded. In fact, the bifunctional catalytic performance of P/Nb/Ti–Si is much better compared to other reported bifunctional catalysts including sulfated titania–silica aerogel [24], phosphate–vanadium impregnated silica–titania aerogel [3] and sulfated zirconia loaded TS-1 [23] in terms of selectivity and yield of 1,2-octanediol.

As it was claimed, TiO₂ supported SiO₂ materials have only Lewis acidity, but no Brønsted acidity [30]. Therefore, it is believed that existence of Nb or PO₄³⁻ or combination of two has facilitated creation of Brønsted acidity in the samples regardless the loading method applied. In order to further study the role of each element in the prepared bifunctional catalysts and to explain the catalytic behavior of these samples, samples without TiO₂, Nb₂O₅, PO₄³⁻ and SiO₂ were synthesized via the preparation procedure similar with that of P/Nb/Ti–Si which was the best bifunctional catalyst in this work. The activity of the samples was evaluated in the same catalytic reaction. As observed in Fig. 4(f), with absence of TiO₂, the sample P/Nb/Si has produced only 71 μmol 1,2-epoxyoctane and 30 μmol 1,2-octanediol. The dramatic drop of more than 56% in epoxy yield suggested that Ti species contributed as oxidative site. The formation of 1,2-octanediol strongly indicated the presence of Brønsted acid sites in the sample since only Brønsted acidity provides the active site for epoxy to diol transformation.

Sample P/Ti–Si was the weakest oxidative catalyst (Fig. 4(g)). Without Nb₂O₅, the sample produced only 8 μmol 1,2-epoxyoctane, with no detection of any 1,2-octanediol after 24 h of reaction. Even though this sample has very low surface area and porosity as compared to that of TiO₂–SiO₂, both materials have similar catalytic activity in transformation of 1-octene to 1,2-epoxyoctane. It may suggest that the surface area and porosity were not important in the epoxidation. As evidenced, the samples P/Nb/Ti–Si and P/Nb/Si yielded 164 μmol and 71 μmol, respectively, 1,2-epoxyoctane. It was documented that the SiO₂ support has aided formation of more isolated Nb which acted as active site in SiO₂ supported Nb₂O₅ catalyst for the oxidation reaction [26,31]. In another study, the authors claimed that the incorporation of Nb into MCM-41 type silica matrix resulted in formation of active and selective catalyst for the oxidation of hydrocarbons [32]. Here, our results strongly implied Nb₂O₅ would be a more important active site for oxidation compared to that of originated from TiO₂. This finding explains why P/Nb/Ti/Si which possesses more Nb⁵⁺

species (see Fig. 1) has the highest oxidative activity. Besides, it was believed that absence of Nb has caused alteration in Ti species formed due to the direct interaction between PO₄³⁻ and TiO₂ in P/Ti–Si, bringing in the poorer oxidative catalytic performance.

A sample without PO₄³⁻ was prepared in order to study its function as catalyst modifier. Surprisingly, the sample Nb/Ti–Si was a weak catalyst in epoxidation reaction as it only produced 59 μmol 1,2-epoxyoctane (Fig. 4(h)). The epoxy yield was even lesser than that of produced using P/Nb/Si, the sample without TiO₂. Apparently, the PO₄³⁻ treatment has promoted the oxidative active site generation or has strengthened the oxidative active sites. Its role in oxidative active site formation will be discussed in detail in our next report. Similar to sample P/Ti–Si, this sample was totally inactive in diol formation. Therefore, we conclude that the co-existence of PO₄³⁻ and Nb₂O₅ is important for Brønsted acidity generation.

Fig. 4(i) shows that the sample P/Nb/Ti produced limited amount of 1,2-epoxyoctane and 1,2-octanediol. Apparently, the absence of SiO₂ support in this sample has caused remarkably decrease in the catalytic activity (16 times lesser in yield) as compared with P/Nb/Ti–Si. Owing to abundant of OH⁻ groups available on its surface, SiO₂ provided space for better dispersion of TiO₂, Nb₂O₅ and PO₄³⁻, bringing to effective interaction among the elements and hence creating more active sites. It was reported previously that usage of SiO₂ support for Nb₂O₅ has facilitated Brønsted acidity generation [14]. In another work, Ziolk et al. [33] claimed that silanol group present in SiO₂ type support was important to form Nb–OH–Si which gave enhanced acidic character to the material.

It is note-worthy that a relatively economical support of SiO₂ was used in this work. Previously, it had been demonstrated that the oxidative–acidic bifunctional catalyst of vanadium–phosphate impregnated silica–titania aerogel yielded only 151 μmol 1,2-epoxyoctane and 275 μmol 1,2-octanediol under the same reaction condition [3]. The better catalytic performance of niobium–phosphate impregnated silica–titania in the current work strongly suggests the usage of fumed silica, a relatively easy prepared SiO₂ matrix as effective catalyst support. Besides, the finding may also indicate that, as compared to V₂O₅, Nb₂O₅ was definitely a better modifier in improving both oxidative and acidic catalytic activities of TiO₂–SiO₂ materials.

4. Conclusions

An excellent oxidative–acidic bifunctional catalyst of P/Nb/Ti–Si was successfully synthesized. This material was a promising catalyst in the consecutive transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane. Both tetrahedrally coordinated Ti and Nb species acted as oxidative sites for the epoxidation. The phosphoric acid treatment has contributed to the enhanced oxidative activity. Meanwhile, the direct interaction between PO₄³⁻ and Nb₂O₅ was important for the Brønsted acidity formation, bringing to the high yield of diol. As evidenced, SiO₂ support played a key role for the improved bifunctional catalytic performance of the material.

Acknowledgments

The authors acknowledge funding from the Ministry of Higher Education (MOHE) and Universiti Teknologi Malaysia for the Research University Grants (Vote no: Q.J.130000.2526.00H08 and Q.J.130000.2526.02H81). The authors are grateful to Prof. Dr. Sugeng Triwahyono from Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia for the pyridine adsorption analysis. J.M.E. is thankful to Universiti Teknologi Malaysia for the UTM Institutional Zamalah Scholarship.

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