

# Preparation and characterization of bifunctional oxidative and acidic catalysts Nb<sub>2</sub>O<sub>5</sub>/TS-1 for synthesis of diols

Didik Prasetyoko<sup>a,\*</sup>, Zainab Ramli<sup>a</sup>, Salasiah Endud<sup>a</sup>, Hadi Nur<sup>b</sup>

<sup>a</sup> Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

<sup>b</sup> Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor, Malaysia

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## Abstract

Bifunctional oxidative and acidic catalyst was prepared by incorporation of titanium ion (Ti<sup>4+</sup>) and niobic acid in zeolite molecular-sieve. The catalysts being active both in oxidation reactions due to the presence of tetrahedral Ti<sup>4+</sup>, and acid-catalyzed reactions due to the presence of niobic acid. Nb/TS-1 was prepared by hydrothermal synthesis of TS-1, calcination in air and subsequent impregnation of niobium into TS-1. The sample was characterized by XRD, FTIR, UV–vis DR, TPR and pyridine adsorption techniques. The XRD analysis of Nb/TS-1 revealed that the MFI structure of the TS-1 support was found to be intact upon incorporation of niobium. The infrared spectra showed that the tetrahedral titanium in the TS-1 is still remained after impregnation with niobium while based on the UV–vis DR result, the niobium species are in the octahedral structure. On the basis TPR and infrared of hydroxyl groups results, it is concluded that niobium species interacted with the silanols on the surface of TS-1. Pyridine adsorption study shows both Brønsted and Lewis acid sites are present in Nb/TS-1. The catalytic results in the transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane by using Nb/TS-1 indicate that the production of epoxide and diol was correlated with the presence of oxidative and Brønsted acidic sites in the catalyst.

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## 1. Introduction

Development of efficient catalysts is a challenge in catalysis research. One of the interesting fields is the creation of two active sites in a single material catalyst, so-called bifunctional catalysts. The catalysts are potentially active for consecutive processes. Bifunctional oxidative and acid catalysts have been prepared by incorporation of trivalent metal ions (Al<sup>3+</sup>, B<sup>3+</sup>, Fe<sup>3+</sup>, Ga<sup>3+</sup>) and titanium ion (Ti<sup>4+</sup>) together in the framework of zeolites [1]. The catalysts being active both in the oxidation and acid-catalyzed reactions [2]. In a previous study, van Bekkum and co-workers [3] have demonstrated that bifunctional Ti–Al-beta zeolites can lead to acid-catalyzed consecutive reactions. The catalysts were active in epoxidation of alkenes to produce epoxide and diol. However, it is difficult to control the number of oxidative site together

with acidic sites due to some competition between titanium and aluminium to become isomorphously substitute in the framework of zeolites. In order to overcome such problem, a new catalyst system has been designed.

This work focuses on the enhancement of the catalytic performance of bifunctional oxidative and acidic catalysts by incorporation of titanium and niobium into zeolite molecular-sieve. Titanium silicalite (TS-1) molecular-sieves have attracted much attention during the last decade because of their interesting catalytic properties in oxidation reactions [2–6]. Niobium has been loaded on the surface of TS-1 to introduce acidity. The surface acid strength of hydrated niobium oxide, namely niobic acid (Nb<sub>2</sub>O<sub>5</sub>·*n*H<sub>2</sub>O) corresponds to the acid strength ( $H_0 \leq -5.6$ ) of 70% sulfuric acid and exhibits high catalytic activity, selectivity and stability for acid-catalyzed reactions [7,8].

In this paper, we reported the preparation and characterization of bifunctional oxidative and acidic catalyst, Nb/TS-1. Silicalite and TS-1 were prepared by direct hydrothermal syn-

\* Corresponding author. Tel.: +60 75534530; fax: +60 75566162.

E-mail address: [dramadhani@yahoo.com](mailto:dramadhani@yahoo.com) (D. Prasetyoko).

thesis method, whereas Ti/silicalite and Nb/TS-1 were prepared by impregnation of titanium in silicalite and niobium in the TS-1, respectively. By impregnation method, the titanium or niobium position was made to be in octahedral structure located as the extra-framework of silicalite or TS-1. The structure and properties of the catalysts were characterized with various techniques, such as X-ray diffraction (XRD), infrared (FTIR) and UV–vis DR spectroscopies, Temperature programmed reduction (TPR) and pyridine adsorption techniques. The catalytic activity of Nb/TS-1 in the epoxidation of 1-octene was significantly improved in comparison with TS-1.

## 2. Experimental

### 2.1. Preparation of samples

TS-1 was prepared according to a procedure described in the literature [4] with slight modification [9], using tetraethyl orthosilicates (Merck, 98%), tetraethyl orthotitanate, TEOT (Merck, 95%) in isopropyl alcohol, tetrapropylammonium hydroxide (Merck, 20% TPAOH in water), and distilled water. The gel was charged into a 150 ml autoclave and heated at 175 °C under static condition. The material was recovered after 4 days by centrifugation and washed with excess distilled water. A white powder was obtained after drying in air at 100 °C overnight. Silicalite was synthesized by using the same procedure without the addition of TEOT. The calcination of sample to remove of the template was carried out in air at 550 °C for 5 h with temperature rate 1° min<sup>-1</sup>. Ti/silicalite (1 wt.%) were prepared by impregnation technique using TEOT as a precursor. About 0.99 g of silicalite was added into the solution of TEOT (0.0502 g) in isopropanol (50 ml) with stirring. The mixture was stirred for 4 h at 80 °C. The solid was recovered by slowly evaporating the alcohol at 80 °C. The solid material was then calcined in air at 550 °C for 5 h. Here, the prepared silicalite and silicalite loaded with titanium oxide are denoted SIL and Ti/SIL, respectively.

Sample Nb/TS-1, TS-1 loaded with niobium oxide, was prepared by impregnation technique using niobium ethoxide Nb(OC<sub>2</sub>H<sub>5</sub>)<sub>5</sub> (Aldrich, 99.95%) precursor. TS-1 was dried in oven at 200 °C for 24 h. After that, the necessary amount of niobium ethoxide was dissolved in *n*-hexane (Aldrich, >99%) to obtain the desired metal loading, and the required quantity of pre-dried of TS-1 was immediately added to the clear solution with stirring. The mixture was stirred at room temperature for 3 h. The solid was recovered by evaporating the *n*-hexane at 80 °C. The acid hydrolysis was performed by addition of 20 ml solution of 0.5 M HNO<sub>3</sub> in distilled water and aged overnight, followed by heating at 120 °C until dryness. The solid was then washed with distilled water for three times and finally dried at 200 °C for 24 h.

For comparison on the presence of Nb species, experiments were carried out to obtain niobium oxide and niobic acid. Niobic acid was prepared by hydrolysis of niobium

Table 1  
Chemical compositions of the samples and preparation method

Sample	Code	Nb/(Nb + TS-1) (wt.%)	Methods
Titanium silicalite	TS-1	0.81 (gel) <sup>a</sup>	Direct synthesis
Silicalite	SIL	–	Direct synthesis
Ti/silicalite	Ti/SIL	1.0 <sup>b</sup>	Impregnation
Nb <sub>2</sub> O <sub>5</sub> · <i>n</i> H <sub>2</sub> O/TS-1	Nb/TS-1	3.4	Impregnation and hydrolysis
Nb <sub>2</sub> O <sub>5</sub>	NBO	100	Calcination
Nb <sub>2</sub> O <sub>5</sub> · <i>n</i> H <sub>2</sub> O	NBA	100	Hydrolysis
TiO <sub>2</sub>	TIO	–	Hydrolysis and calcination

<sup>a</sup> %Ti = Ti/(Ti + Si) in the initial gel.

<sup>b</sup> %Ti = Ti/TS-1, wt.%.

ethoxide using neutral hydrolysis method, followed by calcination at 200 °C. The hydrolyzed niobium ethoxide is denoted NBA. Niobium oxide was also prepared by calcination of ammonium niobium oxalate at 550 °C for 3 h. The prepared particles were labeled NBO.

Titanium oxide was prepared by hydrolysis of titanium(IV) tetraethoxide (TEOT) at room temperature. The white solid was recovered by filtration, washing with water and drying at 100 °C overnight. Finally, the solid was calcined at 550 °C for 5 h. The thus-prepared particles were labeled TIO. Table 1 summarizes the chemical composition of all the above samples and preparation methods.

### 2.2. Characterizations

All molecular-sieves were characterized by powder X-ray diffraction (XRD) for identification of the crystalline phases in the catalysts using a Bruker Avance D8 diffractometer with the Cu K $\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. Typically, powder samples were ground and spread into a sample holder and then analyzed. The pattern was scanned in the  $2\theta$  range of 5–50° at a step 0.020° and step time 1 s. Infrared (IR) spectra of the samples were collected on a Perkin Elmer Fourier Transform Infrared (FTIR) spectrophotometer, with a spectral resolution of 2 cm<sup>-1</sup>, at temperature 20 °C by KBr pellet method. The framework spectra were recorded in the region of 1400–400 cm<sup>-1</sup>. UV–visible diffuse reflectance (UV–vis DR) spectra were recorded at ambient condition on a Perkin Elmer Lambda 900 UV/VIS/NIR spectrometer. Temperature programmed reduction (TPR) experiments were performed using TPDRO 1100 Thermo Quest CE Instrument as follows. The sample (typically about 0.05 g) was pre-treated in nitrogen at a flow rate of 30 cm<sup>3</sup> min<sup>-1</sup> at 200 °C for 1 h and cooled down to 100 °C. The reduction analysis was performed by heating the sample from 100 up to 1000 °C at a rate of 10 °C min<sup>-1</sup> and held for 5 min at 1000 °C with flowing mixture of 5% hydrogen in nitrogen (H<sub>2</sub>/N<sub>2</sub>) at the rate of 40 cm<sup>3</sup> min<sup>-1</sup>. For hydroxyl groups and acidity study, about 10 mg of the sample was pressed at 2–5 tonnes for a minute to obtain a 13 mm disk. The sample was introduced in the

infrared cell with calcium fluoride,  $\text{CaF}_2$  windows. The sample was heated at  $200^\circ\text{C}$  in vacuum condition for 16 h. The infrared spectra were collected at room temperature using Shimadzu 2000 FTIR spectrometer at  $2\text{ cm}^{-1}$  resolutions. The types of acid sites were examined using pyridine as a probe molecule. Pyridine was adsorbed at room temperature for a minute, continued by desorption at  $150^\circ\text{C}$  for an hour. The infrared spectra were monitored at room temperature.

### 2.3. Catalytic test

The catalyst performance was tested in the epoxidation of the 1-octene using hydrogen peroxide as oxidant. The reaction mixture, i.e. 8 mmol of 1-octene (Sigma, 99%), 15 mmol of  $\text{H}_2\text{O}_2$  in  $\text{H}_2\text{O}$  (Scharlau, 35% extra pure) in 10 g acetone (J.T. Baker) as solvent and 0.8 mmol of cyclooctane (Fluka, >99%) as an internal standard were placed in a  $25\text{ cm}^3$  round bottom flask equipped with a magnetic stirrer and condenser. An amount 0.05 g catalyst was then added in the solution. The reaction was carried out in oil bath with stirring at  $70^\circ\text{C}$ . The aliquots were sampled at regular time intervals. The products of the reaction were analyzed with an HP 6890N GC using Ultra-1 column and HP GC-MSD using HP5 column.

## 3. Results and discussion

### 3.1. Solid characterizations

Fig. 1 shows the XRD patterns of the samples tabulated in Table 1. The XRD pattern of TIO sample indicated that the structure of  $\text{TiO}_2$  was rutile. There is no diffraction line was observed on the XRD pattern from sample NBA prepared by hydrolysis of niobium pentoxide, suggesting that niobic acid is fully amorphous. On the other hand, sample NBO, niobium oxide prepared by calcination of ammonium niobium oxalate at  $550^\circ\text{C}$  shows splitting of the diffraction line around  $2\theta = 29^\circ$ , indicating that the sample is crystalline niobium oxide phase ( $T\text{-Nb}_2\text{O}_3$ ) with orthorhombic structure [10].

The XRD patterns of TS-1, SIL, Ti/SIL and Nb/TS-1 samples revealed that the sample contained framework structures of the MFI type zeolite [11]. For sample Nb/TS-1, the structure of TS-1 is not strongly affected by the presence of impregnated niobium. The XRD patterns show that no diffraction line assigned for crystalline phase of the niobium oxide present. This indicated that niobium was well dispersed on the TS-1. This also suggested that the niobium is present in the form of amorphous niobium oxide hydrate, since it was prepared by hydrolysis of niobium ethoxide and not calcined at temperature higher than  $400^\circ\text{C}$ . In addition, the peak intensity of TS-1 is drastically decreased up to 60% after impregnation of 3.4 wt.% of niobium on the TS-1. It is suggested that niobium is either located on the surface of TS-1 or covering the surface of TS-1. Since the estimated molecular size of  $\text{Nb}(\text{OEt})_5$  (ca. 1.1 nm), the source of Nb sites, is larger than

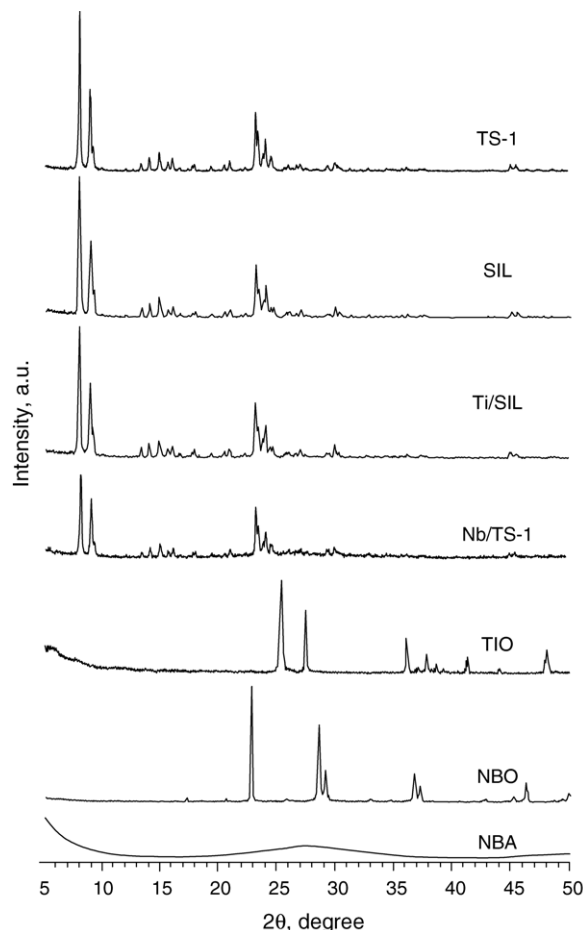


Fig. 1. XRD pattern of the samples.

the size pore-entrance of TS-1 (ca. 0.6 nm), they should be attached to the external surface of TS-1.

The infrared spectra of the samples in the lattice vibration region between  $1400$  and  $400\text{ cm}^{-1}$  are depicted in Fig. 2. Sample NBA shows a major strong band centered at  $586\text{ cm}^{-1}$  and a shoulder band at  $933\text{ cm}^{-1}$ . This spectrum is consistent with the skeletal vibration previously reported for amorphous niobic acid [12]. The spectrum of crystalline phase of niobium oxide (sample NBO) exhibits two strong bands at  $615$  and  $850\text{ cm}^{-1}$ . The broad band at higher frequency ca.  $>850\text{ cm}^{-1}$  is associated with the stretching mode of terminal  $\text{Nb}=\text{O}$  bonds (niobyl species), while the band around  $600\text{ cm}^{-1}$  can be assigned to the stretching of longer bridging  $\text{Nb}-\text{O}-\text{Nb}$  bonds. Samples TS-1, SIL, Ti/SIL and Nb/TS-1 showed similar bands. According to Flanigen [13], the absorption bands at around  $1100$ ,  $800$  and  $450\text{ cm}^{-1}$  were three lattice modes associated with internal linkages in tetrahedral  $\text{SiO}_4$  (or  $\text{AlO}_4$ ) and are insensitive to structure changes. The absorption bands at about  $1225$  and  $547\text{ cm}^{-1}$  are characteristic of MFI-type zeolite associated with the particular structural assembly of the tetrahedral and are sensitive to structure changes.

It is already known that the infrared spectrum of titanium silicalite, TS-1 is characterized by an absorption band at

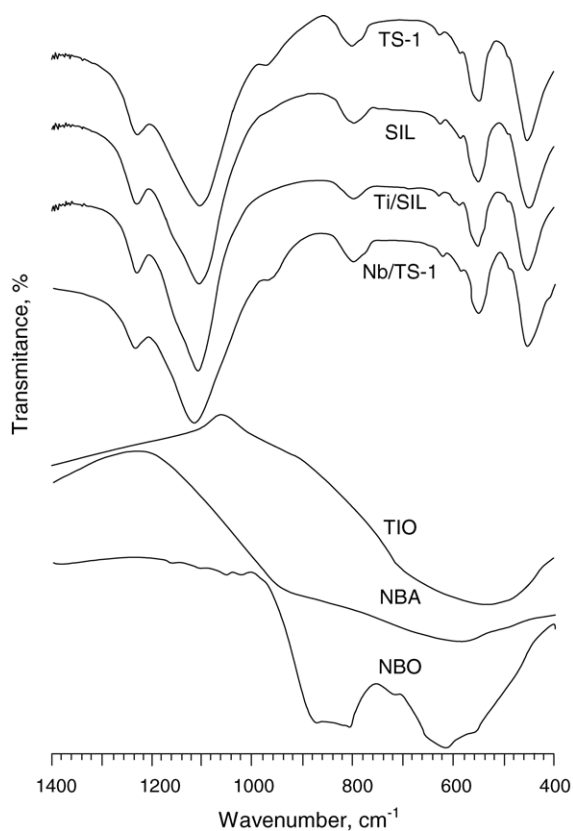


Fig. 2. FTIR spectra of the samples.

around  $960\text{ cm}^{-1}$  [6,14–16]. However, the vibrational modes at around this frequency may be the result of several contributions i.e. the asymmetric stretching modes of Si–O–Ti linkages [14–16], terminal Si–O stretching of SiOH–(HO)Ti “defective sites” and titanyl [Ti=O] vibrations. Our TS-1 sample shows a weak band at  $977\text{ cm}^{-1}$ . This band can be attributed to the titanium in the framework, since silicalite (SIL sample; contains only silica without addition of any titanium) does not show any band at around this frequency. Furthermore, sample Ti/SIL (titanium oxide loaded silicalite, 1 wt.% of Ti) also does not show the band around  $960\text{ cm}^{-1}$ . It is concluded that the TS-1 sample contains Si–O–Ti connections. No additional bands appeared after impregnation of titanium in the SIL sample.

A small band at around  $970\text{ cm}^{-1}$  assigned to the titanium ions in the tetrahedral structure is still present after impregnation of niobium (sample Nb/TS-1). No additional band after impregnation of niobium into the TS-1 can be observed. This finding shows that impregnation of niobium has not effected the MFI structure of TS-1 significantly. Infrared spectroscopy technique also cannot detect the presence of niobic acid in the sample Nb/TS-1, due to low vibration intensity of pure niobic acid itself as compared to TS-1.

The nature and coordination of metal oxide or metal in substituted molecular-sieves can be characterized by UV–vis DR spectroscopy technique. Fig. 3 shows the UV–vis spectra of the samples. The UV–vis spectrum of NBA sample ex-

hibits a maximum band around 295 nm and a shoulder band around 243 nm. This main band (295 nm) attributed to the charge transfer transitions  $\text{O}^{2-}$  to  $\text{Nb}^{5+}$ , which can be associated to the energy gap between the O 2p-valence band and the Nb 4d-conductance band [12]. For TIO sample, the main band at around 340 nm and a strong band at 240 nm are observed, both assigned to the octahedral Ti (Oh). Silicalite (MFI sample) shows two bands at around 213 and 240 nm with very low intensity (0.05) (spectrum was magnified four times). These bands are not assigned to the coordination of titanium or niobium with oxygen due to their low intensity and the sample contains silicon only without any addition of titanium or niobium. For the TS-1 sample, only a single strong band at 215 nm was observed. This band is attributed to ligand-to-metal charge transfer associated with isolated  $\text{Ti}^{4+}$  framework sites (between  $\text{O}^{2-}$  and the central Ti(IV) atoms) in tetrahedral coordination, Td. The band characteristic of octahedral extra-framework titanium was not observed, while Ti/SIL sample shows a broad band at 240 nm attributed to extra-framework titanium oxide suggesting that impregnation of titanium only produce some extra-framework titanium species. Impregnation of niobium on the TS-1 (sample Nb/TS-1) shows a strong band at about 240 nm assigned to octahedral niobium species. Meanwhile, the band characteristic for tetrahedral titanium at about 215 nm cannot be observed due to the overlapping of this band with the band of niobium oxide that has remarkably higher intensity.

Fig. 4 shows the TPR profiles of the samples. Sample NBA prepared by hydrolysis of niobium ethoxide then calcined at  $200\text{ }^\circ\text{C}$  exhibited three regions of hydrogen consumption, i.e. a negative peak at around  $550\text{ }^\circ\text{C}$  and positive peaks at around  $875\text{ }^\circ\text{C}$  and at a higher temperature above  $1000\text{ }^\circ\text{C}$ . The negative peak can be attributed to CO or  $\text{CO}_2$  formation due to carbon residue from the niobium ethoxide that is not

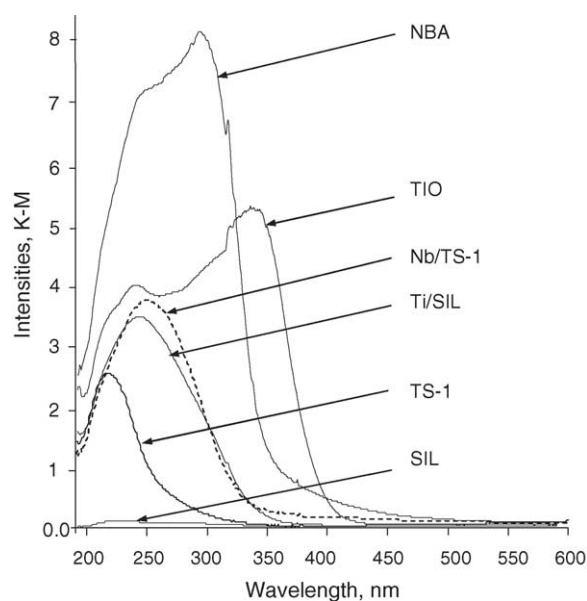


Fig. 3. UV-diffuse reflectance spectra of the samples.

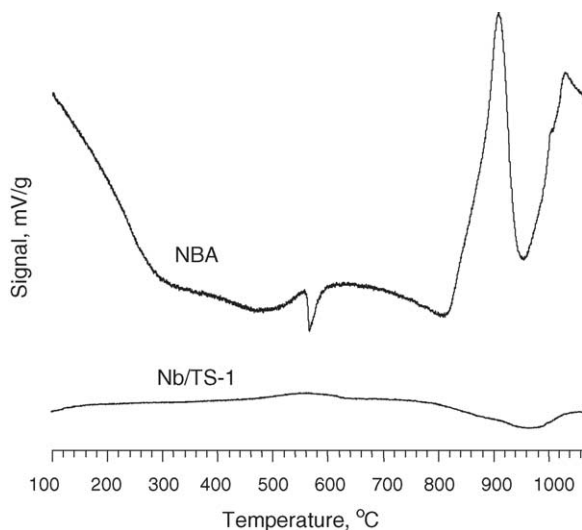


Fig. 4. TPR profiles of the samples.

fully hydrolyzed. The first positive peak was attributed to the reduction of  $\text{Nb}^{5+}$  to  $\text{Nb}^{4+}$  in the form of  $\text{Nb}_2\text{O}_5$  to  $\text{NbO}_2$  [8,17], while for reduction of  $\text{NbO}_2$  to lower oxidation state of niobium,  $\text{NbO}$  needed higher reduction temperature.

Sample Nb/TS-1 does not show any significant peak in this reduction temperature range, although the sample contains niobium. This finding is explained to be due to several factors. Low amount of niobium loading results in high dispersion of niobium on the surface of TS-1 that cause high interaction between niobium and TS-1. Pereira et al. [17] found that high dispersions promote intimate contact between the niobium and the silica surface, Nb–O–Si bonding in relation to Nb–O–Nb bonding prevailing. It also can be explained based on the electronegativity concept that the presence of silicon in the coordination sphere of niobium should increase the electronic density niobium. Thus the reduction of niobium from  $\text{Nb}^{5+}$  to  $\text{Nb}^{4+}$  was more difficult to occur. Recently, Mendes et al. [18] found that 20 wt.% of niobium supported on  $\text{Al}_2\text{O}_3$  did not show any hydrogen uptake as indication of the interaction of niobium with  $\text{Al}_2\text{O}_3$ .

The hydroxyl groups and acidity of the samples were monitored by infrared technique. The wafer sample was put in the glass cell and evacuated at  $200^\circ\text{C}$  for 16 h under vacuum. The infrared spectra were recorded at room temperature. Fig. 5 shows the infrared spectra of the samples TS-1, NBA, NBO and Nb/TS-1 after evacuation at  $200^\circ\text{C}$ . TS-1 shows a sharp peak at around  $3743\text{ cm}^{-1}$  characteristic of hydroxyl silanol groups. Niobic acid (sample NBA) shows a small peak at around  $3700\text{ cm}^{-1}$  and a broad peak centered at around  $3400\text{ cm}^{-1}$  that can be assigned to hydroxyl stretching mode of free Nb–O–H groups and hydroxyl with hydrogen bonding, respectively [12]. On the other hand, crystalline niobium oxide does not show any peak in the region of hydroxyl groups indicating that crystalline niobium oxide does not contain any hydroxyl groups. A different finding

was reported recently by Braga et al. [19] for niobium oxide calcined at  $800^\circ\text{C}$ .

The peak at  $3743\text{ cm}^{-1}$  disappeared as niobium was loaded on the TS-1. A small peak at  $3733\text{ cm}^{-1}$  and broad peak centered at around  $3530\text{ cm}^{-1}$  were observed in Nb/TS-1 sample. Meanwhile, a mechanical mixture of 20% NBA in TS-1 only shows a peak similar to that of TS-1 at around  $3744\text{ cm}^{-1}$  assigned for silanol hydroxyl groups. Although this mixture contains 20 wt.% of NBA, however, no peak at around  $3700\text{ cm}^{-1}$  assigned for Nb–O–H can be observed. It suggests that the amount of hydroxyl groups of Nb–OH in the sample NBA is much lower than the amount of silanol groups of TS-1. For samples Nb/TS-1, a drastic decrease of silanol species present on the surface of TS-1 indicates that there is strong interaction between niobium and TS-1 (niobium bonded with –O–Si, replaced hydrogen atom of silanol species in the TS-1). Since niobic acid does not show any peak in this region, the result clearly suggests that niobium species covered of the surface of TS-1. Therefore, deposition of niobium oxide species on TS-1 consumes surface Si–OH groups of TS-1, as consequently the silanol groups decreased.

The types of acid sites in the samples were monitored by pyridine adsorption. Pyridine was adsorbed at room temperature after evacuation of the sample at  $200^\circ\text{C}$  for 16 h in vacuum. The infrared spectra were collected after evacuation at  $150^\circ\text{C}$  for an hour. Fig. 6 shows the infrared spectra of the samples in the pyridine region. Sample NBO does not show any peak which indicates that crystalline niobium oxide has no acidity. Sample NBA shows the peaks at 1636, 1609, 1575, 1540, 1489 and  $1448\text{ cm}^{-1}$ . The peaks at around  $1540$  and  $1448\text{ cm}^{-1}$  are due to Brønsted and Lewis acid sites,

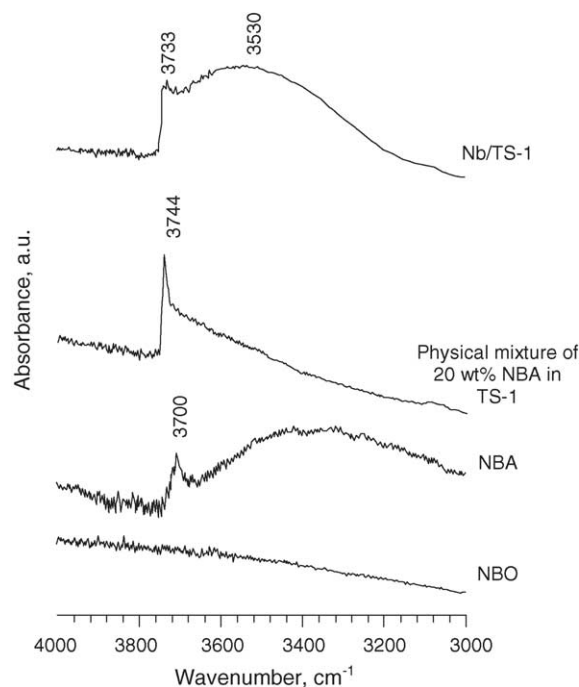


Fig. 5. FTIR spectra of the samples in the hydroxyls region, after evacuation under vacuum at  $200^\circ\text{C}$  for 16 h.

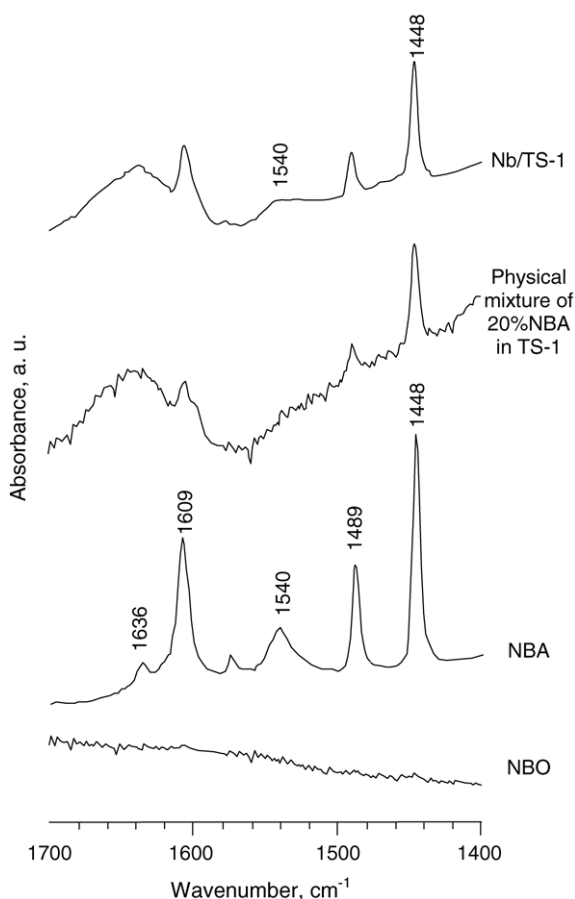


Fig. 6. FTIR spectra of the samples after evacuation under vacuum at 200 °C for 16 h followed by pyridine adsorption at room temperature and evacuation at 150 °C for an hour, in the pyridine regions.

respectively. Similar finding has been reported by Morais et al. [20] for niobic acid. Niobium oxide containing TS-1 (sample Nb/TS-1) show the peaks similar to that of sample NBA. However, the intensity of the characteristic peaks for Brønsted and Lewis acid sites at around 1540 and 1448  $\text{cm}^{-1}$  is lower than that of sample NBA. Jehng and Wachs [21] have reported the evidence of both Brønsted and Lewis acid sites in niobium oxide supported on silica, while Mendes et al. [18] only found Lewis acid sites in the silica supported niobic acid. On the contrary, in this study, a mechanical mixture of niobic acid and TS-1 only shows the peaks at around 1608, 1489 and 1447  $\text{cm}^{-1}$ , which are similar to those of sample TS-1.

### 3.2. Catalytic activity

The bifunctional catalyst Nb/TS-1 was tested in the epoxidation of 1-octene with aqueous  $\text{H}_2\text{O}_2$  in acetone at 70 °C. Samples NBO and NBA showed no noticeable activity toward the formation of 1,2-epoxyoctane, consequently, there is no 1,2-octanediol observed from these reactions. TS-1 shows their activity toward the formation of 1,2-octanediol. However, Nb/TS-1 showed remarkable higher activity (four times

higher in yield and selectivity for 1,2-octanediol) compared to TS-1. It suggested that TS-1 and Nb/TS-1 catalysts in this study contain Brønsted acid sites, since it is well known that the formation of 1,2-octanediol is catalyzed by Brønsted acid sites. However, from the pyridine adsorption studies, only Brønsted acid sites were observed on Nb/TS-1. It is suggested that the Brønsted acid sites might not have originated from the TS-1 catalyst itself, but rather formed during the reaction in the presence of water from the reaction mixtures. Meanwhile, the higher yield observed on Nb/TS-1 is due to the higher amount of Brønsted acid sites, which is responsible in this reaction. In addition, the induction time of the formation of 1,2-epoxyoctane in TS-1 and Nb/TS-1 is observed after reaction for 24 and 3 h, respectively, indicating the higher reactivity of Nb/TS-1 catalyst. The titanium and niobium concentrations of the used Nb/TS-1 catalyst was determined by infrared and UV–vis DR spectroscopies. It is found that no leaching of titanium and niobium has been observed as analyzed by infrared and UV–vis DR spectroscopies, respectively.

## 4. Conclusion

Bifunctional oxidative and acidic catalysts was successfully synthesized by impregnation of niobic acid on the surface of TS-1 (Nb/TS-1). It is demonstrated that the tetrahedral titanium species and niobic acid act as oxidative and acidic active sites, respectively. The catalytic results in the transformation of 1-octene to 1,2-octanediol through the formation of 1,2-epoxyoctane by using Nb/TS-1 indicate that the production of epoxide and diol was correlated with the presence of oxidative and Brønsted acidic sites in the catalyst.

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