

Physical Properties and Bifunctional Catalytic Performance of Phosphate–Vanadium Impregnated Silica–Titania Aerogel

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Abstract The excellent catalytic performance of phosphate–vanadium impregnated silica–titania aerogel as a bifunctional oxidative and acidic catalyst was evaluated in consecutive transformation of 1-octene to 1,2-octanediol through formation of 1,2-epoxyoctane using aqueous H_2O_2 . Phosphate group and vanadium were impregnated onto silica–titania aerogel via wet impregnation method at room temperature, followed by a high calcination temperature. Significant increase of hydrated, tetrahedrally coordinated Ti species was found in phosphate–vanadium impregnated silica–titania sample. Pyridine adsorption study revealed that the combination of phosphate group and vanadium is essential for generation of Brønsted acidic sites. Phosphate–vanadium impregnated silica–titania catalyst produced 1,2-octanediol (275 μmol) with selectivity of 65%. In contrast, no noticeable diol was produced when silica–titania aerogel and phosphate treated silica–titania sample were used.

Keywords Bifunctional catalyst · Silica–titania aerogel · Vanadium · Phosphate · Brønsted acidity

1 Introduction

Development of bifunctional catalysts has attracted much attraction in catalyst research as they are potentially active for consecutive processes. Recently, the bifunctional oxidative and acid catalysts have been prepared by incorporation of Ti^{4+} and sulfated zirconia or niobic acid together in zeolites molecular sieve [1, 2]. However, the production of diols was low, indicating insufficient acidity in the catalysts. Besides, the considerably small pore size in zeolites of $\sim 3\text{--}8 \text{ \AA}$, including titanium silicalite (TS-1), has limited the transformation of diols from epoxides.

Due to their large surface areas and higher porosity, mesoporous materials such as MCM-41 and aerogels have potential applications as catalysts for processing large molecules [3, 4]. Generation of Brønsted acid sites in mesoporous materials were observed in sulfated Al-MCM41 and phosphate-impregnated MCM-41 [5, 6]. However, no any oxidative site was detected on MCM-41 based materials. Similarly, silica aerogel is totally inactive towards epoxidation since no oxidation site formed in this material. Silica–titania aerogel, however, is an excellent catalyst for epoxidation due to the highly distribution of Ti^{4+} species in the catalysts [7]. Unfortunately, they do not possess Brønsted acidity, but only Lewis acidity [8].

Both weak Lewis and Brønsted acid sites were created through 6–27 wt% vanadium deposition on silica, titania and silica–titania aerogels [9]. Besides, the interlayer doping of vanadium oxide on hydrotalcite-type materials facilitated the formation of both Brønsted and Lewis sites [10]. In contrast, the presence of vanadium in Y-zeolite appeared to neutralize the acid sites in this material, resulted in a decrease of Brønsted acid sites [11]. In our previous work [12], the generation of Brønsted acidity in sulfated silica titania aerogel which acted as bifunctional

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catalyst in diol production was reported. In the present work, we demonstrated the significant increase of Brønsted acidity formation through incorporation of both phosphate group and vanadium onto surface of silica–titania aerogel. The physical properties and catalytic performance of the synthesized materials were discussed.

2 Experimental

2.1 Catalyst Preparation

Silica–titania aerogel (ST, molar ratio of Si:Ti = 33:1) was prepared via method as described at elsewhere [12]. Phosphated silica–titania aerogel (PO₄/ST) was prepared by adding 2 g of silica–titania aerogel (ST) into 25 mL of 0.2 M phosphoric acid. Meanwhile, impregnation of 1 wt% of vanadium onto silica–titania aerogel (V/ST) was carried out by dissolving the necessary amount of vanadyl sulfate hydrate (VOSO₄ · H₂O, Fluka) in 25 mL H₂O. In order to study the synergy effect of vanadium and phosphate, V_PO₄/ST was prepared as follows: dissolved 1 wt% of vanadium in 25 mL of 0.2 M phosphoric acid, then added 2 g of silica–titania aerogel into the solution. All the mixtures were stirred vigorously at room temperature for 2 h before drying at 100 °C for 2 days. The dry gel powder was ground and calcined at 500 °C for 7 h.

2.2 Characterizations of Powder Catalysts

The surface area and pore volume of samples was determined by means of BET N₂ adsorption using Qsurf surface area analyzer. The analyzer was calibrated using Al₂O₃ as the standard material prior to analysis. The powder X-ray diffraction (XRD) analysis was carried out for crystallinity of the samples, using a Bruker Advance D8 using Siemens 5000 diffractometer with the Cu K_α (λ = 1.5405 Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. XRD analysis was carried out at a step of 0.02 and step time 1 s over 2θ range of 2°–50°. Diffused reflectance UV spectra were collected under ambient conditions using a Perkin Elmer Lambda 900 DRUV/VIS/NIR spectrometer over the range from 190 to 800 nm. For acidity evaluation, 14 mg sample was pressed into a 13 mm disk and placed in the infrared cell with CaF₂ windows and heated at 300 °C in vacuum for 3 h. The infrared spectra were recorded at room temperature using Perkin Elmer Spectrum One FT-IR spectrometer with 2 cm⁻¹ resolution. The acid sites were examined quantitatively using pyridine as a probe molecule with a tolerance of ±5%. Pyridine was absorbed at room temperature for a minute, continued by desorption at 150 °C for an hour.

2.3 Catalytic Testing

The catalyst performance of the samples was tested in epoxidation of 1-octene using aqueous H₂O₂ (30%) as oxidant. The reaction mixture containing 1-octene (5 mmol), H₂O₂ (8 mmol), acetonitrile (10 mL) as solvent and 100 μL of cyclohexanon as the internal standard was put in a round bottom flask equipped with a condenser. The catalyst (0.050 g) was then added to the solution. The reaction was carried out in an oil bath under stirring at 70 °C for 24 h. The products of the reaction were analyzed using a GC and GC-MS. Three set of experiments were carried out for each catalyst.

3 Results and Discussion

3.1 Physical Properties

Silica–titania aerogel (ST) was semi-transparent and light fluffy powder even after the 500 °C calcination step in air. PO₄/ST was in white even after the 500 °C calcination step in air. However, the changing of colour was observed in the vanadium impregnated samples: V/ST changed from white to yellow; while V_PO₄/ST appeared in pale green after calcination. It is believed that, during this step vanadium in the samples has changed toward a higher oxidation state [13].

1 wt% of vanadium and/or 0.2 M of phosphoric acid were impregnated onto silica aerogel and silica–titania aerogel. It has been suggested that most possibly the vanadium was loaded on the surface of the aerogels instead of loading into the framework of aerogel when an impregnation method was applied [2]. Table 1 shows that a slight decrease of 7% in surface area of ST after introduction of vanadium (V/ST). As for PO₄/ST and V_PO₄/ST, the drastic decrease of ~90% in both surface area and pore volume strongly suggests the presence of phosphate group in a sample tends to a complete destruction of the aerogel mesostructure.

XRD results showed ST and those phosphate and/or vanadium impregnated samples are in amorphous form (Fig. 1). No peaks corresponding to either Ti or V were observed on the diffractograms, indicating that Ti and V

Table 1 Surface area and pore volume of ST and phosphate and/or vanadium impregnated samples

Sample	Surface area (m ² /g) ± 5%	Pore volume (cm ³ /g) ± 5%
ST	550	0.98
V/ST	511	0.97
PO ₄ /ST	44	0.11
V_PO ₄ /ST	39	0.11

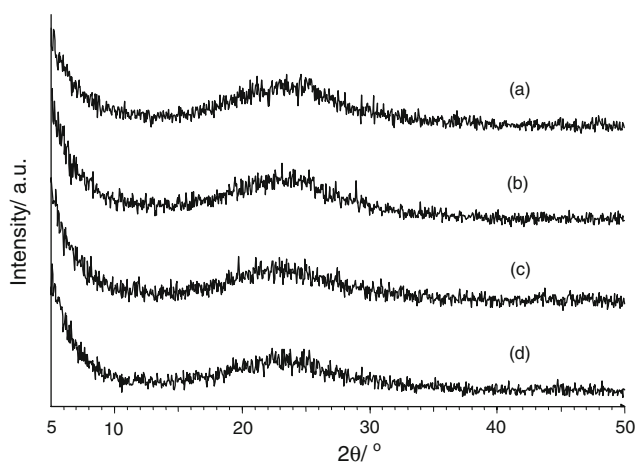


Fig. 1 XRD diffractograms of **a** ST; **b** V/ST; **c** PO₄/ST; and **d** V-PO₄/ST

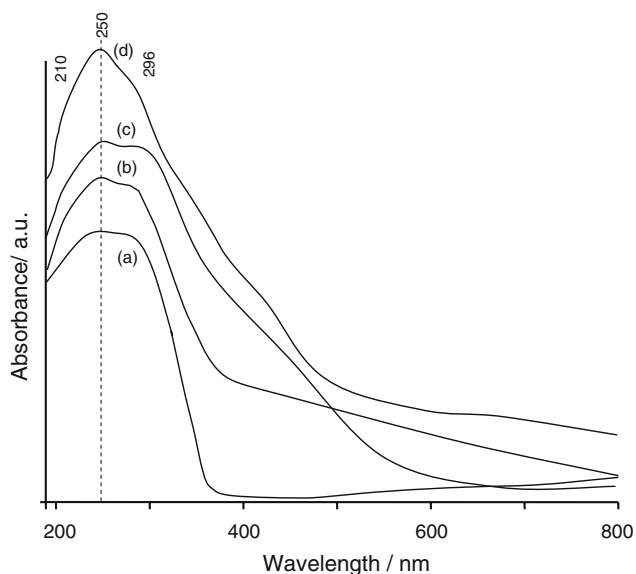


Fig. 2 UV-Vis diffuse reflectance spectra of **a** ST; **b** V/ST; **c** PO₄/ST; and **d** V-PO₄/ST

were highly dispersed on the surface of silica aerogel, or were incorporated into silica framework. It also suggested that Ti presents neither in anatase nor rutile form. Alternatively, the broad and featureless X-ray diffractograms could be attributed to the low content of Ti and V in the samples.

Figure 2 shows the DRUV-Vis spectra of samples. Generally, three absorption bands at 210, 250 and 296 nm associated to Ti species are observed in silica-titania and modified samples. The weak absorption band at 210 nm is attributed to isolated, tetrahedral Ti species. This electronic transition is assigned to a $O^{2-} \rightarrow Ti^{4+}$ charge transfer transition of tetrahedral Ti species. Meanwhile, the band at 296 nm is assigned to either octahedrally coordinated or polymeric Ti species. Obviously, some of the framework

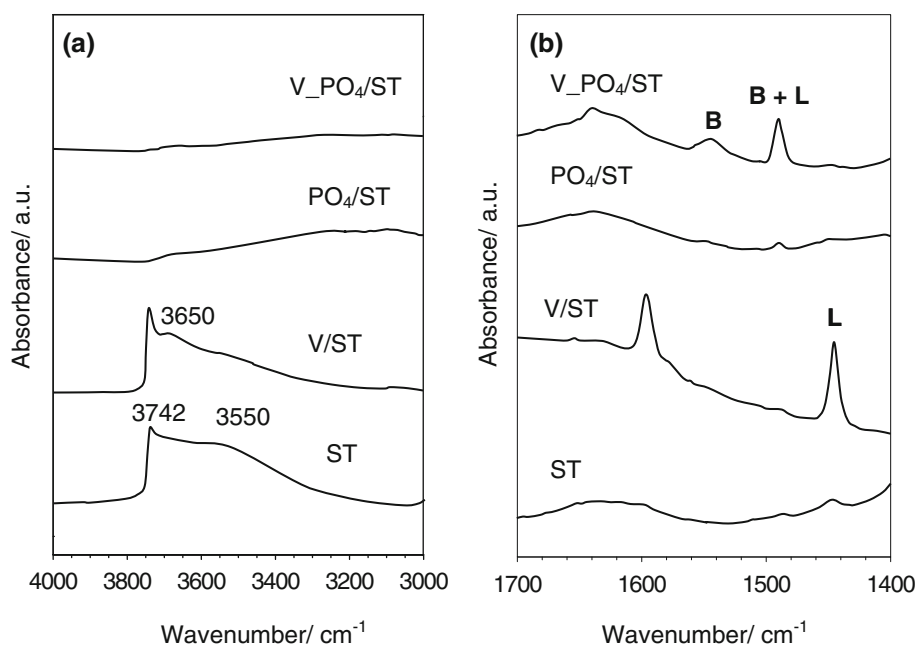
tetrahedral Ti were transformed to extraframework octahedral Ti structure during vanadium or phosphate loading onto ST. Similar transformation has been reported sulfated TS-1 [8]. However, a more intense band at 250 nm is observed on V-PO₄/ST; associated with hydrated tetrahedral Ti species. The finding strongly suggests that V-PO₄/ST is more hydrophilic and treatment with both vanadium and phosphoric acid facilitates the hydration of Ti. In other words, it is apparent that there is a significant increase in the amount of hydrated tetrahedral titanium species on the surface of the aerogel upon co-existence of vanadium and phosphate group. Apparently the Ti species in V-PO₄/ST are linked to a continuous chain of tetrahedrally coordinated silicate polymer, even though the morphology of aerogel is amorphous in the long range. The existence of vanadium species is evidenced by the existence of a broad shoulder above 360 nm.

3.2 Acidity

Figure 3 shows the FTIR spectra of the ST and phosphate and/or vanadium impregnated samples after evaluation at 150 °C for 1 h after pyridine adsorption. In the region of hydroxyl group (Fig. 3a), the peak at 3,742 cm^{-1} , which is assigned as silanol hydroxyl groups, can be clearly observed for ST and V/ST. However, this band was diminished in those phosphate-impregnated samples, implying that the phosphate groups are located in the space/sites previously occupied by silanols groups after the destruction of aerogel structure. It is also possible that phosphate groups reacted with Si-OH groups and hence led to enhancement of Brønsted acidity sites. Besides, a broad peak centered at 3,550 cm^{-1} that observed in ST and V/ST could be assigned to hydroxyl with hydrogen bonding.

Figure 3b illustrates that the infrared spectra of the samples in the pyridine region. The spectrum of ST shows two weak adsorption bands at 1,597 and 1,446 cm^{-1} which are corresponded to pyridine interacting with Lewis acid sites. This finding coincides with previous study that Brønsted acidity does not exist in such sample [8]. On the other hand, it was reported that unsupported vanadia possesses both Lewis and Brønsted acidity [14]. A decrease in Lewis acidity and an increase in Brønsted acidity were observed when vanadia was supported on a metal oxide support [15]. The decrease of Lewis acidity was related to the coordination of VO_x species on the metal oxide support [16]. In this study, however, two intense adsorption bands 1,600 and 1,446 cm^{-1} corresponded to pyridine interaction with Lewis acid sites were observed in V/ST. The significant increment of Lewis acidity when vanadium is supported on silica-titania aerogel (V/ST) strongly implies the interaction between Si and V favoured the generation of Lewis acid sites only. There was no noticeable Brønsted

Fig. 3 The FTIR spectra of ST and phosphate–vanadium impregnated samples after pyridine adsorption and evacuation at 150 °C for 1 h in **a** hydroxyl region, **b** pyridine region (L = Lewis acidity, B = Brønsted acidity)



acid site detected in V/ST. This finding contradicts to Reicher et al. [9] who reported the presence of both Brønsted acid and Lewis acid sites in vanadium grafted silica–titania aerogel. The discrepancy could be attributed to the low concentration of vanadium (only 1 wt%) used in this study or possibly caused by the different sources and incorporation method used in catalyst synthesis.

Evidently, the amount of acid sites calculated from pyridine adsorption data in Table 2 indicates that loading of phosphate onto ST tends to devastate the Lewis acid sites. Besides, no significant change was found after addition of phosphate group onto ST. Nevertheless, additional peaks at 1,641 and 1,547 cm^{-1} which are attributed to adsorbed pyridine bound associated to Brønsted acid sites were observed in the spectrum of V_PO₄/ST. This phenomenon could be explained by differences in the local environment of vanadium sites with and without the presence of phosphate groups on the surface of aerogel. Since there was no Brønsted acid site formed in ST, V/ST, and PO₄/ST samples, we strongly propose that the combination of phosphate–vanadium is essential to generate Brønsted acid sites in silica–titania aerogel.

Table 2 Amount of acid sites calculated from pyridine-FTIR data of ST and phosphate and/or vanadium impregnated samples at 150 °C

Catalyst	Lewis acid (μmol pyridine g^{-1})	Brønsted acid (μmol pyridine g^{-1})
ST	9.7	0
V/ST	16.6	0
PO ₄ /ST	0	0.7
V_PO ₄ /ST	0	8.2

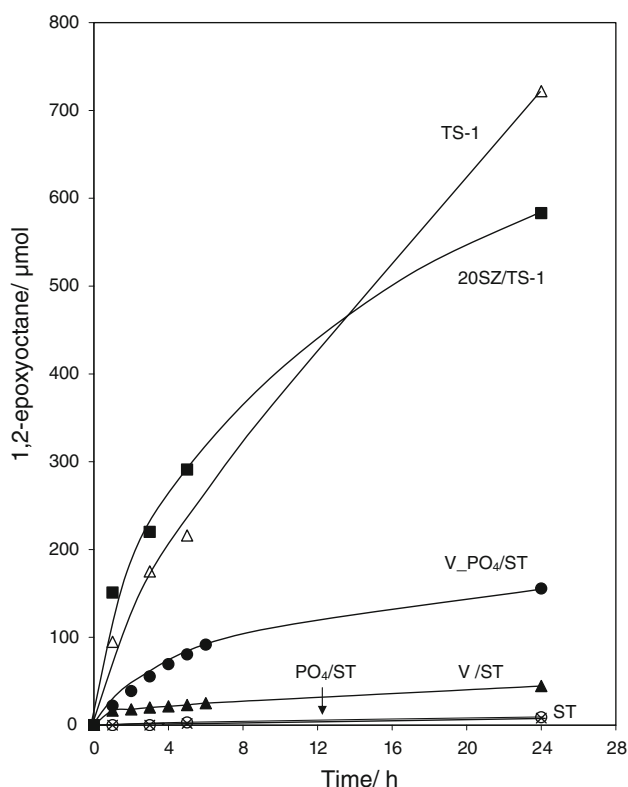
3.3 Catalytic Activity

The catalytic properties these phosphate and/or vanadium impregnated samples were studied in the catalytic epoxidation of 1-octene at 70 °C. Results showed that, among these samples, V_PO₄/ST was the best catalyst for epoxidation, followed by V/ST, PO₄/ST and ST. As evidenced, the existence of more hydrated, isolated Ti tetrahedrally coordinated species in V_PO₄/ST (Fig. 2) which acts as oxidative site in epoxidation reaction was responsible for the high production of 1,2-epoxyoctane with 1-octene conversion of 86% (Table 3). Besides, it is believed that V impregnated onto silica aerogel, V⁵⁺ = O at surface might perform as oxidative site in the reaction [17]. This argument is supported by the fact that the catalytic activity in epoxidation reaction of catalysts containing vanadium (V_PO₄/ST and V/ST) is higher than that of vanadium free catalysts (PO₄/ST and ST), suggesting that the vanadium plays a role as oxidative site (see Fig. 4 and Table 3). The alternative possibility is the oxidative strength of Ti was enhanced significantly after addition of phosphate and vanadium. In absence of phosphate group, a weaker oxidative site of Si–O–Ti–O–V was formed in V/ST. On the other hand, ST and PO₄/ST were inactive toward epoxidation, indicating impregnation of phosphate group alone onto ST had devastated the Ti species as oxidative site in the material. Only 22 and 18% of 1-octene were converted using ST and PO₄/ST catalysts, respectively, after 24 h of the reaction.

The catalytic performance of titanium silicalite (TS-1) and 20 wt% sulfated zirconia loaded TS-1(20SZ/TS-1) is included for comparison [2]. The results revealed that the

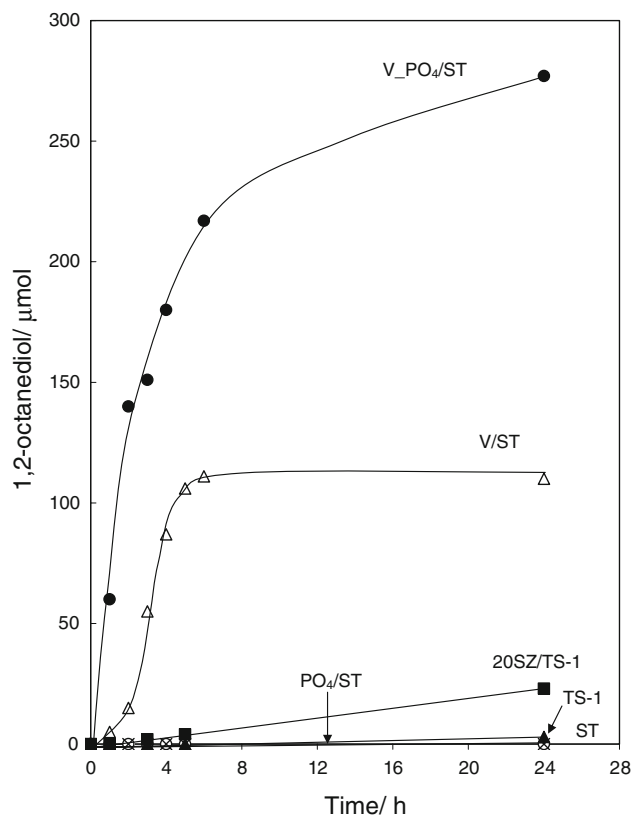
Table 3 Catalytic performance of samples on transformation of 1-octene to 1,2-octanediol through formation of 1,2-epoxyoctane at 70 °C for 24 h

Catalyst	Conversion of 1-octene (%)	Yield of products (μmol)		Selectivity of products (%)	
		1,2-epoxyoctane	1,2-octanediol	1,2-epoxyoctane	1,2-octanediol
ST	22 ± 1.7	8 ± 1.5	0	100	0
V/ST	74 ± 3.2	45 ± 4.7	110 ± 6.3	29	71
PO_4/ST	18 ± 1.8	9 ± 1.2	0	100	0
$\text{V_PO}_4/\text{ST}$	86 ± 3.8	151 ± 8.6	275 ± 11.8	36	65

**Fig. 4** The yield of 1,2-epoxyoctane on the epoxidation of 1-octene using ST and phosphate and/or vanadium impregnated samples with H_2O_2 as oxidant

catalytic activity of TS-1 and 20SZ/TS-1 in producing 1,2-epoxyoctane is much better (4–5 times higher in yield) than those phosphate–vanadium impregnated samples (Fig. 4). Their outstanding catalytic performance was associated with isolated Ti tetrahedrally coordinated species that highly distributed in the framework of these materials [2]. One should realize that the lesser yield of epoxides observed in $\text{V_PO}_4/\text{ST}$ and V/ST as compared to TS-1 and 20SZ/TS-1 could be explained by the fact that more epoxides have been transformed to diols by using these catalysts.

Figure 5 shows the yield of 1,2-octanediol on the epoxidation of 1-octene. Among these catalysts, $\text{V_PO}_4/\text{ST}$ has

**Fig. 5** The yield of 1,2-octanediol on the epoxidation of 1-octene using ST and phosphate and/or vanadium impregnated samples with H_2O_2 as oxidant

contributed to the highest yield of 1,2-octanediol with selectivity of 65%. It is widely accepted that the formation of diols from epoxides is catalyzed by Brønsted acidic sites. Although no Brønsted acid sites were found in the pyridine adsorption studies on V/ST , trace of 1,2-octanediol was observed in the reaction. The production of diol suggests that the Brønsted acid sites might have formed during the reaction in the presence of water from the reaction mixtures. Apparently, high amount of tetrahedrally Ti and Brønsted acidity are essential for an excellent bifunctional catalyst in epoxidation reaction of 1-octene, rather than high surface area and pore volume.

Meanwhile, 20SZ/TS-1 is a weaker catalyst in the consecutive transformation to form diols due to its relatively small pore size and insufficient amount of Brønsted acidic sites. Besides, it may also suggest that the acid strength generated from phosphate–vanadium is much higher than that of sulfated zirconia in 20SZ/TS-1. As expected, TS-1, ST and PO₄/ST showed no noticeable activity toward the formation of 1,2-octanediol since these materials do not possess Brønsted acidity site. Moreover, negligible amount of epoxides produced has definitely restricted the formation of diol.

4 Conclusion

Bifunctional oxidative and acidic catalysts have been successfully synthesized by impregnation of vanadium and phosphoric acid on the surface of silica–titania aerogel. The catalysts were evaluated in consecutive transformation of 1-octene to 1,2-octanediol through formation of 1,2-epoxyoctane using aqueous H₂O₂. Titanium tetrahedrally coordinated and vanadium in phosphate–vanadium impregnated silica–titania acted as oxidative sites in the catalyst. It has also been demonstrated that the interaction between vanadium and phosphate is important for generation of Brønsted acidic sites, bringing to high yield of diol.

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