Properties and Bifunctional Catalytic Activity of Niobium-Doped Silica-Titania: Effect of Phosphoric Acid Treatment

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Abstract
The effect of phosphoric acid treatment on the physical-chemical properties and catalytic activity of the niobium-doped silica-titania bifunctional catalyst was investigated. As part of the synthesis procedure to produce $x\text{PO}_4^-$/Nb/TiO$_2$-SiO$_2$, different concentrations of phosphoric acid ($H_3\text{PO}_4$) were used ($x=0, 0.05, 0.10, 0.15, 0.20, 0.25 \text{ M}$). As shown by XRD analysis, the samples synthesized using 0–0.20 M $H_3\text{PO}_4$ were in amorphous form, as featureless diffractograms were obtained, indicating the $\text{PO}_4^-$ groups were dispersed homogeneously on the surface of Nb doped SiO$_2$-TiO$_2$. Due to the increased concentration of acid, other compounds were formed in the samples by reactions between $\text{PO}_4^-$ and Nb and/or Ti. Additionally, UV-Vis DRS results indicated that the presence of the $\text{PO}_4^-$ group accelerated the transformation of hydrated tetrahedral Ti species into isolated tetrahedral Ti species. An experimental investigation of the catalytic performance of the catalyst was conducted using 1,2-epoxyoctane as an oxidant for the epoxidation of 1-octene to 1,2-octanediol. It has been demonstrated that $H_3\text{PO}_4$ treatment was essential for oxidative and acidity active site formation. The current research findings strongly suggested that Nb-doped TiO$_2$-SiO$_2$ treated with 0.2 M $H_3\text{PO}_4$ was the most effective bifunctional catalyst in generating 1,2-octanediol.

Keywords
Phosphoric Acid, Oxidative, Brønsted Acid, Titania, Niobium, Silica

1. INTRODUCTION
A diol is a valuable feedstock in the fine chemical industry and a key intermediate in the synthesis of fragrances, pesticides, and pharmaceuticals (Alphy et al., 2021). In the present process, diols are formed via two steps, first by oxidizing alkene to epoxy and then by reacting epoxy with an acidic catalyst to yield diol. Consequently, it has resulted in a labor-intensive, time-consuming, and inefficient process as two reactors are needed. It is therefore highly desirable to develop bifunctional catalysts which contain two different active sites in one material.

The acidic catalysts have been widely used in many kinds of chemical reactions (Mulyatun et al., 2021; Munyentwali et al., 2022). Anionic metal oxides containing sulphates, tungstates, and phosphates, which exhibit a high affinity for acid-catalyzed reactions, have recently received attention in heterogeneous catalysis (Sosa et al., 2022; Lim and Lee, 2016; Lee et al., 2015). Solid acids, also important heterogeneous catalysts, can be utilized in many applications such as hydrocarbon cracking, alkane isomerization, and valorization of biomass. The catalytic activity of the solid acids is greatly influenced by the nature of acid sites due to the presence of Brønsted and Lewis acidity (Ekhsan et al., 2014). It was claimed that the co-existence of Brønsted and Lewis acid sites has improved the acidity of the solid catalysts.

For the last two decades, titanium dioxide or titania (TiO$_2$) and TiO$_2$-based heterogeneous catalysts have been intensively investigated for diol production (Wada et al., 2017; Lee and Hamdan, 2008). In fact, these materials have been widely applied as effective catalysts in pollutant removal, the pigment in paint products, and oxidation reactions (Koh et al., 2017; Chen et al., 2022; Ling et al., 2020; Leong et al., 2022). It was documented that TS-1, a TiO$_2$-containing silicalite was a promising oxidative catalyst attributed to the presence of tetrahedrally coordinated titanium in a silicate structure (Zhao et al., 2022). However, only Lewis acidity was found in TiO$_2$-SiO$_2$ mixed oxides, without any Brønsted acidity (Wu et al., 2021).

It had been demonstrated that acid treatment increased the acidity of the designed catalysts (Lim and Lee, 2016; Lee and Hamdan, 2008). Both Lewis and Brønsted acidic sites...
were generated in titania and alumina upon loading of phosphoric acid (Ortiz-Islas et al., 2005). In addition, silica treated with phosphoric acid showed high Bronsted acidity (Kahraman et al., 2005). In other work, the interaction between vanadia and phosphate was claimed to be important for the Bronsted acid site formation in a titanium-silica bifunctional catalyst. The presence of phosphoric acid was also important in strengthening the oxidative catalytic activity of the catalysts.

Previous studies reported that iron phosphate (FePO₄) was an ideal catalyst for oxidation reactions because it possessed both redox and acidic properties. This oxidative dehydration proved to be particularly selective for FePO₄. Despite this, this material did not have a high oxidation catalytic activity (Tan et al., 2016). The coordinated titania and niobium species, which were tetrahedrally coordinated, are also important components of good catalysts that act as oxidative sites. In Nb-impregnated TS-1 catalysts, the presence of niobium compound led to Brønsted acidity formation and sufficient diol production (Ahn et al., 2020).

Thus, here, we present the preparation of a series of phosphoric acid-treated niobium-doped titania-silica. The effect of the phosphate treatment on the physical-chemical properties of the resulting material was investigated. The importance of the phosphoric acid as a modiﬁer of niobium-doped titania-silica bifunctional was examined. Furthermore, the catalytic performance of the synthesized materials was examined in the sequential transformation of 1-octene into 1,2-octanediol by forming 1,2-epoxyoctane.

2. EXPERIMENTAL SECTION

2.1 Synthesis of Materials

Using the sol-gel and impregnation techniques, phosphoric acid concentrations were prepared on modified niobium (Nb) titania-silica (TiO₂-SiO₂). To achieve this purpose, a series of solutions of PO₄³⁻-treated Nb/TiO₂-SiO₂ materials were prepared. Using tetraethylorthosilicate and titanium(IV) isopropoxide, respectively, as SiO₂ and TiO₂ sources, the catalyst support of Si/Ti = 80:1 molar ratio was prepared using the sol-gel method according to previously reported methods (Ekhsan et al., 2014). After stirring TEOS, ethanol, HNO₃, and H₂O (mol ratios 1: 1: 0.6: 4) for 30 minutes at room temperature, a solution of these components was obtained. Titanium(IV) isopropoxide (TTIP, Aldrich, 97%), acetylacetone and ethanol (mol ratio = 1: 0.5: 100) were added to the mixture and stirred at room temperature for 30 minutes. After stirring the clear solution for 1 hour, the mixture was dried at 80°C to get a clear gel. Following the drying of the wet gel at 110°C overnight, it was calcined at 500°C for 5 hours to produce SiO₂-TiO₂ powder.

As a part of the impregnation process, 1.8 g of SiO₂-TiO₂ was added to the niobium solution. At this stage, 1 wt% of niobium(V) ethoxide was prepared by dissolving it in sufficient amounts of niobium(V) ethoxide (Nb(OC₂H₅)₅) (Aldrich, 99.95%) in 10 mL of n-hexane. A stirring process at room temperature was followed by overnight drying at 110°C and stirring at room temperature. During the calcination process, the powder was ground and calcined at 500°C for five hours. The material produced was labeled as Nb/SiO₂-TiO₂.

The phosphoric acid of different molarity was used for the further modification of the catalysts via the wet impregnation method. The final products were labeled as xPO₄³⁻/Nb/SiO₂-TiO₂, where x = 0.05-0.25 M. All the synthesized catalysts were labeled for each sample based on the concentration of phosphoric acid it contains, for example, 0.05PO₄³⁻/Nb/SiO₂-TiO₂ for 0.05 M H₃PO₄ treated Nb/SiO₂-TiO₂ sample.

2.2 Characterizations

For the determination of the surface area of all samples, Micromeritics ASAP2010 surface area analyzer was used to conduct BET N₂ adsorption-desorption on each sample. Al₂O₃ was used as the standard material to calibrate the analyzer prior to analysis. The crystalline phase of the catalysts was examined using powder X-Ray Diffraction (XRD). The XRD analysis was performed at 40 kV and 40 mA, using a Bruker Advance D8 equipped with Siemens 5000 diffractometer, with Cu Kα radiation (λ = 1.5405 Å) as the diffracted monochromatic beam. Scans of the spectra were performed in the range 2θ of 2°-60° at a step of 0.030° and a time step of 1 s. In addition, infrared measurements were conducted on a Perkin Elmer Spectrum One FT-IR spectrometer via the KBr pellet technique, with a scan time of 10 s and spectral resolution of 2 cm⁻¹. Diffuse reflectance UV spectra were collected to determine Ti and Nb species that existed in the samples. With a Perkin Elmer Lambda 900 DRUV/VIS spectrometer, the analysis was performed under ambient conditions over a range of 190 to 800 nm.

2.3 Catalytic Testing

In order to evaluate the bifunctional catalytic properties of the synthesized samples, the sequential reaction of generation of 1,2-octanediol via the conversion of 1,2-epoxyoctane from 1-octene was followed. The chemical reaction is shown in Figure 1.

For this purpose, 1-octene (15 mmol, Aldrich, 98%), 30 mmol hydrogen peroxide in H₂O (Qrec, 30%), and acetonitrile (10 mL, Merck, 99.8%) as solvent were added into a flask equipped with a magnetic stirrer and a condenser. Besides, 250 μL cyclooctane (Fluka, 99%) as the internal standard was out into the flask. The solution was then treated with 0.05 g
catalyst. The reaction was conducted in an oil bath at 70°C for 24 hours with stirring. Finally, the reaction products were analyzed using an HP Agilent 6890N gas chromatograph with an Ultra-1 column.

3. RESULT AND DISCUSSION

3.1 Properties of Materials

All the prepared materials existed in light white and fluffy powder despite calcination at 500°C for 5 hours. XRD patterns of all the PO₄⁻/Nb/SiO₂-TiO₂ samples are shown in Figure 2. As can be observed, the samples Nb/SiO₂-TiO₂ and those treated with 0.20 M or less H₃PO₄ did not exhibit any peaks in the X-ray diffractograms, strongly suggesting that they were amorphous. An H₃PO₄ treatment has been claimed to facilitate well dispersion of Nb on catalyst supports (Onoda and Matsukura, 2015). The amorphous nature of the samples could be also due to the small amount of both TiO₂ and Nb in the samples. As for sample 0.25PO₄⁻/Nb/SiO₂-TiO₂, its XRD diffractogram included some unidentified peaks. The phenomenon might be explained by the possible reactions of H₃PO₄ with Nb and Ti, which generated other compounds in the material. Since impurities are present in 0.25PO₄⁻/Nb/SiO₂-TiO₂, this material was not further characterized and tested for catalytic behavior.

According to Table 1, both the surface area and pore volume of the materials are reduced upon the addition of Nb and PO₄⁻. As a result of using 0.15 and 0.20 M H₃PO₄ in the synthesis of the catalyst, a reduction of ~90% in surface area was detected. As a result of the use of phosphoric acid, the materials exhibited a coalescence process during the calcinations, leading to a drastic decrease in both surface area and pore volume (Lee et al., 2011). A similar phenomenon was also observed on FePO₄/SiO₂ catalysts (Ebert et al., 2017).

The FTIR analysis of the resulting materials revealed different functional groups, as shown in Figure 3. As can be seen in all spectra, the characteristic vibration bands of SiO₂ were detected at 466 and 1100 cm⁻¹, corresponding to the bending and stretching vibrations of Si-O-Si, respectively (Ling et al., 2020). Additionally, the weak band at 2341 cm⁻¹ was attributed to the presence of Nb. The bands at 1651 and 3400 cm⁻¹ were associated with stretching of the O-H atoms and water hydration, respectively. It has been observed that as the concentration of PO₄⁻ in the sample increased, the intensity of the O-H group decreased. There may be an explanation for this by replacing the O-H group on the surface of the samples with the PO₄⁻ group. However, no bands were observed corresponding to H₃PO₄. Perhaps this was caused by the low concentration of H₃PO₄ applied in the synthesis process.

| Materials           | Surface Area (m²/g) | Pore Volume (cm³/g) |
|---------------------|---------------------|---------------------|
| SiO₂                | 572                 | 0.32                |
| Nb/SiO₂-TiO₂        | 602                 | 0.37                |
| 0.05PO₄⁻/Nb/SiO₂-TiO₂| 350                 | 0.23                |
| 0.10PO₄⁻/Nb/SiO₂-TiO₂| 300                 | 0.19                |
| 0.15PO₄⁻/Nb/SiO₂-TiO₂| 32                  | 0.11                |
| 0.20PO₄⁻/Nb/SiO₂-TiO₂| 38                  | 0.12                |

A Si-O-Ti bond was observed in all spectra at 799 cm⁻¹, as depicted in Figure 3. Similarly, the band at ~970 cm⁻¹ may overlap absorptions of the Si-O-Ti bond, also related to tetrahedral Ti, and be connected to surface Si-OH vibrations.
Interestingly, the band appeared to disappear when the concentration of H$_3$PO$_4$ was high. For the PO$_4^-$ treated Nb/SiO$_2$-TiO$_2$ samples, only a weak shoulder was observed at $\sim 1000 \text{ cm}^{-1}$. According to this finding, there is a dramatic reduction in Si-O-Ti and Si-O-Si bonding in SiO$_2$-TiO$_2$, following H$_3$PO$_4$ treatment. It has been described that a small band around 970 cm$^{-1}$ is a result of the interaction between Si-O-M within the silicalite structure (Vicentini et al., 2021). Despite adding Nb, a transition metal to the samples, an additional peak was not observed at this wavenumber. There could be an explanation for this phenomenon in the overlapping with the Si-OH stretching peak, which made it difficult to identify the band precisely (Lee et al., 2011).

Figure 4 illustrates the UV-Vis DRS spectra for the xPO$_4^-$/Nb/SiO$_2$-TiO$_2$. There was an intense band present at 270 nm for all materials. The band corresponds to the hydrated Si-OH stretching peak, which made it difficult to identify the band precisely (Lee et al., 2011).

Table 2. Product Yields of the Materials in Transformation of 1-octene to 1,2-oxirane-1-oxide

| Materials                  | Yield of 1,2-epoxyoctane (µmol) | Yield of 1,2-oxirane-1-oxide (µmol) |
|----------------------------|---------------------------------|-------------------------------------|
| Nb/SiO$_2$-TiO$_2$         | 59                              | 0                                   |
| 0.05PO$_4^-$/Nb/SiO$_2$-TiO$_2$ | 382                             | 0                                   |
| 0.10PO$_4^-$/Nb/SiO$_2$-TiO$_2$ | 333                             | 0                                   |
| 0.15PO$_4^-$/Nb/SiO$_2$-TiO$_2$ | 195                             | 0                                   |
| 0.20PO$_4^-$/Nb/SiO$_2$-TiO$_2$ | 164                             | 461                                 |

However, 1,2-oxirane-1-oxide was only yielded when 0.20PO$_4^-$/Nb/SiO$_2$-TiO$_2$ was used as a catalyst in the reaction. It could be observed that 0.20PO$_4^-$/Nb/SiO$_2$-TiO$_2$ was an effective bifunctional catalyst after 24 hours since it yielded 461 µmol 1,2-oxirane-1-oxide. It was reported previously by our group that 0.20PO$_4^-$/Nb/SiO$_2$-TiO$_2$ possessed 14.6 µmol/g Lewis acid and 2.4 µmol/g Brønsted acid as confirmed via pyridine adsorption analysis (Ekhsan et al., 2014). Since the existence of Brønsted acid sites in V$_x$PO$_4$/ST catalysts has been reported to be due to the coexistence of PO$_4^-$ and V compounds (Lee et al., 2009), the interaction between PO$_4^-$ and Nb compounds in the prepared samples could be important to generate the Brønsted acid sites. For samples Nb/SiO$_2$-TiO$_2$ treated with lesser amount of H$_3$PO$_4$ ($x = 0.05, 0.10, 0.15$ M), no diol was produced. This could be due to the insufficient amount of PO$_4^-$ for the formation of Brønsted acidity with Nb in the samples. As with Nb/TiO$_2$-SiO$_2$, Nb/SiO$_2$-TiO$_2$ had no Brønsted acid sites, so it was inactive in the epoxide-diol transformation.
4. CONCLUSION
Bifunctional catalysts of PO$_4^-$/treated Nb/SiO$_2$-TiO$_2$ were synthesized via sol-gel and impregnation methods. It was observed that the hydrated tetrahedral Ti species present as the most predominant species, and the amount of this Ti species increased with the increase of PO$_4^-$ concentration. After 24 hours of reaction, 0.05 M PO$_4^-$ treated Nb/SiO$_2$-TiO$_2$ proved to be the most efficient oxidative catalyst, strongly suggesting the PO$_4^-$ treatment has increased significantly the oxidative active sites in the samples. More importantly, the current results revealed that 0.20 M PO$_4^-$ treated Nb/SiO$_2$-TiO$_2$ is a promising bifunctional catalyst for the transformation of 1-octene to 1,2-octanediol through the generation of 1,2-epoxyoctane. The research findings indicated that a sufficient amount of PO$_4^-$ was crucial to generate Brønsted acidity for the transformation of 1,2-epoxides to diol.

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