Tungsten-oxide modified silica-titania oxidative-acidic bifunctional catalyst for diol synthesis

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GRAPHICAL ABSTRACT

ABSTRACT

Oxidative-acidic bifunctional catalysts of tungsten oxide modified silica-titania, xW/TiO_2-SiO_2 (x=1, 5, 10 wt%) were successfully synthesized and characterized. Both XRD and UV-Vis analyses results indicated presence of WO_3 phase in samples with higher dopant amount. It also revealed tetrahedral Ti and octahedral coordinated existed as the dominant species in the samples. FTIR analysis suggested formation of Si-O-W in the tungsten oxide modified samples. The catalytic performance of the samples was evaluated via consecutive transformation of 1-octene to 1,2-octanediol through the conversion of 1,2-epoxyoctane using aqueous H_2O_2 as oxidant. While TiO_2-SiO_2 and $1W/TiO_2$-SiO_2 showed no catalytic activity in yielding diol, samples $5W/TiO_2$-SiO_2 and $10W/TiO_2$-SiO_2 exhibited bifunctional catalytic activity. It has been demonstrated that sample $10W/TiO_2$-SiO_2 was the best oxidative-acidic bifuntional catalyst which produced 321 µmol 1,2-epoxyoctane and 51 µmol 1,2-octanediol after 24 h reaction.

Keywords: Bifunctional catalyst; Oxidative; Tungsten oxide; Silica-titania

1.0   INTRODUCTION

A large segment of the modern chemical industry is based on selective catalytic oxidation processes [1]. More than 60% of the chemicals and intermediates synthesized via catalytic processes are the products of oxidation. In the early-eighties, titanium silicalite-1 (TS-1) was first reported by Taramasso *et al.* in 1983 [2]. Using H_2O_2 as oxidant, TS-1 has shown great capability in oxidation and epoxidation of olefins. Silica-titania aerogel was then introduced considering its excellent catalytic properties in epoxidation [3]. Later, alternative low cost SiO_2 support was employed [4]. On the other hand, acidic catalysts which include alumina, zeolites and metal oxides are also important in catalyzing reactions such as esterification and hydrolysis. These materials serve as an alternative to homogeneous acid catalysts [5]. However, monofunctional catalysts are less useful when production of certain chemicals require more than a single step. More than one reactor has to be equipped when the process is to be catalyzed by different catalysts.

As such, bifunctional catalysts are developed to overcome the problem. Bifunctional catalysts consist of two different active sites which are capable of catalyzing two different reactions in a single material. A bifunctional catalyst with oxidative and acidic sites could aid in diols formation from alkene though epoxidation and subsequent hydrolysis. Indeed, diols serve as important feedstocks in fine chemistry as well as intermediates for agrochemicals [6]. Diols contribute to high water solubility, hygroscopicity and reactivity with many organic compounds. Presently, the production of diols involves dual steps of reaction in separate chambers. As such, high cost production is involved and the process is time-consuming. In view of this, an effective bifunctional catalyst is needed for rapid production of diols at a lower cost.

One of the vital challenges is to design a highly effective catalyst combining oxidative and acidic properties. In the past decades, various oxidative-acidic bifunctional catalysts have been reported. Prasetyoko *et al.* [7] had initiated the design of an oxidative-acidic bifunctional catalyst by using sulphated zirconia loaded on TS-1. Even so, only samples with high loading of sulfated zirconia showed catalytic activity towards transformation of 1-octene to 1,2-octanediol through 1,2-epoxyoctane. It was claimed that metal oxides such as V, Mo, W and Nb could act as redox centers and their presence had influenced formation of both Lewis and Brønsted acidity sites on various supports [8]. This was evidenced in previous studies using vanadium and niobium oxides as modifier for silica-titania [9, 10].

Silica-titania has been evidenced as a good catalyst for epoxidation owing to the highly dispersion of Ti^{4+}

species in the catalyst, which corresponds to Lewis acidity [11] Nevertheless, Brønsted acidity is needed for transformation of diols from epoxides. As such, vanadium and niobium oxides were loaded on silica-titania in conjunction of generating Brønsted acidity. However, the performance is less satisfactory in terms of selectivity and yield of diols.

Due to similar properties of transition metals in Group 5 and 6, tungsten oxide was selected as modifier for TiO_2 to enhance the formation of both oxidative and acidic sites on catalysts. Although catalyst which contains tungsten oxide had been synthesized using titanium-silicate (TS-1) as support reported in Prasetyoko *et al*. [12], the amount of Brønsted acid formed as well as catalytic activity did not increase significantly with even at very high tungsten loading. As such, it is worth to explore the effect of impregnation of tungsten oxide using a different support, which is silica-titania.

2.0   EXPERIMENTS

2.1   Synthesis of bifunctional catalysts

SiO_2-TiO_2 with molar ratio of Si:Ti=33:1 was synthesized via sol-gel method as described elsewhere [9,13]. A mixture of tetraethylorthosilicate (TEOS, Alrich, 99.8%), ethanol (EtOH), H_2O and HNO_3 was stirred at room temperature for 30 minutes. Later on, a mixture containing titanium(IV) isopropoxide (TTIP, Aldrich, 97%). EtOH and acetylacetone was added into previously prepared solution and stirred under the same condition. Subsequently, the mixture was dried at 353K until a clear gel was obtained. The resulting wet gel was dried at 383K overnight and calcined at 773K for 5 h to yield TiO_2-SiO_2 powder.

Tungsten oxide was wet impregnated on TiO_2-SiO_2 powder. In conjunction of this, *x* wt% of W was prepared by dissolving sufficient amount of ammonium tungstate pentahydrate $(NH_4)_{10}W_{12}O_{41}.5H_2O$ (Qrec, 99.99%) in 10 mL of H_2O. The mixture was stirred vigorously at room temperature for 1 h, followed by drying at 383K overnight. The obtained solid was ground and calcined at 773K for 5 h. The resulted material was denoted as *x*W/TiO_2-SiO_2 (where x=1, 5, 10 wt%).

2.2   Characterization

The crystal structure and crystallinity of the catalyst was determined with X-ray diffraction (XRD) recorded on a powder diffractometer (Bruker Advance D8, 40 kV, 40 mA) using a Cu Kα radiation source in the range of 2θ = 10 - 60°.

In order to investigate Ti and W species formed in the synthesized materials, diffused reflectance UV spectroscopy analysis was carried out using Perkin Elmer Lambda 900 DRUV/Vis spectrometer. The samples were scanned over the range from 200 to 800 nm.

Infrared measurements were performed using a Thermo Scientific Nicolet iS10 FT-IR spectrometer using KBr pellet technique to identify the type of bonding present in the materials. The spectra were recorded in the region of 400-4000 cm^{-1} using a spectral resolution of 2 cm^{-1}.

2.3   Catalytic testing

The catalytic performance of tungsten oxide modified samples was evaluated through the consecutive formation of 1,2-octanediol via transformation of 1,2-epoxyoctane from 1-octene. The reaction mixture containing 1-octene (15 mmol, Merck, 97%), H_2O_2 (30 mmol, Merck, 30%) in acetonitrile (10 mL, Merck, 99.9%) was placed in a round bottom flask equipped with a condenser. The reaction was carried out in an oil bath at 343 K for 24 h under stirring condition. The products of the reaction were analyzed on a Shimadzu GC 2014 chromatograph using a HP-5 column.

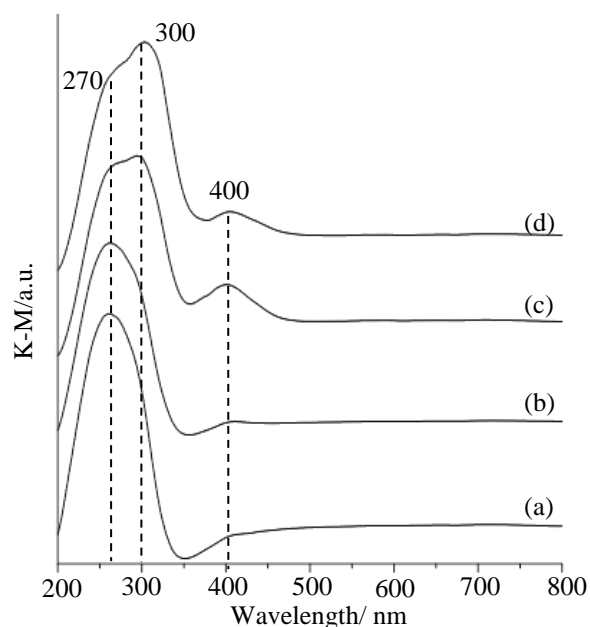## 3.0   RESULTS AND DISCUSSION

3.1   Physical properties

TiO_2-SiO_2 synthesized was light and fluffy powder even after calcination at 773 K for 5 h. Colour changes were observed in tungsten oxide loaded samples: *x*W/TiO_2-SiO_2 changed from white to yellow and increase in colour intensity with higher tungsten loading.

Figure 1 shows the X-ray diffractograms of the synthesized materials. XRD pattern indicated that TiO_2-SiO_2 was an amorphous material. Similar finding was reported previously [10]. No characteristic peak corresponds to TiO_2 was observed, indicating that TiO_2 was highly dispersed on the surface of SiO_2, or were incorporated into SiO_2 framework. A broad peak at a low diffraction angle from 20º to 30º corresponds to the amorphous-state SiO_2 shells surrounding tungsten-sulphate [13]. For species loaded with tungsten oxide, small peak was observed at 2θ = 23.1º for 5 and 10wt% tungsten loaded samples. This peak was indexed to monoclinic WO_3 (JCPDS 43-1035), indicating presence of crystalline WO_3 in the samples as a result of heat treatment. Interestingly, the peak intensity of WO_3 of 10W/TiO_2-SiO_2 was lower than that of 5W/TiO_2-SiO_2. This could be due to lower sample amount of 10W/TiO_2-SiO_2 used in the XRD analysis. Notably, the XRD pattern of the samples showed only a small peak with low intensity. A possible explanation to this is due to amorphous nature of silica-titania. This also indicates tungsten species were distributed homogeneously throughout the support material [14].
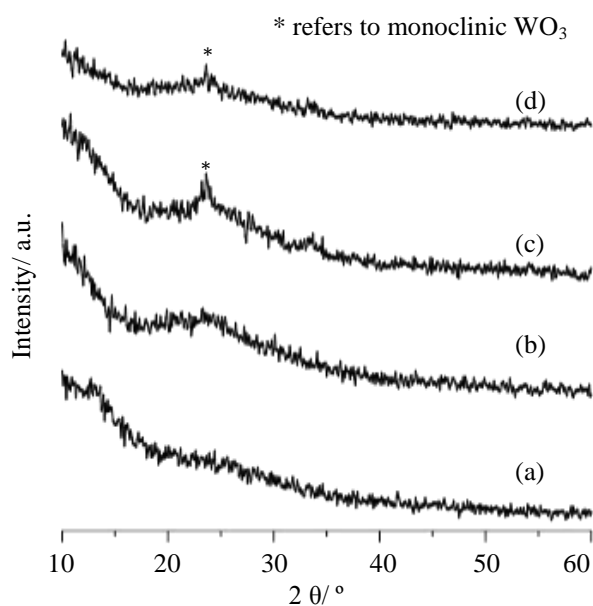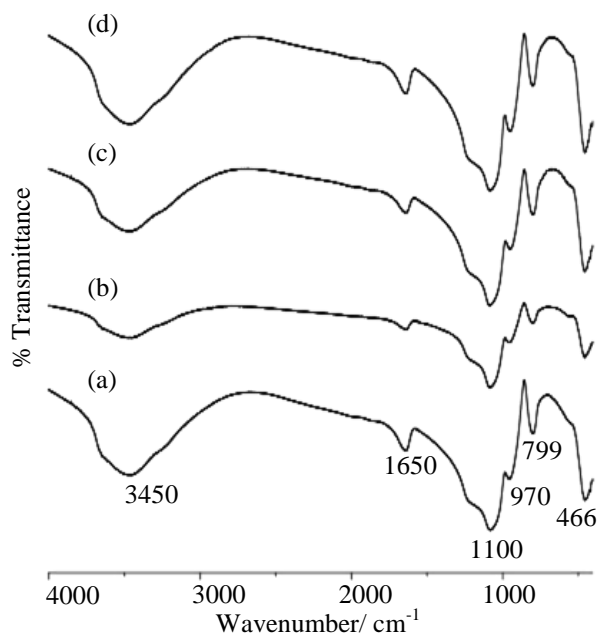
Fig. 1 XRD patterns of (a) TiO_2-SiO_2, (b) $1W/TiO_2$-SiO_2, (c) $5W/TiO_2$-SiO_2 and (d) $10W/TiO_2$-SiO_2

Fig. 2 DRUV-Vis spectra of (a) TiO_2-SiO_2, (b) $1W$ TiO_2-SiO_2, (c) $5W/TiO_2$-SiO_2 and (d) $10W/TiO_2$-SiO_2

Figure 2 depicts DRUV-Vis spectra of the samples. As can be seen, there was only a major peak at around 270 nm for TiO_2-SiO_2, which is associated to tetrahedrally coordinated Ti species. Indeed, tetrahedral Ti species is widely acknowledged 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 [10]. Meanwhile, the peak observed at around 300 nm in xW/TiO_2-SiO_2 (x = 1, 5, 10 wt%) was linked to the creation of octahedral or polymeric Ti species. A possible explanation to this is some tetrahedral Ti framework was transformed into octahedral structure after impregnating with tungsten oxide. The intensity of this peak increased with higher loading of tungsten. The broad band at around 400 nm as observed in materials modified with tungsten oxide was associated to $O^{2-} \rightarrow W^{6+}$ charge transfer transition, as in the case of monoclinic WO_3 [15]. This also explains the appearance of pale yellow colour of the samples. This transformation of some tetrahedral Ti framework to octahedral structure is due to the presence of the acid [13].

FTIR spectra of samples (Figure 3) show typical silicate absorptions at 466 and 1100 cm^{-1} that were associated to Si-O-Si bending and stretching vibrations respectively [16]. The peak at 799 cm^{-1} is corresponded to Si-O-Ti or Si-O-W bond. As can be seen (Fig. 3 (b-d), the tungsten oxide loading affected the formation of the bondings. Meanwhile, the peak at 970 cm^{-1} was linked to surface Si-OH vibrations and possibly overlaps absorptions of Si-O-Ti bond [17]. Apart from that, a broad band at 3450 cm^{-1} and a small peak at 1650 cm^{-1} were attributed to stretching and bending frequency of hydroxyl groups, respectively. As compared among the tungsten oxide modified samples, the intensity of these two bands increased with the increase of W content in the sample. This may imply higher loading of W enhanced hydrophilicity property of the resulted materials. Surprisingly, no typical band of W=O or O-W-O was observed. In the literature [18], W=O and O-W-O band could be detected at 962 cm^{-1}. Possibly, these bands were overshadowed by Si-OH and Si-O-Ti stretching frequency.

Fig. 3 FTIR spectra of (a) TiO_2-SiO_2, (b) $1W/TiO_2$-SiO_2, (c) $5W/TiO_2$-SiO_2 and (d) $10W/TiO_2$-SiO_2

3.2   Catalytic performance

The evaluation of catalytic performance was conducted at 343 K for 24 h through the consecutive transformation of 1-octene to 1,2-octanediol via the formation of 1,2-epoxyoctane using H_2O_2. Traces of 1,2-epoxyoctane (80 µmol) and no 1,2-octanediol were detected in TiO_2-SiO_2 catalyzed reaction. After impregnation of 1wt% W, sample $1W/TiO_2$-SiO_2 produced higher yield of 1,2-epoxyoctane (104 µmol), without formation of any 1,2-octanediol. The results strongly suggested that TiO_2-SiO_2 served merely as a weak oxidative site for epoxidation. Apparently, the tungsten oxide modification has promoted the oxidative active site generation or has strengthened the oxidative active sites.

Further increased amount of W dopant has increased the yield of 1,2-epoxyoctane. Samples $5W/TiO_2$-SiO_2 and $10W/TiO_2$-SiO_2 produced 168 and 132 µmol 1,2-epoxyoctane, respectively. Interestingly, formation of 1,2-octanediol was detected in the reactions which were catalyzed using these two samples. The results strongly indicated that these samples were bifunctional catalysts to produce diol from alkene via single step reaction. The detection of the diol strongly implied the presence of Brønsted acid sites in the samples since only Brønsted acidity provides the active site for epoxy to diol transformation [10].

The current results suggested that $10W/TiO_2$-SiO_2 was the best oxidative-acidic bifunctional catalyst to produce 51 µmol 1,2-octanediol after the reaction. In the literature, niobium oxide modified TiO_2-SiO_2 was a weak catalyst in epoxidation reaction as it only produced 59 µmol 1,2-epoxyoctane, without any yield of 1,2-octanediol after 24 h reaction [10]. Therefore, it could be concluded that tungsten oxide might be a better modifier than niobium oxide in an oxidative-acidic bifunctional catalyst design.

Table 1 Product yields of TiO_2-SiO_2 and xW/TiO_2-SiO_2 samples in transformation of 1-octene to 1,2-octanediol through formation of 1,2-epoxyoctane at 343 K for 24 h.

Catalyst	Yield of 1,2-epoxyoctane (μ mol)	Yield of 1,2-octanediol (μ mol)
TiO_2-SiO_2	80	0
$1W/TiO_2$-SiO_2	104	0
$5W/TiO_2$-SiO_2	168	44
$10W/TiO_2$-SiO_2	321	51

4.0   CONCLUSION

New tungsten oxide impregnated silica-titania oxidative-acidic bifunctional catalysts have been successfully synthesized. Tetrahedrally coordinated Ti species acted as active oxidative sites. Presence of tungsten oxide was believed to strengthen the oxidative sites. Besides, introduction of 5 wt% or more W has generated Brønsted acidity in the samples. The results showed that sample $10W/TiO_2$-SiO_2 was a good oxidative-acidic bifunctional catalyst to produce 321 µmol 1,2-epoxyoctane and 51 µmol 1,2-octanediol at 343 K for 24 h.

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