Catal Lett (2009) 128:177–182
DOI 10.1007/s10562-008-9727-7

Tungsten Oxides-Containing Titanium Silicalite for Liquid Phase Epoxidation of 1-octene with Aqueous Hydrogen Peroxide

Didik Prasetyoko · Hamzah Fansuri · Zainab Ramli · Salasiah Endud · Hadi Nur

Received: 12 May 2008 / Accepted: 10 October 2008 / Published online: 4 November 2008
© Springer Science+Business Media, LLC 2008

Abstract Tungsten oxides (WO_3) have been supported on the titanium silicalite (TS-1) by impregnation method. The solids have been tested for epoxidation of 1-octene with aqueous H_2O_2 in acetone as solvent. It was found that the presence of tungstate species in the catalysts enhanced the rate of the formation of epoxide. Diol as a site-product was also observed due to the acidic properties of the catalysts.

Keywords Titanosilicalite-1 · Tungsten oxides · Epoxidation

1 Introduction

Since the discovery of the titanium silicate-1 activity in the epoxidation of terminal alkene by aqueous hydrogen peroxide[1], the structures, properties and catalytic activities of the titanium-containing materials, such as TS-1 [1–3], Ti-beta [4, 5], Ti-MCM-41 [6, 7] and Ti-containing amorphous silica [8] have been widely investigated. The investigations concluded that the catalytic activities of Ti-containing molecular-sieves depend on the preparation method, size of substrate and solvents [4, 7, 9, 10]. Because the epoxidation reaction occurs in the internal pore of Ti-containing molecular-sieves, pore opening become a determining factor to the catalyst activity because the substrates have to be able to access the active sites in the middle of the pore. Therefore, bigger substrates need bigger pore size. TS-1 has small pore size but it has higher catalytic performances for small substrates than other Ti-containing molecular-sieves [9].

The development of the Ti-containing molecular-sieves catalysts in order to increase their catalytic activity towards epoxides is still progressing. Capel-sanchez et al. [11] reported the effect of alkali addition to the performance of TS-1 catalyst. They observed that the selectivity to epoxide increased as the ratio of Lewis to Brønsted acid sites increased as a result of alkali addition. However, the addition slightly reduce the catalyst's conversion [11, 12]. Meanwhile, in the epoxidation reaction, it is well known that the interaction between titanium and oxidizing agents to form titanium-oxo species should occur before the reaction with alkene to produce epoxides [13, 14].

In this present study, we are showing that the catalytic activity of TS-1 towards the epoxidation of 1-octene with aqueous hydrogen peroxide could be enhanced by deposition of tungsten oxide on the surface of TS-1.

2 Experimental

2.1 Preparation of Materials

Titanium silicalite (TS-1, 3% of titanium, mol%) was prepared according to a procedure described earlier [1]. The WO_x/TS-1 catalysts were prepared by impregnation technique using an aqueous solution containing sufficient amount of ammonium metatungstate hydrate $(NH_4)_6$

D. Prasetyoko (✉) · H. Fansuri
Department of Chemistry, Faculty of Mathematic and Sciences, Institut Teknologi Sepuluh Nopember (ITS), Surabaya 60111, Indonesia
e-mail: didikp@chem.its.ac.id

Z. Ramli · S. Endud
Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 Johor, Malaysia

H. Nur
Ibnu Sina Institute for Fundamental Science Studies, Universiti Teknologi Malaysia, 81310 Johor, Malaysia

$H_2W_{12}O_{41} \cdot 18H_2O$, to produce materials with WO_3 loading in the ranges of 2–25 wt%. The suspension was heated at 110 °C for 3 h under stirring condition, followed by drying at 110 °C for 24 h and calcination at 550 °C for 6 h. The samples were denoted by their weight percentage of WO_3 on TS-1. Table 1 shows the amount of WO_3 loading and preparation condition.

2.2 Characterization

The catalyst structure was characterized by XRD and infrared spectroscopy techniques. The catalyst samples were characterized by powder X-ray diffraction (XRD) for the crystallinity and phase content of the solid materials using a Bruker Advance D8 Difractometer with Cu Kα ($\lambda = 1.5405$ Å) radiation as the diffracted monochromatic beam at 40 kV and 40 mA. The pattern was scanned in the 2θ ranges from 5° to 50° at a step size 0.010° and step time 1 s. The acidity of samples was determined by infrared spectroscopy technique using pyridine as a probe molecule. The wafer of the sample (10–12 mg) was locked in the cell equipped with CaF_2 windows, and evacuated at 400 °C under vacuum for 4 h. After evacuation, the cell was allowed to cooling down to room temperature then the pyridine adsorption process was carried out. Excess pyridine was evacuated at 150 °C for 1 h. Then, the infrared spectra of the sample were recorded at room temperature in the region of 1,400–1,700 cm^{-1} using Shimadzu Fourier Transform Infrared (FTIR).

2.3 Catalytic Activity

The catalyst performance was tested in the epoxidation of 1-octene using aqueous H_2O_2 (30%) as an oxidant. The reaction mixture containing 1-octene (8 mmol), H_2O_2 (8 mmol) and acetone (10 g) as solvent was placed in a round bottom flask equipped with a condenser. The catalyst (0.05 g TS-1 based) was then added to the mixture. The reaction was carried out in an oil bath under stirring at 70 °C. The products of the reaction were analyzed by a Hewlett-Packard 6890N gas chromatograph using an Ultra-1 column and a Hewlett-Packard GC-MSD instrument using an HP5 column.

3 Results and Discussion

3.1 Structural Characterization of WO_3/TS-1 Materials

The XRD patterns of the TS-1 and WO_3/TS-1 samples with various tungsten loading and condition are shown in Fig. 1. Generally, the MFI structure of TS-1 was still retained after dispersion of WO_3 on the surface of TS-1. The peak intensities of the crystalline WO_3 in the WO_3/TS-1 samples increase as the amount of WO_3 loading increase due to the higher concentration of WO_3 on the surface of the TS-1 support. The peaks corresponding to the crystalline phase of WO_3 appear at $2\theta = 23.1$, 23.7, 24.4, 33.2–34.6, and 41.5°, in which the peaks at $2\theta = 23$–25° overlapping with the peaks of TS-1, is only observed for the WO_3/TS-1 samples with high amount of tungsten loading, ca. 10, 15 and 25 wt%. The crystalline phase of WO_3 were not observed for the WO_3/TS-1 samples with low loading amount of WO_3, ca. 2, 5 and 7 wt%. The result demonstrates that crystalline WO_3 appears only in samples with high loading while the WO_3 exists as highly dispersed species in the low loading samples. Wang et al. [15] reported that the characteristic peaks of crystalline WO_3 were clearly seen for the samples with high loading amount of WO_3, ca. >6% and 10%, depending on the nature of silica support. The peak intensities of the crystalline WO_3 in the WO_3/TS-1 samples increase with the increase of WO_3 loading, due to the increase of the WO_3 concentration on the surface of the TS-1 support.

Table 1 : Amount of WO_3 loading, acidity and catalytic activity of the samples

Sample	WO_3 (wt%)	Brønsted (μmol/g)	Lewis (μmol/g)	Peak area at[a] 1,490 cm^{-1}	TOF[b] (10^{-1} h^{-1})
TS-1	0	0	48	0.29	–
2WO_3/TS-1	2.4	12	45	0.40	26
5WO_3/TS-1	4.9	11	52	0.59	49
7WO_3/TS-1	7.2	11	55	0.69	93
10WO_3/TS-1	9.7	14	47	0.54	n.t.[c]
15WO_3/TS-1	14.6	15	59	0.73	68
25WO_3/TS-1	24.9	12	45	0.38	72

[a] Area of the peak characteristic for the mixture of Brønsted and Lewis acid sites, in cm^{-2}

[b] TOF is calculated on the basis of the total Brønsted acid in the catalysts for the production of 1,2-octanediol in the epoxidation of 1-octene with H_2O_2 at 70 °C for 3 h

[c] Not tested

The surface concentration of metal dispersed in the support can be calculated quantitatively based on the amount of metal oxide loading [15]. Based on the graph of the surface concentration of the tungsten versus the ratio of the diffraction peak intensity of WO_3 to that of TS-1 (I_{WO_3}/I_{TS-1}; 2θ: 34.17°/23.04°) in various WO_3 loading, the dispersion capacity of tungsten on the titanium silicalite support was evaluated to be 0.35 W^{6+} cations/nm^2, by extrapolating the straight line to get the intercept on the abscissa [16].

The acidity of tungsten oxide loaded TS-1 samples was investigated by infrared spectroscopy using pyridine as the probe molecule. Figure 2 shows the infrared spectra of the samples at various tungsten loadings after evacuation at 150 °C under vacuum for an hour. Sample TS-1 shows peaks at around 1,606, 1,490, and 1,447 cm^{-1}. The peak at around 1,606 and 1,447 cm^{-1} are assigned to Lewis acid sites, suggesting that TS-1 possesses only Lewis acid. Meanwhile, all WO_3/TS-1 samples show peaks at around 1,637, 1,606, 1,544, 1,490, and 1,447 cm^{-1}. The small peak at around 1,544 cm^{-1} and the strong peak at around 1,446 cm^{-1} indicate that all the samples contain both Brønsted and Lewis acid sites.

The calculated amount of both Brønsted and Lewis acid sites in the samples are tabulated in Table 1. It was found that Brønsted acid sites were formed in the TS-1 upon introduction of tungsten oxide even at low tungsten loading, such as in 2WO_3/TS-1. However, as the amount of tungsten loading increased, there was no significant increase in the Brønsted acid sites and even at very high tungsten loading (25 wt%) the amount of Brønsted acid sites seems to decrease slightly. This finding indicates that

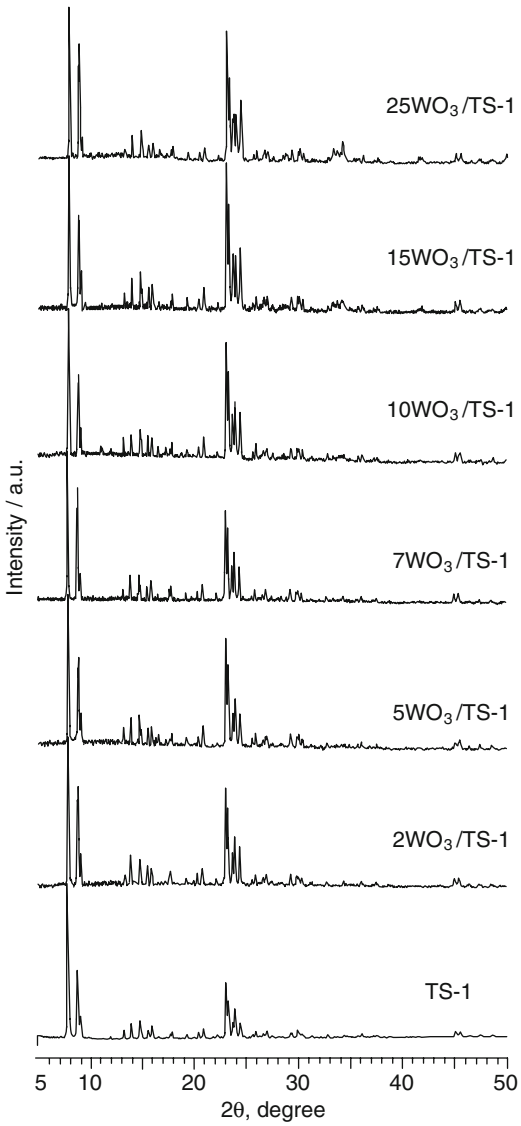

Fig. 1 XRD patterns of the TS-1 and tungsten-coated TS-1 samples

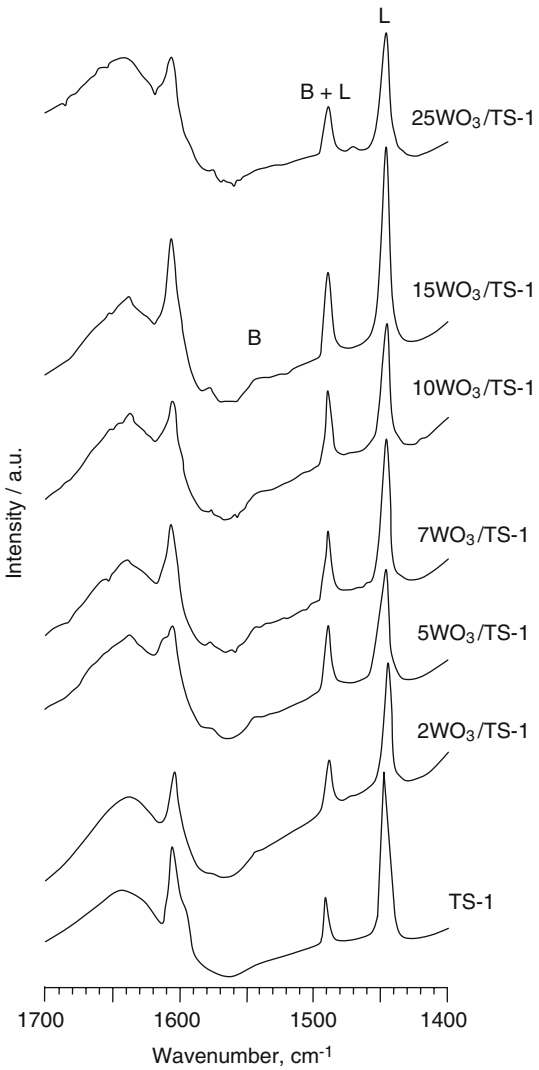

Fig. 2 Infrared spectra of the samples after evacuation at 400 °C in vacuum followed by pyridine adsorption at room temperature and desorption at 150 °C for 1 h

the creation of Brønsted acid in the TS-1 occurs only at low tungsten oxide loading. Further addition of tungsten oxide (at the higher loading amount) does not create any of Brønsted acid sites. It is further suggested that the formation of Brønsted acid sites is due to the reaction of tungsten with the surface silanol groups on the TS-1 to form the new bonding i.e. Si–O–W. Therefore, once all silanol reacted with tungsten, the additional tungsten will not form any more Brønsted acid sites. The excess tungsten creates tungsten oxide as bulk oxide, as can be observed in the infrared spectra of the framework vibration (not shown). Consequently, amount of atomic interaction of W–O–Si bond is lower as compare to W–O–W bond. For Lewis acid, addition of tungsten on TS-1 at low and high loadings does not significantly change the amount of Lewis acid sites. It suggests that tungsten oxide supported on TS-1 does not increase Lewis acid sites significantly, although according to Meijers et al. [17], tungsten oxide itself possesses Lewis acid sites. Meanwhile, Lucas et al. [18] have reported that the HZSM-5 acidity decreased after impregnation by tungsten.

Table 1 also shows the area of the peak at around 1,490 cm^{-1} that can be assigned to total amount of acid sites (Brønsted and Lewis). The table shows that the area increases as WO_3 loading increases up to 7 wt%. Wang et al. [15] reported that the height of ammonia desorption peak increased with the increased of WO_3 loading up to 6 wt%. It means that the total amount of acid sites increases up to monolayer coverage. In this study, it is suggested that the coordinately bonding of tungsten species with hydroxyl groups on the surface of TS-1 can be correlated with Brønsted acid sites. Martin et al. [19] reported the formations of Brønsted acid sites in the tungsten oxide supported silica. The formation of Brønsted acid sites in the supported tungsten oxide on the various supports such as alumina, titania, zirconia, silica and mixed oxides have also been reported [20–22].

3.2 Catalytic Activity

The activity of the TS-1 and WO_3/TS-1 catalysts were tested in the epoxidation of 1-octene using H_2O_2 as the oxidant at 70 °C for 3 h. The main products of the reaction were 1,2-epoxyoctane and 1,2-octanediol. Figure 3 shows the graph of the rate of formation of 1,2-epoxyoctane vs. reaction time. All samples show activity towards the epoxidation of 1-octene. Compare to WO_3/TS-1 catalysts, sample TS-1 shows the lowest rate of the formation of 1,2-epoxyoctane. Therefore, the high rate of 1,2-epoxyoctane formation observed in the reaction mixture catalyzed by samples WO_3/TS-1 may be due to the presence of WO_3 in the catalysts. However, the yield of 1,2-epoxyoctane decreased as WO_3 loading increased in all reaction time. Since among the catalysts used in the reaction have the similar amount of TS-1, this finding suggest that in this condition, the WO_3 is not active in the epoxidation of 1-octene, but low concentration of WO_3 improves catalytic activity. Furthermore, for the activity of WO_3/TS-1 catalysts, it can be seen in Fig. 3 that the rate of 1,2-epoxyoctane formation increased very rapidly at the initial stage, and then further increased gradually with the reaction time up to 3 h.

The high rate of the formation of 1,2-epoxyoctane observed in the initial stage of reaction time on WO_3/TS-1 catalysts can be explained in term of the hydrophilicity of the catalysts. Generally, in the catalytic reaction by heterogeneous catalysts, the first step of the reaction involve adsorption of the substrate on the surface of the catalysts to form intermediate, followed by reaction in the catalyst, and finally desorption of the product from the catalyst. In this reaction, the 1-octene is a non-polar molecule, while H_2O_2 is a polar molecule. Therefore, 1-octene will be adsorbed immediately at the catalyst with high hydrophobicity. Sample TS-1 has higher hydrophobic properties than WO_3/TS-1. Consequently, when catalyst TS-1 is added into the solution of 1-octene and H_2O_2, the adsorption of 1-octene on the TS-1 is faster than that of H_2O_2. Meanwhile, it is known that in the epoxidation of alkene, the active sites is oxo-titanium complex which is formed by interaction of titanium species with hydrogen peroxide [13, 14]. Therefore, it is expected that the faster interaction of H_2O_2 with titanium in the TS-1 result the faster formation of oxo-titanium species. As a results, the formation of 1,2-epoxyoctane was found to increased. Therefore, based on these

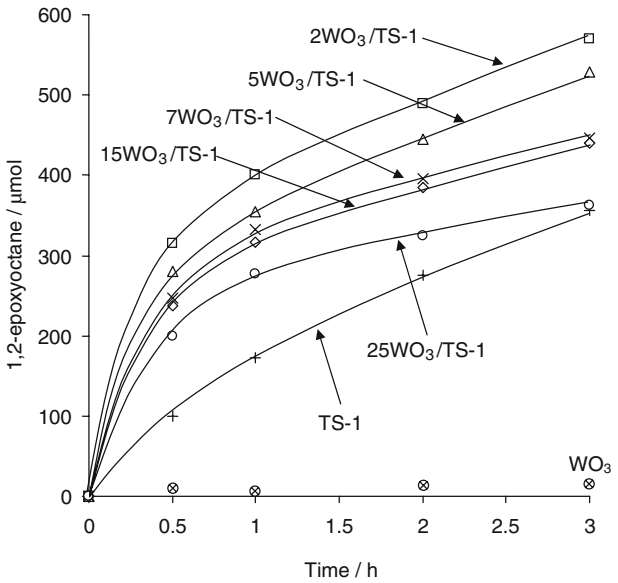

Fig. 3 The formation of 1,2-epoxyoctane from 1-octene epoxidation using aqueous H_2O_2 at 70 °C catalyzed by TS-1 and WO_3/TS-1

finding, it is concluded that the high rate of the formation of 1,2-epoxyoctane observed on the samples WO_3/TS-1 may due to the higher hydrophilicity of these catalysts than TS-1.

Figure 4 shows the dependence of the TOF (mol oxide/mol titanium/h) on the amount of WO_3 loading in WO_3/TS-1 for the epoxidation of 1-octene with aqueous H_2O_2 at 70 °C for 1 h. All WO_3/TS-1 catalysts showed higher TOF than the parent TS-1. Among the WO_3/TS-1 catalysts, it is found that the TOF decreased sharply with an increasing amount of WO_3 loading. This finding suggests that the capability of substrate to access the oxo-titanium active sites inside the pore of TS-1 is easier at lower amount of WO_3 loading. The pore opening of TS-1 is blocked by tungsten oxide at the high amount of WO_3 loading. This explanation is supported by the finding that the rate of formation of 1,2-epoxyoctane after 1 h of reaction time decreased on sample $7WO_3$/TS-1 (Fig. 3). Based on the XRD data (the graph is not shown), it was found that the dispersion capacity of tungsten on the titanium silicalite is 0.35 W^{6+}/nm^2, which close to the 7 wt% of WO_3 on TS-1. Meanwhile, the higher activity observed in the sample with lower WO_3 loading indicated that only small amount of WO_3 is needed to increase the hydrophilicity of TS-1 for the formation of oxo-titanium species.

The yields of 1,2-octanediol versus reaction time using various catalysts are depicted in Fig. 5. It is found that the yield of 1,2-octanediol increased as the amount of WO_3 loading increased. The highest yield of 1,2-octanediol was observed on the sample $25WO_3$/TS-1 at every reaction time. It is known that the formation of 1,2-octanediol from

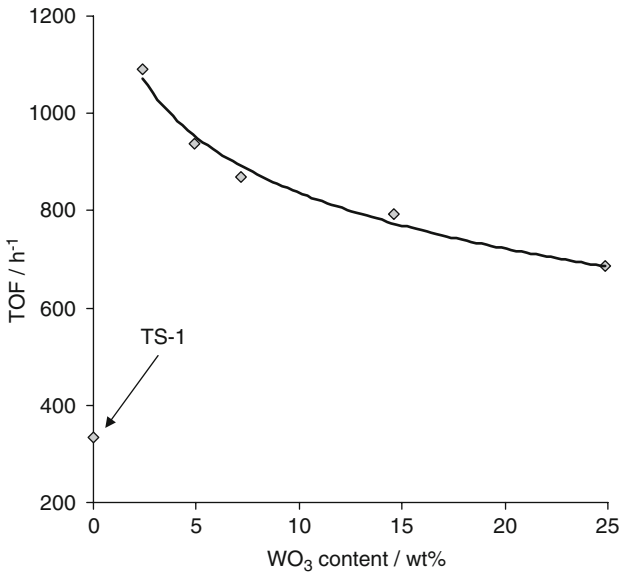

Fig. 4 Dependence of TOF (mol epoxide per mol Ti, per h at 0.5 h of reaction time) on the WO_3 content for epoxidation 1-ocetene with aqueous hydrogen peroxide at 70 °C in acetone

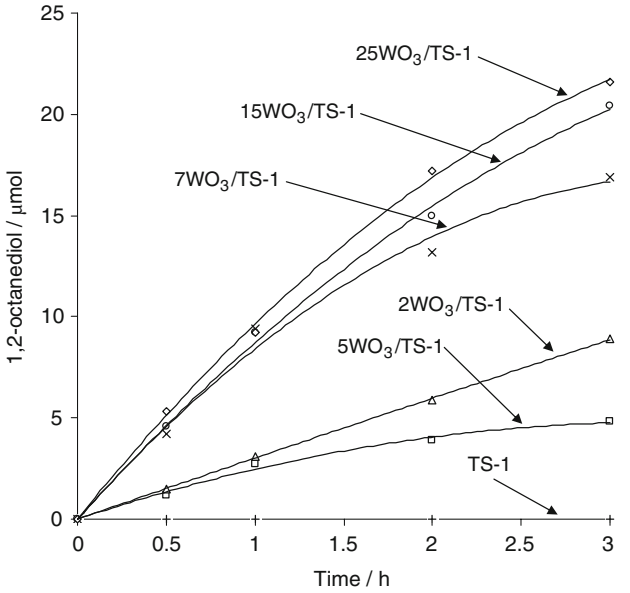

Fig. 5 The formation of 1,2-octanediol from 1-octene epoxidation using aqueous H_2O_2 at 70 °C catalyzed by TS-1 and WO_3/TS-1

1,2-epoxyoctane is catalyzed by both Brønsted and Lewis acid sites. In this study, it is found that the yield of 1,2-octanediol increased as the amount of Brønsted and Lewis acid sites increased. Therefore, catalysts with high amount of Brønsted and Lewis acid sites showed high yields of 1,2-octanediol. However, when the yield of 1,2-octanediol is divided by the amount of Brønsted acid sites, it is observed that its ratio increased as the increased of tungsten loading up to 7 wt% (value of monolayer coverage). Therefore, it can be explained that the effective Brønsted acid sites are located in immediate vicinity of the titanium sites (oxidative sites) that was generated by the interaction of W-O-Si in the surface of TS-1. The increased of 1,2-octanediol observed in high loading of WO_3 due to the higher amount of Lewis acid sites presence in the catalysts. In WO_3/TS-1 catalysts, it shows that the turn over frequency, TOF, increased as the WO_3 loading increased up to sample $7WO_3$/TS-1, and then decreased in samples with higher WO_3 loading (Table 1). Hence, it is concluded that the highest catalytic activity can be observed in the catalysts with monolayer coverage containing the highest W-O-Si bond. Meanwhile, for selectivity of 1,2-octanediol, it is found that the highest selectivity was observed in sample $25WO_3$/TS-1 due to high amount of Brønsted and Lewis acid sites involved during the reaction.

4 Conclusions

Impregnation of tungsten oxides (WO_3) onto titanium silicalite (TS-1) was studied. The XRD data showed that after

incorporation of tungsten oxide, the MFI structure of TS-1 still remained although with lower crystallinity. In the epoxidation of 1-octene with aqueous H_2O_2 in acetone as a solvent, the WO_3/TS-1 catalysts showed higher activity than the initial TS-1 due to higher hydrophylicity of the WO_3/TS-1 catalysts. Brønsted acid sites have been generated in the WO_3/TS-1 catalysts. It was found that all WO_3/TS-1 catalysts with different amounts of tungsten loading contain similar amount of Brønsted acid sites. Consequently, the activities of the catalysts for the formation of 1,2-octanediol from 1-octene were found to be similar. It was suggested that the Brønsted acid sites were formed due to formation of Si–O–W bond in the WO_3/TS-1 catalysts.

Acknowledgments We gratefully acknowledge funding from the Ministry of Science Technology and Innovation Malaysia (MOSTI), under IRPA grant No. 09-02-06-0057 SR0005/09-03 and Directorate General of Higher Education, Indonesia, under *Hibah Kompetensi* grant No. 1108/I2.7/PM/2008.

References

1. Taramasso M, Perego G, Notari B (1983) U. S. Patents No. 4,410,501
2. Clerici MG, Ingallina P (1993) US Patent No. 5,221,795
3. Clerici MG, Ingallina P (1998) Catal Today 41:351
4. van der Waal JC, Rigutto MS, van Bekkum H (1998) Appl Catal A: Gen 167:331
5. Krijnen S, Sánchez P, Jakobs BTF, van Hooff JHC (1999) Microporous Mesoporous Mater 31:163
6. Blasco T, Corma A, Navarro MT, Pariente JP (1995) J Catal 156:65
7. Li KT, Lin CC (2004) Catal Today 97:257
8. Kochkar H, Figueras F (1997) J Catal 171:420
9. Perego C, Carati A, Ingallina P, Mantegazza MA, Bellussi G (2001) Appl Catal A: Gen 221:63
10. Capel-Sanchez MC, Campos-Martin JM, Fierro JLG (2005) J Catal 234:488
11. Capel-Sanchez MC, Campos-Martin JM, Fierro JLG (2003) Appl Catal A: Gen 246:69
12. Tatsumi T, Koyano KA, Shimizu Y (2000) Appl Catal A: Gen 200:125
13. Srinivas D, Manikandan P, Laha SC, Kumar R, Ratnasamy P (2003) J Catal 217:160
14. Bonino F, Damin A, Ricchiardi G, Ricci M, Spano G, D'Aloisio R, Zecchina A, Lamberti C, Prestipino C, Bordiga S (2004) J Phys Chem B 108:3573
15. Wang Y, Chen Q, Yang W, Xie Z, Xu W, Huang D (2003) Appl Catal A: Gen 250:25
16. Prasetyoko D, Ramli Z, Endud S, Nur H (2004) In: Proc. 2nd Annual Fundamental Science Seminar, 207
17. Meijers S, Gielgens L, Ponec V (1995) J Catal 156:147
18. Lucas A, Valverde JL, Rodriguez L, Sanchez P, Garcia MT (2001) Appl Catal A: Gen 171:195
19. Martin C, Malet P, Solana G, Rives V (1998) J Phys Chem B 102:2759
20. Gutiérrez-Alejandre A, Castillo P, Ramýrez J, Ramis G, Busca G (2001) Appl Catal A: Gen 216:181
21. Macht J, Baertsch CD, May-Lozano M, Soled SL, Wang Y, Iglesia E (2004) J Catal 227:479
22. Mamede AS, Payen E, Grange P, Poncelet G, Ion A, Alifanti M, Pârvulescu VI (2004) J Catal 223:1