

Reactivity of Titanium-Based Porous Catalysts for the Epoxidation of Camphene to Epoxide

Zainab Ramli¹ and Siti Aminah Setu @ Sabtu²

¹Ibnu Sina Institute for Fundamental Science Studies,
Universiti Teknologi Malaysia, 81310 UTM, Skudai, Johor D.T
e- mail: zainab@kimia.fs.utm.my

²Dept. of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Skudai, Johor D.T.

Abstract : Titanium-based microporous and mesoporous catalysts with variation of pore sizes were evaluated as heterogeneous epoxidation catalysts in this study. The microporous titanium silicalite-1 (TS-1) and titanium ferrierite (Ti-FER) as well as mesoporous titanium-ITQ6 (Ti-ITQ6) and titanium-MCM41 (Ti-MCM41) were prepared and tested in the epoxidation of camphene using aqueous hydrogen peroxide as oxidant. All catalysts were characterized by X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) spectroscopy techniques. The advantage of the mesoporosity of Ti-ITQ6 and Ti-MCM41 were displayed in the epoxidation of camphene compared to microporous TS-1 which displayed no activity for the camphene epoxidation. On the other hand microporous Ti-FER showed some activity for the epoxidation of camphene, owing to the presence of tetrahedral Ti on the outer surface layer of the Ti-FER crystal.

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Introduction

Epoxidation of olefinic compounds over Ti based catalysts and H₂O₂ as oxidant has gained considerable interest recently. Two types of Ti-based catalysts have been extensively investigated: Ti-substituted zeolites and Ti-mesoporous materials [1]. Titanium silicalite-1 (TS-1) [2,3] molecular-sieves has been widely research because of its interesting catalytic properties in many oxidation reactions [4-6]. However its activity and selectivity is restricted to the oxidation of relatively small organic molecules due to diffusion limitations and size exclusion effects. An obvious limitation is its pore size of 5.6 x 5.3 Å, limiting its catalytic potential only to linear hydrocarbons or monofunctionalized benzene derivatives [7]. In contrast, MCM-41 [8,9] possesses uniformly sized mesopores. However, this material does not show short-range order and has closer resemble to amorphous material compared to zeolite [10].

In view of this, a new type of mesopores titanium-containing molecular sieve, titanium-ITQ6 (Ti-ITQ6) will be studied. A new mesoporous zeolitic material Ti-ITQ6 has been obtained by the direct synthesis of a layered titanosilicate precursor, followed by delamination process [11]. A significant difference, however, between the delaminated zeolites and the mesoporous MCM-41 and SBA-type materials is that the former have short-range order owing to the zeolitic nature of the layers, and are thus

more stable thermally and hydrothermally[12]. Titanium is tetrahedrally coordinated in framework positions and, while the zeolite derived from the precursor has little activity owing to geometrical constraints, the delaminated Ti-ITQ6 material is more active and selective, similar to those of Ti-beta for the epoxidation of olefins with H₂O₂ [11].

The present study aims at evaluating the reactivity of the Ti-based catalysts based on its porosity in the epoxidation of bulky molecules. Thus, the synthesis of mesoporous Ti-ITQ6 for oxidation reaction of bulkier substance will be covered in this research. For comparative purposes, mesoporous siliceous Ti-MCM41, microporous titanium silicalite, TS-1 and titanium ferrierite, Ti-FER types of zeolite have also been studied. The catalysts prepared were characterized using XRD and FTIR spectroscopy. The activity and selectivity of the catalysts have been tested in the oxidation of bulky olefin, camphene [7].

Experimental

Catalyst Preparation and Characterization

Siliceous Ti-PREFER was first synthesized by using direct hydrothermal method according to the procedure described by Corma *et al.* [11]. The Ti-ITQ6 sample was prepared by swelling the laminar precursor of Ti-PREFER based on procedures described by Concepción *et al.* [12]. The Ti-PREFER material was suspended in an aqueous solution of

cetyltrimethylammonium bromide (CTABr) (2.0 g) and tetrapropylammonium hydroxide (TPAOH) (10.0 g) and followed by refluxing for 16 h at 95°C. Delamination was performed by placing the slurry in an ultrasound bath for 1 h, and then reducing the pH to below 2. Finally, the solid phase was washed thoroughly with water, dried at 100°C, and calcined at 580°C for 7 h yielding Ti-ITQ6. Microporous Ti-FER was prepared by direct calcination of a portion of Ti-PREFER at 580°C.

Siliceous Ti-MCM41 was prepared by using direct hydrothermal method [13,14]. Two different solutions were prepared. For solution A, tetraethylorthotitanate (TEOT) (0.4 g) in isopropanol (10 mL) and tetraethylorthosilicate (TEOS) (11.9 g) were mixed at 35°C followed by cooling to 0°C. Solution B was prepared by mixing tetramethylammonium hydroxide (TMAOH) (4.0 g), distilled water (62.7 g), and CTABr (21.0 g), followed by cooled to 0°C. Solution B was added to the solution A at 0°C and then heated between 80 – 90°C for 4 h. Water was then added and the resulting gel was placed in a PTFE bottle which was then further heated at 98°C in an oven for 3 days. Finally, the solid was filtered and washed using hot water, dried at 110°C overnight and calcined at 500°C for 16 h.

TS-1 was synthesized according to a procedure described previously [15]. TEOS (66.9 g) and TEOT (0.8 g) in isopropanol (10 ml), were mixed at 35°C followed by cooling to 0°C. TPAOH (120 g) was slowly added into the mixture followed by heating in the temperature range 80 – 90°C for 4 h. Then, the gel formed was then autoclaved at 175°C under static condition for 4 days. Finally the solid was centrifuged, washed with distilled water, dried at 100°C overnight and calcined at 550°C for 16 h.

Characterization of the catalysts

Characterization using XRD for identification of the crystalline phases of the samples was done using a Bruker Advance D8 Diffractometer with the Cu K α ($\lambda = 1.5405 \text{ \AA}$) scanned in the 2θ range of 2 - 40° for Ti-PREFER as well as every sample after each treatment. The framework spectra were recorded in the region of 1400-400 cm^{-1} using a Perkin Elmer FTIR, employing the KBr pelleting method.

Catalytic testing

In order to investigate the effect of pore sizes on the catalytic performances, the prepared titanium

catalysts, Ti-ITQ6, Ti-FER, Ti-MCM41, and TS1 were tested for the epoxidation of camphene using hydrogen peroxide as oxidant. The reaction mixture containing camphene (10 mmol), H_2O_2 (10 mmol), 0.1 g catalyst and acetonitrile (10 g) as solvent were refluxed at 70°C with continuous stirring for 24 h. The aliquots were analyzed with GC-FID using Ultra 1 (methyl siloxane, 25 m length x 0.2 mm internal diameter) capillary column and the identification of the products was confirmed using GC-MSD spectroscopy.

Results and Discussion

Characterization of Catalysts

The phase crystallinity and structure of the prepared samples were characterized by XRD. The XRD pattern of the starting laminar material, Ti-PREFER and Ti-ITQ6 as well as Ti-MCM41 and TS-1 samples are shown in Figure 1.

The XRD pattern of Ti-PREFER shows a sharp peak at 2θ 6.7° indicating that the sample has a very high crystalline structure. Practically, the XRD pattern of both Ti-PREFER and Ti-FER samples are similar, showing high crystallinity. However, the sharp peak at d_{200} of Ti-PREFER was shifted from 2θ 6.7° to 2θ 9.5° in Ti-FER indicating decreased in interlayer spacing, forming 3-dimensional FER type material. Ti-FER has been characterized before as microporous solid [16]. On the other hand, XRD pattern of Ti-ITQ6 sample shows broader and less intense peaks indicating that the material has changed to the amorphous phase. In this case the highly crystalline framework of Ti-PREFER has collapsed due to the delamination process.

The XRD pattern of Ti-MCM41 shows 3 diffraction lines at 2θ 2.223°, 3.818° and 4.00° with different intensities. The pattern has been assigned to a hexagonal lattice which confirmed the framework of the Ti-MCM41 [14]. The most intense peak relative to the d_{100} plane is usually taken to indicate the degree of crystallinity [15] or how ordered is the synthesized Ti-MCM41. Thus the intense d_{100} peak indicates that the Ti-MCM41 is a highly ordered mesoporous material. The XRD diffractogram of TS-1 shows the highest peak at 2θ 7.9° which has similar XRD pattern characteristic of MFI structure type of zeolite [17].

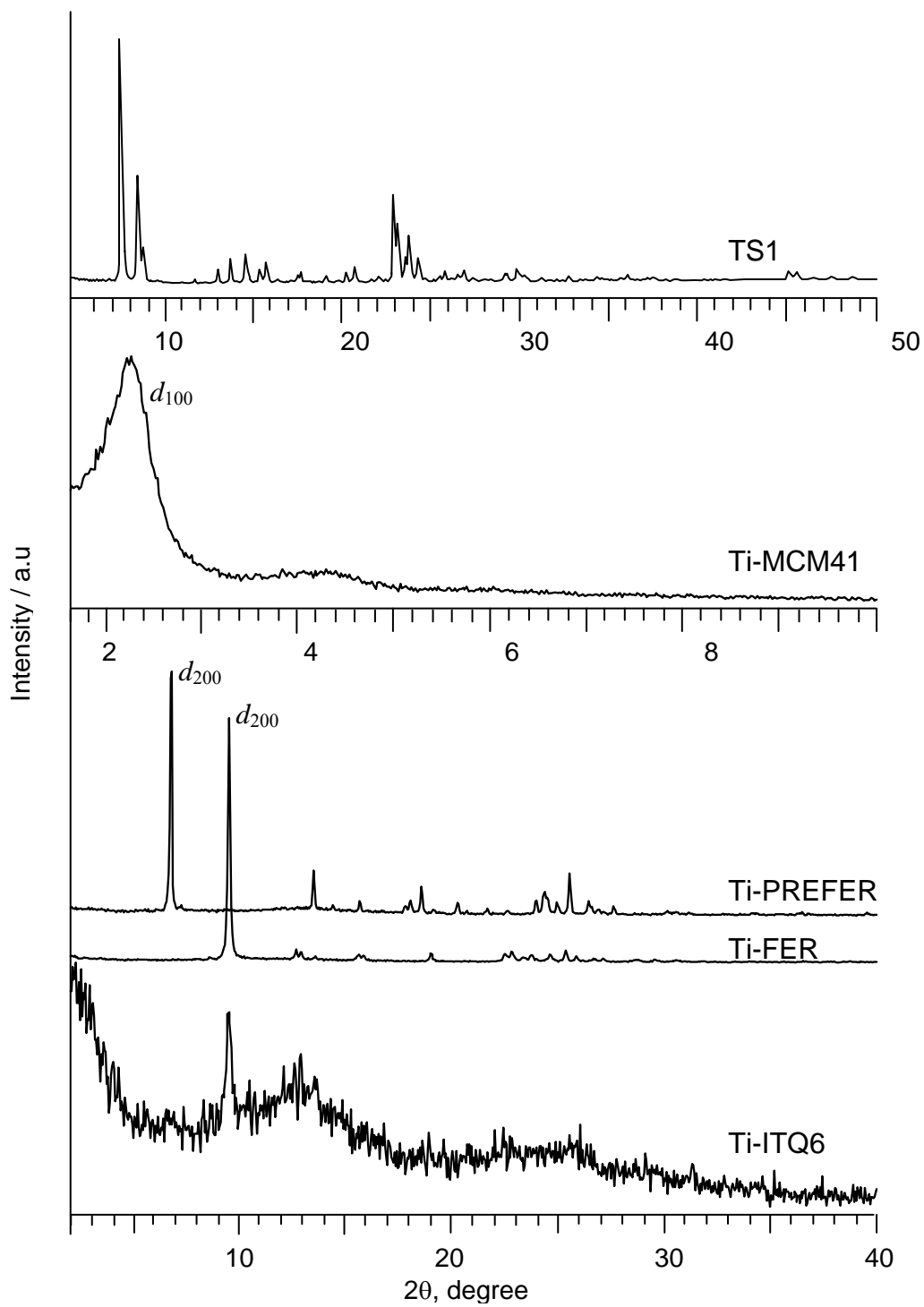


Figure 1 : XRD diffractogram of the samples

FTIR characterization technique is conducted to identify the presence of specific bonding or the functional groups in the samples. The infrared spectra of the samples in the lattice vibration region between 1400 and 400 cm^{-1} are depicted in Figure 2. The infrared spectra of Ti-PREFER and Ti-ITQ6 display bands at 1080, 960, 800, and 460 cm^{-1} , almost similar to that of Ti-MCM41 sample. The vibration band at 1070 cm^{-1} is assigned to Si-O-Si asymmetric stretching vibration, 800 cm^{-1} for the Si-O-Si symmetric stretching vibration and the peak at 450 cm^{-1} is assigned to Si-O-Si bending. The band at *ca.*

610 cm^{-1} is assigned to the double ring vibration of the zeolite framework which exists in Ti-PREFER and Ti-FER. This band is sensitive to the structure changes and disappeared in Ti-ITQ6 sample indicating that it has lost its double-ring structure due to the delamination process. TS-1 sample shows five peaks at *ca.* 1230, 1100, 800, 550 and 450 cm^{-1} , characteristic of MFI type of zeolites [16]. A small band at *ca.* 970 cm^{-1} assigned to titanium ions in the tetrahedral coordination is clearly visible in all the spectra except for Ti-FER sample.

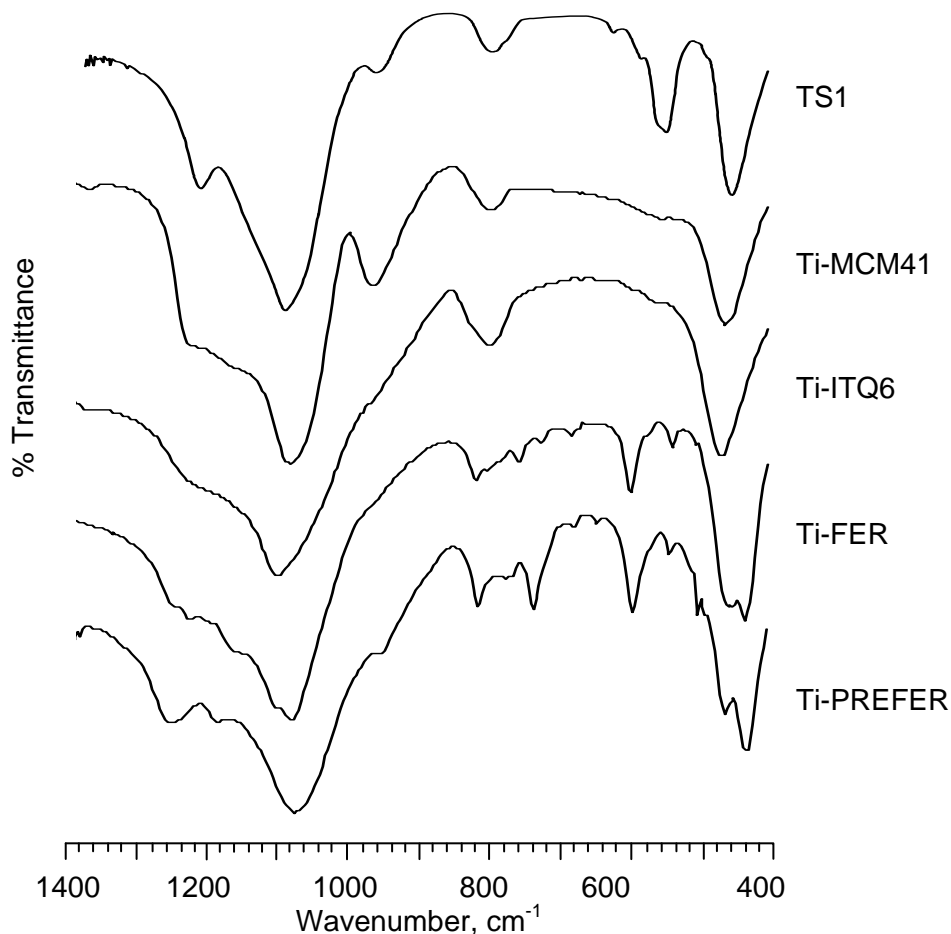


Figure 2: FTIR spectra of the samples.

Catalytic Activity

Catalyst performance was investigated for the epoxidation of camphene. Figure 3 shows general reaction of the oxidation of camphene and Figure 4 shows camphene oxidation reaction catalyzed by the Ti-ITQ6, Ti-FER, Ti-MCM41 and TS-1 samples. All samples showed activity towards the formation of products, i.e. camphene oxide, 3-camphenilanol and 3-camphenilanol.

The control reaction that has been carried out in the absence of catalyst at the same condition showed

very low conversion without any selectivity towards camphene oxide as the desired product. The camphene oxide is produced in the presence of Ti arranged in the tetrahedral form. The reactivity of mesoporous Ti-ITQ6 and Ti-MCM41 were found almost similar with the conversion of about 25%.but higher than microporous Ti-FER which gave 20%. In general, this conversion indicates that both catalysts are fairly active for the reaction and might due to the lack of active sites especially for the Ti-ITQ6.

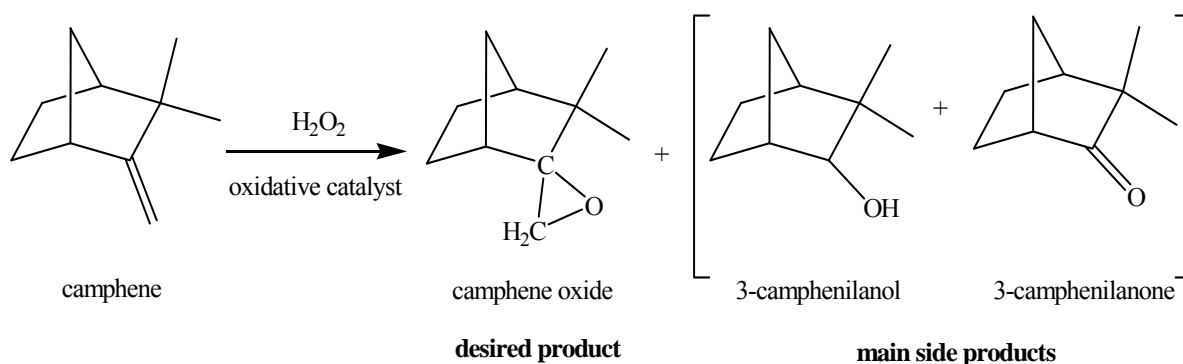


Figure 3: The oxidation reaction of camphene using H_2O_2 oxidant and its products

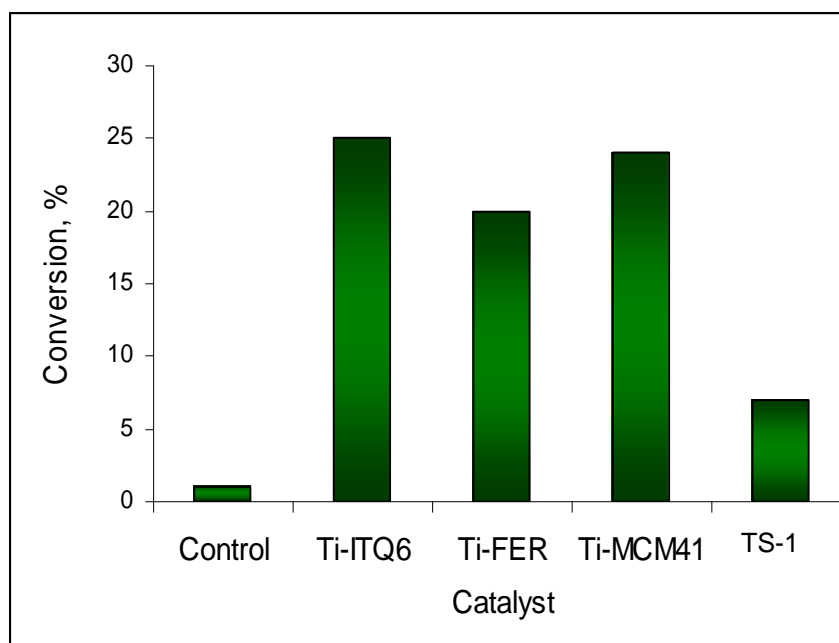


Figure 4: Catalytic activity of each sample in oxidation of camphene.

The selectivity of the products catalyzed by each sample is presented in Figure 5. Only Ti-ITQ6, Ti-MCM41 and Ti-FER produced camphene oxide indicating that they contain active tetrahedral-Ti sites. Ti-ITQ6 and Ti-FER showed lower selectivity for camphene oxide which are 26 and 20% respectively as compared to Ti-MCM41 (34%). In principle, one would expect that if some tetrahedral Ti were expelled from the framework structure and agglomerates, producing small TiO_2 crystallites which usually in the octahedral form and not active for epoxidation, this should be reflected in a decrease in the catalytic activity for the formation of camphene oxide. From the XRD pattern in Figure 1, it showed that Ti-ITQ6 has an amorphous-like structure, suggesting that Ti-ITQ6 has less amount of tetrahedral Ti as a result of the delamination process of Ti-PREFER. However the production of camphene oxide by Ti-ITQ6 proved that an appreciable amount of tetrahedral Ti is still present even though the structure is amorphous.

Ti-MCM41 is active in the epoxidation but its activity and selectivity are low considering the highly ordered mesoporous material displayed by the XRD pattern. This presumably may be due to the relatively hydrophobic interior of M41S-type materials or to inaccessibility of titanium sites due to its incorporation inside the silica walls [7]. However the selectivity of camphene oxide is the highest among

the catalysts used suggesting that the number of active sites containing tetrahedral Ti is the highest.

One would expect that less camphene oxides would be produced from reaction catalysed by microporous Ti-FER based on its crystalline phase of the sample and its microporous property which hinders the bulky molecules from entering the pore to the active sites inside the pores. However the amount of camphene oxide produced was just slightly less than what had been obtained by Ti-ITQ6. This suggests that it has more or less similar amount of active sites situated at defect sites on the surface of the crystal. Since the Ti-FER is obtained from the calcined Ti-PREFER it has different phase from ferrierite (FER), suggesting that the distribution of Ti in Ti-PREFER are more on the outer layers of the crystal. Calcination process results in the formation of defect sites with the active sites on the outer surface of the crystal which are accessible by camphene.

In contrast, no camphene oxide was produced from microporous TS-1. Apparently all the active sites in TS-1 are located inside the pores which render it inactive in the epoxidation of camphene. The bulky camphene is too large to enter the channels of the zeolite. It also shows that TS-1 has a negligible outer surface activity.

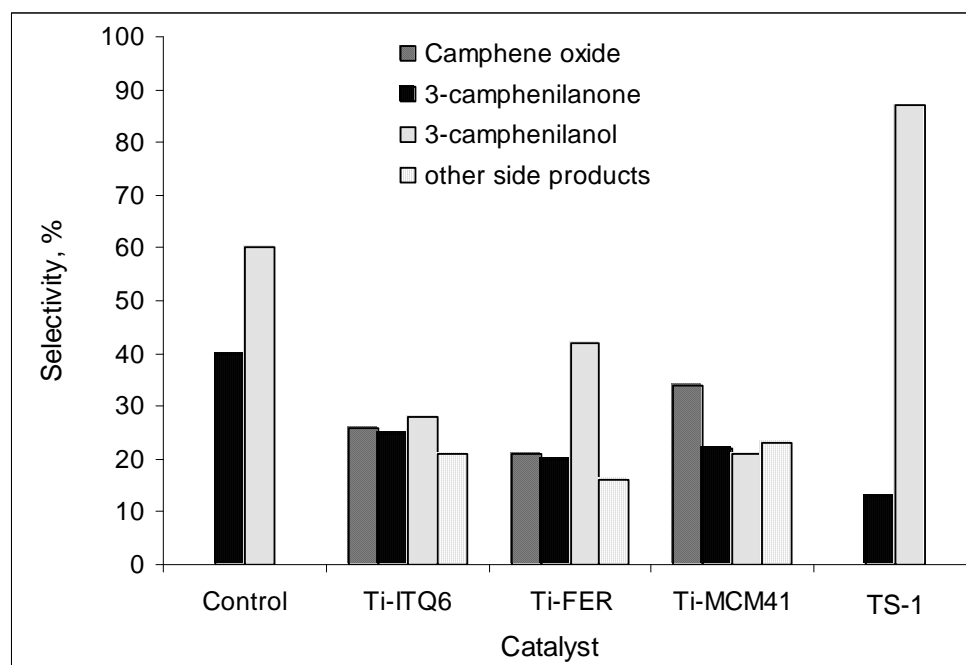


Figure 5 : Product selectivity from the oxidation reaction of camphene catalyzed by each sample.

In addition, the low selectivity for camphene oxide shown by the catalysts was also due to the presence of impurities such as water molecule or acid in the reaction mixture giving side products; ketone and alcohol. The water molecule which has been produced in this oxidation reaction can react further with the reactant to produce more side products. Thus, there is competition between the formations of epoxide with other side products.

Conclusions

All mesoporous Ti-based catalysts produced, Ti-ITQ6 and Ti-MCM6 are active for the epoxidation of camphene where bulky camphene can get access to the active sites while microporosity in TS-1 hinders it inactive. Mesoporous Ti-ITQ6 has been synthesized by delamination of layered precursor Ti-PREFER. Ti-ITQ6 is active in the oxidation of camphene to epoxide, thus proved the presence of tetrahedral Ti form in the framework even though the structure has collapsed during the delamination process.

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