

Catalytic Efficiency of Titanium Dioxide (TiO₂) and Zeolite ZSM-5 Catalysts in the *in-situ* Epoxidation of Palm Olein

M Z Mohd Yunus, S K Jamaludin*, S F Abd. Karim, A Abd. Gani and A Sauki

¹ Faculty of Chemical Engineering, Universiti Teknologi MARA, 40450 Shah Alam, Selangor, MALAYSIA

sitikhatijah@uitm.edu.my

Abstract. Titanium dioxide and zeolite ZSM-5 are the commonly used heterogeneous catalysts in many chemical reactions. They have several advantages such as low cost and environmental friendly. In this study, titanium dioxide and zeolite ZSM-5 act as catalyst in the *in-situ* epoxidation of palm olein. Epoxidation of palm olein was carried out by using *in-situ* generated performic acid to produce epoxidized palm olein in a semi-batch reactor at different temperatures (45°C and 60°C) and agitation speed of 400 rpm. The effects of both catalysts are studied to compare their efficiency in catalyzing the *in-situ* epoxidation. Epoxidized palm olein was analyzed by using percent of relative conversion to oxirane (RCO%) and fourier transform infrared spectroscopy (FTIR). Surface area of the catalysts used were then characterized by using BET. The results indicated that titanium dioxide is a better catalyst in the *in-situ* epoxidation of palm olein since it provides higher RCO% compared to Zeolite ZSM-5 at 45°C.

1. Introduction

Palm olein is a type of vegetable oil that is obtained from fractionation of palm oil. It consists of 53.5% unsaturated fatty acid and 46.5% saturated fatty acid, with iodine value ranging from 55.6 to 61.9 [1]. Since palm olein contains unsaturated fatty acid, it can be chemically adjusted to value added products by epoxidation process. Epoxidation can be defined as the conversion of unsaturated carbon-carbon double bond into an epoxide which is a cyclic ether with three atom ring [2]. The common process of epoxidation is by reacting performic acid with the unsaturated oil, also known as peracid epoxidation. According to Campanella et al. [3], this process can be conducted by reacting the unsaturated bond of the vegetable oils with formic acid, which acts as the oxygen carrier and hydrogen peroxide that acts as oxygen donor. Formic acid is more favored in most reactions due to its high reactivity. Figure 1 and figure 2 illustrate the reaction between formic acid and hydrogen peroxide to form performic acid and reaction of performic acid with unsaturation in fatty acid to form epoxide, respectively.

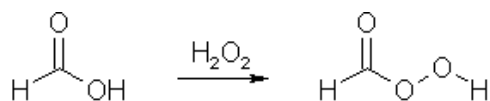


Figure 1. Reaction between formic acid and hydrogen peroxide to form performic acid.

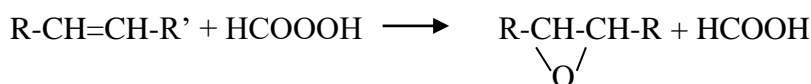


Figure 2. Reaction between performic acid and unsaturated fatty acid to form epoxide.

Epoxide has been used as an intermediate for organic synthesis of various chemicals such as alcohols, glycols, olefinic compounds, lubricants, plasticizer and stabilizer for polymers due to high oxirane reactivity [4]. Besides that, epoxides that obtained from the renewable raw materials and from their alkyl esters have many usages in daily life such as plasticizers and polymer stabilizers [5]. The catalysts used in this study are titanium dioxide (TiO_2) and zeolite ZSM-5. Both catalysts are heterogeneous which basically have many advantages since it is easy to separate by filtering the product and the catalyst can be recovered again in the manufacturing process. Titanium dioxide or TiO_2 basically is a pure white pigment that occurs naturally as crystal and has been applied widely since the surface properties of the rutile has many benefits and become ideal model system in the science of metal oxides [6]. Zeolite Socony Mobil-5 (ZSM-5) also has many applications in recent years. Zeolite ZSM-5 which is made up of various crystalline structures has large open pores in a very regular arrangement since it is composed by many pentasil units linked together to form a chain. Its ability to catalyze organic reactions under solvent-free conditions is one of its attractiveness, among many others [7].

In this study, the effects of temperatures and catalyst types on the epoxidation of palm olein were investigated. Characterization of both catalysts was also done with the intention to investigate the catalyst that performs better in catalyzing the reaction. Here, the characterization of catalyst basically refers to the surface area of the catalyst.

2. Methodology

2.1. Materials

Palm olein used in this study was obtained from a local refined palm olein manufacturing company in Malaysia. Formic acid (CHOOH , 98% purity) and hydrogen peroxide (H_2O_2 , 30 w/w % solution) were used as oxygen carrier and oxygen donor respectively in epoxidation and were purchased from Merck Sdn Bhd. All materials were used as obtained without further purification. Hydrobromic acid (0.1N in acetic acid) was used for titration method to determine epoxy content. TiO_2 and Zeolite ZSM-5 catalysts were purchased from Merck Sdn Bhd.

2.2. Epoxidation of palm olein

The reaction was carried out at two different temperatures (45°C and 60°C) to investigate the effects of different temperatures on epoxidation. The molar ratio of hydrogen peroxide to formic acid to unsaturation in palm olein (H_2O_2 : HCOOH : $\text{C} = \text{C}$) remained constant at 1:1:1. The first set of epoxidation was carried out at temperature 45°C and agitation speed of 400 rpm. The reaction was then carried out at three different conditions; no catalyst, which acts as control variable, 1 g of TiO_2 added and 1 g of zeolite ZSM-5 added. The reaction started with 100 g of palm olein and formic acid loaded into 250 mL reactor equipped with mechanical agitator that was used to ensure homogeneity of the reactor content. After about 30 minutes palm olein acidified with formic acid, hydrogen peroxide was added at the flow rate of 2 ml/s to accomplish the reaction.

2.3. Analytical procedure

The sample was retrieved every 3 minutes to determine the oxirane (epoxide) oxygen content which then was used for the calculation of relative conversion of double bond to oxirane, RCO%. The experimental oxygen oxirane content (OOC_{exp}) value in the epoxidized palm olein was determined by direct titration using hydrobromic acid solution in glacial acetic acid, according to AOCS Tentative Method Cd 9-57 [8], as in equation (1):

$$\text{OOC}_{\text{exp}} (\%) = 1.6 \times x (V-B) / W \quad (1)$$

where N is the normality of HBr, V is the volume of HBr solution used for blank (in mL), B is the volume of HBr solution used for titration (in mL) and W is the weight of sample (in gram). The iodine value (IV) of palm olein used, which indicates the degree of unsaturation in the palm olein was calculated based on AOCS Standard Method Cd 1d-92, as in equation (2):

$$IV (g I_2 / 100g \text{ sample}) = (B-S) \times N \times 12.69 / \text{mass of palm olein} \quad (2)$$

where B is the volume of titrant for blank run (in mL), S is the volume of titrant for sample (in mL) and N is the normality of sodium thiosulfate. The iodine value then applied to calculate theoretical oxirane oxygen content (OO_{theo}) [9], as in equation (3):

$$OO_{theo} = (IV_{oA} / 2A_I) / (250 + (IV_{oA} / 2A_I) A_o) \times A_o \times 100 \quad (3)$$

where IV_o is initial iodine value, A_o is the molar mass of oxygen and A_I is the molar mass of iodine. Then, the percentage of relative conversion to oxirane is calculated using equation (4):

$$RCO\% = OO_{exp} / OO_{theo} \times 100\% \quad (4)$$

Thereafter, the sample was analyzed using FTIR to determine the presence of oxirane ring in the epoxidized oil.

2.4. FTIR spectroscopy analysis

The sample was observed by using Fourier Transform Infrared Spectroscopy to examine the change in functional group before and after the reaction. The typical infrared spectrum of functional groups corresponding to their absorption range is shown in table 1 [10]:

Table 1. Characteristic absorption for functional group based on FTIR analysis.

Functional group	Characteristic Absorption (cm^{-1})
Alcohol	3200-3600
Carbon-carbon double bond	1620-1680
Carboxylic acid	1670-1820
Epoxy / oxirane ring	1210-1320

3. Results and discussion

To study epoxidation of palm olein, series of reactions were conducted by using *in situ* method which is reaction of the palm olein with the performic acid. This reaction samples were analyzed by several methods such as oxirane oxygen content (OOC), percent of relative conversion to oxirane (RCO%), and Fourier Transform IR (FTIR). Since the study was conducted to investigate the efficiency of the catalyst used (TiO_2 and Zeolite ZSM-5), the activities of the different catalyst were compared in the epoxidation of palm olein.

3.1. Effect of temperatures

Epoxidation was conducted at 45°C and 60°C, at 400 rpm agitation speed. Based on figure 3, the maximum yield of epoxidized palm olein obtained was 5.55% as indicated by the highest percentage of RCO% point at 10 min reaction time when the reaction was conducted at 45°C. On the other hand, the highest percentage of RCO% obtained was 2.22% at 60°C.

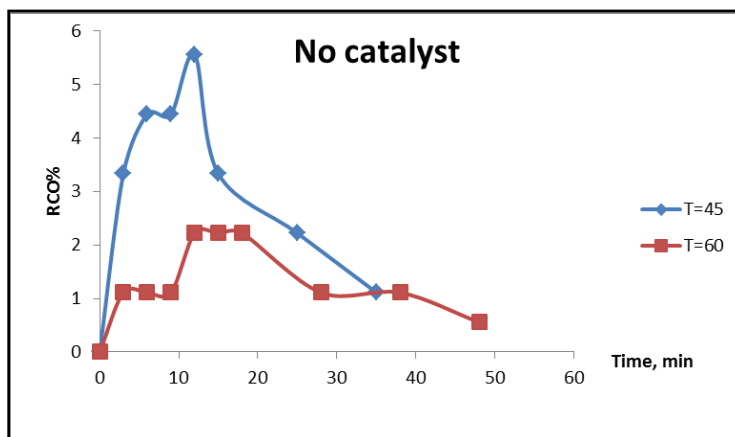


Figure 3. Conversion (RCO%) and the rate of epoxidation of palm olein for non-catalytic epoxidation.

The value of RCO% at 45°C was observed to be higher than at 60°C. This could be due to fact that at high temperatures, epoxidation occurred but was partially hydroxylized through oxirane cleavage, resulting in lower epoxy content [11]. Since the reaction has possibility for side reactions such as oxirane cleavage, epoxidation basically needs to be carried out at lower temperature. However, different temperatures lead to different results when different catalysts were used. This can be shown in figure 4 and figure 5 where the effect of temperatures on the reaction with different types of catalyst basically influences the RCO% of epoxidized palm olein.

As shown in figure 4, the value of RCO% in epoxidation at 45°C basically increase earlier as compared to 60°C but reach the maximum value only at 3.33%, less than if the reaction were carried out at 60°C. This shows that Zeolite ZSM-5 provides better stability at lower temperature but less conversion if compared to the epoxidation at higher temperature. This is because the content of aluminum in Zeolite ZSM-5 helps to lower the activation energy of the reaction, resulting in higher RCO% at 60°C compared to 45°C [12]. However, the RCO% decreased rapidly from peak value at 60°C due to the degradation of epoxy ring, as compared to the rate of epoxy ring degradation at 45°C which is much slower, leading to better ring stability as exhibited at around 7-18 minutes reaction time.

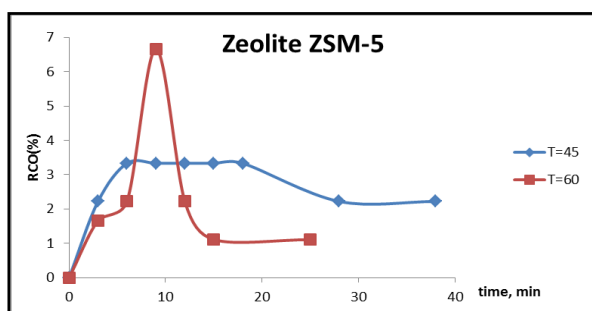


Figure 4. Conversion (RCO%) and the rate of epoxidation of palm olein with zeolite ZSM-5 as catalyst.

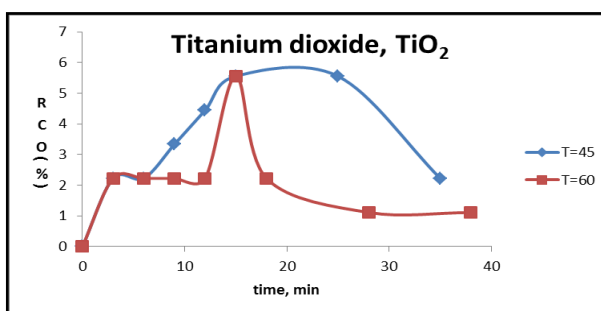


Figure 5. Conversion (RCO%) and the rate of epoxidation of palm olein with TiO₂ as catalyst.

In contrast to Zeolite ZSM-5, the value of RCO% for epoxidation using TiO₂ as catalyst is higher at 45°C which is about 5.55%, as illustrated in figure 5. Moreover, TiO₂ provides higher stability of oxirane ring at 45°C. According to Kim [13] who had carried out the epoxidation of methyl oleate with Ti-SiO₂, the conversion of the reaction increases when the temperature increased but then the selectivity decreases.

3.2. Effect of catalyst

To investigate the effect of heterogeneous catalyst on the epoxidation, different catalyst has been used and was conducted at different temperatures (45°C and 60°C). The types of catalyst varied are zeolite

ZSM-5 and titanium dioxide (TiO_2) while no catalyst acted as controlled variable. Figure 6 and figure 7 show the effect of different catalysts in the epoxidation at 45°C and 60°C.

Based on figure 6, both catalysts show the ability to achieve the epoxy ring stability at 45°C, as indicated by longer duration of peak conversion maintained before ring degradation started to take place (from 7 to 18 minutes reaction time for zeolite ZSM-5 and from 12 to 25 minutes reaction time for TiO_2). However, TiO_2 contributes to higher RCO% compared to Zeolite ZSM-5. This is because the content of titanium in TiO_2 influences the activity of the catalyst in epoxidation. This statement is supported by the research from Kim [13], which stated that the main factor that influences the catalytic activity is the catalyst framework or its structure. However, the result was different when the temperature was increased to 60°C, as illustrated in figure 7.

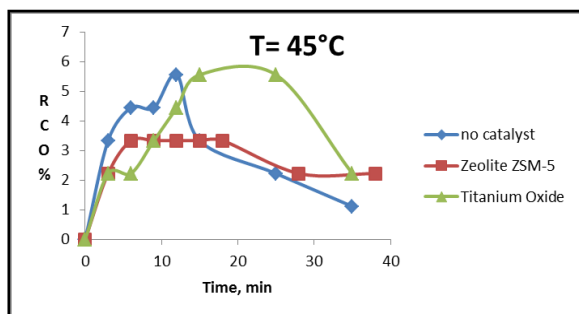


Figure 6. Effect of catalyst on the epoxidation at 45°C.

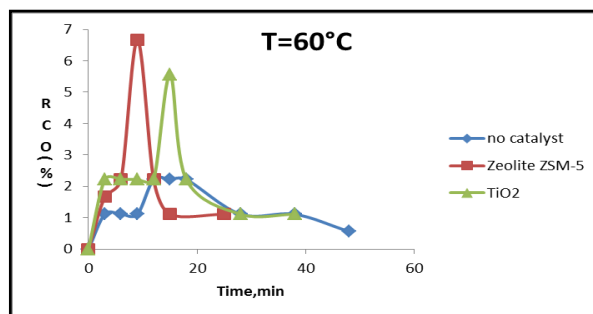


Figure 7. Effect of catalyst on the epoxidation at 60°C.

The effect of catalyst was different when the temperature increases. In figure 7, Zeolite ZSM-5 shows the highest percentage of RCO% compared to TiO_2 and the system without catalyst. Therefore, it can be concluded that Zeolite ZSM-5 catalyst is more efficient when the temperature is high. Besides that, the BET surface area of Zeolite ZSM-5 is larger than TiO_2 as shown in figure 9, thus providing more active sites for the reaction. However, the stability of epoxy ring decreases when the temperature increased, leading to ring opening. This was evidenced by the sharp drop of RCO% once the conversion reached the highest value.

3.3. FTIR of epoxidized palm olein

At the end of the reaction, the product sample was analyzed by using Fourier Transform Infrared Spectroscopy (FTIR) to examine the presence of oxirane group in the epoxidized palm olein. FTIR spectrum of epoxidized palm olein is shown in figure 8.

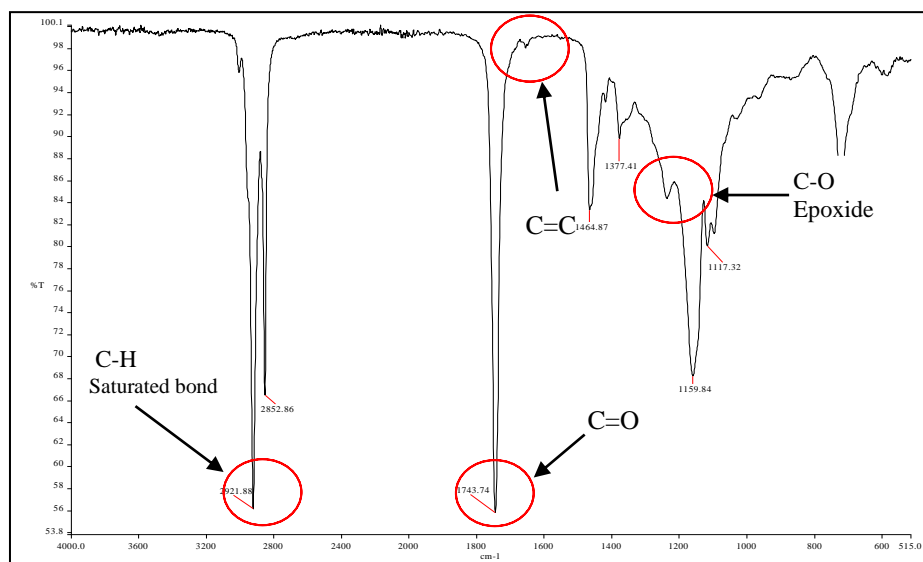


Figure 8. FTIR Spectrum of epoxidized palm olein.

The presence of epoxidized palm olein can be observed according to the absorption band signal as labeled in figure 8 (C-H saturated bond at 2921.88 cm^{-1} , C=O at 1743.74 cm^{-1} and epoxide bond C-O at 1210 cm^{-1}). The observation of epoxide signal band confirms the formation of oxirane ring in the epoxidized palm olein.

3.4. Characterization of catalyst

Zeolite ZSM-5 and TiO_2 were prepared into two different sample bottles and was characterized by using nitrogen adsorption analysis to determine the parameter such as pore volume (V_p) and the BET surface area (A_{BET}). BET surface area of the prepared catalyst was compared in figure 9, which indicates different nitrogen adsorption isotherm for the catalysts.

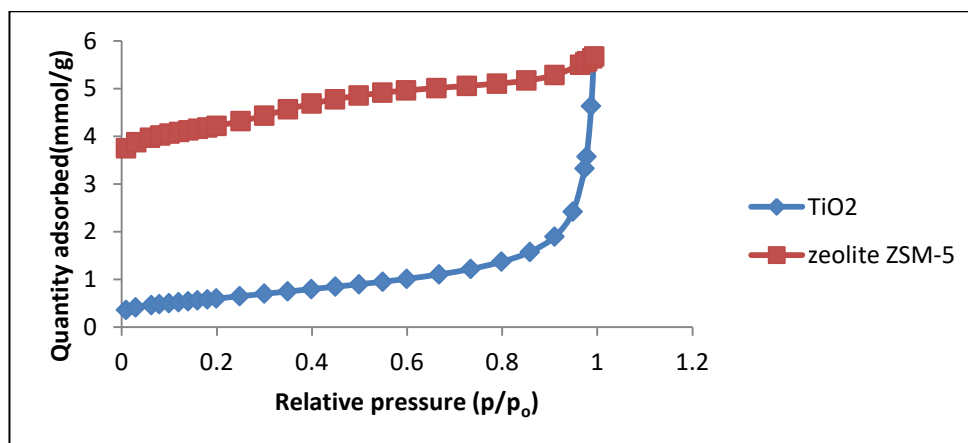


Figure 9. Nitrogen adsorption isotherm for the catalysts.

Table 2. Summary of BET surface area A_{BET} and pore volume (V_p) of the catalysts.

Sample	A_{BET} (m^2/g)	V_p (cm^3/g)
TiO_2	48.8972	0.12343
Zeolite ZSM-5	355.7150	0.15782

Based on table 2, it was observed that BET surface area and the pore volume of zeolite ZSM-5 was larger than TiO_2 . This characteristic indicates that zeolite ZSM-5 catalyst provides more active sites for the epoxidation process which leads to higher conversion of the reaction. Wu et al. [14] provided similar result according to the BET surface area of TiO_2 and zeolite where TiO_2 supported by zeolite provide large BET surface area ($542.51\text{ m}^2/\text{g}$) if compare to TiO_2 ($4.1952\text{ m}^2/\text{g}$).

4. Conclusion

The efficiency of catalysts was determined based on the percentage of RCO in the epoxidation of palm olein. It can be concluded that TiO_2 has better performance in catalyzing the epoxidation since it is able provide higher oxirane content compared to zeolite ZSM-5 at 45°C . It shows the catalyst is preferable since the reaction should be carried out at lower temperature to avoid oxirane ring opening. Zeolite ZSM-5 has the best performance at higher temperature (60°C). However, the main factors that indicate the better catalyst is the catalyst's ability to provide high conversion and better epoxy ring stability in the epoxidation simultaneously at lower temperature. Therefore, TiO_2 was chosen as the best catalyst since it provides highest percentage of RCO (5.55%) and also epoxy ring stability at longer time when conducted at low temperature (45°C).

Acknowledgments

The authors would like to thank the Ministry of Education Malaysia for the financial support via Research Acculturation Grant Scheme (RAGS) (600-RMI/RAGS 5/3 (67/2015). The authors would like to thank the Faculty of Chemical Engineering, Universiti Teknologi MARA Shah Alam, Selangor for the use of services and facilities in conducting the research leading to this paper.

References

- [1] Gunstone F D 2002 *Vegetable Oils in Food Technology : Composition, Properties and Uses* (Oxford: Blackwell Publishing)
- [2] Padmasiri K G, Michael O and Laleen K 2009 Epoxidation of some vegetable oils and their hydrolysed products with peroxyformic acid - optimised to industrial scale *J. Natn. Sci. Foundation Sri Lanka* **37(4)** 229
- [3] Campanella A, Fontanini C and Baltanas M 2008 High yield epoxidation of fatty acid methyl esters with performic acid generated in situ *Chem. Eng. J.* **144(3)** 466
- [4] Flávia de A C, Felipe K S, Leandro S M M, Selma G F L, Rodrigo O M A D S and Ivana C R L 2012 Epoxidation of oleic acid catalyzed by PSCI-Amano lipase optimized by experimental design *Journal of Molecular Catalysis B: Enzymatic* **81** 7
- [5] Luis R, David E and Fernando C 2013. Hydroxylation of vegetable oils using acidic resins as catalysts. *Industrial Crops and Products* **43** 183
- [6] Diebold U 2003 Structure and properties of TiO₂ surfaces: A brief review *Appl. Phys. A* **76** 681
- [7] Massah A R, Kalbasi R J, Khalifesoltani M and Kordesofla F M 2013 ZSM-5-SO₃H: An efficient catalyst for acylation of sulfonamides amines, alcohols, and phenols under solvent-free conditions *ISRN Organic Chemistry* **2013** Article ID 951749
- [8] American Oil Chemists' Society 1963 *Tentative Method of Oxirane Oxygen: AOCS Cd 9-57* (Illinois)
- [9] Petrovic Z S, Zlatanovic A, Lava C C and Sinadinovic-Fiser S 2002 Epoxidation of soybean oil in toluene with peroxyacetic and peroxyformic acids - kinetics and side reactions *Eur. J. Lipid Sci. Technol.* **104** 293
- [10] Noorfazlida M, Mohd J J, Siti K J and Ahmad R M D 2014 Formation of dihydroxystearic acid from hydrolysis of palm kernel oil-based epoxidized oleic acid. *J. Appl. Sci. & Agric.* **9(11)** 86
- [11] Kim N 2014 Epoxidation and di-hydroxylation of camelina sativa oil *K-State Research Exchange (K-Rex)* Kansas State University Electronic Theses 1-74
- [12] Choudary V R and Pataskar S G 1986 Thermal decomposition of TPA-ZSM-5 zeolites: effect of gas atmosphere and Si/Al ratio *Thermochimica Acta* **97** 1-10
- [13] Kim K 2012 Epoxidation of vegetable oils using the heterogeneous catalysis, amorphous Ti-SiO₂ *RWTH Publications* RWTH Aachen University Electronic Theses 1-113
- [14] Wu L P, Li X J, Yuan Z H and Yong C 2009 The fabrication of TiO₂-supported zeolite with core/shell heterostructure for ethanol dehydration to ethylene *Catalysis Communications* **11** 67-70