CHAPTETER VII

STYRENE OXIDATION WITH H_2O_2 OVER Fe- AND Ti-SBA-1 MESOPOROUS SILICA

7.1 Abstract

The catalytic activity of M-SBA-1 (M = Fe and Ti) synthesized using silatrane as precursor was studied in the liquid phase oxidation of styrene using hydrogen peroxide as oxidant. The influence of various reaction parameters, viz. reaction temperature and time-on-stream, affecting the activity and selectivity of styrene were studied. At 80°C, the selectivity of benzaldehye and styrene oxide reached 74 and 11%, respectively, at styrene conversion of 67% over 4%Fe in SBA-1 while those of styrene oxide and benzaldehyde reached 48 and 50%, respectively, at styrene conversion of 69% over 2%Ti in SBA-1.

7.2 Introduction

Since the incorporation of transition-metal ions in the silica framework may improve the catalytic performance of SBA-1 support, many researchers have tried to introduce transition-metal into the silica framework of SBA-1 [1-3]. In recent years, metal ion-incorporated SBA-1, such as Fe^{3+} and Ti^{4+}, has attracted much attention as oxidation catalyst [4-6], especially, tri-substituted molecular sieves displaying the redox catalytic activities [6-8]. These successful studies show that incorporation of transition metal ions into the framework of the porous materials is a capable method for the designable preparation of the novel catalysts [9].

Styrene epoxidation is of interest in both academic and commercial fields for the synthesis of two important products, styrene oxide and benzaldehyde, in the presence of hydrogen peroxide [8-11]. The use of hydrogen peroxide for oxidizing organic substrates generates various types of products, depending on the catalyst and reaction conditions used [7]. The aim of our study is thus to investigate the oxidation of styrene in the presence of hydrogen peroxide over Fe- and Ti-SBA-1. The influences of the catalyst, as well as of the reaction parameters, on the catalytic activity and the product selectivity in the styrene oxidation are investigated.

7.3 Experimental

7.3.1 Materials

Fumed silica (SiO_2, 99.8%) (Sigma-Aldrich), titanium dioxide (TiO_2) (Carlo Erba), triethanolamine (TEA) (Carlo Erba), tetraethylenetriamine (TETA) (FACAI, Thailand), ethylene glycol (J.T. Baker, USA), acetronitrile (Labscan, Asia), ferric chloride ($FeCl_3$) (Sigma-Aldrich), hexadodecyltrimethylammonium bromide (C_{16}TMAB) (Sigma-Aldrich), H_2SO_4 (Labscan, Asia) and NaOH (Labscan, Asia) were used without treatment. Styrene monomer (Labscan, Asia) and hydrogen peroxide (H_2O_2, aqueous 30%) (Ajax Finechem) were used for catalytic activity.

7.3.2 Preparation of mesoporous M-SBA-1 (M = Fe^{3+}, Ti^{4+})

7.3.2.1 Sol-Gel Process

Metal incorporated SBA-1 was performed as follow; solution A was prepared by adding C_{16}TMAB (0.44g) to water (30 ml) and stirring for 0.5 h to obtain a clear solution. Solution B was prepared by dissolving silatrane (5 mmol, 1.4g), synthesized following the procedure described in references [10], in 14 ml of 0.3 M H_2SO_4 and NaOH (1.7 mmol, 0.068g) by stirring for 0.5 h. The required amount of metal precursor (titanium glycolate synthesized according to reference [11] and $FeCl_3$) was added to solution B and stirring continued for 0.5 h and then added to the solution A under vigorous stirring that continued for 4 h. Added the water (30 ml) to this mixture before aging for 2 days at ambient temperature to form a white precipitate. The product was filtered, washed with distilled water, and dried at room temperature overnight. The template was removed by calcination (560°C / 6 h) in a Carbolite Furnace (CFS 1200) at a heating rate of 0.5°C/min.

7.3.2.2 Incipient Wetness Impregnation Method

Incipient wetness impregnation was used to incorporate metal (M = Fe^{3+}, Ti^{4+}) onto the SBA-1 support, synthesized following the procedure described in reference [14], using 2 and 4 wt% titanium glycolate and $FeCl_3$ precursor, respectively. The precursor was dissolved in water and dropped onto the catalyst supports, SBA-1. Evaporation of water was carried out at 100°C in the oven for 12 hr, followed by calcination (600°C/5 h) in a Carbolite Furnace (CFS 1200) at a heating rate of 10°C/min.

7.3.3 Catalytic Reaction

The epoxidation of styrene is carried out in a 50 ml glass flask to be heated with an oil bath. In a typical run, styrene (1.04 g, 10 mmol), an aqueous 30% H_2O_2 (1.14 g, 10 mmol), were mixed in 10 ml of CH_3CN. The catalyst (50 mg) was added in the reaction and heated at 80°C with continuous stirring. During the reaction, the products were analyzed (by withdrawing small aliquots after specific interval of time) using a gas chromatography (GC) equipped with a capillary column (DB-WAX, 30 Mx0.25 mm) and a FID detector.

7.4 Results and Discussion

7.4.1 Catalyst characterization

Surface areas, pore volumes, and pore sizes of all samples are summarized in Table 7.1. N_2 adsorption-desorption isotherms (Fig. 7.1) of all M-SBA-1 samples showed type IV adsorption isotherms, indicating the mesopore characteristic, with a narrow pore size distribution. These results are in good agreement with our previous study [14].

XRD patterns of M-SBA-1 (Fig. 7.2) display three well resolved diffraction peaks in the region of $2\theta = 1.5\text{-}3°$, indexed as {200}, {210}, and {211} reflections with respect to a cubic lattice [15]. Diffuse reflectance UV-visible spectra of these samples are shown in Fig. 7.3. The Fe-SBA-1 showed a strong UV band at ~230 nm associated with a shoulder at 290 nm consistent with Laporte-allowed ligand-to-metal charge transfer, involving isolated $Fe^{3+}O_4$ co-ordination [4]. A characteristic band above 320 nm typical of octahedral co-ordination ($Fe^{3+}O_6$) was absent; indicate that these materials are free of ferric oxide species similar to those found in iron hydroxide, iron oxyhydroxide and iron oxide [16-19]. The Ti-SBA-1 samples show an absorption band centered at 220 nm, being characteristic of the charge-transfer transition associated with regular $Ti^{4+}O_4$ framework tetrahedra. Octahedral co-ordination ($Ti^{4+}O_6$) as the distinctive feature at 330 nm is missing [6-8]. All the above characterizations clearly indicate that the metals are incorporated into the silica framework of SBA-1.

7.4.2 Catalytic activity of M-SBA-1 in the styrene epoxidation

Oxidation of styrene, catalyzed by Ti-and Fe-SBA-1, uses H_2O_2 as an oxidant given two main products, benzaldehyde and styrene oxide, in the reaction with small amount of styrene glycol and benzoic acid. The catalytic results for the epoxidation of styrene over Ti- and Fe-SBA-1 with different metal contents are presented in Fig. 7.4.

The reaction without the metal loaded occurs at a very low rate. The main product was benzaldehyde, resulted from a nucleophilic attack of H_2O_2 to styrene oxide, followed by a cleavage of the intermediate hydroxy-hydroperoxystyrene, and also from a cleavage of the C=C bond [8]. Using the Ti- and Fe incorporated SBA-1 catalysts; the conversion of the styrene is sharply increased. This indicates that the metal species in the framework of SBA-1 is the activated site for the oxidation reaction [5, 6]. It is noticeable that Ti-SBA-1 catalyst performs better than Fe-SBA-1 catalyst under the same reaction conditions. It can be revealed that Ti^{4+} in the framework is more active than Fe^{3+} for the oxidation of styrene. As can be seen that when increasing the Ti content up to 2 wt%, the conversion of styrene was increased at a maximum value of 69 ± 1 % and the selectivity of benzaldehyde and styrene oxide were 50% and 48%, respectively. These results were consistent with those reported by Ji and coworkers [6], using commercial precursors and large head group of template under strongly acidic condition to prepare Ti-SBA-1, and showing that the styrene conversion and the selectivity for desired epoxide increased with increasing Ti content (0.9-2.5 wt%). At titanium loading of 2 wt%, it exhibited a maximum value of the styrene conversion at 45.1% and epoxidation selectivity at 40%. Comparing to our study of Ti-SBA-1, synthesized using a small head group of template and home-made metal alkoxide precursors, under much milder acidic condition, less amount of the catalyst is needed to provide higher conversion (2 wt% Ti). It is worth noticing that the catalyst with 2 wt% Ti synthesized by Ji and coworkers showed the XRD result with distorted pattern, indicating some collapse of the SBA-1 structure. This might be a reason why their styrene conversion and the epoxidation selectivity were less. Ti-SBA-1 at 2 wt% Ti content synthesized by impregnation was also studied to compare with the catalyst synthesized via the sol-gel process, and it was found that the conversion of styrene is at 59% and selectivity of benzaldehyde and styrene oxide is at 54 and 29%, respectively. It can be concluded that, for the epoxidation of styrene, Ti^{4+} incorporated inside the framework is more active than outside the framework.

In case of Fe-SBA-1, the increased in Fe content up to 4 wt% increases the conversion of styrene at a maximum value of 67 ± 1 % with the selectivity of benzaldehyde and styrene oxide at 74 and 11%, respectively. When the Fe content exceeded 4 wt%, the conversion of styrene rather slightly decreased. As compared to Fe impregnated SBA-1 at 4 wt%, the conversion of styrene reached 65% with the selectivity of benzaldehyde and styrene oxide at 67 and 14%, respectively. The result demonstrates that the metal active sites incorporated inside the framework of SBA-1 probably account for the epoxidation of styrene with hydrogen peroxide [19]. In the earlier report, Thitsartarn and coworkers studied styrene epoxidation over one-dimensional mesoporous Fe-MCM-41 [20], and showed that the selectivity of styrene oxide reached 65% at a styrene conversion of 22% over 1% loaded Fe. Comparing to our three-dimensional mesoporous Fe-SBA-1, relatively higher conversion was obtained over our catalyst. A possible reason is that the cubic structure of three-dimensional mesopore of SBA-1 is more favorable for diffusion of reactant. As mentioned earlier that the conversion of styrene over the neat SBA-1 is very low, indicating that Fe^{3+} incorporated inside the framework is indeed the active site for epoxidation of styrene. This result is in accordance with the conclusion that the tetrahedrally coordinated and atomically isolated iron sites were responsible for the oxidation of styrene [6, 19].

Figure 7.5 demonstrates the styrene conversion as a function of reaction time at 80°C reaction temperature. When the reaction time is fixed at 4 h, using 2 wt% Fe catalyst, the styrene conversion is 66%, the selectivity of benzaldehyde and styrene oxide are 73, 11%, respectively, though the reaction time was further prolonged, the conversion of styrene and the selectivity of styrene oxide have slightly changed. However, this conversion is still higher than the one observed by Wang and coworkers [19].

At 2 h reaction time, 2 wt% Ti in Ti-SBA-1 catalyst provided the corresponding styrene conversion and the selectivity of benzaldehyde and styrene oxide of 69, 50 and 48%, respectively. The selectivity to styrene oxide decreases with the reaction time while that to benzaldehyde increases with a slightly increasing in other products. It could be attributed to secondary oxidation of the epoxide and the formation of benzaldehyde through the cleavage of the C=C bond [6, 8].

7.5 Conclusion

SBA-1 with the metals Ti^{4+} and Fe^{3+} incorporated into the framework were synthesized via the sol-gel method and also incipient wetness impregnation method. Both Fe- and Ti-SBA-1 catalysts show good activity and selectivity in the oxidation of styrene. The selectivity of benzaldehye and styrene oxide reached 74% and 11%, respectively, at the styrene conversion of 67% over 4 wt% Fe in SBA-1 while those of styrene oxide and benzaldehyde reached 48 and 50%, respectively, at the styrene conversion of 69% over 2% Ti in SBA-1. However, Ti-SBA-1 revealed better performance (both the activity and the selectivity) in the styrene conversion to styrene oxide. Moreover, when compared with the impregnated catalyst, the sol-gel synthesis catalyst showed better performance for the conversion of styrene.

7.6 Acknowledgements

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7.7 References

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Table 7.1 BET analysis of M-SBA-1 synthesized at different degree of loading

Material		Physical Properties			Crystallographic Properites	
Designation	Metal Doping (wt %)	BET Surface Area (m^2/g)	Pore Volume (cm^3/g)	Average Pore Diameter (nm)	d_{210} (nm)	a_0 (nm)
SBA-1	0	1435	0.75	2.12	3.62	8.09
Fe 2%	2	1164	0.61	2.11	3.65	8.16
Fe 4%	4	1175	0.61	2.11	3.68	8.23
Fe 6%	6	1062	0.54	2.10	3.71	8.30
Ti 2%	2	1101	0.57	2.07	3.77	8.43
Ti 4%	4	1029	0.56	2.17	3.80	8.51
Ti 6%	6	880	0.51	2.34	3.83	8.58

[a] Lattice parameters a_0 were calculated based on the formula $a_0 = \sqrt{5}d_{210}$

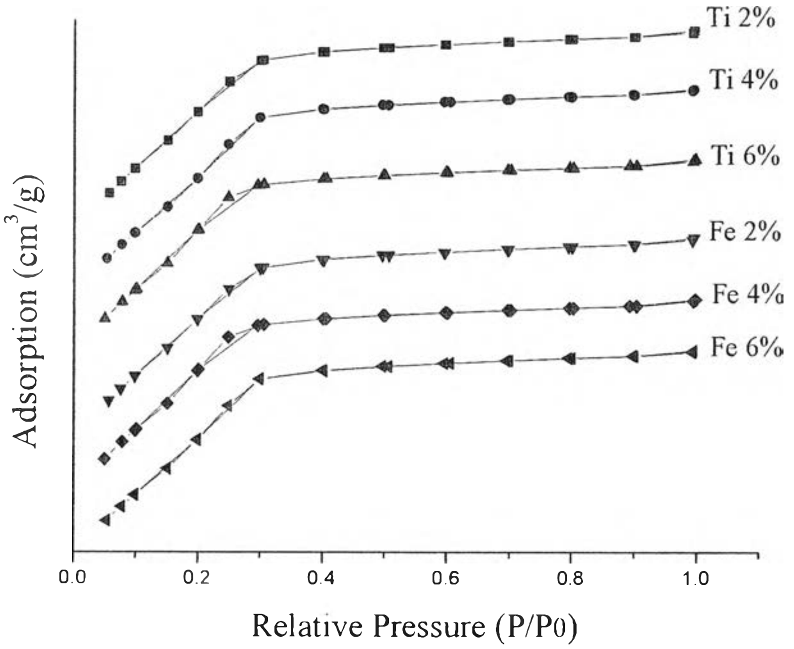

Figure 7.1 The nitrogen adsorption–desorption isotherms of the calcined FeSBA-1 and Ti-SBA-1 samples prepared at different degrees of loading.

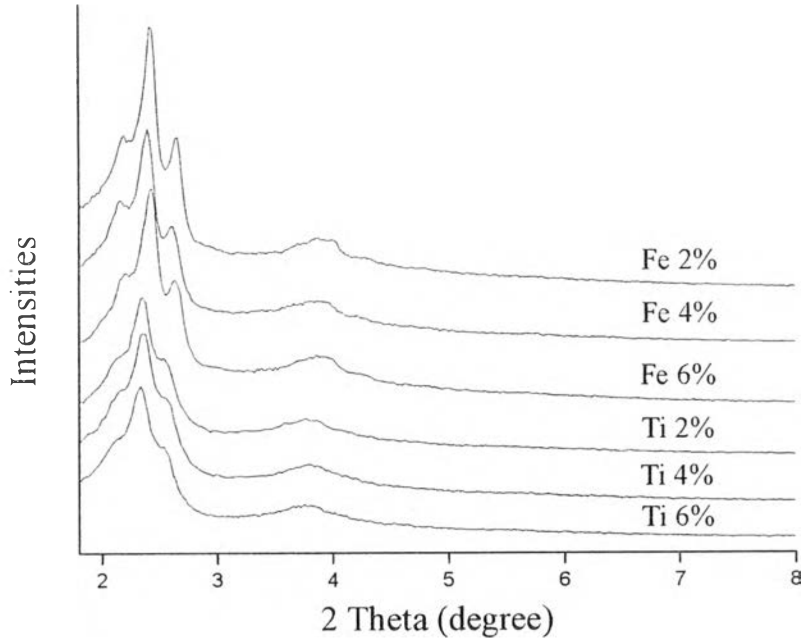

Figure 7.2 XRD patterns of the calcined FeSBA-1 samples (A) and TiSBA-1 samples (B) prepared at different degrees of loading.

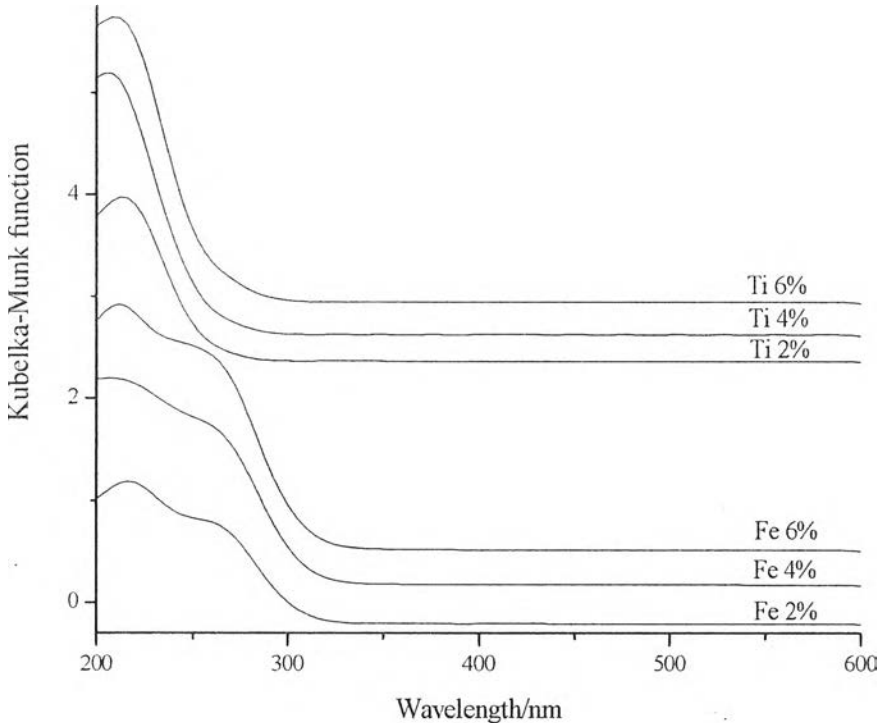

Figure 7.3 Diffuse reflectance UV-vis spectra of the calcined FeSBA-1 samples (A) and TiSBA-1 samples (B) prepared at different degrees of loading.

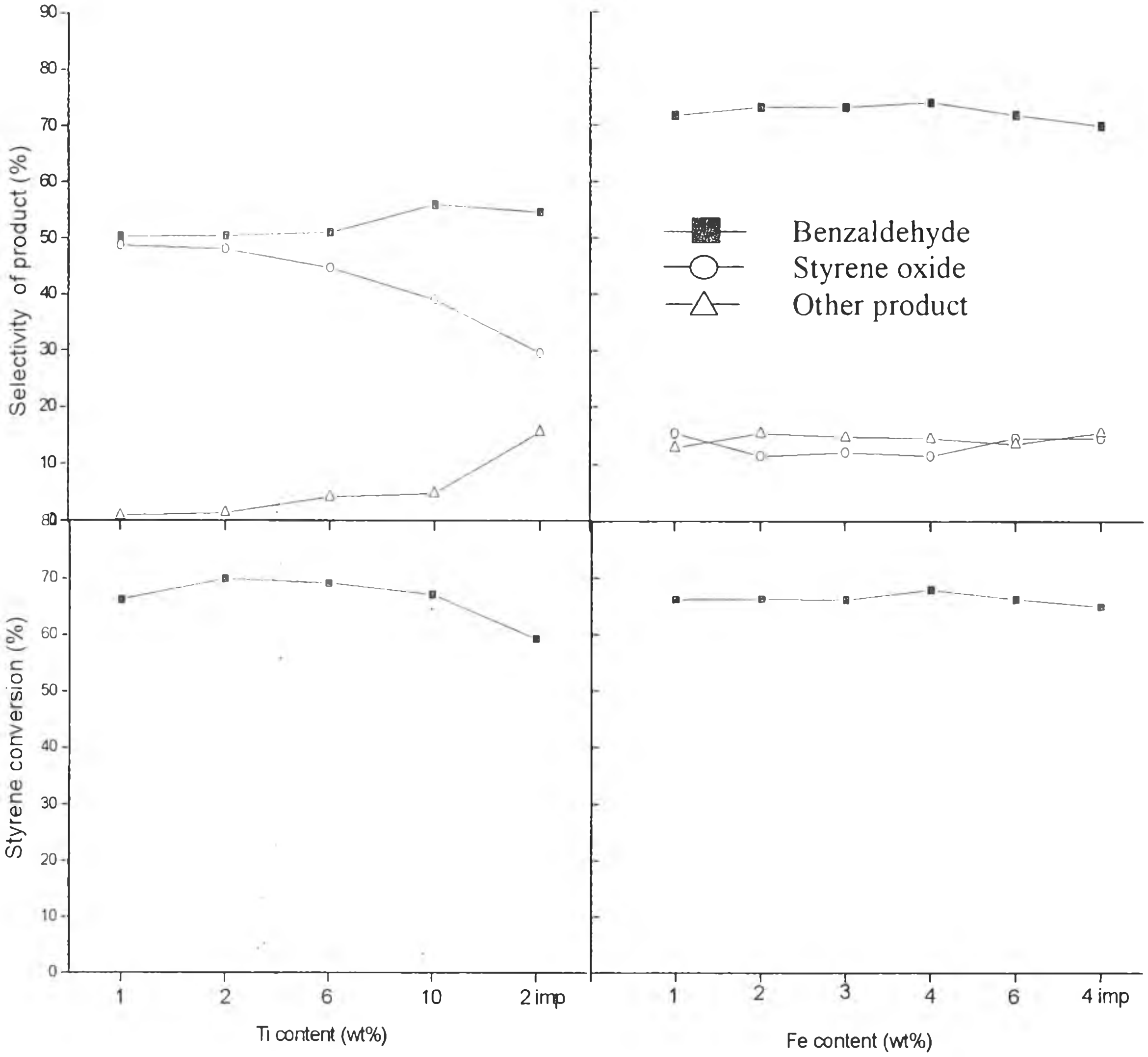

Figure 7.4 Effect of the metal content on epoxidation of styrene carried out at 80°C reaction temperature for 2 h (Ti-SBA-1) and 4 h (Fe-SBA-1) reaction time with 50 mg catalyst.

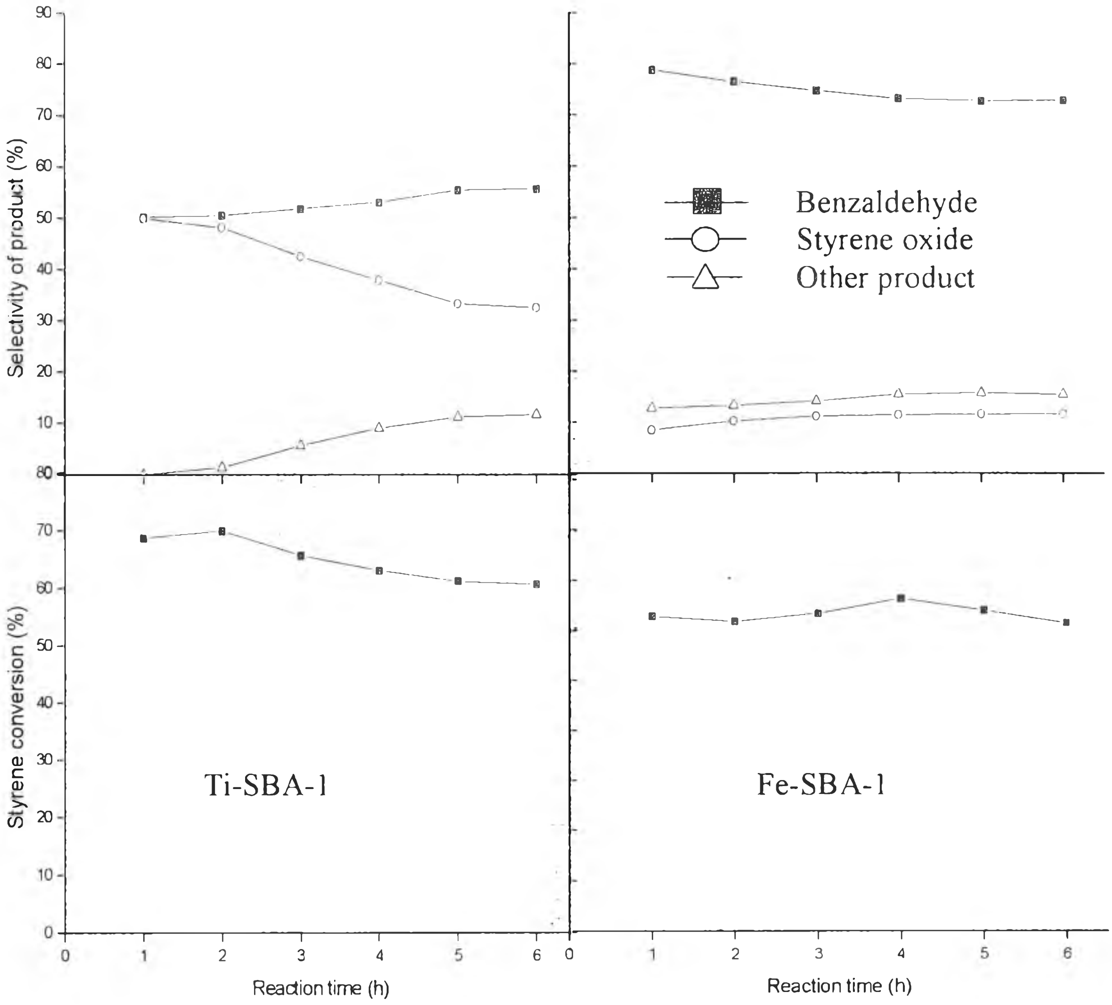

Figure 7.5 Effect of the reaction time on the epoxidation of styrene using 50 mg catalyst at 80°C reaction temperature.