CHAPTER V
RESULTS AND DISCUSSION

The results and discussion in this chapter are divided into two sections. In the first section, the catalyst characterization using AAS, BET, XRD, IR and SEM is described. Next, the catalytic hydroxylation reaction of benzene to phenol is discussed.

5.1 Catalyst characterization

5.1.1 Determination of composition content and BET surface area of the catalyst

The results of mole ratio of Si/Ti and BET surface area of TS-1, which were analyzed by atomic absorption spectroscopy (AAS) and BET surface area are summarized in Tables 5.1.

Table 5.1 The mole ratio of Si/Ti and BET surface area

Catalyst samples	Mole ratio of Si/Ti	BET surface area (m^2/g)[a]
TS-1	27	265

[a] Measurement error is $\pm 2\%$.

5.1.2 X-ray diffraction (XRD)

The X-ray diffraction is a technique which can identify the crystal structure. Figure 5.1 shows the XRD patterns of TS-1 zeolite. The XRD pattern indicated similarly six main peaks at 2θ as 8, 8.8, 14.8, 23.1, 24 and 26.7 from reference [The JCPDS (1996)] using CuKα radiation.
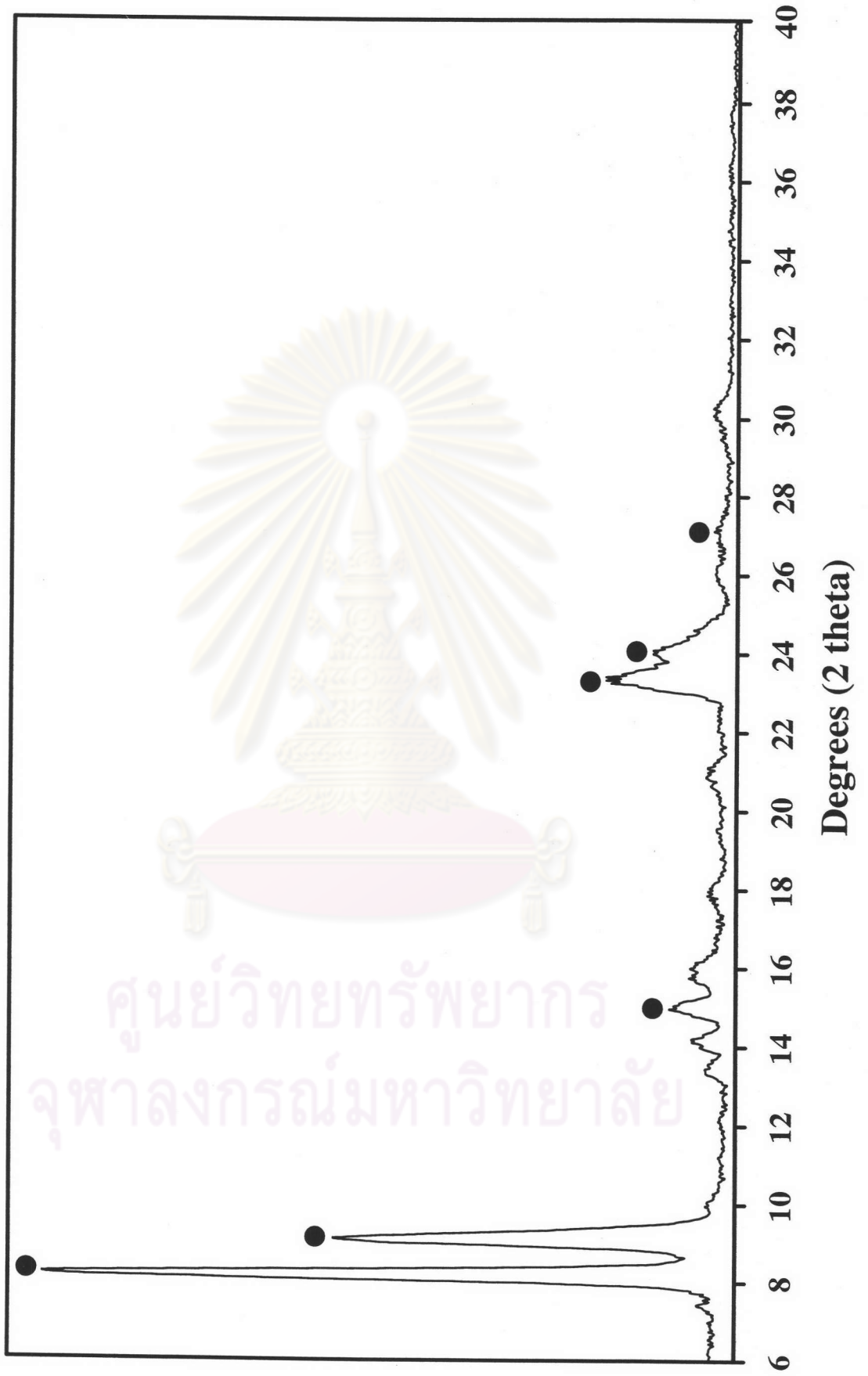
Figure 5.1 XRD spectra of the TS-1 zeolite

The pattern obtained is the pattern typical for a crystalline zeolite having a MFI structure. The result indicated that the catalyst contained well-defined single-phase XRD pattern and was consistent to those already reported for TS-1 (Taramasso *et al.*, 1983). Although the peaks were identified to that of TS-1, it showed less crystalline compared with TS-1 synthesized employing the recipe in the original patent. We believe that this difference strongly suggests that the methodology of catalyst preparation have an influence on the characteristic of TS-1 catalyst.

5.1.3 Fourier transform Infrared (FT-IR)

A comparative IR spectrometric study was performed to obtain information concerning the existence of framework titanium. It is well known that the vibrational spectrum of TS-1 is characterized by an absorption band in the 900–975 cm^{-1} region (Taramasso *et al.*, 1983). It has been suggested that the presence of a 960–975 cm^{-1} band is a necessary, but not sufficient, condition for catalytic activity (Huybrechts *et al.*, 1991). Thus, defective orthorhombic silicalites, with fully hydroxylated nanocavities generated by extraction of a few adjacent (SiO_4) units, have been characterized by an extra-broad IR absorption at *ca.* 970 cm^{-1} (Perego *et al.*, 1986) as shown in Figure 5.2.
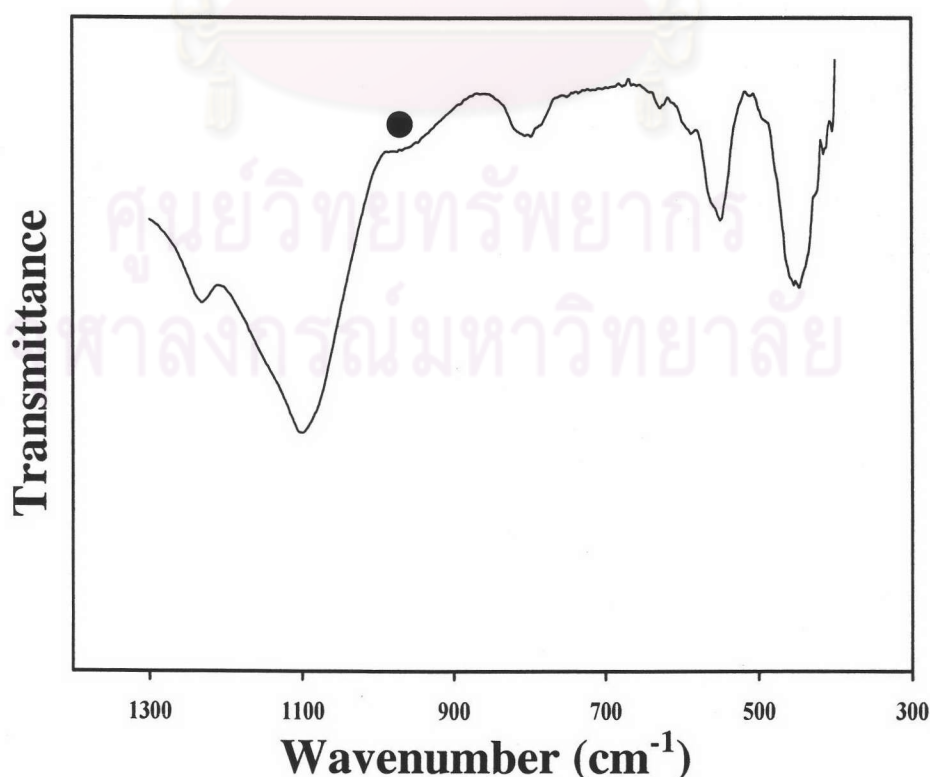

Figure 5.2 The IR spectra patterns of TS-1 catalysts

5.1.4 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is used to determine the catalyst granule morphology. Figure 5.3 displays scanning electron micrographs of TS-1. The crystalline morphology was nearly spherical sample. These particles were not neatly crystallized, the outer surface was covered with amorphous gel. It is suggested that this amorphous gel occurs during the catalyst preparation. It has an influence on the characteristic of TS-1 catalyst. The crystal sized is almost identical (≈ 5 μm).
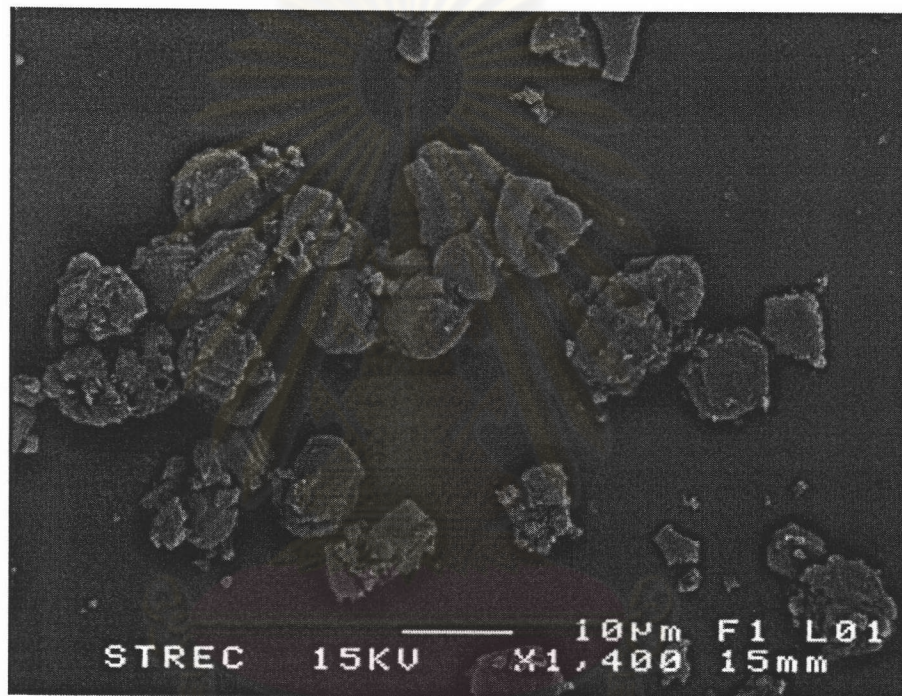

Figure 5.3 SEM micrograph of catalyst granule at the external surface at 1400x magnification.

5.2 Catalytic reaction

5.2.1 Performance comparison for co-current operation and periodic operation

Performance comparison experiments were conducted for the two cases of interest: (i) co-current operation, and (ii) periodic operation. Figure 5.4 shows the conversion profiles with time for co-current and periodic operation. The conversions for co-current operation nearly did not change with time. Both benzene and H_2O_2 solutions are allowed to flow homogeneously in the reactor for the co-current operation. Thus, H_2O_2 is the main surface species initially, benzene still have chance to competitively adsorb on the catalyst surface. Later, the surface will become saturated with H_2O_2 and the system approaches an equilibrium. The main product (phenol) is dissolved by the H_2O_2 at the same time. Thus, the catalytic may be unchanged.

In the case of periodic operation, both benzene and H_2O_2 were periodically introduced into the reactor. H_2O_2 was fed through the reactor to adsorb on the catalyst first and then following by the benzene vapor. Figure 5.4 shows that the periodic operation has higher benzene conversion than co-current operation. The performance enhancement (%) was about 30%. The calculation was shown below:

$$\text{Performance enhancement, } \% = \frac{\text{Conv.(US)-Conv.(SS)}}{\text{Conv.(SS)}} \times 100$$

where: Conv.(US) is conversion of benzene under periodic operation;
Conv.(SS) is conversion of benzene under co-current operation. (Khadilkar *et al.*, 1999)

The way commonly occurred under co-current operation in trickle beds was poor catalyst wetting, especially under low liquid flow rates. On-off liquid pulses were an alternative to steady liquid flow. Higher liquid flow pulses should improve external catalyst wetting since at higher liquid flow rates, external catalyst wetting was greater, as had been demonstrated (Stradiotto *et al.*, 1999).

It appears likely that at low liquid flows, co-current benzene conversions were lower than periodic ones because of the nonuniform distribution of liquid and thus in liquid-poor regions in bed. The wetting influences the hydroxylation rate. As a result, the gas reactant may be quite accessible to the catalyst, but without the second reactant presents on most of the surface, the net effect decreases reactor throughput. The importance of periodic addition of liquid reactant is to increase the efficiency of wetting, higher liquid flow pulses during the liquid cycle period, thereby increasing the benzene conversion.
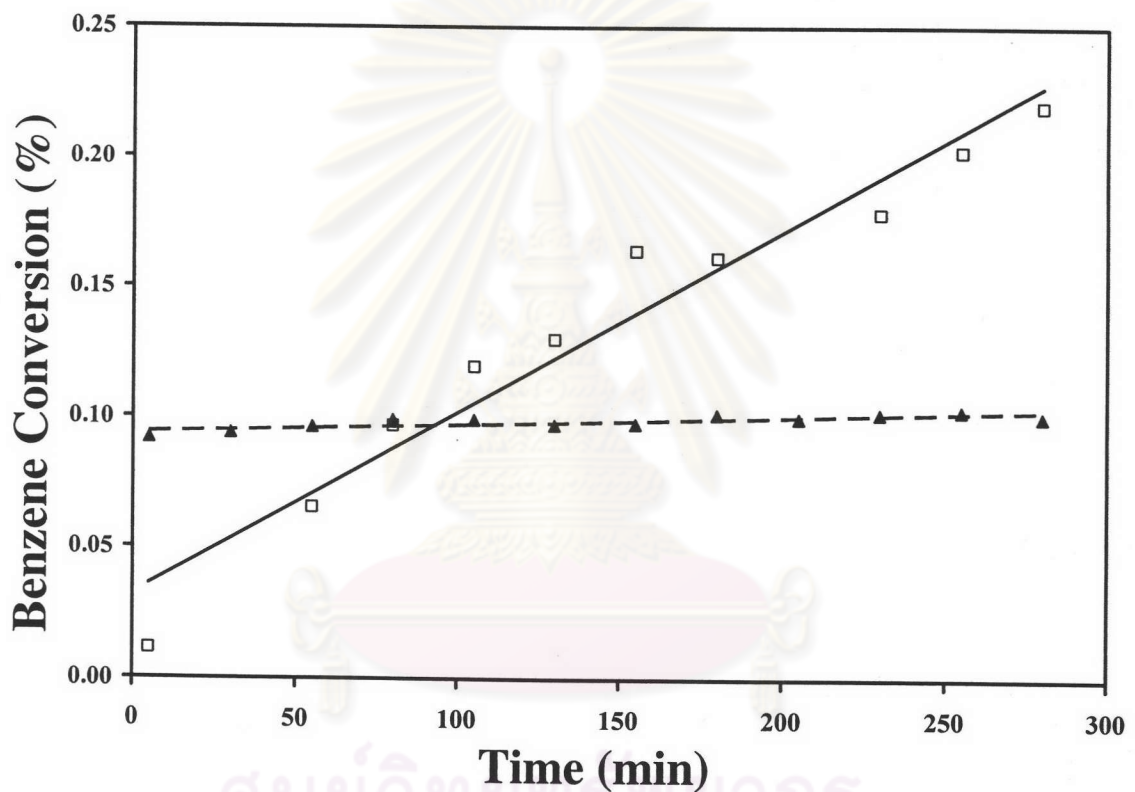

Figure 5.4 Comparison between co-current operation and periodic operation: ($\square$, —) co-current operation; ($\blacktriangle$,— — —) periodic operation with τ = 25 min and s = 0.8. Result under both operation were plotted at concentration of benzene = 2.38 mol/m^3, 1 g of the catalyst.

5.2.2 The effect of cycle period on periodic operation performance

This part, the cycle period was varied. For all cases, the period time of H_2O_2 cycle remained constant at 5 min, but the period time of benzene cycle was varied between 10 to 20 min. It can be observed from Figure 5.5 and Figure 5.6 that cycle period has an influence on benzene conversion. The longer cycle period, the higher conversion. This is suggested that the cycle period is longer, it means the reaction time is longer too. The H_2O_2 was fed through the reactor to adsorb on the catalyst first and then following by the benzene. Benzene will react with the H_2O_2 that adsorbs on catalyst surface to form the product during the cycle period of benzene. With longer reaction time, more phenol is formed on the catalyst surface (as shown in higher benzene conversion). H_2O_2 was fed in the liquid phase and benzene was fed as gas phase, thus it can be determined that H_2O_2 is excessively enough for benzene. It means that the gaseous benzene represents the rate limiting reactant as mention above that the H_2O_2 cycle period is constant at 5 min with flow rate 0.3 ml/min.
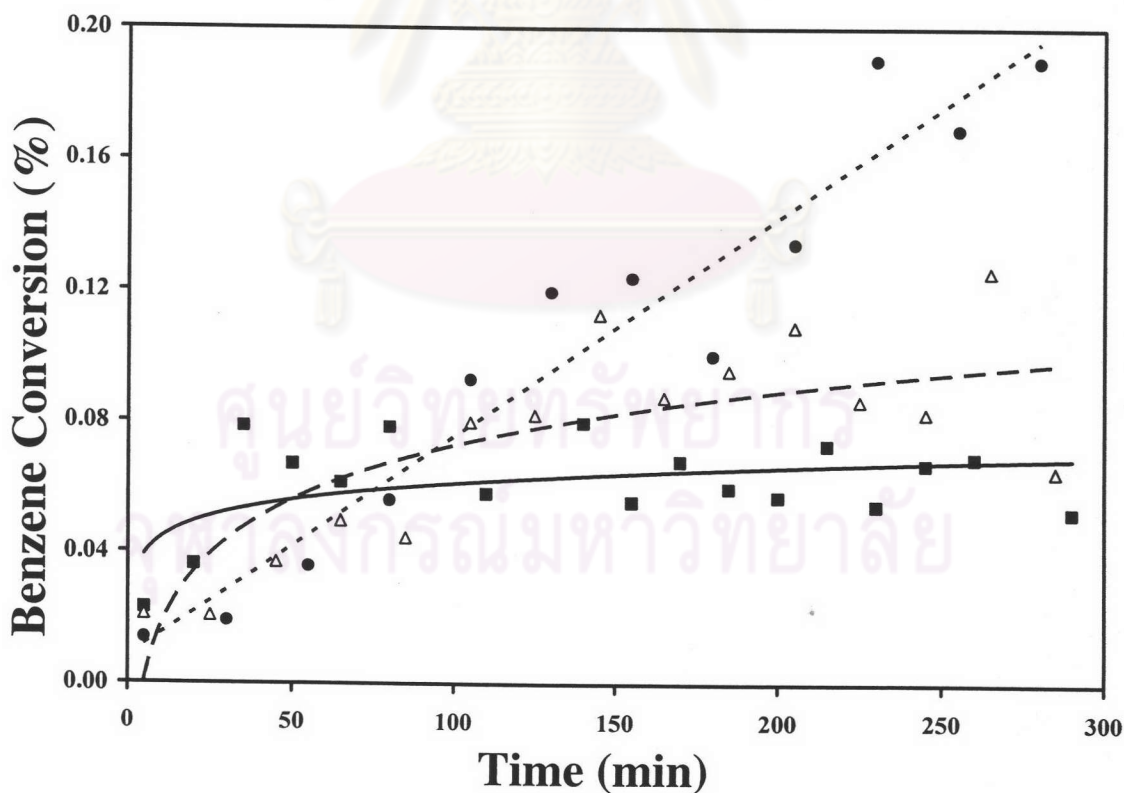

Figure 5.5 Effect of cycle period on conversion of benzene under periodic operation: (■, ——) $\tau = 15$ min and $s = 0.67$; (Δ,— — —) $\tau = 20$ min and $s = 0.75$; (●,- - -) $\tau = 25$ min and $s = 0.80$. Results were plotted at concentration of benzene $= 2.22$ mol/m^3, 1 g of the catalyst.

Moreover, Figure 5.5 shows that at the longer cycle period, the benzene conversion approached the constant value slowly than the shorter cycle period. The shortest cycle period (15 min) rapidly approached the constant value of conversion and behaved like the co-current operation. It is suggested that the reaction time is not long enough in order to desorp phenol from the catalyst surface. Thus, phenol accumulates on the catalyst surface, eventually inhibiting further oxidation for the next cycle and results loss in catalytic activity. Thus, conversion becomingly unchange and would decrease benzene conversion faster than the higher cycle period.
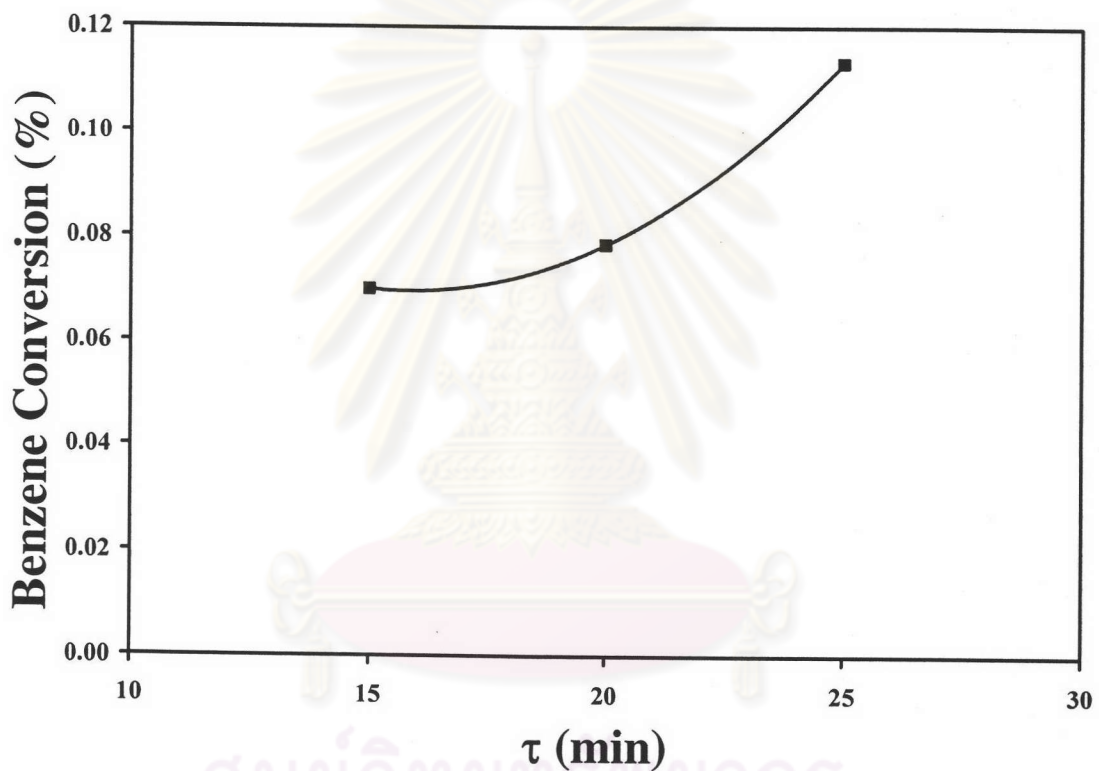

Figure 5.6 Effect of cycle period on conversion of benzene under periodic operation at concentration of benzene = 2.22 mol/m^3, 1 g of the catalyst. Results were determined as the overall conversion of benzene during the reaction time (300 min).

5.2.3 The effect of concentration of benzene on periodic operation performance

From section 5.2.2, we can conclude that the cycle period equal to 25 min give the highest benzene conversion in the range of experiment. Thus, the cycle period equal to 25 min were chosen to study the effect of benzene concentration. The experimental result showed that concentration of benzene had an influence on conversion as indicated in Figure 5.7. The higher concentration of benzene, the higher benzene conversion. As we mentioned before that benzene was the rate limiting reactant. It is suggested that higher quantity of benzene adsorbed on catalyst surface further reacted with H_2O_2 to form the higher quantity of phenol during the cycle period of benzene too (as shown in higher benzene conversion).
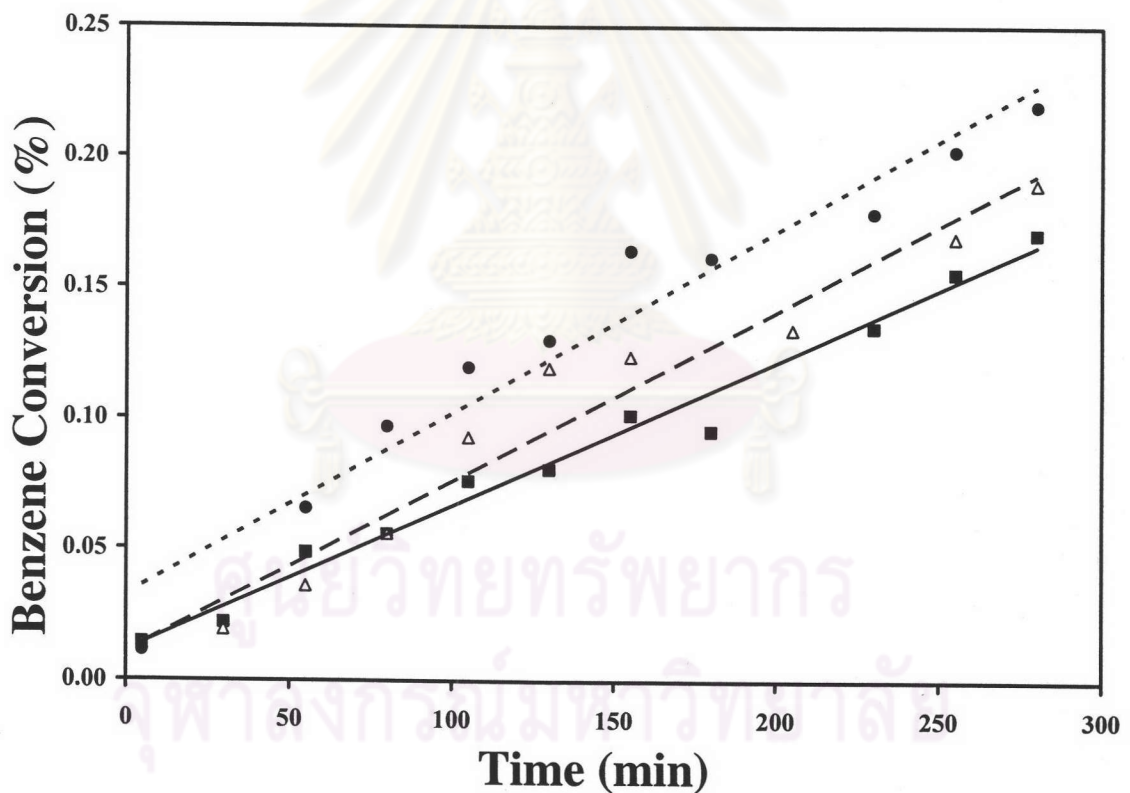

Figure 5.7 Effect of concentration of benzene on conversion of benzene under periodic operation: (■, ——) C_{C6H6} = 1.94 mol/m^3; (Δ,— — —) C_{C6H6} = 2.07 mol/m^3; (●,- - -) C_{C6H6} = 2.38 mol/m^3. Results were plotted at τ = 25 min, s = 0.80 and 1 g of the catalyst.

However, the conversion seemed to increase with increasing the concentration of benzene, Figure 5.8 shows the limitation for increasing value of conversion. When concentration of benzene reached the value about 2.3 mol/m^3, the conversion gradually increased and approached a constant. This phenomenon can be discussed by the same way as in section 5.2.2. It is suggested that the higher in quantity of benzene make they are the main species that cover on the catalyst surface. The phenol which formed on the catalyst surface was hardly desorped back to the bulk reactant in the reactor. Thus, the phenol accumulated on the catalyst surface, eventually inhibiting further oxidation for the next cycle. Finally, we can conclude that the benzene mass transfer is the important role for this system.
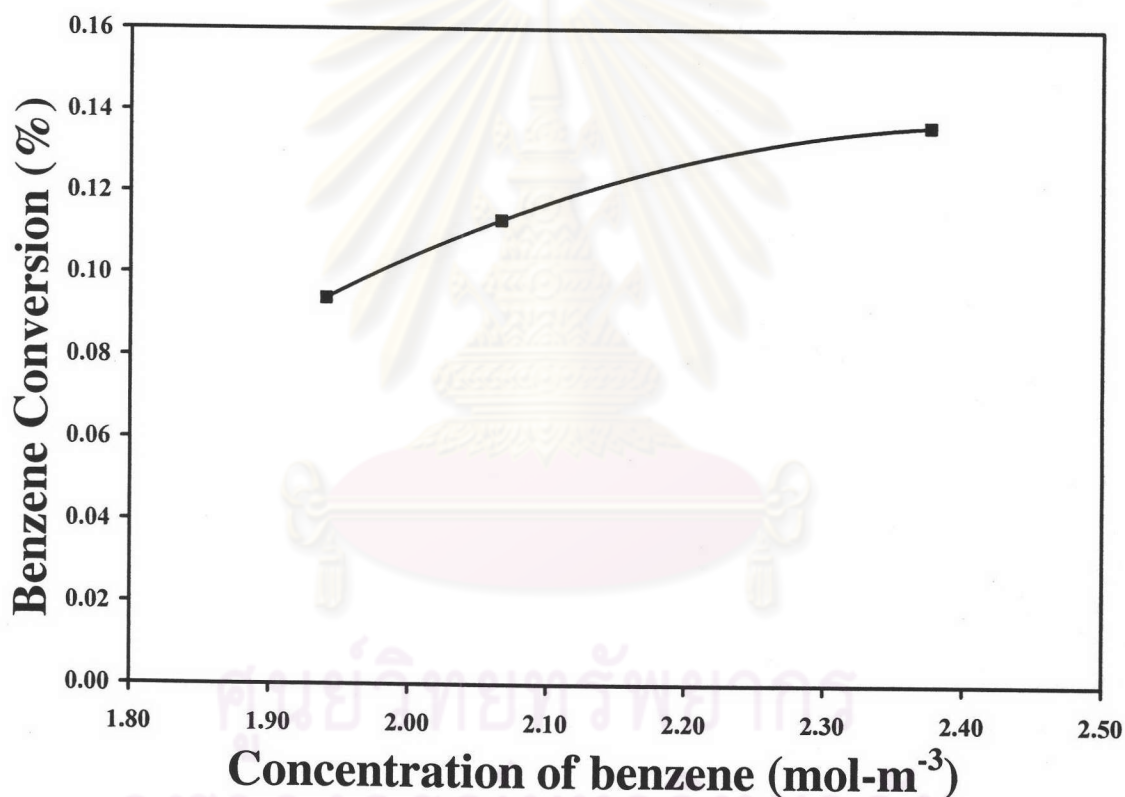

Figure 5.8 Effect of concentration of benzene on conversion of benzene under periodic operation at τ = 25 min, s = 0.80 and 1 g of the catalyst. Results were determined as the overall conversion of benzene during the reaction time (300 min).

5.2.4 The effect of weights of catalyst on periodic operation performance

The effect of catalyst weights are discussed at the cycle period 25 min and concentration of benzene 2.38 mol/m^3. The main objective in this section is to prove whether the weight of catalyst has effect on the overall conversion as the results shown before have very low conversion compared with other literatures. Figure 5.9 shows that the system with 1 g of catalyst have higher benzene conversion than the system with 2 g of catalyst. The results showed the opposite trend that they were expected to be. It is suggested that the bed thickness may play some role in the system. In the system that have more bed thickness, the liquid pockets occurred. In this case, the liquid pockets are the aqueous H_2O_2 that approaches to bed and further oxidation with benzene to form phenol. By the characteristic of phenol make them favorably dissolve in H_2O_2. The benzene conversion was calculated from the overall amount of phenol in aqueous H_2O_2 that passed through the reactor. Thus, the liquid pockets which trap in the bed will further reduce the quantity of phenol. A better way, the bed diameter should be increased instead of the bed thickness. Moreover, the higher flow rate of benzene and H_2O_2 is preferably chosen to diminish the remain liquid pockets.
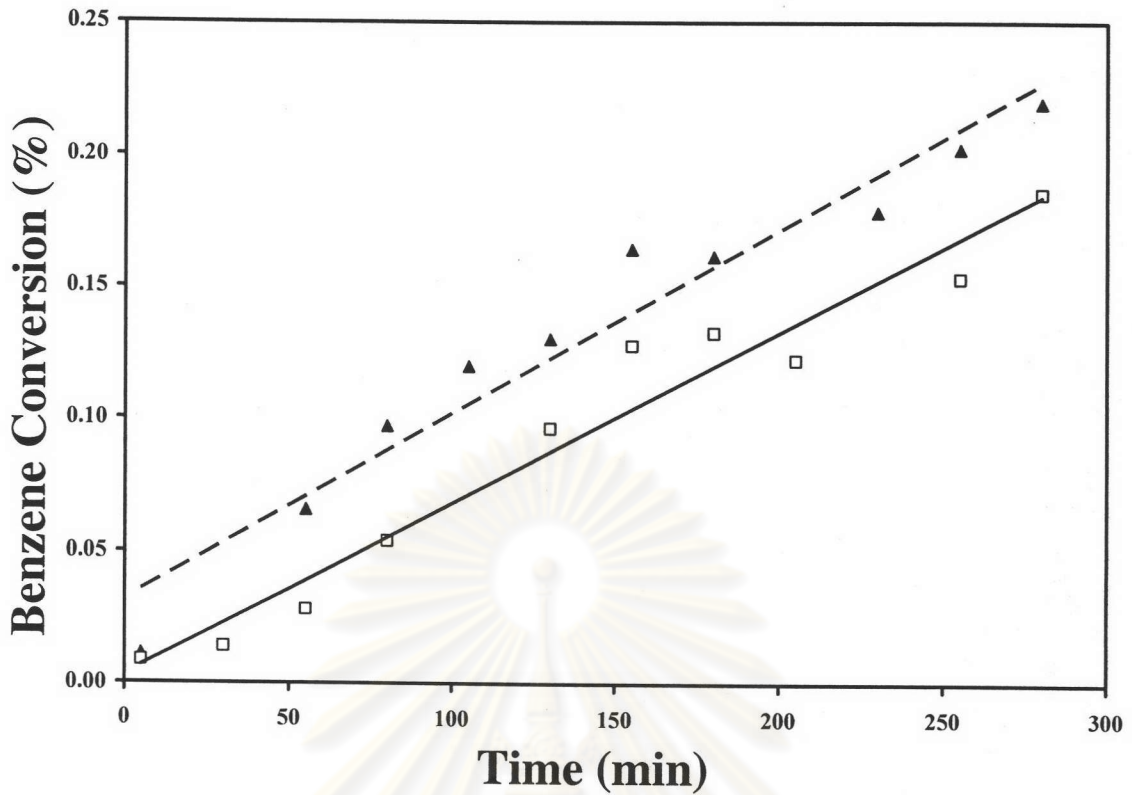
Figure 5.9 Effect of weight of catalyst on conversion of benzene under periodic operation: (▲,— — —) 1 g of catalyst; (□,——) 2 g of catalyst. Results were plotted at $\tau = 25$ min, $s = 0.80$ and concentration of benzene $= 2.38$ mol/m^3.