



## CHAPTER II

### LITERATURE REVIEW

TS-1 catalyzed processes are advantageous from the environmental point of view as the oxidant is aqueous  $H_2O_2$ , which turns into water, and the reactions, operated in liquid phase under mild conditions, show very high selectivity reducing problems and cost of by-product treatment. TS-1 can catalyze a variety of useful oxidation reactions and the hydroxylation of benzene by  $H_2O_2$  to phenol in the presence of TS-1 is also well known.

This chapter divides the reviewed works into two parts, i.e., (a) the different Si/Ti ratio of TS-1 catalyst and the hydroxylation of benzene by  $H_2O_2$  over the TS-1, (b) the pretreatment of the catalyst with acid solution to improve the performance of the catalyst. An attempt will also be made to summarise the present knowledge and understanding of various factors influencing the conversion of the hydroxylation of benzene reaction under periodic operation. In the last section of this review, comments on previous studies that have direct influences on the aims of this study are given.

#### 2.1 Literature reviews

##### 2.1.1 The TS-1 catalyst and the hydroxylation of benzene by $H_2O_2$ over the TS-1

Kraushaar-Czarnetzki and Van Hooff (1989) reported that TS-1 could also be obtained from [Al]ZSM-5 by dealumination and subsequent treatment with titanium tetrachloride. The obtained TS-1 exhibited the same catalytic properties as hydrothermal synthesized TS-1 of high purity. Moreover, their experimental result showed that the selectivity of their catalyst was strongly affected by the presence of small amounts of non-framework titania.

Thangaraj *et al.* (1990) studied the hydroxylation of benzene with  $\text{H}_2\text{O}_2$  over various zeolites. They found that benzene remained unreacted over silicalite-1,  $\text{TiO}_2$  (both amorphous and crystalline), and also in the absence of catalysts. The selectivity for the conversion of  $\text{H}_2\text{O}_2$  to hydroxyl benzenes decreased in the order  $\text{TS-1} > \text{Fe-TS-1} > \text{Al-TS-1} > \text{Fe-ZSM-5} > \text{Al-ZSM-5}$ . The selectivity to phenol, however, followed the reverse order. An interesting feature was that while phenol was the only product over pure acid zeolites (Fe-ZSM-5 and Al-ZSM-5), *p*-benzoquinone, the secondary product was formed in appreciable quantities over titanium-containing zeolites (TS-1, Fe-TS-1 and Al-TS-1). The selectivity for *p*-benzoquinone decreased in the order:  $\text{TS-1} > \text{Fe-TS-1} > \text{Al-TS-1}$ . The acid strength of these zeolites followed the reverse trend i.e.,  $\text{Al-TS-1} > \text{Fe-TS-1} > \text{TS-1}$ . Protonation of phenol over acid zeolites probably suppressed the further electrophilic reaction leading to dihydroxy benzenes.

TS-1 samples of different particle size were synthesized and investigated by Van der Pol *et al.* (1992). Smaller particles were more active than larger particles. From calculation of the Weisz modulus they concluded that large zeolite particle were not fully utilized because of pore diffusion limitations. The product distribution was also influenced by particle size.

Martens *et al.* (1993) studied the hydroxylation of phenol with  $\text{H}_2\text{O}_2$  on EUROTTS-1 catalyst. They reported that the calcinations conditions of EUROTTS-1 was critical. An increase of calcinations temperature from 400 to 500°C resulted in a substantial increase in activity. Static calcinations generated less active catalysts, probably due to incomplete removal of template or its residues. The higher *ortho/para* ratio in the hydroxylated products observed on EUROTTS-1 that was calcined under static conditions was used as an indication to show that the active sites in the interior of the crystals were partially blocked. In the presence of small amounts of solvent, a replacement of acetone by methanol resulted in an increase of the *p*-selectivity of EUROTTS-1.

Weitkamp *et al.* (1997) investigated samples of TS-1 which had different mole ratio of Si/Ti. They observed that samples prepared according to two different synthesis procedures could differ significantly in their hydrophobic/hydrophilic

surface properties. For Si/Ti ratio above ca. 40, value of hydrophobic/hydrophilic decreased linearly with increasing titanium content which had been attributed to the increased formation of polar Si-O-Ti bridges in the zeolite framework. For TS-1 samples with higher titanium content, Value of hydrophobic/hydrophilic strongly depended on the method of preparation and was considerably influenced by the formation of additional titanium-containing species in extra-framework positions. From the results of the catalytic characterization in the hydroxylation of phenol they could concluded that, in particular, TS-1 samples with high titanium content were the more active, the lower their value of hydrophobic/hydrophilic.

Bengoa *et al.* (1998) studied the influence of TS-1 structural properties and operating conditions on benzene catalytic oxidation with  $H_2O_2$ . They mentioned that small changes in the preparation conditions led to the presence of extra-framework titanium. In the benzene hydroxylation reaction using TS-1 prepared by the method of Thangaraj *et al.* (1990), the presence of sodium traces in the solid or  $CH_3OH$  in the reaction mixture changed the activity drastically. These results were attributed to a deactivation of active  $Ti^{4+}$  sites. In addition, the synthesis conditions might be controlled carefully to get pure TS-1, since the presence of extra-framework titanium inhibited benzene hydroxylation.

Bhaumik *et al.* (1998) studied the influence of solvent conditions on benzene catalytic oxidation with  $H_2O_2$ . It had been demonstrated that using a tri-phase system (solid-liquid-liquid), in the absence of an organic co-solvent, a considerable increase in the conversion of benzene during the oxidation by the TS-1/ $H_2O_2$  system could be achieved. Vigorous stirring was needed for the reaction to occur in the tri-phase system. Since the surface of titanium silicalite was relatively hydrophobic in nature, the benzene reactant competed more favorably with water for the diffusion and adsorption under the tri-phase conditions, resulting in higher conversion. Apart from enhancement in activity the present tri-phase method offered distinct advantages in easier product separation and thus contributed to the development of an eco-friendly process.

The use of environmentally detrimental organic solvent created problems in product separation and solvent recycle which were energy intensive steps. Hence, it

was important to develop suitable methodology where the oxidation reactions catalyzed by TS-1 using  $\text{H}_2\text{O}_2$  as an oxidant could be carried out in the absence of organic solvents. In 1999, Kumar *et al.* tried to investigate the enhancement in the reaction rates in the hydroxylation of aromatics over TS-1/ $\text{H}_2\text{O}_2$  under solvent-free triphase conditions. They reported that the reaction rates of the hydroxylation of aromatics (such as benzene, toluene and anisole) were enhanced under triphase conditions (solid-liquid-liquid) compared to that obtained under biphasic conditions in the presence of a co-solvent (solid-liquid). While in the presence of a co-solvent (like acetone, acetonitrile or methanol) a long induction period was observed, in the solvent-free conditions the induction period was almost absent. In the case of substituted benzenes *para*-hydroxy product was predominantly obtained under the triphase conditions. However, in the biphasic condition the formation of *ortho*-isomer was preferred. Probable factors responsible for an enhancement in the activity and a change in regions-selectivity were suggested to be: Relative hydrophobic nature and restricted pore dimensions of TS-1; Diffusive resistance faced by the substrate with an organic co-solvent in biphasic while such a resistance was minimized in triphase.

Li *et al.* (2001) reviewed the effect of titanium species in TS-1 prepared by hydrothermal method on the catalytic activity. They reported that the form of titanium atoms incorporated into the framework of TS-1 synthesized using tetrapropylammonium bromide as template differed from that using the classical method. But the symmetry of TS-1 changed from monoclinic to orthorhombic with the increase of titanium content in both methods. The  $\text{Ti-O}_2^-$  originated from framework titanium and  $\text{H}_2\text{O}_2$  had the moderate stability and might be active site in oxidation reaction. TS-1 synthesized using tetrapropylammonium bromide as template did not contain anatase, but contained a kind of partly condensed titanium species with six-fold coordination. The titanium species might correspond to 270-280 nm band in UV-VIS spectra and also could form  $\text{Ti-O}_2^-$ . But, this kind of  $\text{Ti-O}_2^-$  was very stable and could not be catalytic active site. Therefore, the six-fold coordination titanium species might be inactive in both the oxidation reaction and the decomposition of  $\text{H}_2\text{O}_2$ . The hypothesis had been further proved by the phenomena that the titanium species was easily washed off using acid, and acid treating would not influence the catalytic performance of TS-1.

Liu *et al.* (2004) studied the influence of pretreatment with aqueous solution of  $\text{CH}_3\text{COOK}$ ,  $\text{NaAc}$ ,  $\text{NH}_4\text{Ac}$ ,  $\text{NH}_4\text{Cl}$ , or  $\text{HNO}_3$ . They found that the TS-1 framework structure was not destroyed and titanium in the framework was not removed and its surface area changed hardly, but some extra-framework  $\text{TiO}_2$  could be removed partly, which led to the slight increase of the crystalline of catalyst and the amount decrease of acid sites on the surface of the catalyst. As a result, the activity, selectivity, utilization of  $\text{H}_2\text{O}_2$  and the hydroquinone/chatacol ratio of product for hydroxylation of phenol were improved. When the TS-1/diatomite catalyst was pretreated by a base solution, the framework silicon of catalyst was dissolved partly and the framework structure of TS-1 is destroyed, causing the decrease of the crystallinity and surface area of catalyst and the increase of acid sites on the surface of catalyst. As a result, the catalytic activity of the TS-1/diatomite catalyst for hydroxylation of phenol descended or deactivated completely.

Kong *et al.* (2004) studied the selective oxidation of thiophene by hydrogen peroxide with different  $\text{SiO}_2/\text{TiO}_2$  ratio of TS-1 catalyst. The catalyst was treated using  $\text{HCl}$  (2 mol/l) four times, part of the non-framework titanium species will be washed off and the activity of the catalyst increased greatly. These results indicate that framework titanium was crucial for thiophene oxidation. The unique role played by framework titanium might be that they could interrupt conjugation during the reaction. This breakage of the aromatic of thiophene ring was critical for oxidation of thiophene by hydrogen peroxide under mild conditions. Non-framework titanium in the catalyst was not the active site for thiophene oxidation.

Hulea and Dumitriu (2004) studied Ti-containing molecular sieves with MFI(TS-1), BEA(Ti-beta) and MCM-41 topologies for the styrene oxidation in liquid phase by hydrogen peroxide was performed. The major reactions were epoxidation of styrene oxide into phenylacetaldehyde(PhAA) as well as its oxidative cleavage into benzaldehyde (BzA) and formaldehyde. A high selectivity to PhAA was observed over TS-1, whereas the BzA formation was predominant on Ti-beta and TiMCM-4. Because of the diffusion limitation of the reactants and shape-selectivity towards the transition state and the product distribution depended on the nature of the catalyst. Thus, the selectivity to PhAA was very high for all catalysts of MFI type (smaller

pore opening), whereas the BzA was formed in large amount in the presence of Ti-beta and TiMCM-41 (larger pores).

Liu et al. (2005) studied deactivation and regeneration of TS-1/diatomite catalyst for hydroxylation of phenol in a fixed-bed reactor. They found that the TS-1/diatomite catalyst would be deactivated during the hydroxylation of phenol by  $H_2O_2$  in the fixed-bed reactor, and the catalytic activity and selectivity to products decrease with an increase of reaction time. However, the crystallinities of the TS-1/diatomite catalyst have changed a little, and the framework structure of TS-1/diatomite catalyst have changed a little, and the framework structure of TS-1 zeolite and the amount of titanium in the framework had not changed. Compared with the fresh catalyst, the BET surface area and pore volume of the deactivated catalyst decrease significantly, and the channels of the TS-1/diatomite catalyst were blocked by the organic by-products deposited on the catalyst surface, resulting in the reversible deactivation of the catalyst. The deposition on the TS-1/diatomite catalyst could be removed by calcining at  $550^\circ C$  in air or refluxing with dilute hydrogen peroxide, which could recover completely the performance of the TS-1/diatomite catalyst for phenol hydroxylation.

### 2.1.2 The periodic operation in various reactions

Under periodic operation can solvable many problem which occurred on varying reaction followed to below

Periodic operations of catalytic processes have been investigated for many years. The literature up to almost the end of 1992 has been summarized in an excellent review by Silveston *et al.* (1995).



**Table 2.1** A list of reactions studied under periodic operation from 1968-1992 (Silveston *et al.*, 1995)

Authors	Year	Process	Forced parameter	Investigated effects
Lehr <i>et al.</i>	1968	EtOH dehydration to diethyl ether	Flow	Study of process nature
Denis and Kabel	1970	As above	Flow	Selectivity
Wandrey and Renken	1973	Hydrocarbons oxidation (propene, cyclohexene)	Concentration	Product distribution
Renken <i>et al.</i>	1974	EtOH dehydration to diethyl ether	Concentration	Selectivity
Helmrich <i>et al.</i>	1974	Ethylene hydrogenation	Concentration	Rate
Baiker and Richarz	1976	As above	Concentration	Rate
Renken <i>et al.</i>	1976	Ethylene oxidation	Concentration	Selectivity
Dautzenberg <i>et al.</i>	1977	Fischer-Tropsch synthesis	Concentration	Product distribution
Briggs <i>et al.</i>	1977-80	SO <sub>2</sub> oxidation	Concentration	Rate
Leupold and Renken	1977	Ethyl acetate from ethylene and acetic acid	Concentration	Rate
Al-Taie and Kershenbann	1978	Butadiene hydrogenation	Concentration	Selectivity
Bilimoria and Bailey	1978	Acetylene hydrogenation	Concentration	Selectivity
Crone and Renken	1979	Styrene polymerization	Concentration	Rate, product distribution
Cutlip	1979	CO oxidation	Concentration	Rate
Abdul-Kareem <i>et al.</i>	1980	As above	Concentration	Rate
Lee <i>et al.</i>	1980	Saponification of diethyl adipate	Concentration	Selectivity
Silveston and Hudgins	1981	SO <sub>2</sub> oxidation	Concentration	Rate
Jain <i>et al.</i>	1982-83	NH <sub>3</sub> synthesis	Concentration	Rate
Wilson and Rinker	1982	NH <sub>3</sub> synthesis	Concentration	Rate
Adesina <i>et al.</i>	1984	Fischer-Tropsch synthesis	Concentration	Rate
El-Masry	1985	Claus reaction	Concentration	Rate
Nappi <i>et al.</i>	1985	Low-pressure methanol	Concentration	Rate
Müller-Erlwein and Guba	1988	Methacrolein from isobutyraldehyde	Concentration	Selectivity
Haure <i>et al.</i>	1989	SO <sub>2</sub> oxidation in trickle bed	Flow	Rate
Saleh-Alhamed <i>et al.</i>	1992	Propylene oxidation to acrolein	Concentration	Selectivity
Strots <i>et al.</i>	1992	SO <sub>2</sub> oxidation in CSTR	Concentration	Conversion

Haure *et al.* (1989) founded that periodic operation, switching between reactant and water in the form of gas and liquid phase, had rate of oxidation sulfurdioxide with sulfur catalyst more than continuous operation. Because of periodic operation made catalyst refresh and reduced temperature when system switches to water in.

Adesina *et al.* (1995) founded that when the periodic operation was used in reaction of Fischer-Tropsch, it allowed switching a catalyst which led to the product distribution of the paraffin products was changed. The Ru and Co catalysts

could produce the lower mean carbon number, while Mo catalyst could produce the higher mean carbon number. However, Fe catalyst could stimulate strongly for only CH<sub>4</sub> formation, whereas the product distribution of the other hydrocarbon products was unchanged.

Gulari *et al.* (1995) found that oxidation of carbon monoxide with Pt and Pd catalysts under periodic operation could increase rate of reaction than transient operation because carbon monoxide which covered on transient operation's catalyst inhibit the reaction.

Aida and Kawakami (1997) found that during the reduction of NO with hydrocarbon in steady operation, its intermediate (NO<sub>2</sub>) could be oxidized to provide NO<sub>3</sub> when the system still had oxygen in the system. However, when the reactions were progress in periodic operation, NO<sub>2</sub> could react with hydrocarbon to provide product. In this case, oxygen did not present in the process, when the system was switched to hydrocarbon in without the oxygen.

Yamada and Goto (1997) found that the catalytic activity of hydrogenolysis for deprotection of amino acid in a trickle bed reactor containing gas-liquid-liquid-solid four phases gradually decreased due to the deposit of phenylalanine (main product) on the surface of the catalyst. This problem could be solved by periodic operation with flow of organic and aqueous solutions in the reaction period and with flow of only aqueous solution in the washing period.

Stradiotto *et al.* (1999) found that under steady-state reaction rates of hydrogenation of crotonaldehyde were lower than periodic flow interruption in a trickle bed that appeared likely at low liquid flows. Because the catalyst was not uniformly and only fractionally wetted, the gas reactant might be quite accessible to the catalyst, without the second reactant presented on most of the surface. The importance of periodic addition of liquid reactant was to increase the efficiency of wetting, and, despite the probability of greater diffusion resistance from the liquid phase, to enhance the likelihood that the two reactant streams were in contact over a wide portion of the total catalyst surface, thereby increasing the overall rate of reaction.



The operation of a trickle-bed reactor in the pulsing flow regime was well known for its advantages in terms of an increase in mass and heat transfer rates. Boelhouwer *et al.* (2001) mentioned that the advantages associated with pulsing flow might then be utilized to improve reactor performance in terms of an increase in capacity and the elimination of hot spots, while interfacial contact times were comparable to trickle flow. During the periodic operation of a trickle bed, continuity shock waves were initiated in the column due to the step-change in liquid flow rate. This resulted in the division of the column into a region of high liquid holdup and a region of low liquid holdup. At high enough gas flow rates, the inception of pulses took place in the liquid-rich region. Analysis of the performed experiments indicated that besides gas and liquid flow rates, an additional criterion for pulse inception was the available length for disturbances to grow into pulses. For self-generated pulsing flow this resulted in the upward movement of the position of the point of pulse inception with increasing gas flow rate. With liquid-induced pulsing flow this means that higher gas flow rates were necessary to induce pulses as the length of the liquid-rich region decreased.

An  $\alpha$ -methyl styrene hydrogenation over Pd/Al<sub>2</sub>O<sub>3</sub> under periodic operation was studied by Turco *et al.* (2001). In this reaction the transport of H<sub>2</sub> from the liquid phase to the Pd surface was largely rate controlling. An attempt to exploit the inertial effects by varying the gas loading in a down flow co-current trickle bed was not successful. On the contrary the periodic modulation in liquid loadings could result in significant increases in rates of reaction even when there was no change in bed temperature as a result of modulation. The improvement probably resulted from inertial effects which allow foaming created at high liquid flow rates to persist when the liquid flow rate was reduced to a low value and the system should have reverted to a trickling regime without foam.

Pimporn *et al.* (2003) found that the benzene conversion under periodic operation were higher than those under comparable co-current operation and many key parameters such as total cycle period, concentration of benzene, and weight of catalyst had result in periodic operation. The higher cycle period was found to enhance benzene conversion because of the longer contact time of the reaction. The

higher concentration of benzene was found to enhance benzene conversion due to the higher amount of benzene at the same period time. The liquid pocket which was trapped in the bed increased when increasing the catalyst weight or the bed depth.

Carlsson *et al.* (2004) studied the activity Pt/Al<sub>2</sub>O<sub>3</sub> catalysts for propane oxidation and compare with step-response operation. The activity of step-response experiment for lean compositions drops probably due to a high O coverage (O self-poisoning) which leads to Pt oxide formation. Periodic operation was usefully in this reaction about quantity of the composition on the catalyst surface.

Massa *et al.* (2005) studied phenol oxidation in periodically operated trickle bed reactor. They found that cycling experiments could improve the performance. Many operations were emphasized to investigate variables, such as gas reactant concentration at the catalytic surface, liquid reactant concentration inside/outside the catalyst, wetting condition, liquid holdup, etc.

## 2.2 Comment on previous works

From the previous studies e.g. about the reaction, there are many researches about the hydroxylation of aromatic by H<sub>2</sub>O<sub>2</sub> over the TS-1. However there are only some researches about the hydroxylation of benzene by H<sub>2</sub>O<sub>2</sub> although this is a simple reaction (it yields only two products). From the reviewed literatures, the Si/Ti ratio of TS-1 catalysts had the influence on catalytic activity. Because of a large number of Ti led to more activity on active site, Li *et al.* (2001). The particle size of TS-1 catalysts had the influence on catalytic activity. It resulted that large zeolite particle were not fully utilized because of pore diffusion limitations, van der Pol *et al.* (1992). Thus, the hydroxylation reaction might occur primarily on the external surface of catalyst particle. Rate controlling step then would be the film type mass transfer from the liquid phase to TS-1. The periodic switching of flows that controlled the wetting efficiency (which affected the mass transfer rate) should increase the rate of reaction and yield, Lange *et al.* (1999). The effect of pretreatment with acid solution makes them more activity than that unpretreat, Liu *et al.* (2004).

Although, the periodic operation can improve the rate of the hydroxylation of benzene reaction, but the previous studies did not show research in the periodic operation. Thus, the hydroxylation of benzene by  $\text{H}_2\text{O}_2$  using the different Si/Ti ratio of TS-1 as the catalysts under periodic operation is chosen to be studied in this research and effect of pretreatment with  $\text{HNO}_3$  in various concentrations. From Liu *et al.* (2004), it is indicate that the activity increases due to  $\text{TiO}_2$  anatase is removed to surface TS-1 catalyst. Therefore, pretreatment is occurs in this research too.