CHAPTER III
LITERATURE REVIEWS

There are several studies of titanium silicalite-1 (TS-1) catalysts. Many researchers have found knowledge about TS-1, especially modified TS-1 for several reactions. This chapter divides the reviewed works into three parts, i.e., (a) effect of the synthetic method of titanium silicalite-1 (TS-1), (b) effect of the modified TS-1 for several reactions and (c) effect of cobalt on catalyst properties. An attempt will also be made to summarise the present knowledge and understanding of various factors influencing the properties of catalysts and catalytic performance. In the last section of this review, comments on previous studies that have directly influenced the aims of this study are given.

3.1 Literature reviews

In 1983, Taramasso, and co-worker reported the synthesis of a titanium-substituted analogue of silicalite, given the name titanium silicalite-1 or TS-1. The new material opened a new field in heterogeneously catalyzed various oxidation reaction such as the epoxidation of alkenes, the oxidation of alcohols, the phenol hydroxylation etc. in both gas and liquid phases. The product has proved to be an extremely useful oxidation catalyst, particularly in conjunction with peroxide. In epoxidations and related reactions, TS-1 is an active and selective catalyst. So, the investigation of preparation TS-1 was quite undertaken in a lot of laboratory. Some of the more prominent studies and the modified TS-1 for several reactions are summarized below.

3.1.1 Effect of the synthetic method of titanium silicalite-1 (TS-1)

The difficulty in the synthesis of metallo-silicates arises because of the formation of stable insoluble metal oxide/hydroxide precipitate, either during preparation of gel or during the crystallization of the metallo silicate. The normal pHs of the gels for the synthesis of the metallo silicates are around 9-13. Under such

alkaline conditions, Ti^{+4} has a strong tendency to form insoluble amorphous TiO_2 species, unlike silicates or aluminates which dissolve under alkaline conditions.

To overcome the above difficulties in the synthesis of TS-1, several routes are tried to synthesize TS-1 with no amorphous extra- framework titanium species.

From the early research about the preparation and characterization of the TS-1 catalyst, [Taramasso et al., (1983)] has investigated the classical synthesis of TS-1. The material is prepared by using a source of silicon oxide, a source of titanium oxide and alkali free tetrapropylammonium hydroxide (TPAOH) is used as the template. TS-1 contains low levels (up to about 2.5 atom %) of titanium substituted into tetrahedral positions in the silicalite lattice and is produced under severe conditions and at high cost, which makes the synthesis difficult to be industrialized. In order to reduce the cost of TS-1, tetrapropylammonium bromide (TPABr) can be used as the template to synthesize TS-1 instead of using the expensive template TPAOH.

Atom planting method was introduced by Kraushaar et al. (1988) where highly siliceous zeolites are treated with titanium chloride vapor at high temperature. Ti-mordenite, which has not been synthesized under hydrothermal conditions, has been synthesized by this atom planting method.

Another research of Padovan et al. (1989) had synthesized the TS-1 by wetness impregnation method of SiO_2- TiO_2 co-precipitate. The dried SiO_2-TiO_2 co-precipitate is impregnated with a required quantity of TPAOH solution similar to the pore volume of the solid and the subsequent treatment leads to the formation of TS-1 without the formation of TiO_2 species. After that, Uguina et al. (1994) has successfully synthesized TS-1 from SiO_2-TiO_2 co gel using modified Padovan's method.

Gao et al. (1995) synthesized TS-1 using aqueous solution of TiC_{l3} as the titanium source and thereby avoiding the precipitation of TiO_2. After 2-5 days of autoclaving at 160 °C, TS -1 was obtained without any trace of extra-framework titanium species.

Furthermore, the research of Kumar et al. (1996) had studied the synthesis of metallosilicate in presence of complexing agent such as oxalic acid, acetyl acetone. The use of this complexing agent may prevent the formation of metal oxide/hydroxide precipitate by complexing with the metal ion used in the synthesis. TS-1 has been synthesized successfully using acetylacetone as the complexing agent without formation of extra-framework TiO_2 species. After that, Kumar et al. (2002) has developed a new method for synthesizing TS-1 using tetraethyl orthosilicate (TEOS), tetrabutyl orthotitanate (TBOT), and orthophosphoric acid (H_3PO_4) were used as the silica source, titanium source, and promoter, respectively. Tetrapropylammonium hydroxide (TPAOH) was used as the templating agent for the synthesis of the TS-1 sample. This method gives particles in the size range 100 nm – 200 nm with almost uniform particle size distribution.

After that, Shibata et al. (1997) has created a new synthesis route for MFI-type titanosilicates (TS-1) using methylamine along with tetrapropylammonium bromide (TPABr), silica or silicon tetrachloride and titanium tetrachloride, thus avoiding the use of costly TPAOH and Ti-alkoxide, has been investigated. The presence of titanium ions in the reaction gel slowed down the crystallization of MFI zeolites, while addition of hydrogen fluoride as a co-mineralizer into the gel dramatically improved the crystallization kinetics. Reduced initial amounts of methylamine in the gel led to an increase of the apparent crystallization rate of the zeolite and to a remarkable decrease of the amount of framework Ti, suggesting that high concentration of methylamine is needed for the Ti incorporation into the growing MFI crystallites.

The synthesis of TS-1 by using TPABr and n-butylamine as the template and the base respectively is presented in the research of Wang et al. (2002). The addition of base used to neutralize the residual acidity of the catalyst favor the reaction, the catalyst shows high activity and selectivity upon the adequate amount of base. The catalytic properties were investigated in detail over the synthesized and catalytic activity testing used epoxidation of propylene.

3.1.2 Effect of the modified TS-1 for several reactions

Unless the properties of the catalysts influenced catalytic performance, there is another factor affected it such as the reaction. Many researches have tried to apply TS-1 to catalytic oxidation of many organic compounds with aqueous hydrogen peroxide as the oxidant under mild condition. Therefore, Notari et al. (1990) investigated to use TS-1 as the catalyst for the production of two industrial chemicals: catechol and hydroquinone. They have been produced by the hydroxylation of phenol with H_2O_2. In the conversion of cyclohexanone into cyclohexanone oxime in the presence of ammonia and H_2O_2, TS-1 offers a substantial reduction in coproduct formation [Thangaraj et al. (1990)].

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

Furthermore, the research of Weitkamp et al. (1997) investigated samples of TS-1 which had different mole ratios of Si/Ti. They observed that samples prepared according to two different synthesis procedures could differ significantly in their hydrophobic/hydrophilic surface properties. From the results of the catalytic characterization in the hydroxylation of phenol they concluded that, in particular, TS-1 samples with high titanium content were the more active.

Schuster et al. (2001) investigated the activity of titanium and vanadium containing zeolitic and non-zeolitic materials in the oxidative dehydrogenation of propane to propene. Using TS-1 as the catalyst showed the optimum performance. The propane and oxygen partial pressure had no influence on the selectivity, and the mass transport limitation in the macropores and mesopores could be neglected. They assumed that the reaction probably took place on the outer surface of the TS-1 crystallites on Lewis acid sites, the exact reaction mechanism nor the exact active site were not clear. In addition, increasing the Lewis acidity by a sulfation of TS-1 in both

the gas phase and the liquid phase prior to the reaction resulted in an increase of the conversion of up to 17% with selectivity about 74%.

Moreover the next research of Wang et al. (2003) investigated the effect of the different supports (TiO$_2$, SiO$_2$, silicalite-1, HZSM-5, TS-1), the TS-1 preparation and the reaction conditions on propylene epoxidation using oxygen as the oxidant in a fixed-bed quartz glass reactor. They found that only TS-1 was the suitable support and the Si/Ti ratio of TS-1 had a great effect on the propylene epoxidation. With an increase in the Si/Ti ratio of TS-1, both the propylene conversion and the selectivity to propylene oxide increased. The Si/Ti ratio was 64, the catalyst exhibited optimum performance, 0.92% propylene conversion and 91.21% propylene oxide selectivity.

The other observation on the preparation and properties of colloidal silicalites-1, TS-1, silicalite-2 and TS-2 was studied by Cundy and Forrest (2004). The research showed that colloidal silicalite-1 and TS-1 have been prepared by hydrothermal synthesis using both conventional and microwave heating. The degree of framework substitution depend on synthesis temperature (optimum conditions for heteroatom incorporation about 100-175°C). Higher temperatures favour the formation of products with greater levels of framework titanium but there is also an increase in the formation of extra-framework anatase impurity. Increasing levels of titanium in the synthesis composition reduce the overall growth rate of the colloidal TS-1 product and also tend to increase the crystal size.

3.1.3 Effect of cobalt on catalyst properties

Reuel and Bartholomew (1984) studied the effect of support and dispersion on the CO hydrogenation activity/selectivity properties of cobalt. They found that the specific activity and selectivity of cobalt in CO hydrogenation is a function of support, dispersion, metal loading and preparation. The order of decreasing CO hydrogenation activity at 1 atm and 225°C for catalysts containing 3wt% cobalt was Co/TiO$_2$ > Co/SiO$_2$ > Co/Al$_2$O$_3$ > Co/C > Co/ MgO. The specific activity of cobalt best correlated with dispersion and extent of reduction. In the Co/Al$_2$O$_3$ system,

activity and selectivity for high molecular weight hydrocarbons increased very significantly with increasing cobalt loading.

In 1996, Inui et al. reported that the MFI-type silicates incorporated with various contents of cobalt ions were synthesized by the rapid crystallization method. However, a considerable amount of cobalt could be incorporated stably into the zeolite framework, up to a Co/(Si+Co) atomic ratio of about 0.0025. Even at a Co/(Si+Co) atomic ratio of above 0.0025, a consideration amount of cobalt ions could be highly dispersed in the internal domain of the zeolite pore matrix.

The research of Riva et al. (2000) has studied the effect of metal-supported interaction in Co/SiO$_2$ and Co/TiO$_2$ catalysts and their effect on the dispersion and reducibility of cobalt. They found that the interaction is much stronger in the case of titania, as indicated by the formation of a surface compound between cobalt and titania that is more resistant to reduction than Co$_3$O$_4$. On the contrary the behavior of silica supported sample is very similar to that of unsupported Co$_3$O$_4$ under reduction treatments. Besides, the degree of interaction between cobalt and the support affected not only the response of cobalt to reduction, but also its dispersion. They also found that cobalt spread on titania during reduction and trended to sintering on silica.

In addition, Pirutko et al. (2001) synthesized metal modified TS-1 catalyst by hydrothermal synthesis and cobalt is the one of metal used for loading into TS-1 catalyst. From a part of this research, they synthesized and studied TS-1 containing cobalt by 1.6% weight and they found that it has the MFI crystal structure which is the same as TS-1 containing other metals i.e. aluminium, chromium, iron, vanadium and rubidium.

Ruiz et al. (2005) investigated the addition of transition metals (Co, Cu) on hydrothermally treated TiO$_2$ for gas sensing. Their result showed that the hydrothermal treatment was appropriated for preparing colloidal suspensions of nano-TiO$_2$ resistant to grain growth and phase transformation. The hydrothermally treated titanium dioxide was impregnated with Co or Cu transition metals. It could be mentioned that Co and Cu are promising as additives to titania based gas sensors.

After that, the catalytic behaviors of mixed TiO_2-SiO_2-supported cobalt (Co) Fischer–Tropsch (FT) catalysts via carbon monoxide (CO) hydrogenation were investigated in the research of Jongsomjit et al. (2005). The various weight ratios of TiO_2/SiO_2 were prepared, then the consequently impregnated with the cobalt precursor. The decreased activities had to be attributed to the less number of reduced cobalt metal surface atoms for catalyzing the reaction. However, longer chain hydrocarbons such as C_2–C_5 can be obtained substantially with increasing the amounts of titania in the mixed supports. It can be concluded that the presence of titania apparently inhibited the chain growth probability during CO hydrogenation. And another research of them showed both highly dispersed cobalt oxide species along with the presence of rutile phase in titania could play an important role on the number of reduced cobalt metal surface atoms for Co/TiO_2.

Yao et al. (2005) investigated that cobalt-doped mesoporous titania with anatase crystalline structure, prepared using 1-dodecylamine as template by cogellation method, appears to be an efficient catalyst for the oxidation. of cyclohexane to cyclohexanol and cyclohexanone at 100°C by using acetic acid as the solvent.

Moreover, Somanathan et al. (2006) have synthesised mesoporous Co-MCM-41 molecular sieves with various Si/Co ratios: 25, 50, 75 and 100 by direct incorporation of cobalt into the framework through hydrothermal method. Using acetylene as a carbon precursor at 750°C, Co-MCM-41 (100) catalytic template showed the best results with particularly high selectivity for single walled carbon nanotubes(SWCTs). The catalytic template maintains its crystallinity after successive reaction, which suggests that Co-MCM-41 is a very stable template for producing SWNT under harsh conditions.

Furthermore, the research of A' lvarez et al. (2006) focused on the preparation of Co/Al_2O_3 catalysts to be used in the removal of pyruvic acid from water by ozonation. A series of Co/Al_2O_3 catalysts were prepared by the incipient wetness impregnation method using γ-Al_2O_3 support and $(CH_3COO)_2Co·4H_2O$ solutions, followed by calcination at 500–800 °C. Depending on preparation conditions (i.e.,

calcination atmosphere, temperature and metal loading), one or more of the following Co-containing compounds were identified: CoO, Co$_3$O$_4$ and CoAl$_2$O$_4$. The results found that calcining impregnated γ-Al$_2$O$_3$ (2 wt.%) at 500 °C in either nitrogen or air generates CoO or Co3O4 as the main cobalt phase, respectively and calcining impregnated γ-Al$_2$O$_3$ (2–5 wt.%) in air at 800 °C gives rise to the formation of cobalt aluminate as the major phase. The Differences in catalytic activity among the various Co/Al$_2$O$_3$ catalysts investigated were attributed to the different Co active phases deposited on the γ-Al$_2$O$_3$ surface. The following sequence of increasing activity can be inferred from experimental results: CoO, CoAl$_2$O$_4$ and Co$_3$O$_4$. All the Co/Al$_2$O$_3$ catalysts prepared showed good stability as the percentage of cobalt leached out was rather low.

3.2 Comment on previous works

From the reviewed literatures, the preparation of catalyst, there are many researches studied about different methods such as impregnation, co-precipitation, deposition-precipitation, ion exchange and incorporation for preparing TS-1. Nowadays, the interested second metal was introduced to TS-1 framework to improve TS-1 properties. In a previous research [Sangngaem N. (2006)], has studied the effect of cobalt addition which can be incorporated into the TS-1 structure by hydrothermal method without any interference to the main TS-1 structure. Though, this work showed that the incorporation of cobalt increases the amount of the weak acid site while the amount of the strong acid site decreases. The Co-TS-1 catalysts exhibit higher catalytic activity for the dehydration reaction and selectivity toward propylene than the unmodified TS-1. Although, the preparation of Co-TS-1 by using incorporation has been reported but the factor that effected for preparing Co-TS-1 catalysts have not yet investigated. Therefore, the factor of Co-TS-1 preparation by using incorporation is concerned to study in this research.