

CHAPTER III

EXPERIMENT



This chapter will discuss the synthesis methodology of the catalyst both of the standard TS-1 synthesis procedure and the previously used synthesis procedure of the V/TS-1 including an expanded discussion about the problem of metal quantity controlling in the catalyst structure. The alternative procedure considerations and the several alternative procedures are later discussed. The catalyst characterization and the catalytic reaction are also explained. The chemicals, apparatus and standard synthesis procedure of TS-1 are explained in section 3.1. The previously used synthesis procedure of V/TS-1 is discussed in section 3.2. Section 3.3 illustrates the several alternative procedures and its considerations. The composition, the structure and the surface properties of the synthesized catalysts characterized by various techniques are discussed in section 3.4. Finally, the details of the catalytic reaction are illustrated in section 3.5.

3.1 The standard synthesis procedure of TS-1 catalyst

Since this research focuses on the synthesis methodology of the titanium silicalite-1 (TS-1) catalyst and the vanadium modified TS-1 (V/TS-1) catalyst; therefore, the details of synthesis procedures are important to understand. Example of the standard synthesis procedure of TS-1 catalyst with the molar ratio of silicon/titanium was set at 50 is demonstrated as follows. List of chemicals and the reagents used to prepare the TS-1 catalyst are shown in Table 3.1 and 3.2 respectively. The preparation procedure is shown in Figure 3.1.

Table 3.1 List of chemicals for TS-1 catalyst preparation.

Chemicals	Grade	Supplier
Titanium (IV) butoxide 97%		Aldrich
Tetrapropylammonium bromine 98%		Aldrich
Sodium chloride	Analytical	APS
Sodium hydroxide	Analytical	Merck
Sulfuric acid	Analytical	Aldrich
Sodium silicate solution	Extra pure	Merck

Table 3.2 The reagents used to prepared TS-1 catalyst (Si/Ti = 50)

Gel solution preparation		Decant solution preparation	
A1 Solution		A2 Solution	
Ti[O(CH ₂) ₃ CH ₃] ₄ *	2.297 g	Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g
TPABr	5.720 g	TPABr	7.530 g
NaCl	11.930 g	De-ionized water	60.00 ml
De-ionized water	60.00 ml	H ₂ SO ₄ (conc.)	3.40 ml
H ₂ SO ₄ (conc.)	3.40 ml		
B1 Solution		B2 Solution	
Sodium Silicate	69.000 g	Sodium Silicate	69.000 g
De-ionized water	45.000 g	De-ionized water	45.000 g
C1 Solution		C2 Solution	
TPABr	2.160 g	NaCl	26.270 g
NaCl	40.590 g	De-ionized water	104.00 ml
NaOH	2.390 g		
De-ionized water	208.00 ml		
H ₂ SO ₄ (conc.)	1.55 ml		

* The calculation of Ti[O(CH₂)₃CH₃]₄ used are explained in appendix A.

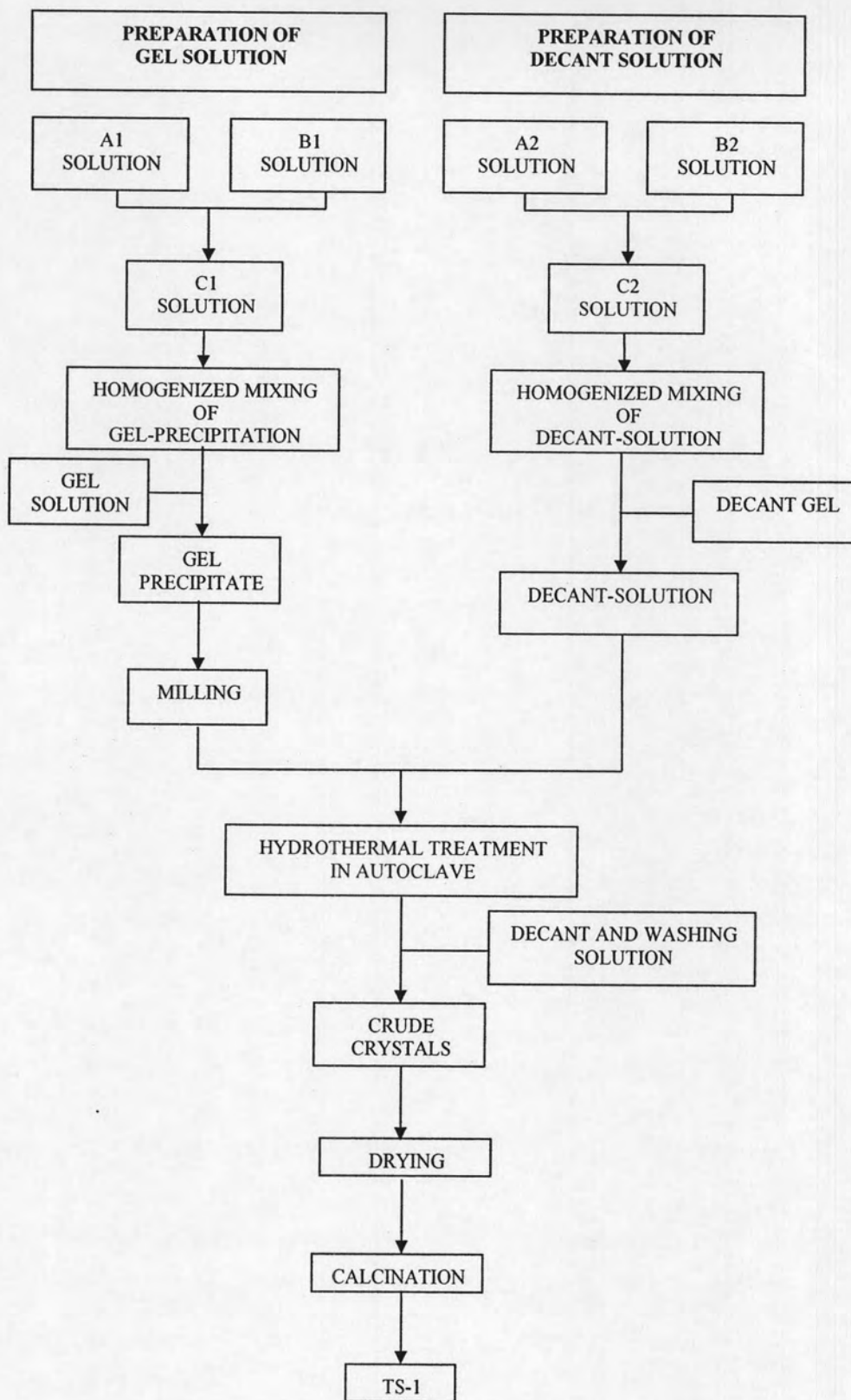


Figure 3.1 The preparation procedure of TS-1 by hydrothermal method.

The synthesized catalyst uses titanium (IV) butoxide ($\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$) and sodium silicate solution ($\text{Na}_2\text{O}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$) as the sources of cations (Ti and Si respectively) for preparation of gel and decant solution. Tetrapropylammonium bromide ($(\text{CH}_3\text{CH}_2\text{CH}_2)_4\text{NBr}$) is used as the organic template. The detail procedures are as follows:

Firstly, the gel is prepared by gradually dropping A1 and B1 solution into C1 solution while stirring with a magnetic stirrer at room temperature. During this step the pH value of the mixed solution is controlled in the range of 9-11. NaOH solution will be added, if necessary, to control the pH of the solution within this range. The mixed solution is further stirred for 2 hours and centrifuged to derive gel.

Secondly, a decant solution is prepared by gradually drop A2 and B2 solution into C2 solution. The methods and conditions of mixing are similar to the preparation of the gel solution. The mixed solution is centrifuged to derive supernatant liquid (decant solution).

Mixing of the prepared gel and decant solution leads to derive solution for crystallization in the next step.

The step of crystallization is shown in Figure 3.2; the mixture of the solution from the previous steps is filled in a glass vessel and placed in a stainless steel autoclave. The mixture is heated from room temperature to 160 °C with a heating rate of 2 °C/min and is further heated from 160 °C to 210 °C with a heating rate of 2 °C/10 min under pressure 3 kg/cm² (gauge) of nitrogen gas, after that the hot mixture is cooled down to room temperature while still remains in the autoclave. The product crystals are washed with de-ionized water until the pH value of the washing water decreases from about 10 to 7. Then, the crystals are dried in an oven at 110 °C for 24 hours.

The dry crystals are calcined in an air stream at 550 °C by heating it from room temperature to 550 °C with a heating rate of 8.6 °C/min and hold at that temperature for 7 hours. The calcined crystals are finally cooled down to room temperature and stored in a dessicator for later use.

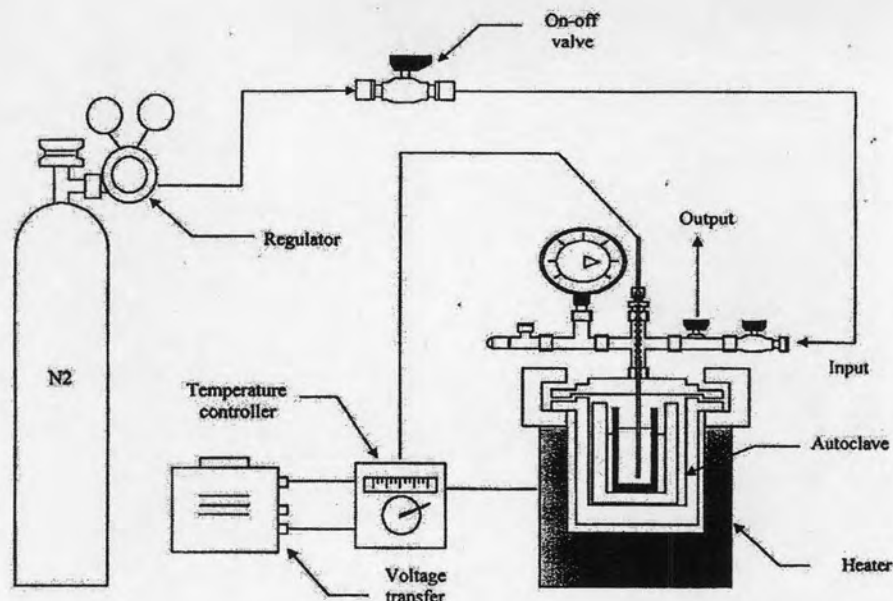


Figure 3.2 The crystallization step of TS-1 catalyst

3.2 The synthesis procedure of V/TS-1 catalyst

From the previous research (Sunphloi, 2005), the V/TS-1 catalysts ($\text{Si/Ti} = 50$, $\text{Si/V} = 20, 30, 50, 70, 100$ and 150 , vanadium source = VCl_3) were synthesized using hydrothermal method. The chemicals, the reagents and the preparation procedures of V/TS-1 used are similar to the preparation of the TS-1 mentioned above. The vanadium salt was added in both gel solution and decant solution (A1 and A2 solution). For example, the compositions of A1 and A2 solution used to prepared V/TS-1 catalyst ($\text{Si/Ti} = 50$, $\text{Si/V} = 100$, vanadium source = VCl_3) are listed in table 3.3 and 3.4. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.3 The compositions of A1 solution used to prepared V/TS-1 catalyst
(add VCl_3 in both of A1 and A2 solution)

Chemicals	Quantity used
$\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$	2.297 g
TPABr	5.720 g
VCl_3^{**}	0.5363 g
NaCl	11.930 g
De-ionized water	60.00 ml
H_2SO_4 (conc.)	3.40 ml

Table 3.4 The compositions of A2 solution used to prepared V/TS-1 catalyst
(add VCl_3 in both of A1 and A2 solution)

Chemicals	Quantity used
$\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$	2.297 g
TPABr	7.530 g
VCl_3^{**}	0.5363 g
De-ionized water	60.00 ml
H_2SO_4 (conc.)	3.40 ml

According to the preparation procedure of V/TS-1 catalyst mentioned above, it has been shown that a problem about how to control the amount of titanium and vanadium in the MFI structure exists. Therefore, this research is set up to provide a better preparation procedure that can control the composition of the prepared catalyst.

In addition to the addition the vanadium salt in both of A1 and A2 solutions presented in the previous work, there are several alternative procedures for adding the vanadium salt in the solutions used to prepare the V/TS-1 catalyst. The alternative procedure considerations will discuss in the next section.

3.3 The alternative procedure considerations of vanadium salt addition

There are several considerations should be considered i.e. which metal compound should be used as a source of the second metal incorporated into the catalyst structure and which solution that the second metal should be added. These considerations are discussed in the section 3.3.1 and 3.3.2 respectively.

3.3.1 Which metal compounds should be used

To select the metal compound used as a source of the second metal incorporated into the catalyst structure. The considerations about the properties of that compound must be considered. For example, the solubility, the interference from the anion and the oxidation state of the interested element. These considerations will be discussed as follow:

3.3.1.1 Solubility

The selected metal compound must dissolve homogeneously in the solution that used as the reagents in the gel solution and the decant solution preparation.

3.3.1.2 Interference from the anion

Since the other anion appeared on the catalyst surface affect the catalyst activity; therefore the interference from the anion must be considered, if the metal exists in the cation or anion part of the compound.

3.3.1.3 The oxidation state of the metal in the compound

One transition metal has many oxidation states. Each oxidation state has its own characteristic; for example, the ability to incorporate into the TS-1 structure. Therefore, the oxidation state of the interested metal in the compound is one of the important factor must be considered.

3.3.2 Which solution that the metal compound should be added

There are various solutions in the catalyst preparation in which the metal compound can be added. The selected solution must dissolve the metal compound homogeneously.

The present research not only study about the effects of the synthesis methodology (i.e. the vanadium salt addition method) but also study about the effect of the vanadium sources contain vanadium in different oxidation states on the incorporation ability into the TS-1 structure. According to the mixed solution used to prepare the V/TS-1 catalyst has water as a solvent, therefore vanadium(III)chloride (VCl_3), vanadyl acetylacetonate ($VO(acac)_2$) and Vanadium(V)oxide (V_2O_5) were chosen as the source of vanadium metal because these vanadium compounds can dissolve in water and have different oxidation states of vanadium (i.e. V^{3+} , V^{4+} and V^{5+} respectively).

3.4 The alternative procedures of vanadium salt addition

The explanation about the alternative procedures of vanadium salt addition is divided in three sections by the type of the vanadium salt. The alternative procedures of VCl_3 , $VO(acac)_2$ and V_2O_5 addition are illustrated in the section 3.4.1, 3.4.2 and 3.4.3 respectively.

3.4.1 Vanadium(III)chloride (VCl_3)

3.4.1.1 Add in A1 and A2 solution

The vanadium salt addition in A1 and A2 solution has already been discussed in section 3.2. The compositions of A1 and A2 solution used to prepared V/TS-1 catalyst ($Si/Ti = 50$, $Si/V = 100$, vanadium source = VCl_3) are listed in table 3.3 and 3.4. The compositions of the remaining solutions are the same as in Table 3.2.

3.4.1.2 Add in A1 solution

The compositions of A1 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VCl_3) are listed in table 3.5. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.5 The compositions of A1 solution used to prepared V/TS-1 catalyst (add VCl_3 into A1 solution)

Chemicals	Quantity used
$\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$	2.297 g
TPABr	5.720 g
VCl_3^{**}	1.0762 g
NaCl	11.930 g
De-ionized water	60.00 ml
H_2SO_4 (conc.)	3.40 ml

3.4.1.3 Add in A2 solution

The compositions of A2 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VCl_3) are listed in table 3.6. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.6 The compositions of A2 solution used to prepared V/TS-1 catalyst (add VCl_3 into A2 solution)

Chemicals	Quantity used
$\text{Ti}[\text{O}(\text{CH}_2)_3\text{CH}_3]_4$	2.297 g
TPABr	7.530 g
VCl_3^{**}	1.0762 g
De-ionized water	60.00 ml
H_2SO_4 (conc.)	3.40 ml

3.4.1.4 Add in B1 solution

The compositions of B1 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VCl_3) are listed in table 3.7. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.7 The compositions of B1 solution used to prepared V/TS-1 catalyst (add VCl_3 into B1 solution)

Chemicals	Quantity used
Sodium Silicate	69.000 g
VCl_3^{**}	1.0726 g
De-ionized water	45.000 ml

3.4.1.5 Add in B2 solution

The compositions of B2 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VCl_3) are listed in table 3.8. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.8 The compositions of B2 solution used to prepared V/TS-1 catalyst (add VCl_3 into B2 solution)

Chemicals	Quantity used
Sodium Silicate	69.000 g
VCl_3^{**}	1.0726 g
De-ionized water	45.000 ml

3.4.1.6 Add in C1 solution

The compositions of C1 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VCl_3) are listed in table 3.9. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.9 The compositions of C1 solution used to prepared V/TS-1 catalyst
(add VCl_3 into C1 solution)

Chemicals	Quantity used
TPABr	2.160 g
NaCl	40.590 g
NaOH	2.390 g
VCl_3^{**}	1.0726 g
De-ionized water	208.00 ml
H_2SO_4 (conc.)	1.55 ml

3.4.1.7 Add in C2 solution

The compositions of C2 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VCl_3) are listed in table 3.10. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.10 The compositions of C2 solution used to prepared V/TS-1 catalyst
(add VCl_3 into C2 solution)

Chemicals	Quantity used
NaCl	26.270 g
VCl_3^{**}	1.0726 g
De-ionized water	104.00 ml

****** The calculation of the amount of VCl_3 used is explained in appendix A.

The preparation of V/TS-1 catalyst (Si/Ti=50, Si/V=100) by adding the amount of VCl_3 in either gel solution or decant solution, instead of adding 0.5363 g of VCl_3 into the A1 solution and another 0.5363 g of VCl_3 into the A2 solution like the previous research, the alternative procedures will add 1.0726 g of VCl_3 (0.5363 g + 0.5363 g) in each solution that used to prepare the gel solution and the decant solution (i.e. solution A1, A2, B1, B2, C1 or C2).

3.4.2 Vanadyl acetylacetonate (VO(acac)₂)

3.4.2.1 Add in A1 and A2 solution

The vanadium salt addition in A1 and A2 solution has been discussed in section 3.2. The compositions of A1 and A2 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VO(acac)₂) are listed in table 3.11 and 3.12 respectively. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.11 The compositions of A1 solution used to prepared V/TS-1 catalyst (add VO(acac)₂ into A1 and A2 solution)

Chemicals	Quantity used
Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g
TPABr	5.720 g
VO(acac) ₂ **	0.8947 g
NaCl	11.930 g
De-ionized water	60.00 ml
H ₂ SO ₄ (conc.)	3.40 ml

Table 3.12 The compositions of A2 solution used to prepared V/TS-1 catalyst (add VO(acac)₂ into A1 and A2 solution)

Chemicals	Quantity used
Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g
TPABr	7.530 g
VO(acac) ₂ **	0.8947 g
De-ionized water	60.00 ml
H ₂ SO ₄ (conc.)	3.40 ml

3.4.2.2 Add in A1 solution

The compositions of A1 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VO(acac)₂) are listed in table 3.13. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.13 The compositions of A1 solution used to prepared V/TS-1 catalyst (add VO(acac)₂ into A1 solution)

Chemicals	Quantity used
Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g
TPABr	5.720 g
VO(acac) ₂ ^{**}	1.7894 g
NaCl	11.930 g
De-ionized water	60.00 ml
H ₂ SO ₄ (conc.)	3.40 ml

3.4.2.3 Add in A2 solution

The compositions of A2 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VO(acac)₂) are listed in table 3.14. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.14 The compositions of A2 solution used to prepared V/TS-1 catalyst (add VO(acac)₂ into A2 solution)

Chemicals	Quantity used
Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g
TPABr	7.530 g
VO(acac) ₂ ^{**}	1.7894 g
De-ionized water	60.00 ml
H ₂ SO ₄ (conc.)	3.40 ml

3.4.2.4 Add in B1 solution

The compositions of B1 solution used to prepared V/Ts-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VO(acac)₂) are listed in table 3.15. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.15 The compositions of B1 solution used to prepared V/Ts-1 catalyst (add VO(acac)₂ into B1 solution)

Chemicals	Quantity used
Sodium Silicate	69.000 g
VO(acac) ₂ **	1.7894 g
De-ionized water	45.000 ml

3.4.2.5 Add in B2 solution

The compositions of B2 solution used to prepared V/Ts-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VO(acac)₂) are listed in table 3.16. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.16 The compositions of B2 solution used to prepared V/Ts-1 catalyst (add VO(acac)₂ into B2 solution)

Chemicals	Quantity used
Sodium Silicate	69.000 g
VO(acac) ₂ **	1.7894 g
De-ionized water	45.000 ml

3.4.2.6 Add in C1 solution

The compositions of C1 solution used to prepared V/Ts-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VO(acac)₂) are listed in table 3.17. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.17 The compositions of C1 solution used to prepared V/TS-1 catalyst
(add VO(acac)₂ into C1 solution)

Chemicals	Quantity used
TPABr	2.160 g
NaCl	40.590 g
NaOH	2.390 g
VO(acac) ₂ **	1.7894 g
De-ionized water	208.00 ml
H ₂ SO ₄ (conc.)	1.55 ml

3.4.2.7 Add in C2 solution

The compositions of C2 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = VO(acac)₂) are listed in table 3.18. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.18 The compositions of C2 solution used to prepared V/TS-1 catalyst
(add VO(acac)₂ into C2 solution)

Chemicals	Quantity used
NaCl	26.270 g
VO(acac) ₂ **	1.7894 g
De-ionized water	104.00 ml

** The calculation of the amount of VO(acac)₂ used is explained in appendix A.

3.4.3 Vanadium(V)oxide (V₂O₅)

3.4.3.1 Add in A1 and A2 solution

This vanadium salt addition in A1 and A2 solution has been discussed in section 3.2. The compositions of A1 and A2 solution used to prepared V/TS-1

catalyst (Si/Ti = 50, Si/V = 100, vanadium source = V₂O₅) are listed in table 3.19 and 3.20. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.19 The compositions of A1 solution used to prepared V/TS-1 catalyst
(add V₂O₅ into A1 and A2 solution)

Chemicals	Quantity used
Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g
TPABr	5.720 g
V ₂ O ₅ **	0.3007 g
NaCl	11.930 g
De-ionized water	60.00 ml
H ₂ SO ₄ (conc.)	3.40 ml

Table 3.20 The compositions of A2 solution used to prepared V/TS-1 catalyst
(add V₂O₅ into A1 and A2 solution)

Chemicals	Quantity used
Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g
TPABr	7.530 g
V ₂ O ₅ **	0.3007 g
De-ionized water	60.00 ml
H ₂ SO ₄ (conc.)	3.40 ml

3.4.3.2 Add in A1 solution

The compositions of A1 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = V₂O₅) are listed in table 3.21. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.21 The compositions of A1 solution used to prepared V/Ts-1 catalyst
(add V₂O₅ into A1 solution)

Chemicals	Quantity used
Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g
TPABr	5.720 g
V ₂ O ₅ **	0.6014 g
NaCl	11.930 g
De-ionized water	60.00 ml
H ₂ SO ₄ (conc.)	3.40 ml

3.4.3.3 Add in A2 solution

The compositions of A2 solution used to prepared V/Ts-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = V₂O₅) are listed in table 3.22. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.22 The compositions of A2 solution used to prepared V/Ts-1 catalyst
(add V₂O₅ into A2 solution)

Chemicals	Quantity used
Ti[O(CH ₂) ₃ CH ₃] ₄	2.297 g
TPABr	7.530 g
V ₂ O ₅ **	0.6014 g
De-ionized water	60.00 ml
H ₂ SO ₄ (conc.)	3.40 ml

3.4.3.4 Add in B1 solution

The compositions of B1 solution used to prepared V/Ts-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = V₂O₅) are listed in table 3.23. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.23 The compositions of B1 solution used to prepared V/Ts-1 catalyst
(add V_2O_5 into B1 solution)

Chemicals	Quantity used
Sodium Silicate	69.000 g
$V_2O_5^{**}$	0.6014 g
De-ionized water	45.000 ml

3.4.3.5 Add in B2 solution

The compositions of B2 solution used to prepared V/Ts-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = V_2O_5) are listed in table 3.24. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.24 The compositions of B2 solution used to prepared V/Ts-1 catalyst
(add V_2O_5 into B2 solution)

Chemicals	Quantity used
Sodium Silicate	69.000 g
$V_2O_5^{**}$	0.6014 g
De-ionized water	45.000 ml

3.4.3.6 Add in C1 solution

The compositions of C1 solution used to prepared V/Ts-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = V_2O_5) are listed in table 3.25. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.25 The compositions of C1 solution used to prepared V/TS-1 catalyst
(add V₂O₅ into C1 solution)

Chemicals	Quantity used
TPABr	2.160 g
NaCl	40.590 g
NaOH	2.390 g
V ₂ O ₅ **	0.6014 g
De-ionized water	208.00 ml
H ₂ SO ₄ (conc.)	1.55 ml

3.4.3.7 Add in C2 solution

The compositions of C2 solution used to prepared V/TS-1 catalyst (Si/Ti = 50, Si/V = 100, vanadium source = V₂O₅) are listed in table 3.26. The compositions of the remaining solutions are the same as in Table 3.2.

Table 3.26 The compositions of C2 solution used to prepared V/TS-1 catalyst
(add V₂O₅ into C2 solution)

Chemicals	Quantity used
NaCl	26.270 g
V ₂ O ₅ **	0.6014 g
De-ionized water	104.00 ml

** The calculation of the amount of V₂O₅ used is explained in appendix A.

3.5 Catalyst Characterization

Various characterization techniques were used in this study in order to clarify the catalyst structure, the morphology and the surface composition. The synthesized V/TS-1 catalysts were characterized by using the following techniques.

3.5.1 X-ray fluorescence spectroscopy (XRF)

The composition analysis of elements in the bulk of the synthesized catalysts was performed by X-ray fluorescence spectroscopy. Firstly, 4 grams of the powder sample was hydraulic compressed to form a sample pallet and then placed into the sample chamber. After vacuuming step, the chemical compositions were analyzed using Oxford Model ED 2000 with energy dispersive X-ray (EDX) technique.

3.5.2 X-ray diffraction (XRD)

The crystallinity of sample powder were performed by a X-ray diffractometer SIEMENS D5000 connected with a computer with Diffract ZT version 3.3 program for fully control of the XRD analyzer. The experiments were carried out by using Ni-filtered Cu-K α radiation. The scans were performed over the 2θ ranges from 6° to 40° with the resolution 0.02° and the number of scan is 10.

3.5.3 Fourier-transform infrared spectroscopy (FT-IR)

To determine whether the titanium was incorporated into the MFI crystal lattice, the synthesized V/TS-1 catalysts were characterized by FT-IR spectroscopy using a Nicolet model Impact 6700 with smart diffuse reflectance mode. The powder samples were placed directly in the sample holder. The sample holder was then inserted into the sample port of the diffuse reflectance accessory and the spectra were recorded at room temperature in the range of wavenumber $400\text{-}1400\text{ cm}^{-1}$.

3.5.4 Brunaur-Emmett-Teller (BET) surface area, pore volume and pore sized analysis

The total surface area, pore volume and pore size of the synthesized catalysts were calculated using BET Micromeritics ASAP 2020. The sample cell which contained 0.3 g of sample was placed into BET Micromeritics ASAP 2020. After degassing step, the surface area and pore volume of catalyst were measured.

3.5.5 Scanning electron microscopy (SEM)

The morphology and the crystal size of the synthesized catalysts was examined using a JEOL JSM-35CF scanning electron microscope. The SEM was operated using the back scattering electron (BSE) mode at 10 kV.

3.5.6 Electron spin resonance (ESR)

The metal species within framework and the state of catalyst were determined by using JEOSL, model JES – RE2X. A tube containing 0.12 gram of the catalyst sample was placed into ESR spectrometer. X band with 9.4 GHz were used as microwave unit, and spectra were recorded between 0 and 500 mT on a microcomputer at 25 °C.

3.5.7 NH₃-Temperature programmed desorption (NH₃-TPD)

The strong acid and weak acid sites of the synthesized catalyst were measured using NH₃-TPD technique determined by measuring the amount of adsorbed ammonia on the surface using Micromeritics Chemisorb 2750. Samples were pre-treated in He at 550 °C for 1 hour and saturated with 10%NH₃/He at 80 °C for 15 minutes. Adsorbed NH₃ was removed by flowing He (50 ml/min) while heating at 10°C/min to 550°C and detected by TCD. The calculation of amount of NH₃ was done and reported by Chemsorp TPx software.

3.6 Catalytic reaction

The gas phase oxidation of 2-propanol was used as a test reaction in this study. The chemical and gases, the equipments used in this reaction and the reaction procedures are described as follows:

3.6.1 Chemical and gases

The chemical and gases used in this reaction are showed in Table 3.27. Airzero and 2-propanol are used as reactants. Ultrahigh purity argon is used as a carrier gas.

Table 3.27 The chemical and gases used in the gas phase oxidation of 2-propanol

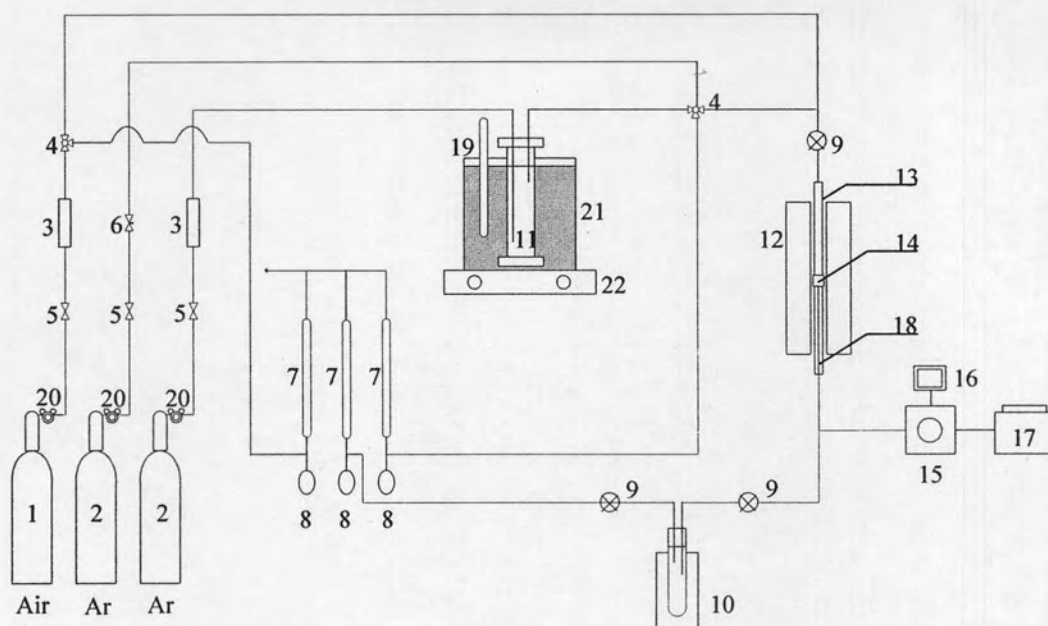
Chemical/gases	Grade	Supplier
2-propanol	Analytical	Fisher scientific
Air	Air zero	TIG
Argon	UHP	TIG

3.6.2 Equipments

Flow diagram of the 2- propanol oxidation system is shown in Figure 3.3. The system consists of a saturator, a microreactor, an automatic temperature controller, an electrical furnace and a gas controlling system.

The microreactor is made from a stainless steel tube. Three sampling points are provided above and below the catalyst bed. Catalyst was placed in the middle of the microreactor between two quartz wool layers.

The gas supplying system consists of three cylinders of gases, one is airzero and the others are the ultra high purity argon, each equipped with pressure regulators (0-120 psig), on-off valves and needle valves for adjusting the flow rate of these gases.



- | | |
|-------------------------|-------------------------------------|
| 1. Air vessel | 12. Furnace |
| 2. Ar vessel | 13. Reactor |
| 3. Mass flow controller | 14. Catalyst bed |
| 4. Three way valve | 15. Temperature controller |
| 5. Gate valve | 16. Digital temperature indicator |
| 6. Needle valve | 17. Variable voltage transformer |
| 7. Rotameter | 18. Thermocouple |
| 8. Rubber cock | 19. Thermometer |
| 9. Sampling point | 20. Pressure regulator |
| 10. Condenser | 21. Water bath |
| 11. Saturator | 22. Heating and stirring controller |

Figure 3.3 Flow diagram of the 2- propanol oxidation system

The composition of the oxygenate compounds in feed and product streams were measured by a Shimadzu GC8A gas chromatograph equipped with flame ionization detector.

A Shimadzu GC8A gas chromatograph equipped with a thermal conductivity detector was used to analyze permanent gases and water. Two columns, a 5A molecular sieve column to separate oxygen and carbon monoxide, a Porapak-Q column to separate carbon dioxide and water were operated in parallel. The operating conditions are shown in the Table 3.28.

Table 3.28 Operating conditions for gas chromatograph.

Gas chromatograph	Shimadzu GC8A	Shimadzu GC8A
Detector	TCD	FID
Column	MS-5A, Porapak-Q	3% SP-1500
Carrier gas	He (99.999%)	N ₂ (99.999%)
Carrier gas flow	25 ml/min	25 ml/min
Column temperature		
- Initial	100 °C	70 °C
- Final	100 °C	120 °C
Heating rate	-	4 °C/min
Detector temperature	130 °C	120 °C
Injector temperature	130 °C	120 °C
Analyzed gas	CO, CO ₂ , H ₂ O	Oxygenates
Detector current	80 mA	

3.6.3 The oxidation procedure

The oxidation procedures are described in the detail below.

1. 0.1 gram of catalyst was packed in the middle of the stainless steel microreactor located in the electrical furnace.

2. 4 ml of 2-propanol was filled in a saturator which placed in the heated water bath. After that, the saturator was connected with the pipeline in the oxidation system as shown in the figure 3.3.

3. The total flow rate was 100 ml/min. Flow rate of 2-propanol, argon and air were adjusted to the required values. The gas mixtures for oxidation reaction were 5 vol% alcohols, 8 vol% oxygen and balance with argon.

4. The reaction was carried out in a microreactor at a temperature range 100-500 °C, atmosphere pressure. The effluent gases were analyzed by using the FID and TCD gas chromatographs. The chromatograph data were converted into mole of propylene, 2-propanol, acetone and CO₂ by calibration curves in Appendix B.

5. The results of catalytic test were calculated in term of percent conversion of 2-propanol. The formula used is shown as followed;

$$\% \text{ A conversion (C)} = \frac{\text{Mole of total products formed}}{\text{Mole of 2 - propanol in feed}}$$

Where total products formed are propylene, acetone and carbondioxide.

To compare the catalytic activity of all synthesized V/TS-1 catalysts the percent conversion of 2-propanol were plotted in the same graph. Mole of 2-propanol used and mole of total products (i.e. propylene, acetone, carbondioxide) formed were plotted in the same graph for each synthesized catalyst to investigate the reaction pathway and to compare the amount of each product formed.