CHAPTER IV

RESULTS AND DISCUSSION

This chapter consists of investigation results of the synthesized catalyst properties with XRF, SEM, XRD, BET, FT-IR, ESR, and NH_3 TPD techniques, and reaction test which are discussed in sections 4.1- 4.9.

4.1 Chemical compositions

Chemical compositions, the atomic ratio Si/Ti and Si/Cr of the synthesized Cr-TS-1 catalysts analyzed by x-ray fluorescence spectroscopy are illustrated in Table 4.1. Data and the calculation of chemical compositions are shown in Appendix F.

Table 4.1 Chemical compositions, the atomic ratio Si/Ti and Si/Cr of the synthesized Cr-TS-1 catalysts by mol of cation

Sample	Si (mol %)	Ti (mol %)	Cr (mol %)	Si/Ti	Si/Cr
Cr(III)-TS-1-A1	99.70	0.12	0.103	814	964
Cr(III)-TS-1-A1A2	99.80	0.17	0.009	584	11458
Cr(III)-TS-1-A2	99.65	0.28	0.003	353	37879
Cr(III)-TS-1-B1	99.37	0.24	0.319	422	312
Cr(III)-TS-1-C1	99.45	0.26	0.231	380	430
Cr(VI)-TS-1-A1	99.66	0.27	0.029	374	3454
Cr(VI)-TS-1-A1A2	99.60	0.32	0.024	308	4132
Cr(VI)-TS-1-B1	99.78	0.19	0.00	524	∞
Cr(VI)-TS-1-C1	99.77	0.20	0.00	489	∞

Table 4.1 shows that the methodology of adding chromium salt in solution and kinds of chromium salt affect the amount of chromium incorporated into TS-1 structure. The Cr(III)-TS-1-B1 sample has the highest amount of chromium whereas the Cr(VI)-TS-1-B1 and Cr(VI)-TS-1-C1 samples do not have chromium. According to the XRF results, it can be concluded that chromium with different oxidation states have different ability to incorporate into the TS-1 structure.

To explain the difference caused by adding the chromium (III) salt [$Cr(NO_3)_3.9H_2O$] in different solutions, the behaviour of Cr^{3+} in an aqueous has to be understood. The simplest ion that chromium (3^+) forms in an aqueous solution is the hexaaquachromium ion $[Cr(H_2O)_6]^{3+}$

$$Cr^{3+} \longrightarrow [Cr(H_2O)_6]^{3+}$$

In the presence of chloride ion (Cl^-), two chloride ions can replace two water molecules of the hexaaquachromium ion to give the tetraaquadichlorochromium III ion.

$$[Cr(H_2O)_6]^{3+} + 2Cl^- \longrightarrow [Cr(H_2O)_4Cl_2]^+ + 2H_2O$$

In the presence of hydroxide ion (OH^-), the hydroxide ions can remove hydrogen ions from the water ligands attached to the chromium ion. Once a hydrogen ion has been removed from three of water molecules, what is left in a complex with no charge.

$$[Cr(H_2O)_6]^{3+} + 3OH^- \longrightarrow Cr(H_2O)_3(OH)_3 + 3H_2O$$

The formed complex [$Cr(H_2O)_3(OH)_3$] does not dissolve in water and form a precipitate.

When added $Cr(NO_3)_3.9H_2O$ in the B1 solution, the dissolve Cr^{3+} ion will react with OH^- ion in the B1 solution and forms complex $Cr(H_2O)_3(OH)_3$. The complex formed, due to its inability to dissolve in water, will be trapped in the gel formed during the gel preparation step. This is the reason while adding $Cr(NO_3)_3.9H_2O$ in the B1 solution yielded a catalyst with the highest Cr content.

When added $Cr(NO_3)_3.9H_2O$ in the C1 solution, the dissolve Cr^{3+} ion will react not only with OH^- ion to form the complex $Cr(H_2O)_3(OH)_3$ but also with Cl- ion to form the complex $[Cr(H_2O)_4Cl_2]^+$. The complex $[Cr(H_2O)_4Cl_2]^+$ can be washed off during the washing step. This cause a loss in chromium which results in lower Cr content when compare with the addition of chromium (III) salt $[Cr(NO_3)_3.9H_2O]$ in the B1 solution.

When added $Cr(NO_3)_3.9H_2O$ in either the A1 or the A2 solution, the Cr^{3+} ion will form mostly the complex $[Cr(H_2O)_4Cl_2]^+$ ion which can be easily washed off during the washing step. The catalysts prepared by adding the $Cr(NO_3)_3.9H_2O$ in the A1 solution Cr(III)-TS-1-A1, A2 solution Cr(III)-TS-1-A2 and A1A2 solutions Cr(III)-TS-1-A1A2, therefore, have a much lower amount of Cr in the obtained catalyst.

Cr^{6+} has different behaviour from Cr^{3+}. In an aqueous solution the Cr^{6+} ion can form a chromate (CrO_4^{2-}) ion or a dichromate ($Cr_2O_7^{2-}$) ion depends on the pH of the solution.

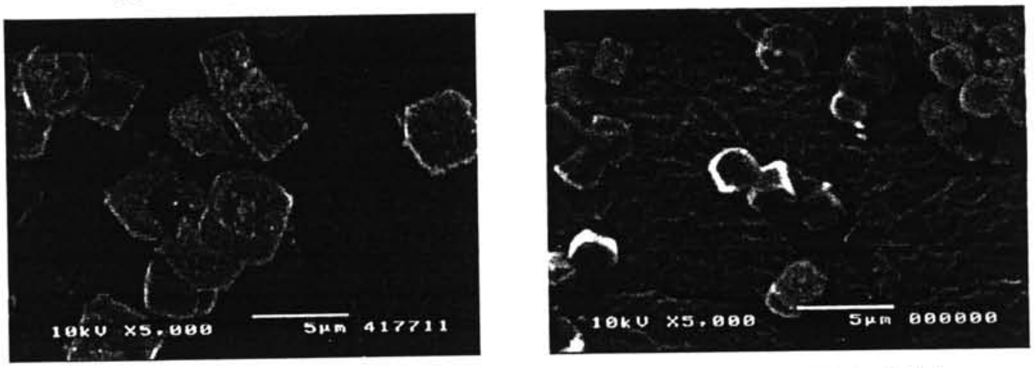
$$\underset{\text{Base}}{CrO_4^{2-}} \quad \underset{+\,OH^-}{\overset{+\,H^+}{\rightleftharpoons}} \quad \underset{\text{Acid}}{CrO_7^{2-}}$$

Both species are very soluble in water. Thus the precipitate chromium species can be easily washed off during the washing step. And in the case of Cr(VI)-TS-1-B1 and Cr(VI)-TS-1-C1 the chromium added was washed off completely. Therefore no chromium was formed in the catalysts Cr(VI)-TS-1-B1 and Cr(VI)-TS-1-C1.

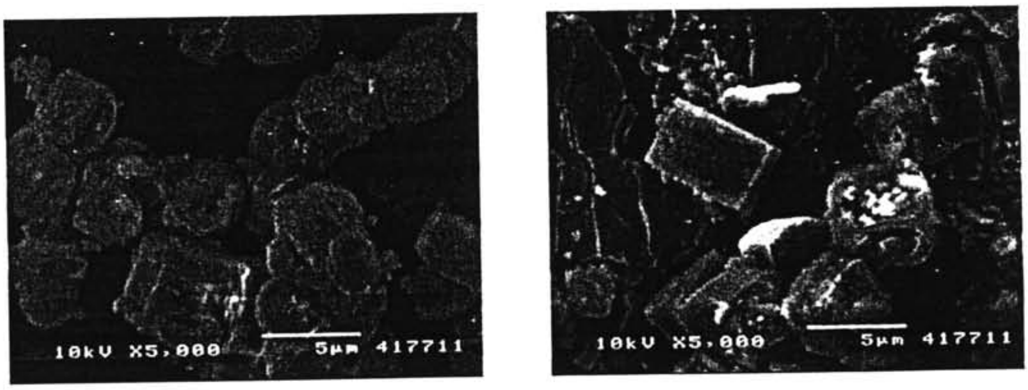
The existence of Cr ion in the catalysts Cr(VI)-TS-1-A1 and Cr(VI)-TS-1-A1A2 is likely due to different reasons. This topic will be discussed later in section of catalytic reaction.

4.2 Morphology

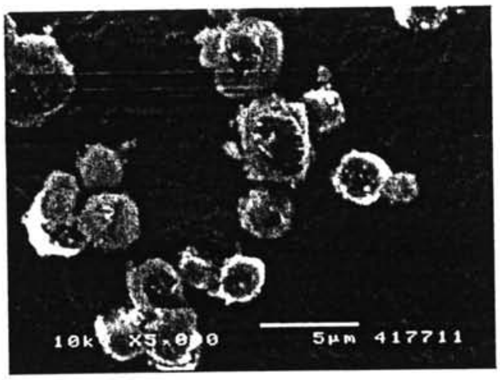
Morphology of the synthesized catalysts was analyzed by scanning electron microscopy are represented in Figures 4.1a and 4.1b.



(a) Cr(III)-TS-1-A1 (b) Cr(III)-TS-1-A1A2

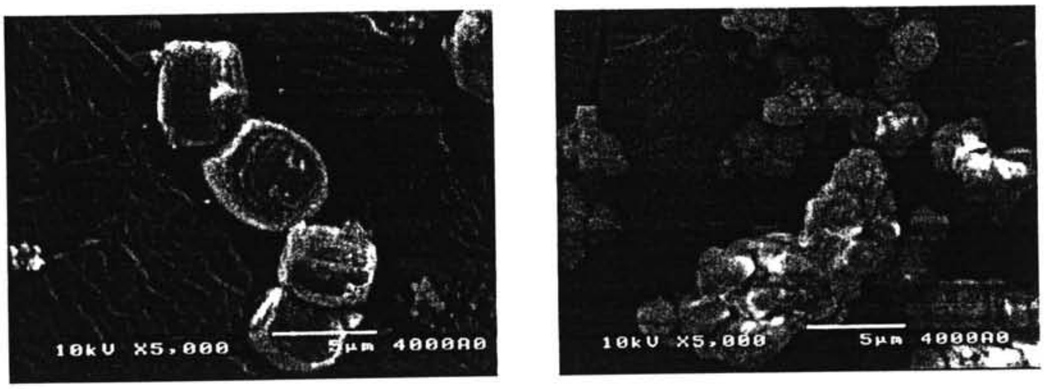


(c) Cr(III)-TS-1-A2 (d) Cr(III)-TS-1-B1

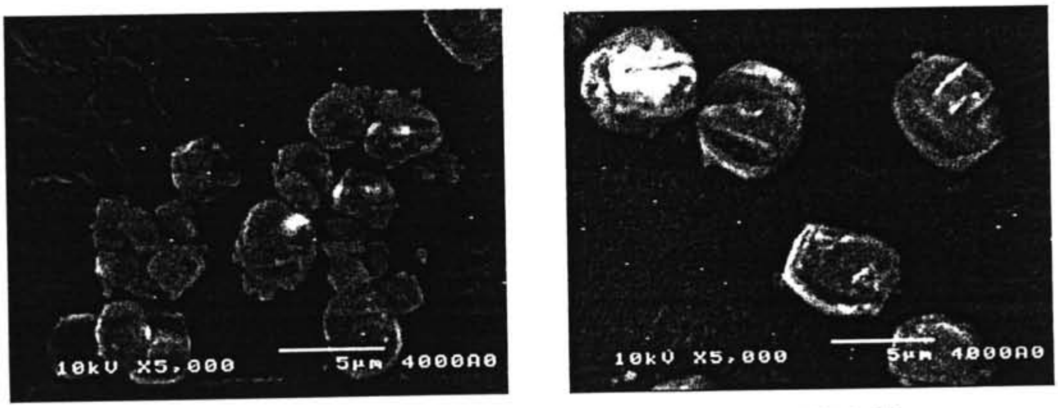


(e) Cr(III)-TS-1-C1

Figure 4.1a SEM micrograph of Cr(III)-TS-1



(f) Cr(VI)-TS-1-A1 (g) Cr(VI)-TS-1-A1A2



(h) Cr(VI)-TS-1-B1 (i) Cr(VI)-TS-1-C1

Figure 4.1b SEM micrograph of Cr(VI)-TS-1

The SEM images show that the synthesized catalysts have various crystalline shapes (e.g. orthorhombic, cubic, sphere). The crystal size of the samples is in the range 2-7 micron. Therefore, it can be concluded that the methodology of adding chromium salt in solution and kinds of chromium salt affect the morphology of the synthesized catalyst.

4.3 Crystalline structure

All samples were investigated by X-ray diffraction. The XRD patterns of the crystalline structure of all samples are shown in Figure 4.2. These patterns show six main characteristic peaks at 2θ as 8, 8.8, 14.8, 23.1, 24 and 29.5 degree, marked with dark circles.

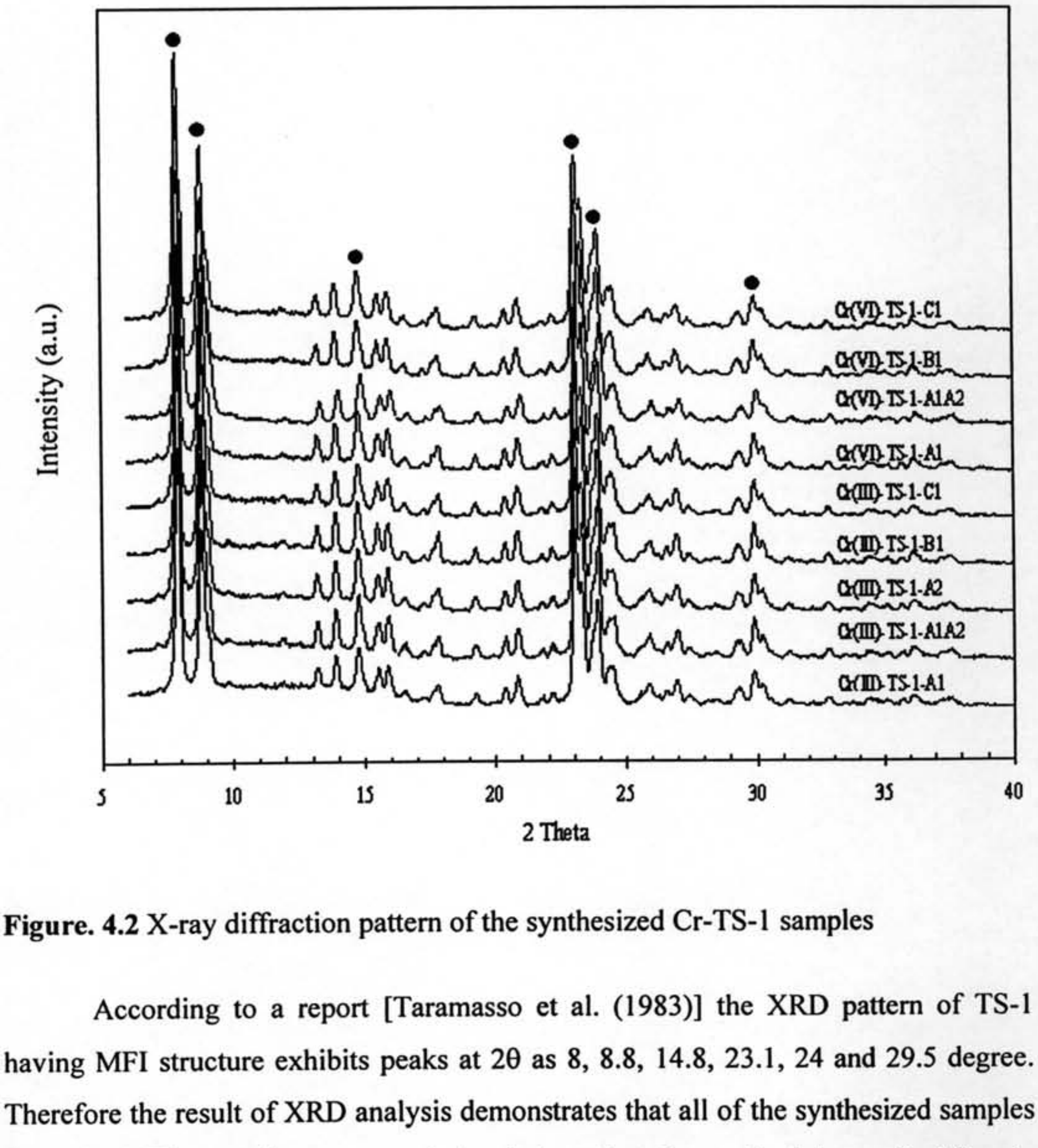


Figure. 4.2 X-ray diffraction pattern of the synthesized Cr-TS-1 samples

According to a report [Taramasso et al. (1983)] the XRD pattern of TS-1 having MFI structure exhibits peaks at 2θ as 8, 8.8, 14.8, 23.1, 24 and 29.5 degree. Therefore the result of XRD analysis demonstrates that all of the synthesized samples have the MFI crystal structure. It is obvious that the methodology of adding in solutions and kinds of chromium salt do not affect the crystalline structure of the obtained catalyst.

4.4 BET surface area and pore volume

BET surface areas and pore volumes of the synthesized samples were analyzed by BET technique. The values are reported in Table 4.2.

Table 4.2 BET surface area and pore volume of the synthesized Cr-TS-1 samples

Sample	BET surface area (m^2/g)	Pore volume (ml/g)
Cr(III)-TS-1-A1	324	0.192
Cr(III)-TS-1-A1A2	325	0.217
Cr(III)-TS-1-A2	322	0.214
Cr(III)-TS-1-B1	307	0.186
Cr(III)-TS-1-C1	317	0.210
Cr(VI)-TS-1-A1	324	0.220
Cr(VI)-TS-1-A1A2	310	0.223
Cr(VI)-TS-1-B1	322	0.207
Cr(VI)-TS-1-C1	324	0.227

From the measurement by BET technique, it was found that surface area and pore volume of all samples are not much different. It is clear that the methodology of adding in solutions and kinds of chromium salt do not affect the surface areas and pore volumes of all samples.

4.5 Location of titanium in MFI structure

To investigate the location of titanium incorporated into the MFI crystal lattice, the samples were analyzed by the FT-IR spectroscopy. The spectra of all samples were measured around 700-1200 cm^{-1}. Those results are represented by Figure 4.3.

From Figure 4.3, it is found that the spectra of all samples exhibit a peak around 960-980 cm^{-1}. It corresponds to the result of a previous study [Huybrechts et al. (1991)], reported that the peak around 960-975 cm^{-1} belong to Ti^{4+} exists in silicate framework. It is obvious that the method of adding chromium salt in various solutions and kinds of chromium salt do not affect the location of titanium ion incorporated in the MFI crystal.

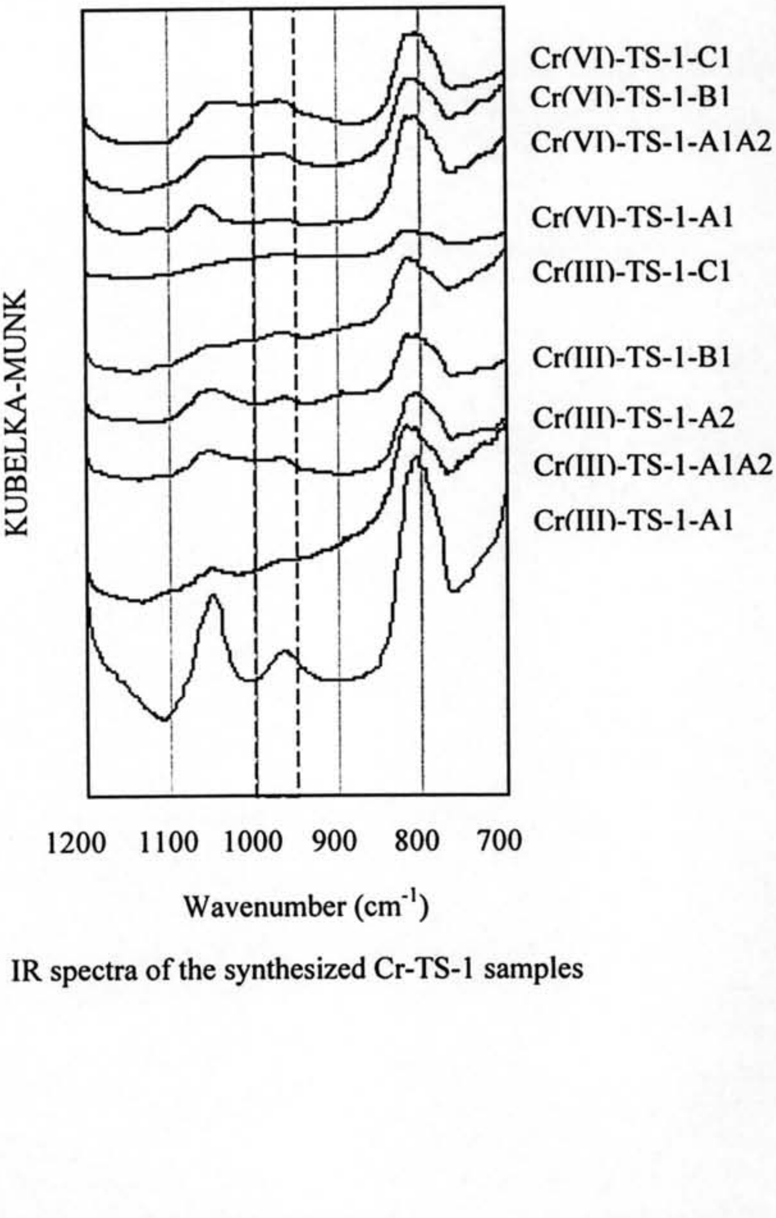


Figure 4.3 IR spectra of the synthesized Cr-TS-1 samples

4.6 Chromium status in Cr-TS-1 framework

Chromium status in Cr-TS-1 framework were investigated by electron spin resonance, e.s.r.. The spectra of the synthesized samples are shown in Figure 4.4. The magnetic field of each sample will be converted to g value as shown Table 4.3.

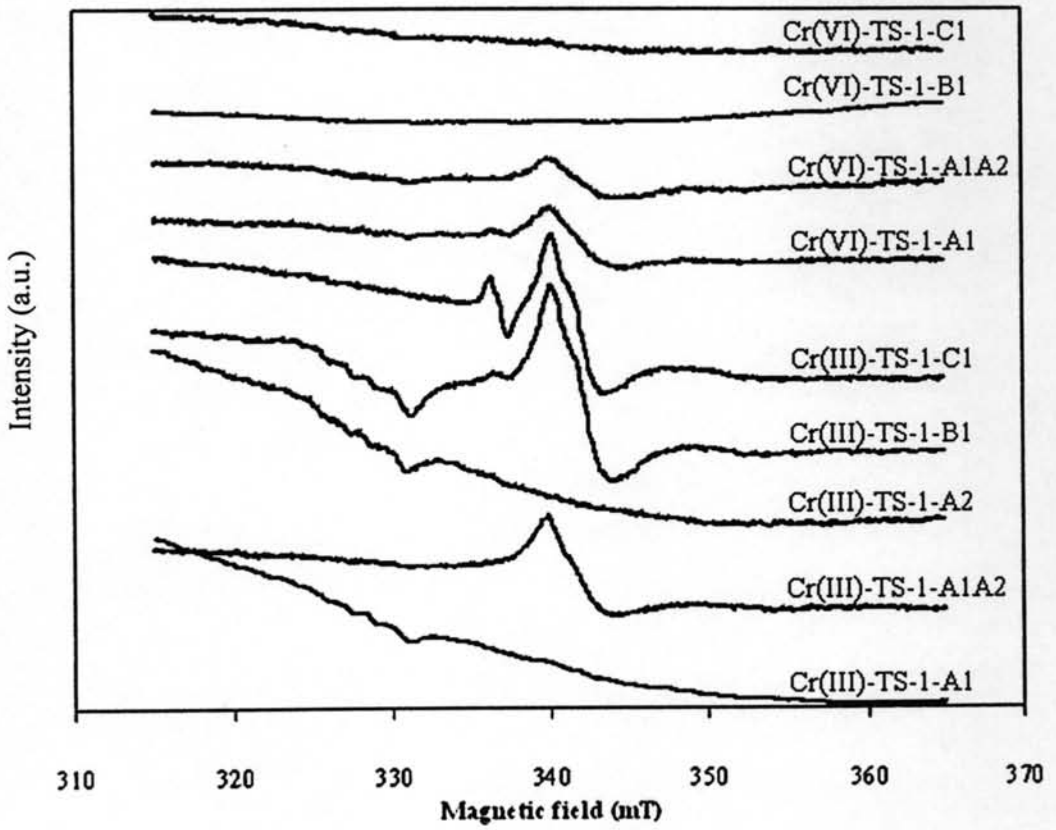


Figure 4.4 ESR spectra of the synthesized Cr-TS-1 samples

Table 4.3 g value of the synthesized Cr-TS-1 samples

Sample	g
Cr(III)-TS-1-A1	-
Cr(III)-TS-1-A1A2	1.974
Cr(III)-TS-1-A2	-
Cr(III)-TS-1-B1	1.972
Cr(III)-TS-1-C1	1.973
Cr(VI)-TS-1-A1	1.973
Cr(VI)-TS-1-A1A2	1.973
Cr(VI)-TS-1-B1	-
Cr(VI)-TS-1-C1	-

It should be noted here that only Cr^{5+} exhibits electron spin resonance phenomenon. The sample(s) do not exhibit e.s.r. phenomenon will not contain Cr^{5+} species. The sample exhibits e.s.r. phenomenon, however, does not have to contain Cr^{5+} species only. Other species (e.g. Cr^{3+} Cr^{6+}) can exist also. The difference in "g" values can indicate the difference in the location of Cr^{5+} species.

The results in Table 4.3 show that Cr(III)-TS-1-A1 and Cr(III)-TS-1-A2 do not contain Cr^{5+} species (no e.s.r. phenomenon was observed). Even though, chromium really exists in the catalyst (from XRF results). Cr(VI)-TS-1-B1 and Cr(VI)-TS-1-C1 do not exhibit e.s.r. phenomenon because there is no chromium in the structure. The e.s.r. results confirm that Cr^{5+} species exists in Cr(III)-TS-1-A1A2, Cr(III)-TS-1-B1, Cr(III)-TS-1-C1, Cr(VI)-TS-1-A1 and Cr(VI)-TS-1-A1A2 catalyst. But one should not conclude that only Cr^{5+} species exists in these samples, other species (Cr^{3+} and Cr^{6+} which do not exhibit e.s.r. phenomenon) can not be excluded. The g value of Cr(III)-TS-1-A1A2, Cr(III)-TS-1-B1, Cr(III)-TS-1-C1, Cr(VI)-TS-1-A1 and Cr(VI)-TS-1-A1A2 catalysts consist of Cr^{5+} bonded in octahedral form outside the framework structure [Giannetto et al.(1997)].

4.7 Catalytic reaction

The synthesized catalysts were tested with the gas phase oxidation reaction of 2-propanol in the fixed bed reactor at 100-500 °C and 1 atm. The feed composition is 5% 2-propanol and 8% oxygen by volume and balanced with argon. The samples were analyzed with gas chromatography described in chapter III. The raw data of samples from GC result were converted to the conversion and selectivity values shown in appendix C.

4.7.1 Mechanism pathways

The catalytic activity testing of the synthesized catalysts with the gas phase oxidation reaction of 2-propanol found that the behaviors of catalysts were similar. The main products of this system are propylene, acetone and carbondioxide. A small amount of acetic acid is also observed. Moreover, the formation of isopropyl ether is a very small that could be neglected.

The results of the catalytic activity testing as illustrated in Figures 4.6a - 4.6i can be concluded that the formation of acetone came from the direct conversion of 2-propanol and possibly formed via the oxidation of propylene as proposal earlier [Chairat (2004)]. The combustion reaction of this system occurs from acetic acid, diisopropyl ether, propylene, acetone and 2-propanol. The reaction pathway of 2-propanol oxidation reaction can show in Figure 4.5.

The conversions of 2-propanol over Cr(III)-TS-1 and Cr(VI)-TS-1 samples as shown in Figures 4.6a - 4.6i are plotted against reaction temperature. It can be said that the reaction quickly proceeded in the range 250-400 °C and rather constant at the reaction temperature higher than 400 °C.

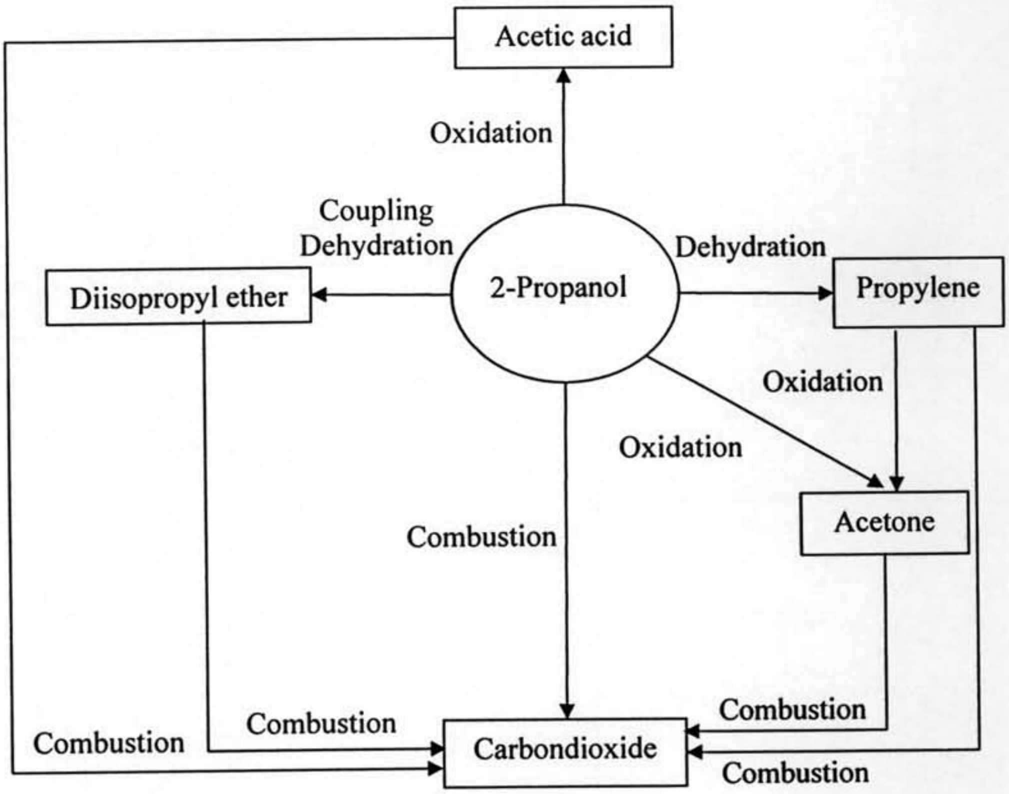


Figure 4.5 The pathway of 2-propanol oxidation reaction

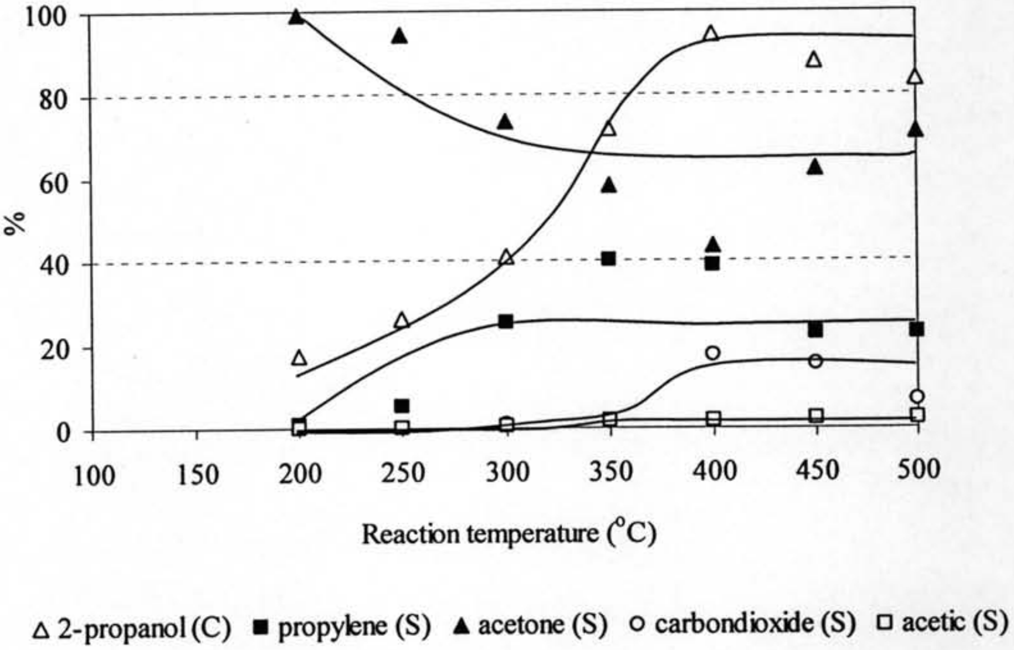


Figure 4.6a Product selectivities of 2-propanol oxidation over Cr(III)-TS-1-A1 (C-Conversion, S-Selectivity)

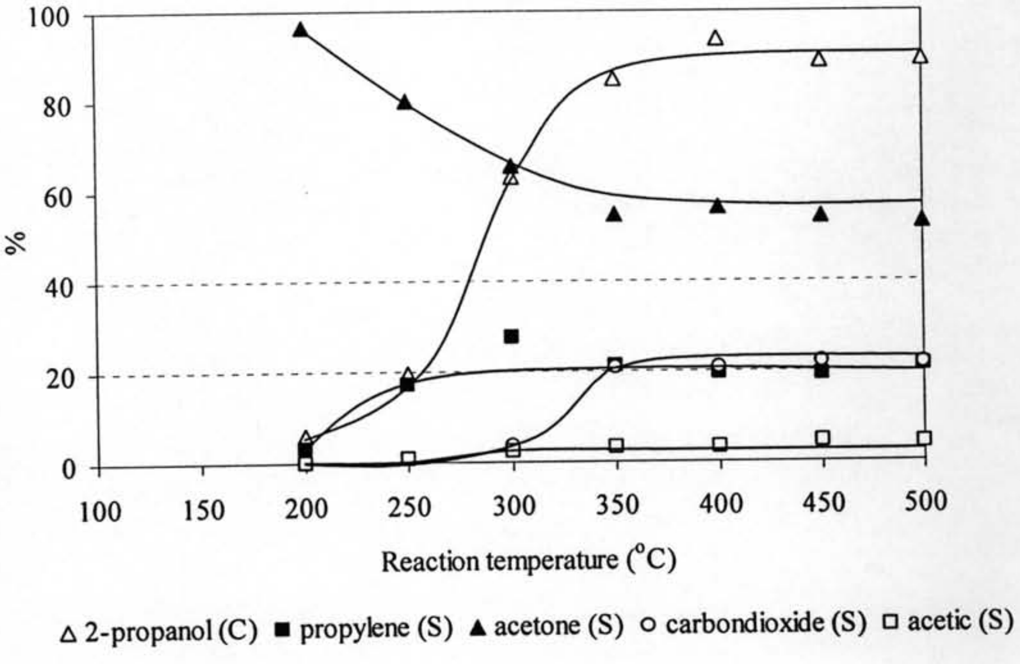


Figure 4.6b Product selectivities of 2-propanol oxidation over Cr(III)-TS-1-A1A2 (C-Conversion, S-Selectivity)

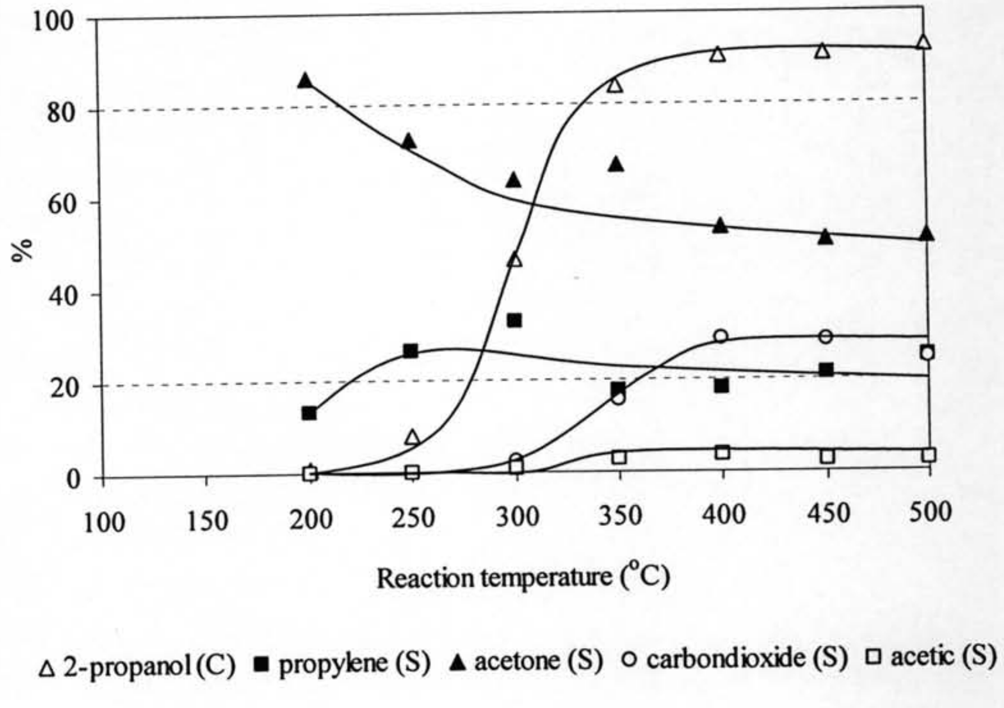


Figure 4.6c Product selectivities of 2-propanol oxidation over Cr(III)-TS-1-A2 (C-Conversion, S-Selectivity)

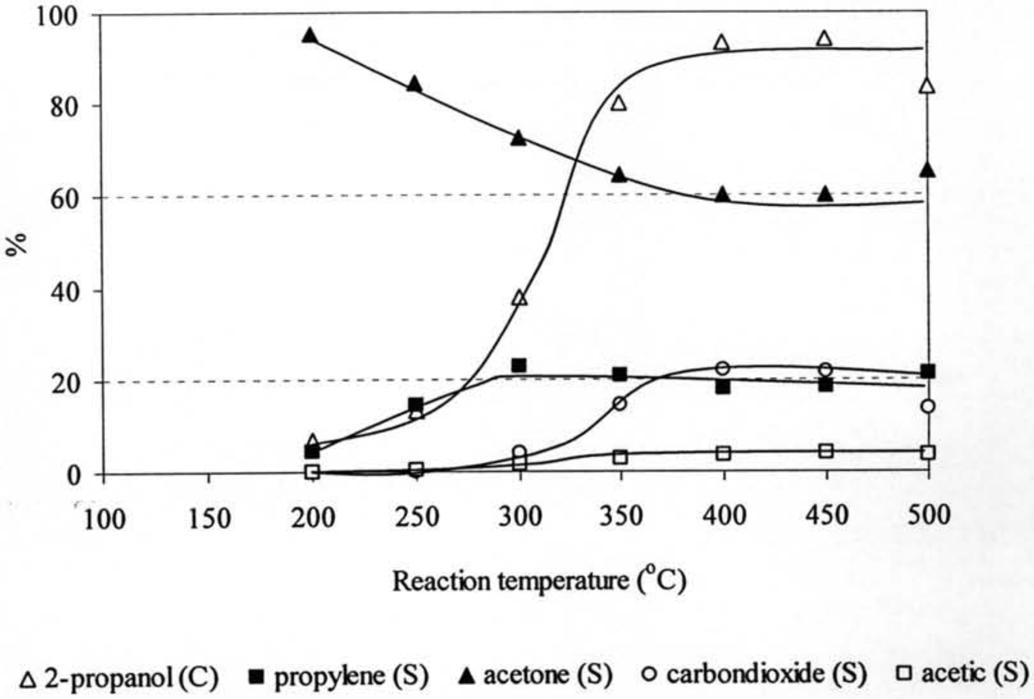


Figure 4.6d Product selectivities of 2-propanol oxidation over Cr(III)-TS-1-B1 (C-Conversion, S-Selectivity)

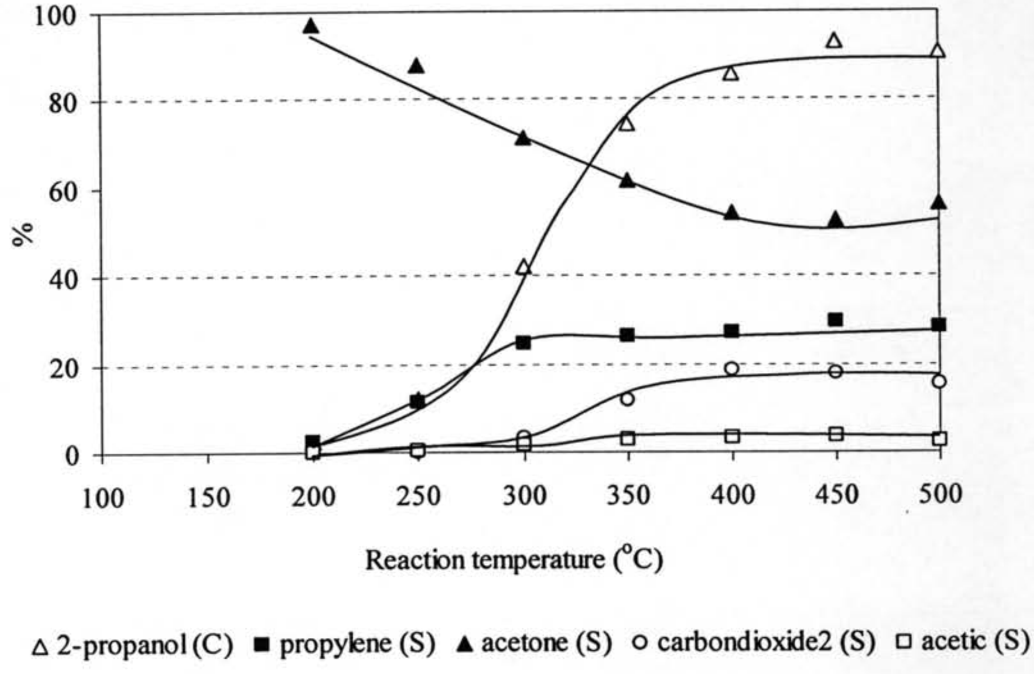


Figure 4.6e Product selectivities of 2-propanol oxidation over Cr(III)-TS-1-C1 (C-Conversion, S-Selectivity)

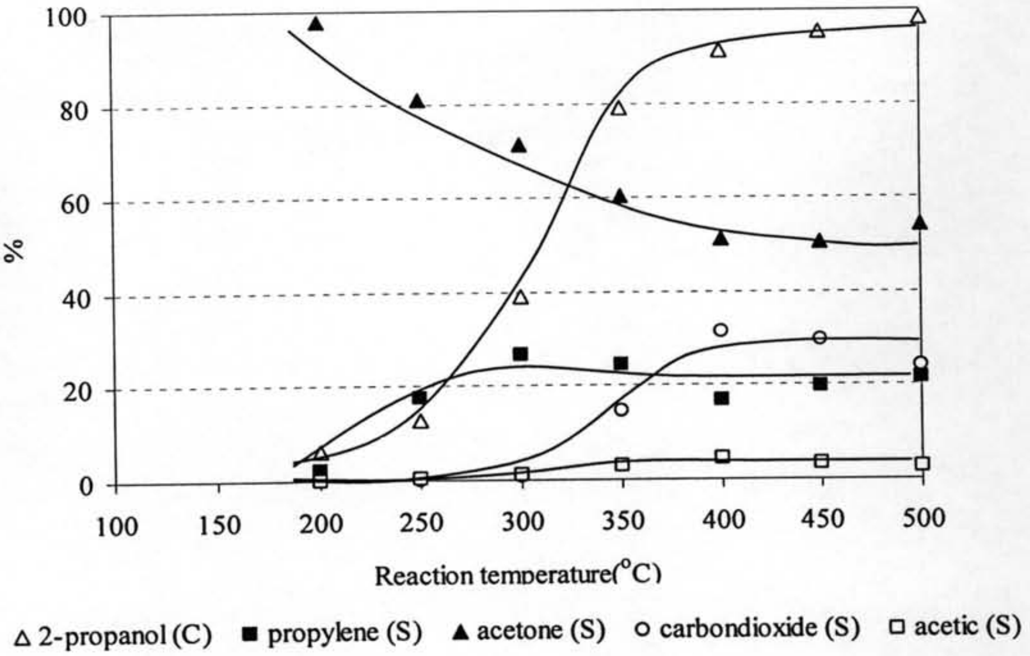


Figure 4.6f Product selectivities of 2-propanol oxidation over Cr(VI)-TS-1-A1 (C-Conversion, S-Selectivity)

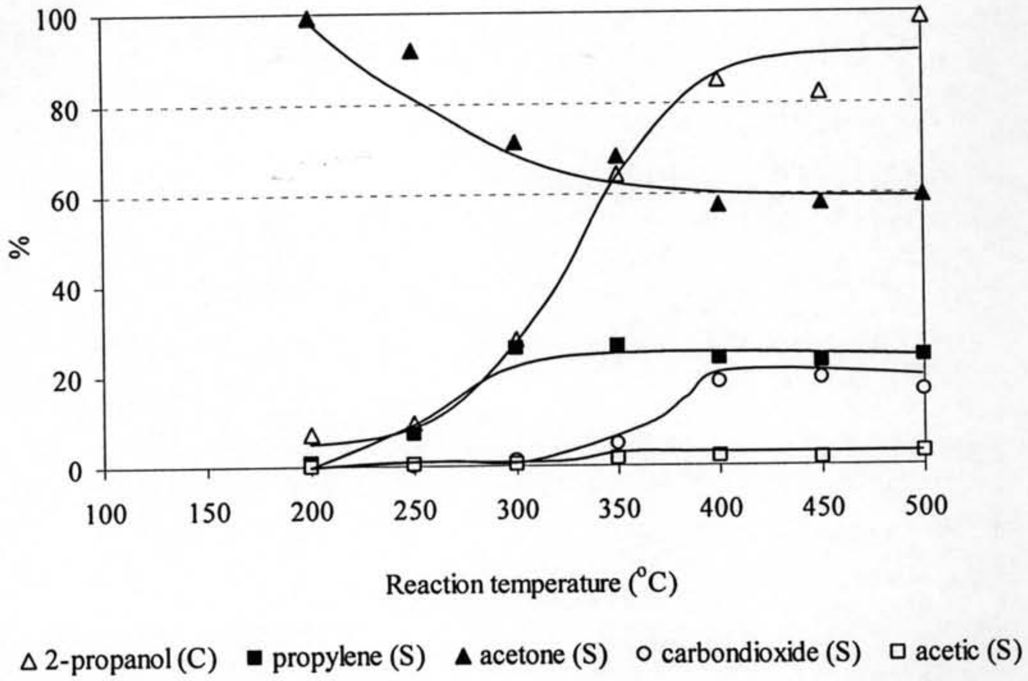


Figure 4.6g Product selectivities of 2-propanol oxidation over Cr(VI)-TS-1-A1A2 (C-Conversion, S-Selectivity)

The effect of the different amount of chromium in catalyst can discuss two cases that are the catalyst with low chromium content group and the catalyst with high chromium content group.

4.7.2 Catalyst with low chromium content group

The catalysts in this group are Cr(III)-TS-1-A1A2, Cr(III)-TS-1-A2, Cr(VI)-TS-1-B1 and Cr(VI)-TS-1-C1. The catalytic behaviors of these catalysts are illustrated in Figures 4.7b, 4.7c, 4.7h and 4.7i. Since the catalyst in this group contain very low amount of Cr or no Cr at all, the catalysts in this group behave in a similar manner in the behavior of a modified TS-1. Therefore, the behavior of the catalysts in this group will not be further discussed.

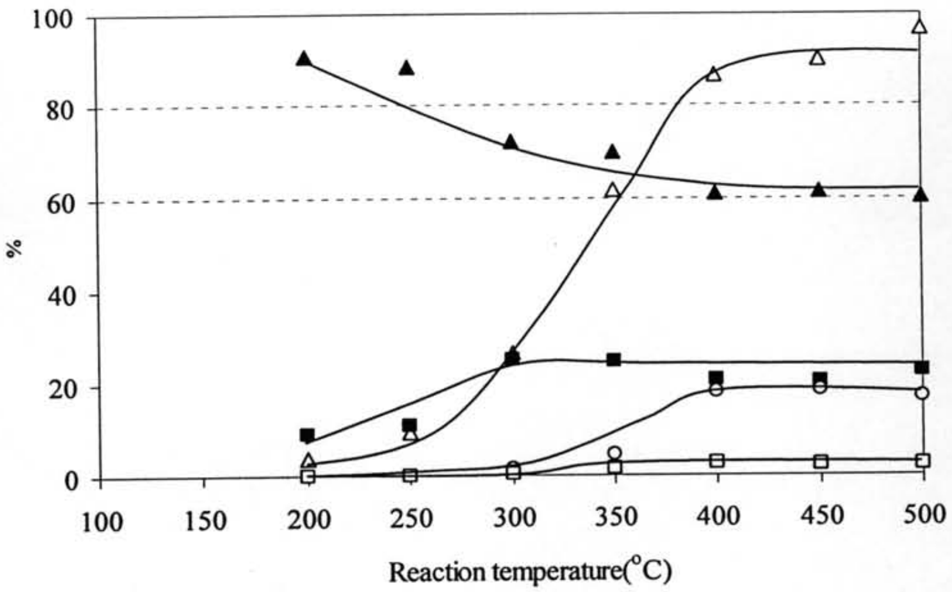
4.7.3 Catalyst with high chromium content group

The catalysts in this group are Cr(III)-TS-1-A1, Cr(III)-TS-1-B1, Cr(III)-TS-1-C1, Cr(VI)-TS-1-A1 and Cr(VI)-TS-1-A1A2. The catalytic behaviors of the catalysts in this group are illustrated in Figures 4.7a, 4.7d, 4.7e, 4.7f and 4.7g. It should be noted that the catalytic activities and selectivities of all the catalysts in this group are similar, independent from the chromium content. Moreover, their behaviors also similar to the behaviors of the catalysts in the low chromium content group and the TS-1. This finding suggests that the chromium presents in the catalyst plays no role in the catalytic oxidation and the dehydration reactions of 2-propanol.

It is generally known that Cr^{6+} is a strong oxidizing agent which Cr^{3+} in the most stable state of chromium ion. It is likely that most of the chromium present in the catalysts is in the 3+ state (and some in the 5+ state as can be seen from the ESR spectra of Cr(III)-TS-1-A1A2, Cr(III)-TS-1-B1, Cr(III)-TS-1-C1, Cr(VI)-TS-1-A1 and Cr(VI)-TS-1-A1A2 catalysts)

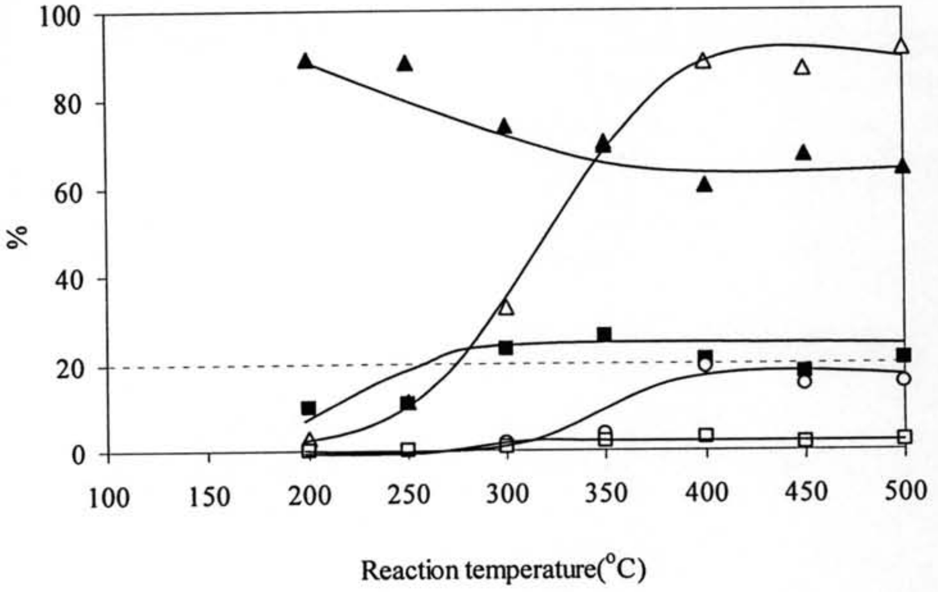
An explanation is needed to explain why the catalysts Cr(VI)-TS-1-A1 and Cr(VI)-TS-1-A1A2 prepared using Cr(VI) salt (CrO_3) but have Cr(III) in the obtained catalysts. A possible explanation is a fraction of the Cr(VI), when dissolved in the A1 solution, acts as an oxidizing agent that oxidized the organic part of $Ti[O(CH_2)_3CH_3]_4$ (i.e. the butoxide part ($-O(CH_2)_3CH_3$) to an aldehyde or a carboxylic acid)

The product of the oxidation reaction is Cr(III) species which is not an active oxidant. The reaction of the Cr(VI) species with the organic part of TPABr is not likely to occur. The experimental results that support this conclusion come from the preparation using the addition of the Cr(VI) salt (CrO_3) in the B1 and C1 solution. The obtained Cr(VI)-TS-1-B1 and Cr(VI)-TS-1-C1 contain no chromium as measured by XRF.



△ 2-propanol (C) ■ propylene (S) ▲ acetone (S) ○ carbondioxide (S) □ acetic (S)

Figure 4.6h Product selectivities of 2-propanol oxidation over Cr(VI)-TS-1-B1 (C-Conversion, S-Selectivity)



△ 2-propanol (C) ■ propylene (S) ▲ acetone (S) ○ carbondioxide (S) □ acetic (S)

Figure 4.6i Product selectivities of 2-propanol oxidation over Cr(VI)-TS-1-C1 (C-Conversion, S-Selectivity)

4.8 Acidity on surface

The acidity on surface of the synthesized catalyst is important for interpretation of the reaction pathway. The acid site of the synthesized catalyst was investigated by ammonia temperature programmed desorption (TPD) technique. The calculation acid site with the peak fitting program is shown in Appendix E. The results are represented in Table 4.4.

Table 4.4 Desorption temperature and acid site quantities of the synthesized Cr-TS-1 samples

Sample	Cr(mole%)	Ti(mole %)	Temperature (°C)		Acid site quantities		
			Weak acid	Strong acid	Weak acid (%)	Strong acid (%)	Total (µmol/g)
Cr(III)-TS-1-A1	0.103	0.12	147	241	47	53	175
Cr(III)-TS-1-A1A2	0.009	0.17	146	242	71	29	174
Cr(III)-TS-1-A2	0.003	0.28	145	227	56	44	133
Cr(III)-TS-1-B1	0.319	0.24	147	247	68	32	132
Cr(III)-TS-1-C1	0.231	0.26	137	231	49	51	132
Cr(VI)-TS-1-A1	0.029	0.27	140	236	75	25	128
Cr(VI)-TS-1-A1A2	0.024	0.32	146	0	100	0	118
Cr(VI)-TS-1-B1	0.00	0.19	139	224	51	49	186
Cr(VI)-TS-1-C1	0.00	0.20	149	229	54	46	187

The total acid sites of the synthesized catalysts are different values. According to adding chromium salt with the different oxidation states affects the different amount of titanium in catalyst structure. The synthesized catalysts have two different types of acid strength, the weaker one desorbs NH_3 at 137-149°C and the stronger one desorbs NH_3 at 224-247°C. The results of the catalytic activity testing of the synthesized catalysts confirm that the amount of chromium existed in catalyst is not significant in 2-propanol oxidation reaction because the behavior of catalyst were similar to TS-1 catalyst. Therefore, it can be concluded that the catalytic activity of the synthesized catalyst does not depend on acid site.