CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the results and discussion are classified into two parts. Firstly, the characterization of H-ZSM-5 and Ag-ZSM-5 catalysts by XRD, SEM, XRF, and NH_3 TPD are described in section 5.1.Secondly, the effects of Si/Al ratio of Ag-ZSM-5 on the silver clusters formation and the results of UV-Vis are explained in section 5.2.

5.1 Catalyst Characterization

5.1.1 X-ray Diffraction Pattern

The structure and crytallinity of the prepared catalysts were analyzed by X-ray diffraction (XRD). The results showed that all of the catalysts have the same structure and crytallinity. XRD pattern of the prepared catalysts correspond with the structure of ZSM-5.The figure 5.1 showed the XRD pattern of H-ZSM-5 catalysts in the different Si/Al ratios from 20 to 150. This indicated that H-ZSM-5 at different Si/Al ratio had the same structure and crytallinity.

XRD pattern of the 3.5wt% Ag-ZSM-5 and 5wt% Ag-ZSM-5 in the different Si/Al ratio from 20 to 150 are shown in Figure 5.2 and 5.3 respectively. XRD pattern of all catalysts have the same pattern as the H-ZSM-5 catalysts. The result indicated that Ag loaded by ion-exchange did not change the main structure of the ZSM-5 catalyst.

XRD pattern of the 3.5wt% Ag-ZSM-5 and 5wt% Ag-ZSM-5 after the reduction with 3% and 100% H_2 are shown in the figure 5.4 to 5.5. The results indicated that after the reduction with H_2, there was no formation of the Ag metal ($2\theta = 38.1°$, $44.3°$ and $44.5°$)[20]. The reductions with hydrogen did not change the main structure of ZSM-5 catalyst.

Figure 5.1 Comparison of XRD pattern of H-ZSM-5 Si/Al from 20 to150

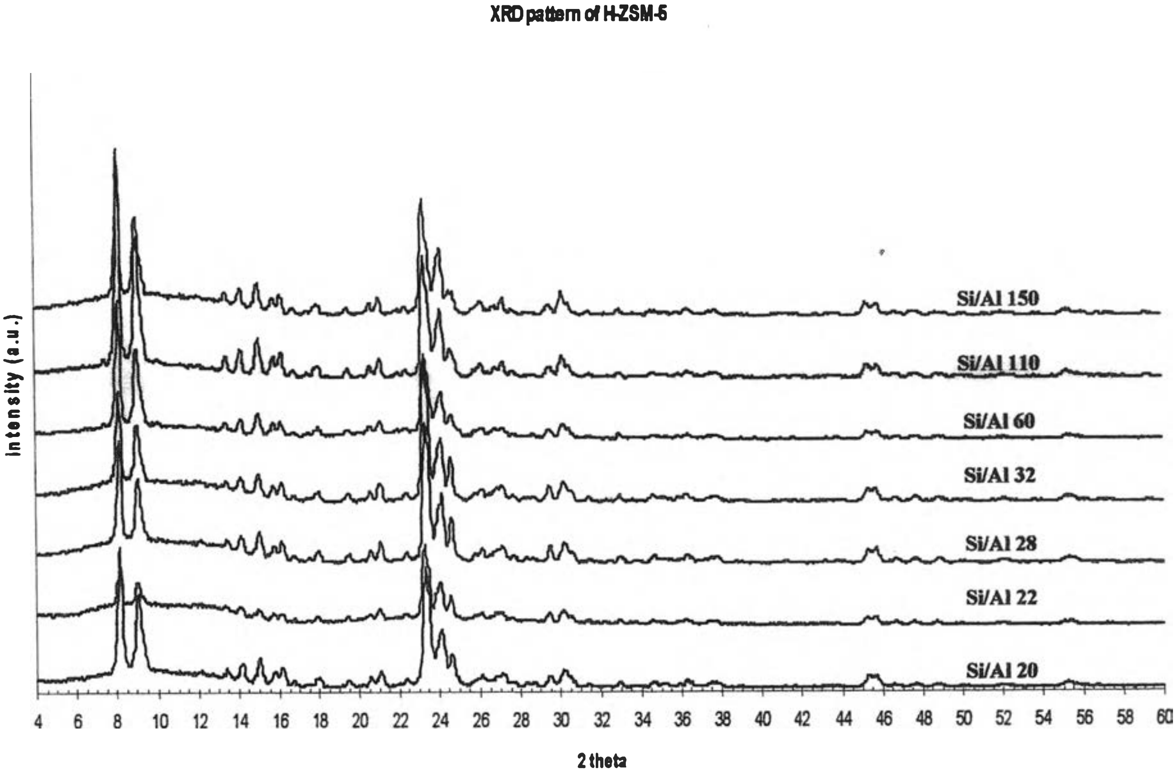


Figure 5.2 Comparison of XRD pattern of 3%Ag-ZSM-5 Si/Al from 20 to150

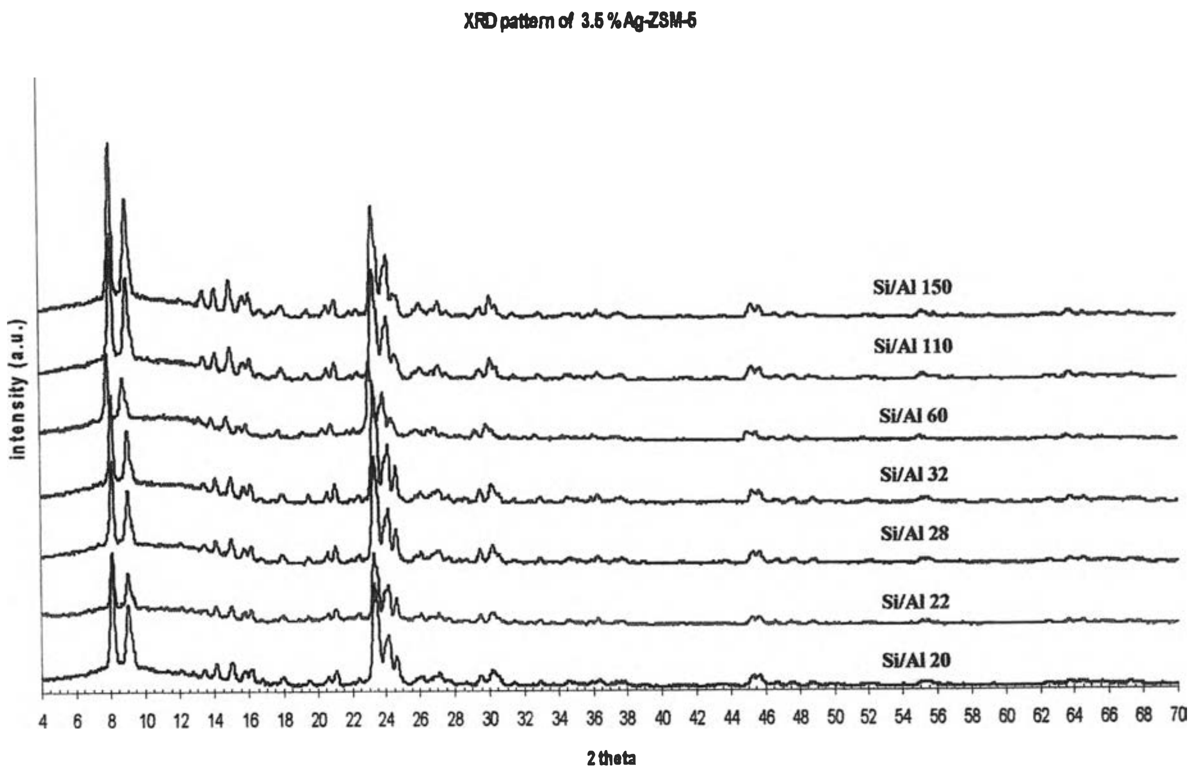


Figure 5.3 Comparison of XRD pattern of 5%Ag-ZSM-5 Si/Al from 20 to150

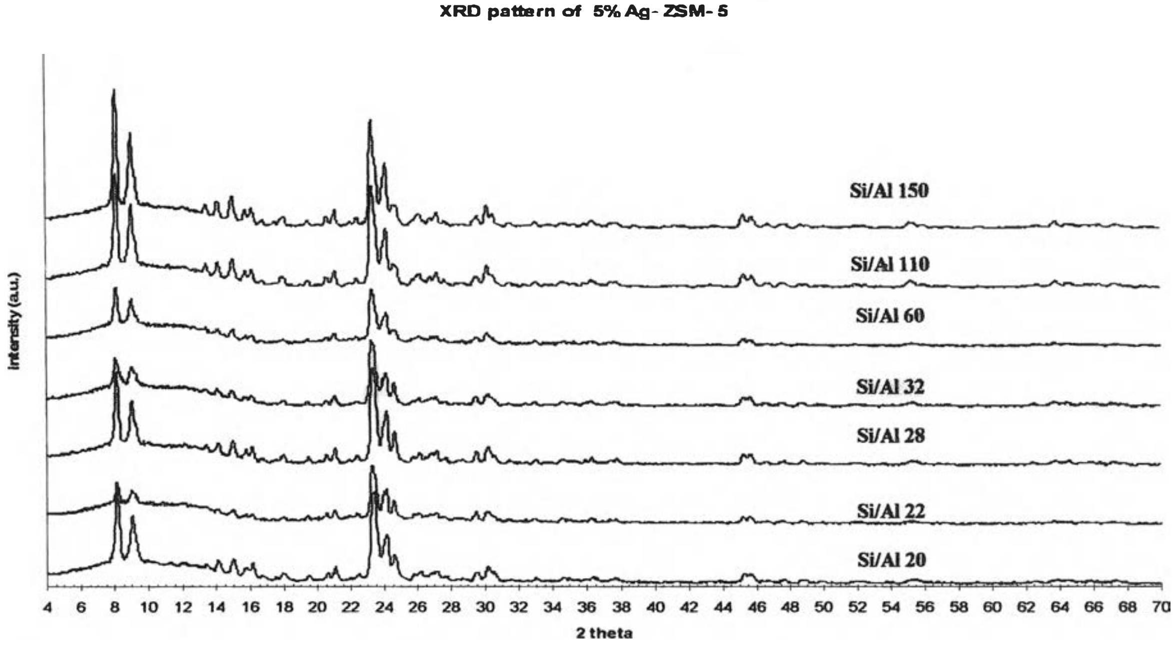
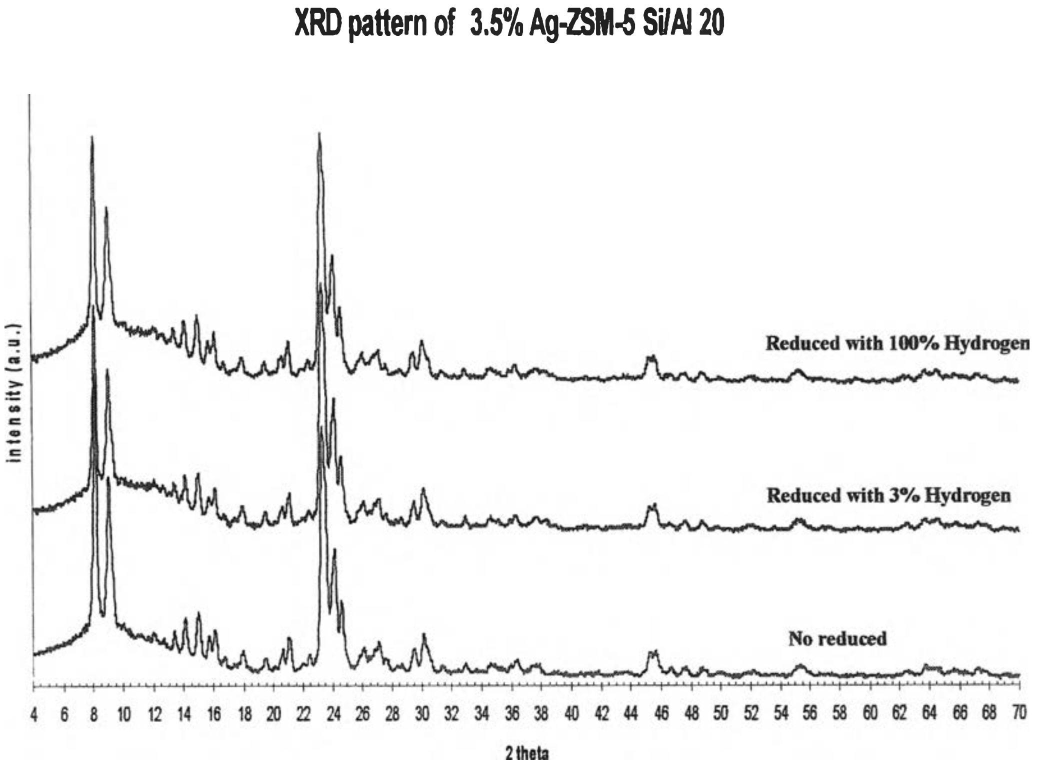
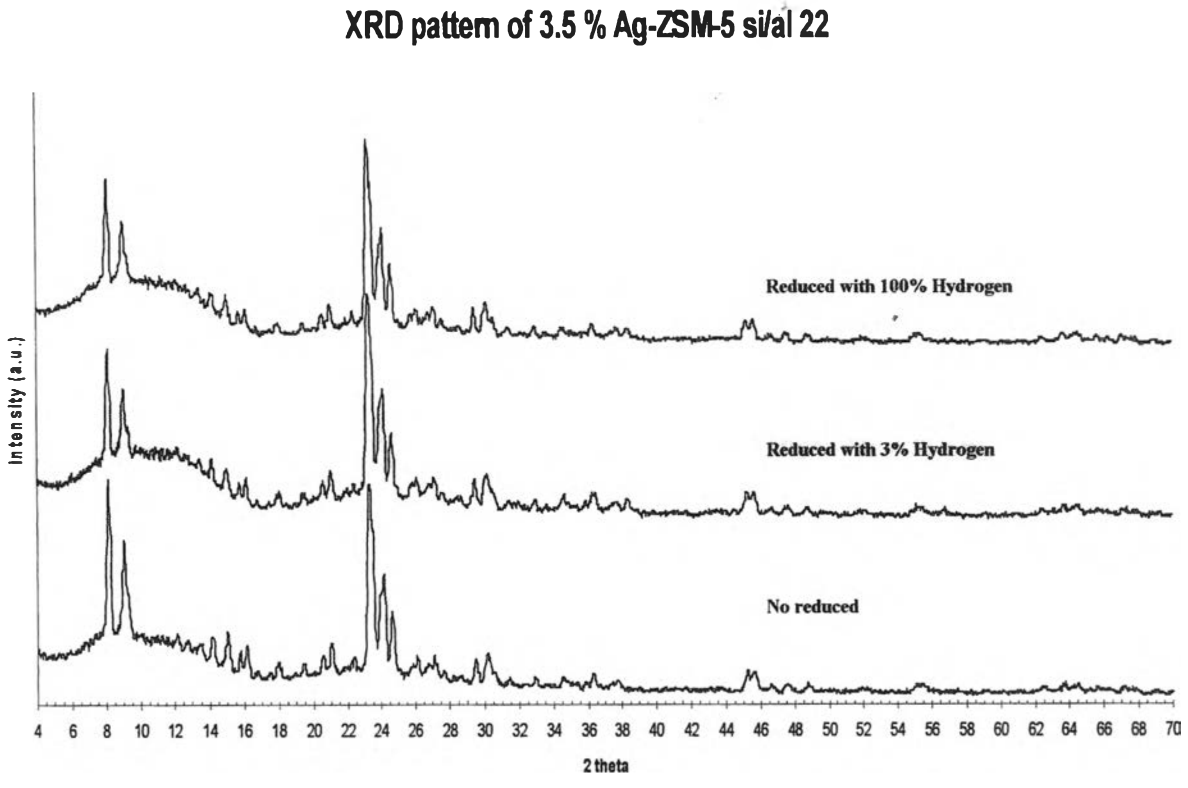


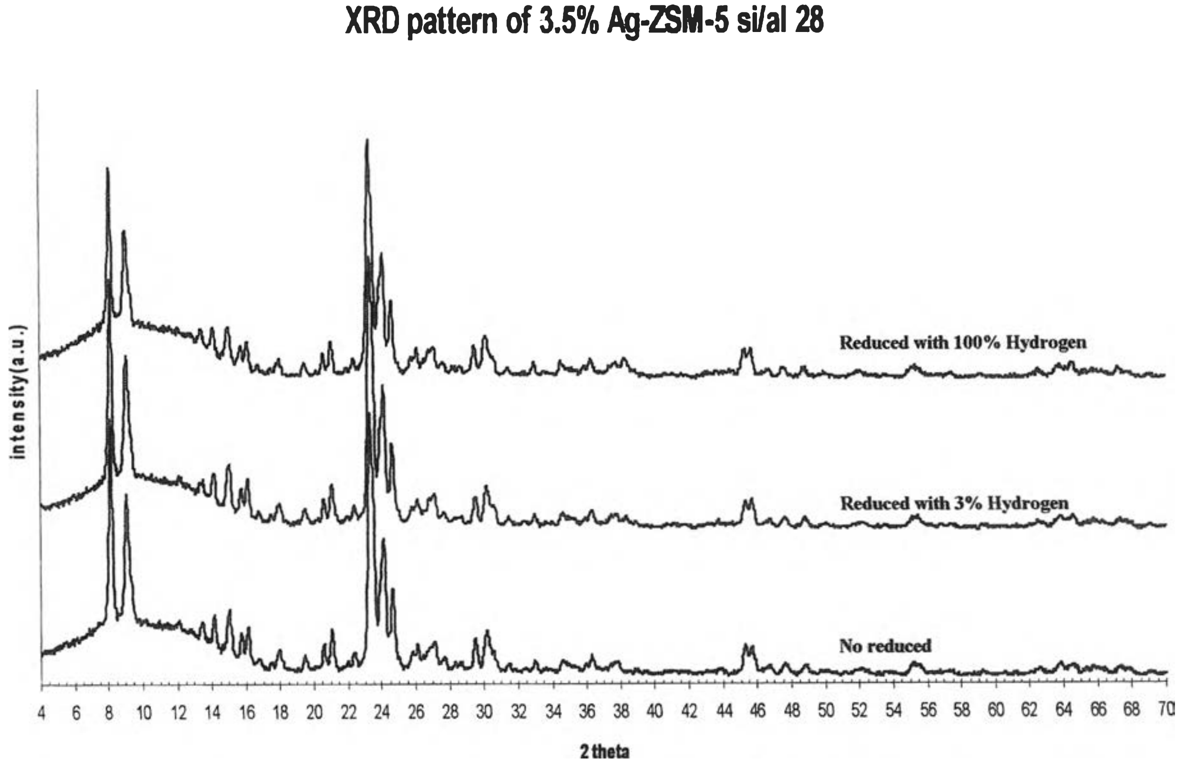
Figure 5.4 Comparison of XRD pattern of 3.5 %Ag-ZSM-5 Si/Al from 20-150 under the reduction with Hydrogen at 300 °C



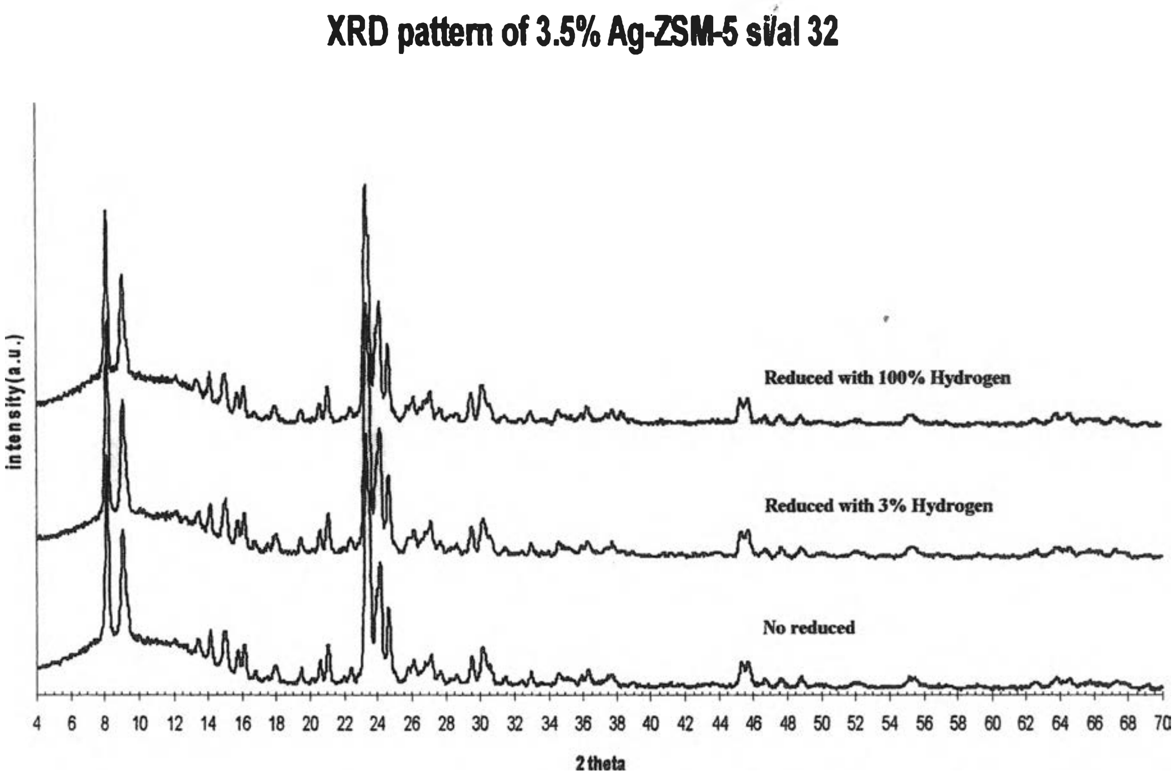
(a) Comparison of XRD pattern of 3.5 %Ag-ZSM-5 Si/Al 20 under the reduction with Hydrogen at 300 °C



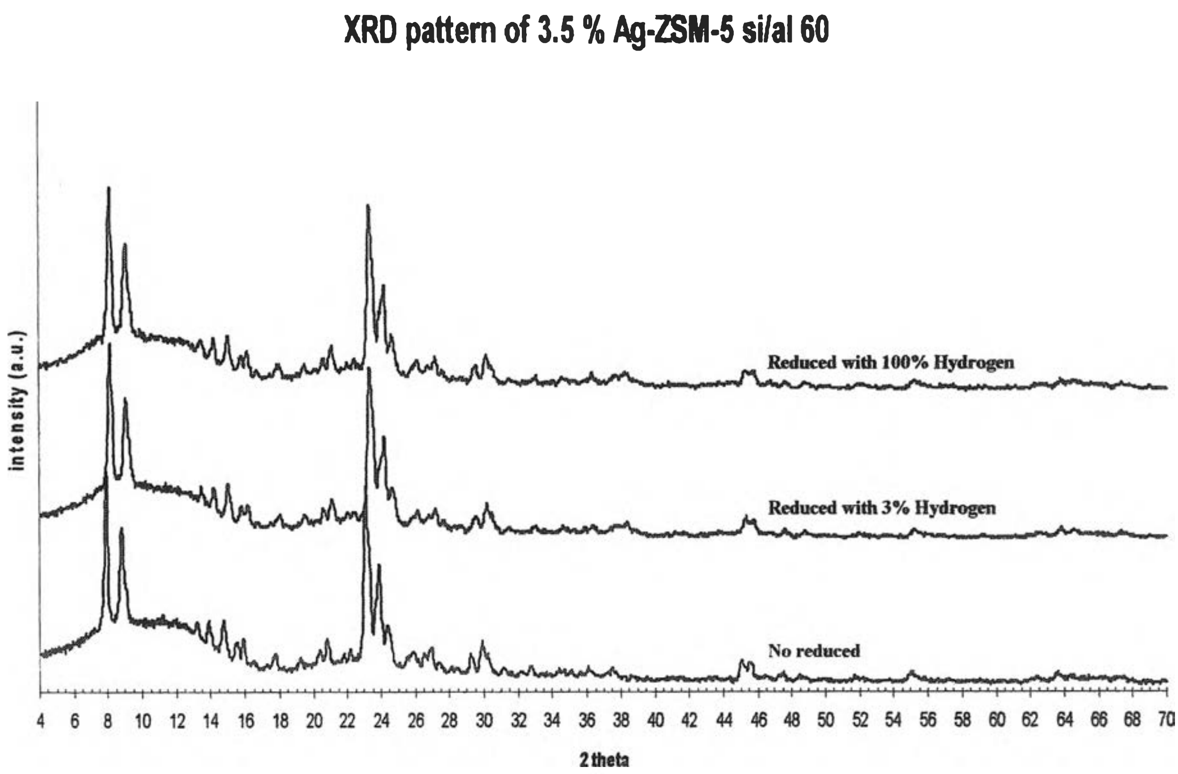
(b) Comparison of XRD pattern of 3.5 %Ag-ZSM-5 Si/Al 22 under the reduction with Hydrogen at 300 °C



(c) Comparison of XRD pattern of 3.5 %Ag-ZSM-5 Si/Al 28 under the reduction with Hydrogen at 300 °C

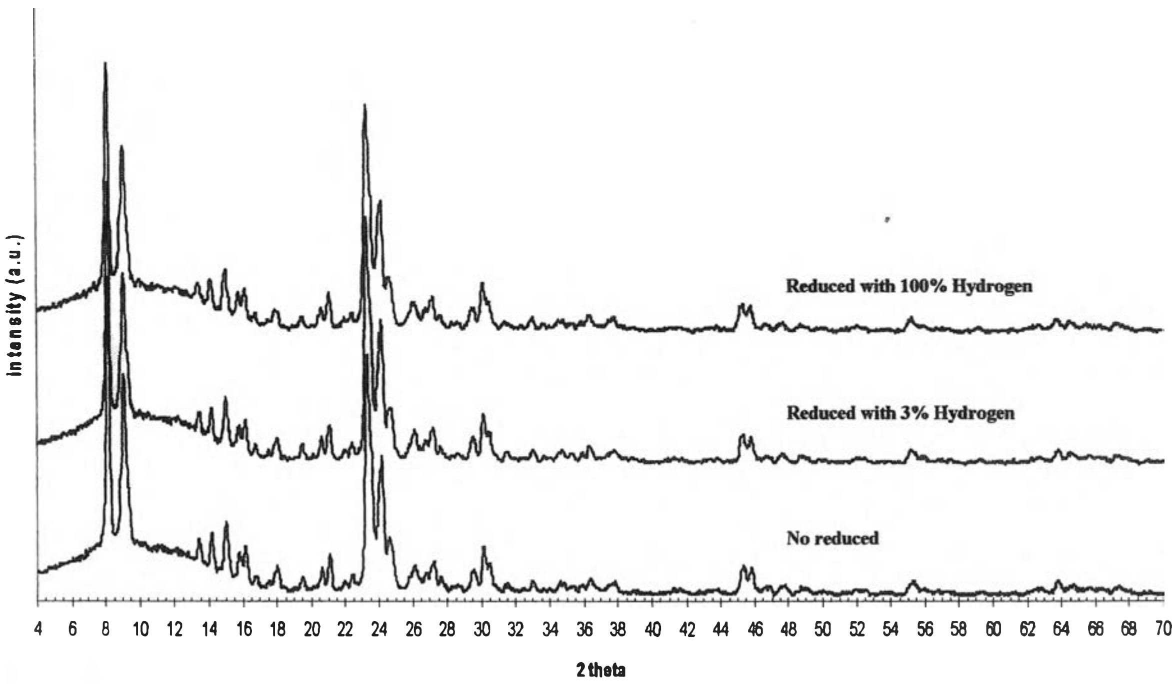


(d) Comparison of XRD pattern of 3.5 %Ag-ZSM-5 Si/Al 32 under the reduction with Hydrogen at 300 °C



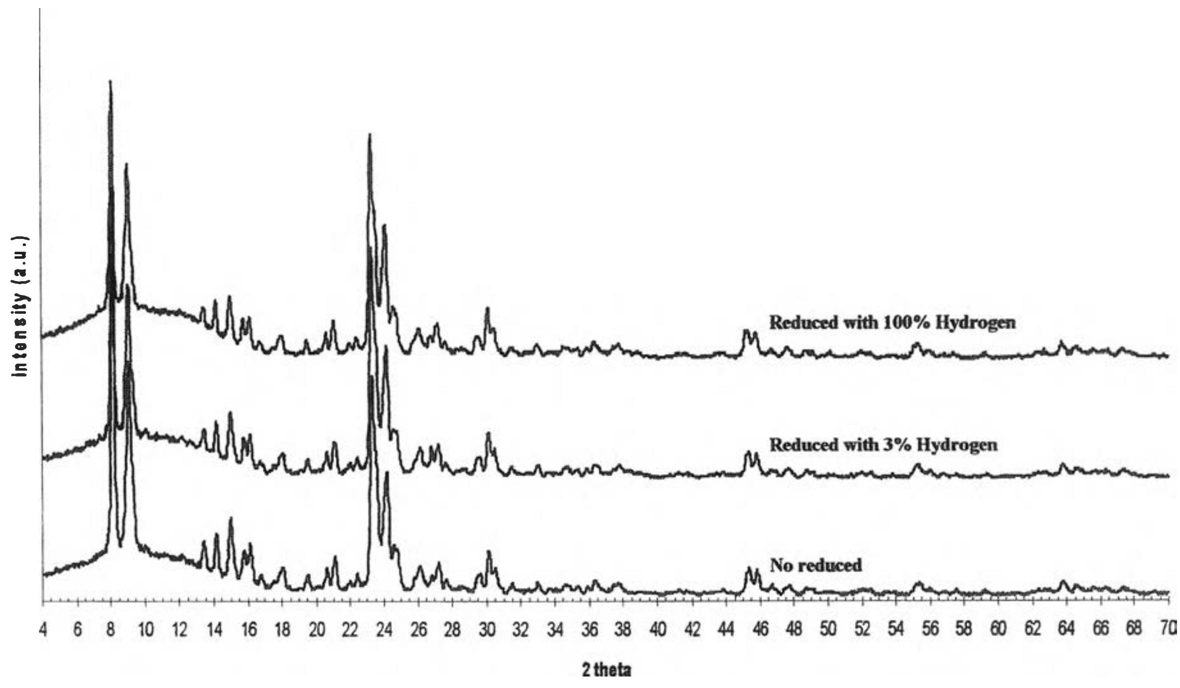
(e) Comparison of XRD pattern of 3.5 %Ag-ZSM-5 Si/Al 60 under the reduction with Hydrogen at 300 °C

XRD pattern of 3.5 % Ag-ZSM-5 si/al 110



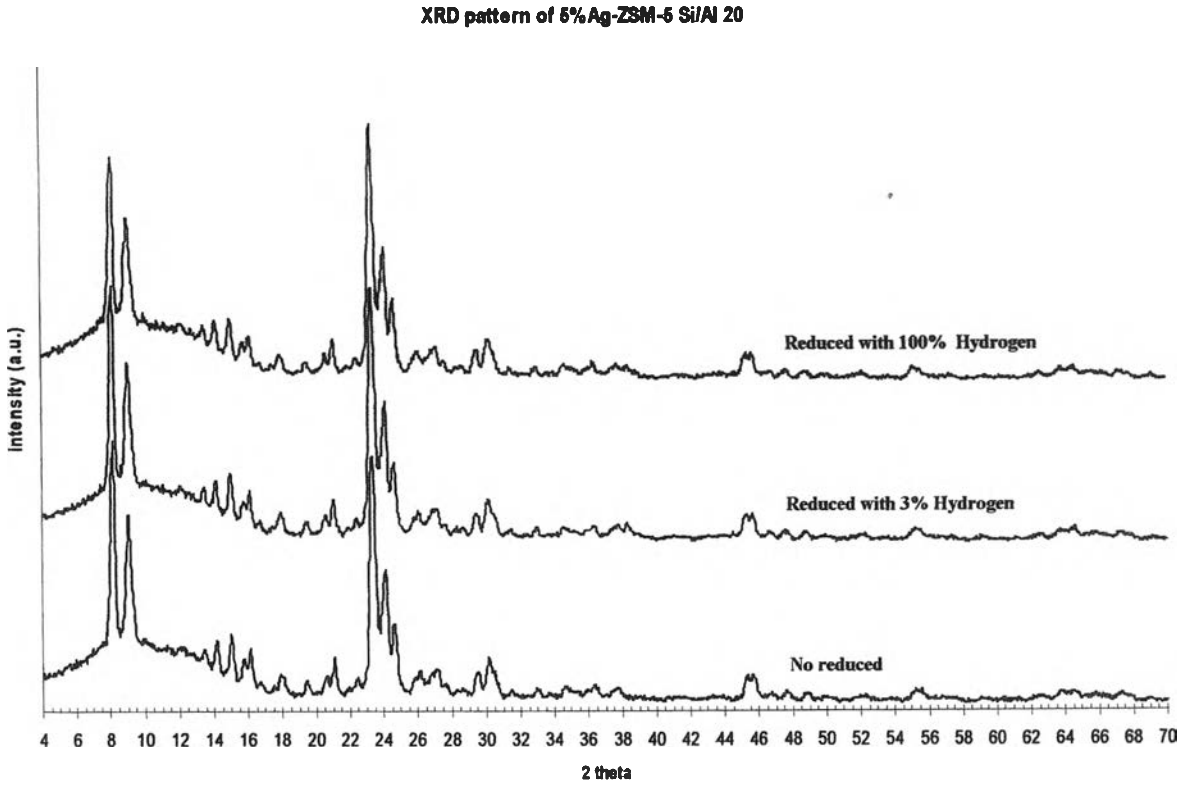
(f) Comparison of XRD pattern of 3.5 %Ag-ZSM-5 Si/Al 110 under the reduction with Hydrogen at 300 °C

XRD pattern of 3.5% Ag-ZSM-5 si/al 150

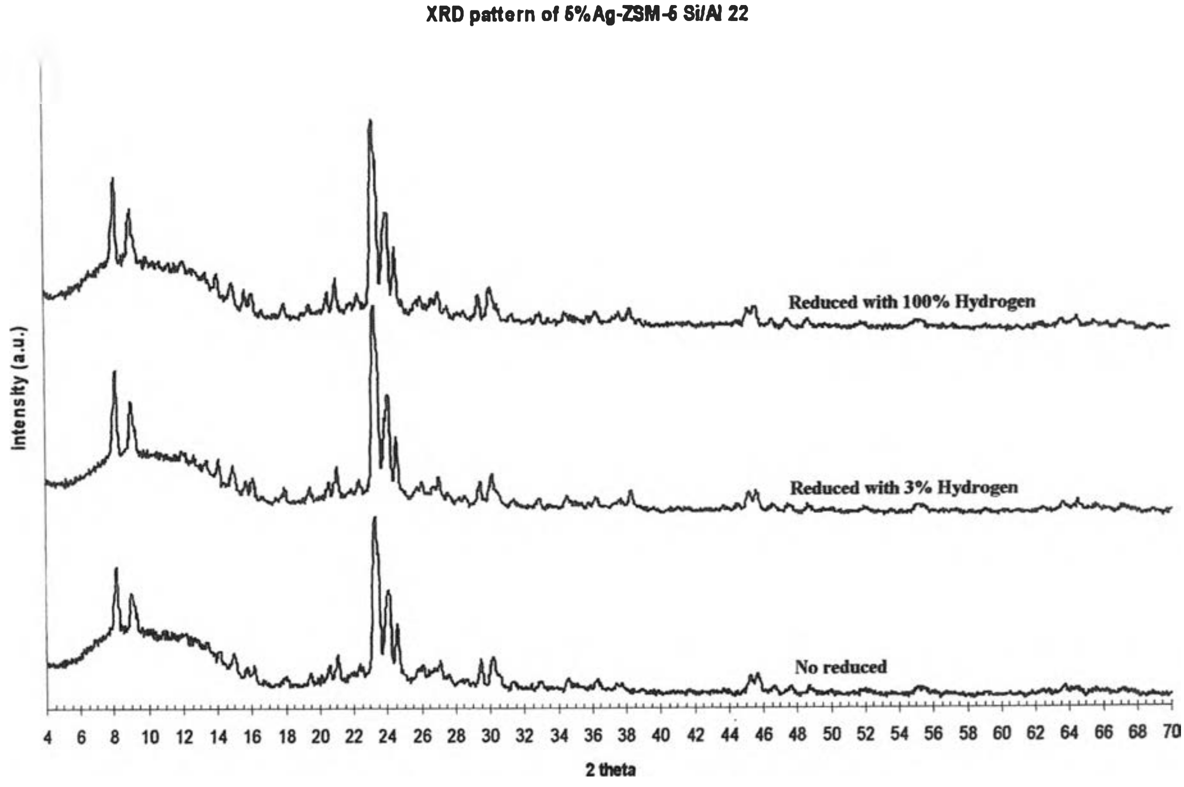


(g) Comparison of XRD pattern of 3.5 %Ag-ZSM-5 Si/Al 150 under the reduction with Hydrogen at 300 °C

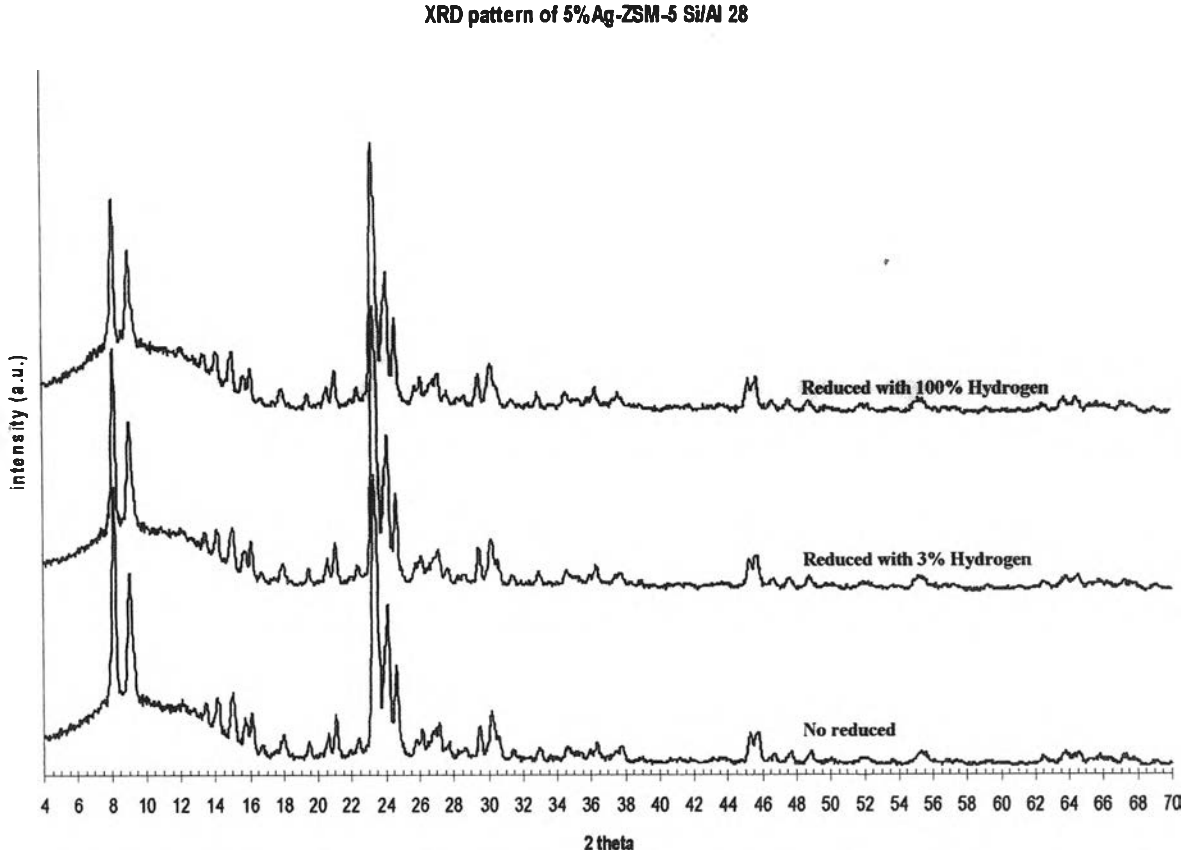
Figure 5.5 Comparison of XRD pattern of 5 %Ag-ZSM-5 Si/Al from 20-150 under the reduction with Hydrogen at 300 °C



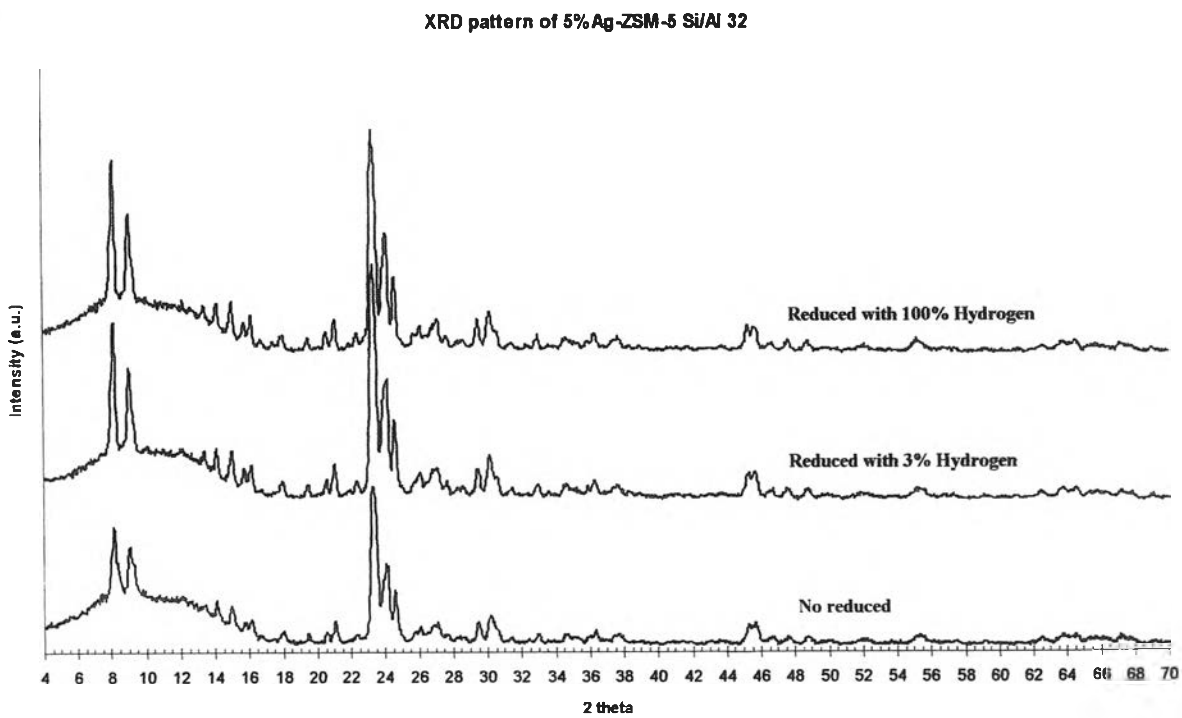
(a) Comparison of XRD pattern of 5 %Ag-ZSM-5 Si/Al 20 under the reduction with Hydrogen at 300 °C



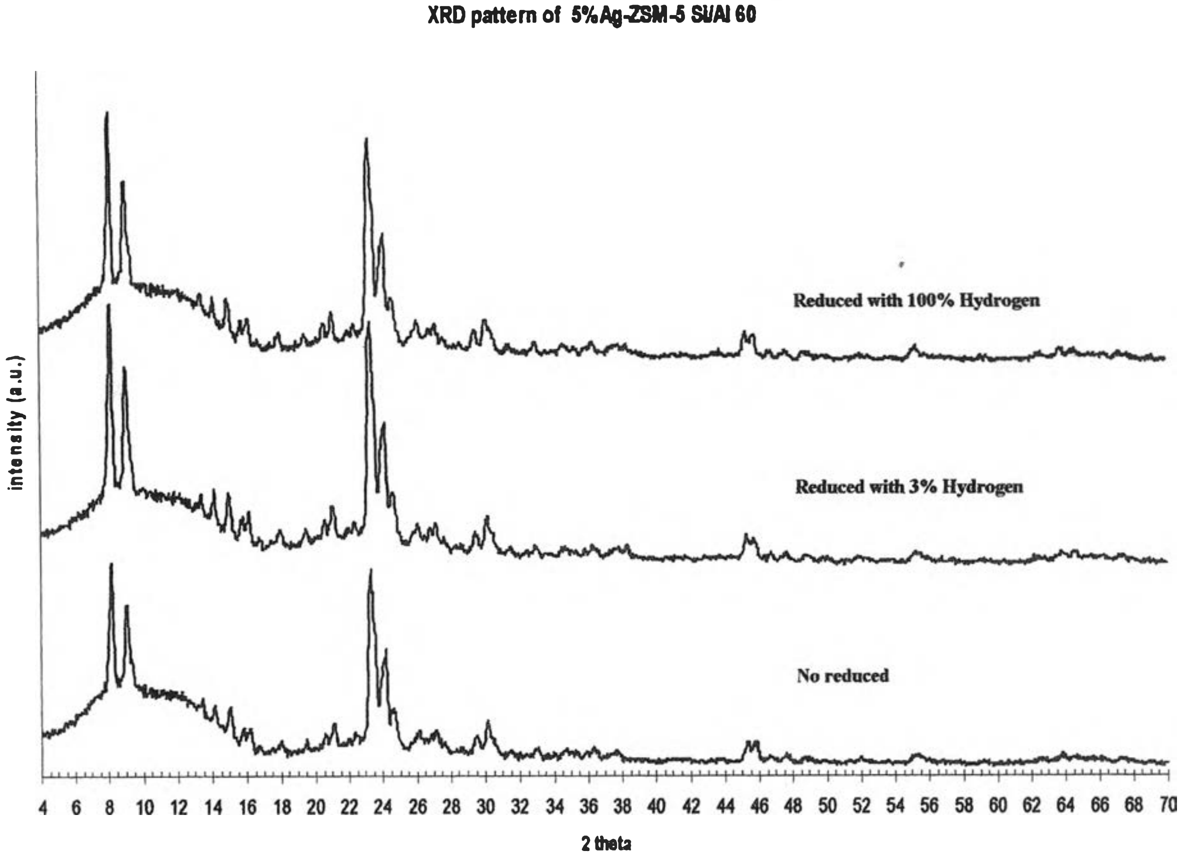
(b) Comparison of XRD pattern of 5 %Ag-ZSM-5 Si/Al 22 under the reduction with Hydrogen at 300 °C



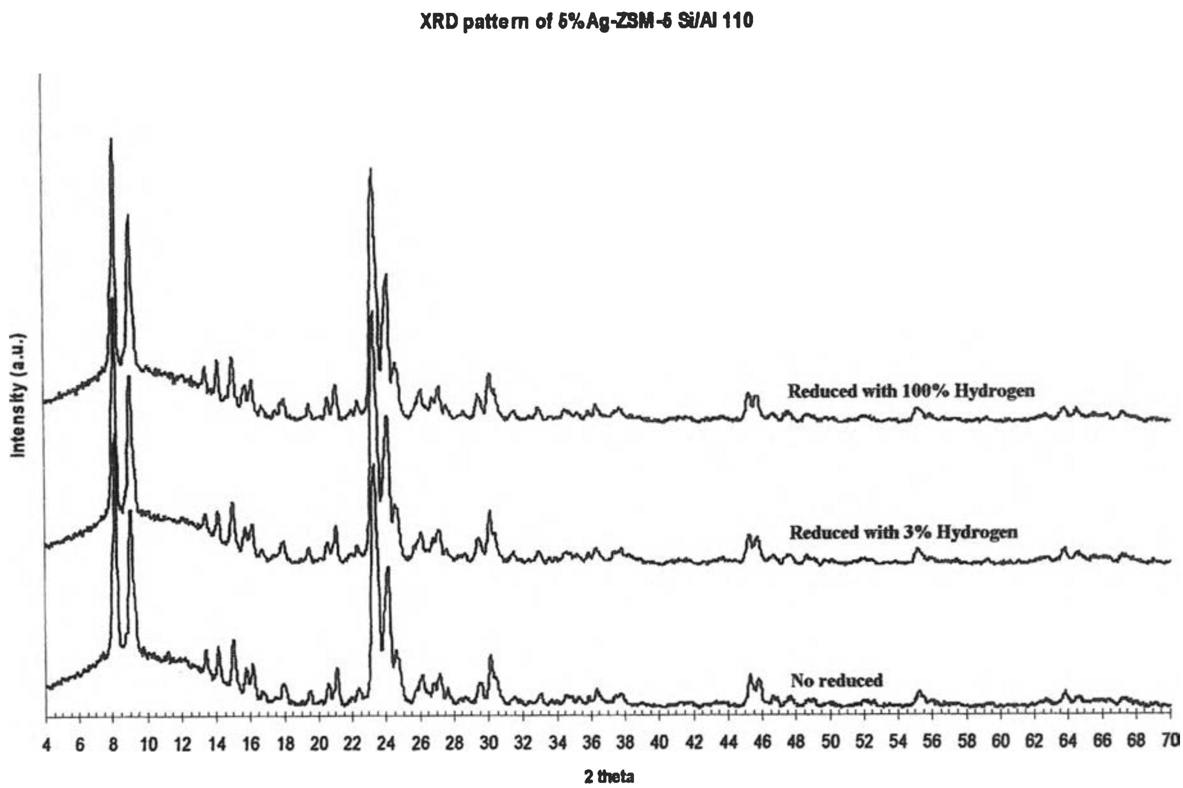
(c) Comparison of XRD pattern of 5 %Ag-ZSM-5 Si/Al 28 under the reduction with Hydrogen at 300 °C



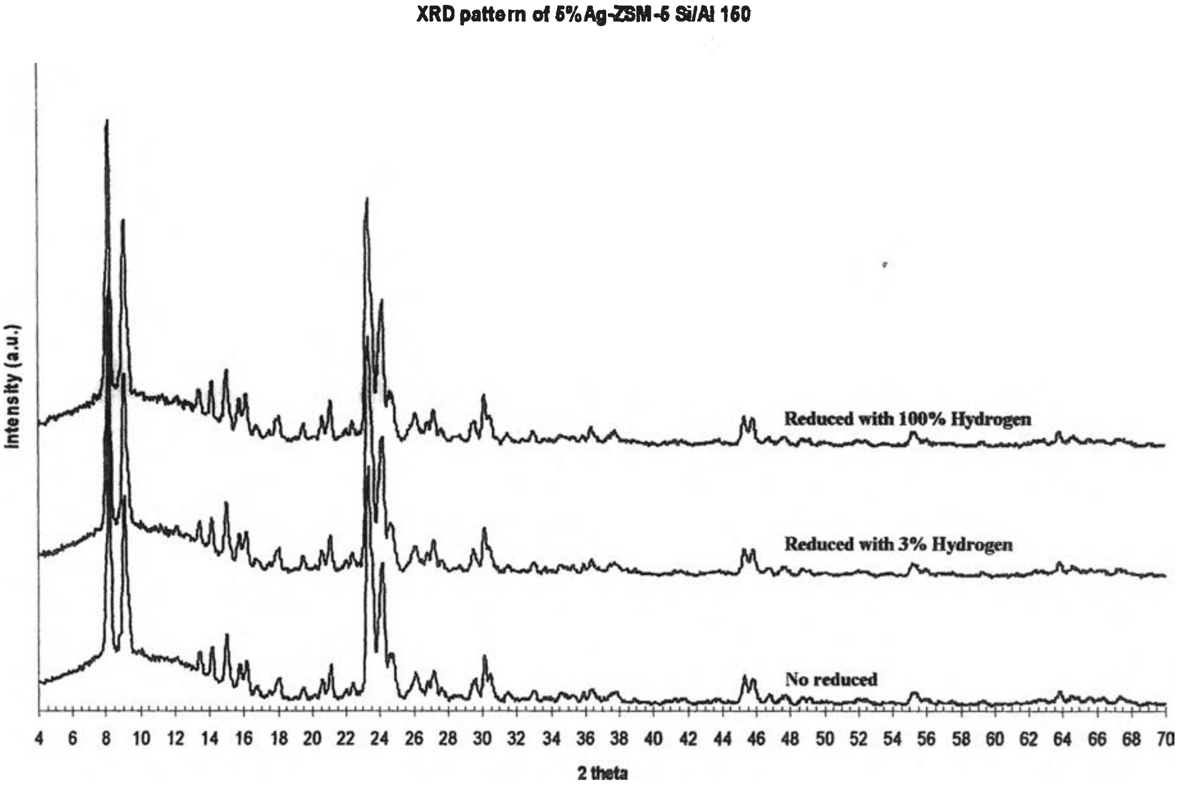
(d) Comparison of XRD pattern of 5 %Ag-ZSM-5 Si/Al 32 under the reduction with Hydrogen at 300 °C



(e) Comparison of XRD pattern of 5 %Ag-ZSM-5 Si/Al 60 under the reduction with Hydrogen at 300 °C



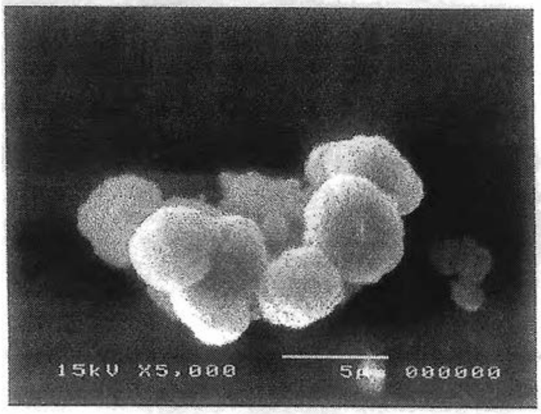
(f) Comparison of XRD pattern of 5 %Ag-ZSM-5 Si/Al 110 under the reduction with Hydrogen at 300 °C



(g) Comparison of XRD pattern of 5 %Ag-ZSM-5 Si/Al 150 under the reduction with Hydrogen at 300 °C

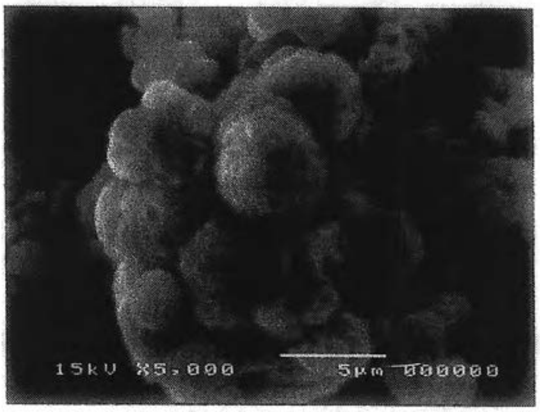
5.1.2 Morphology

Scanning Electron Microscope (SEM) photographs of the prepared catalysts are shown in figure 5.6-5.8 .As shown that all catalysts have crystallized in spherical to cubical shape crystals, which have an average crystal size diameter of 3-7 μm. After the ion exchange the shape and the crystal of catalysts are similar to before ion exchange. This indicated that the Ag exchanged in ZSM-5 did not change the crystals of the catalysts.

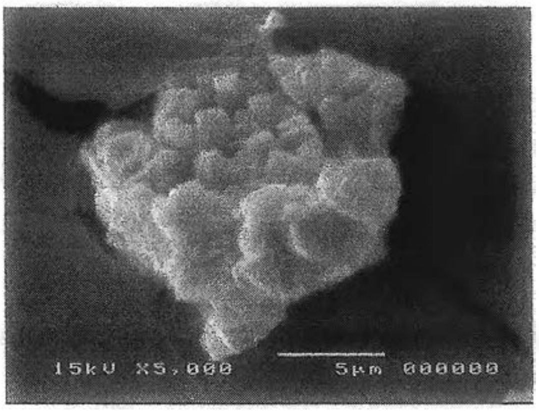


(a) H-ZSM-5 Si/Al 20

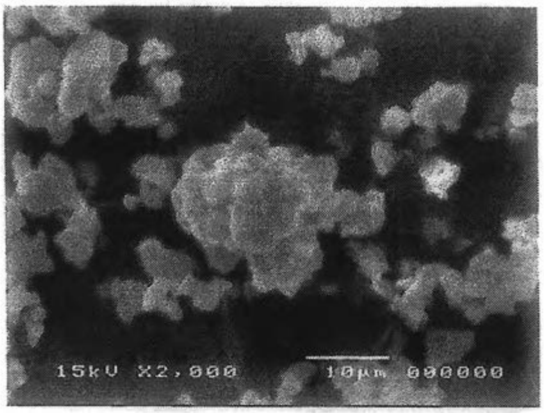
(b) H-ZSM-5 Si/Al 22



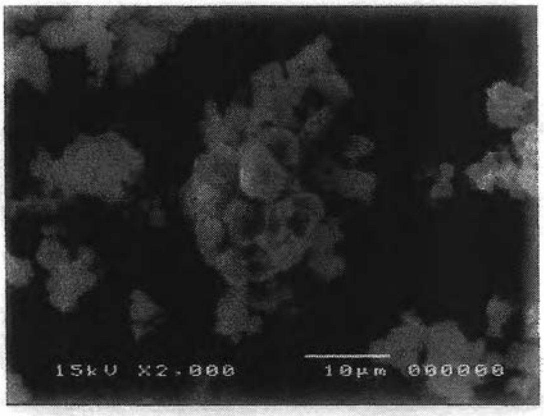
(c) H-ZSM-5 Si/Al 28



(d) H-ZSM-5 Si/Al 32



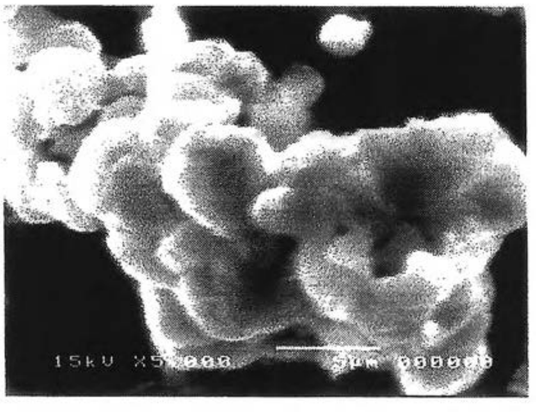
(e) H-ZSM-5 Si/Al 60



(f) H-ZSM-5 Si/Al 110

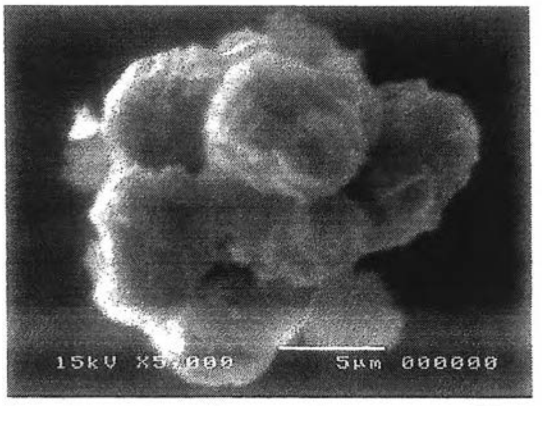
(g) H-ZSM-5 Si/Al 150

Figure 5.6 SEM photographs of H-ZSM-5 Si/Al from 20-150

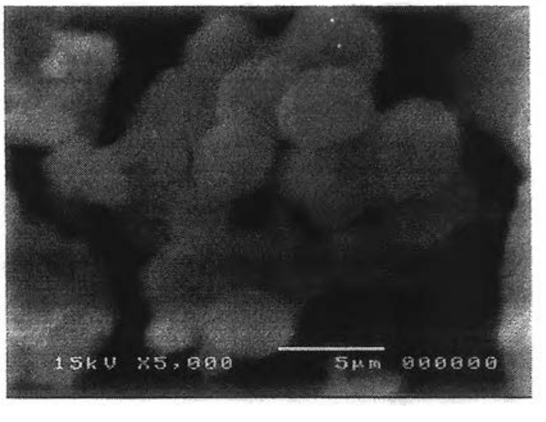


(a) 3.5 %Ag-ZSM-5 Si/Al 20

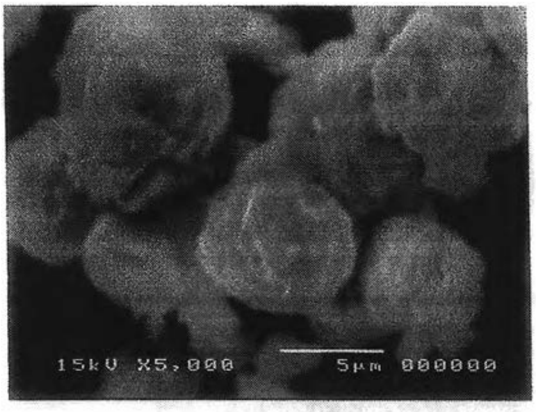
(b) 3.5% Ag-ZSM-5 Si/Al 22



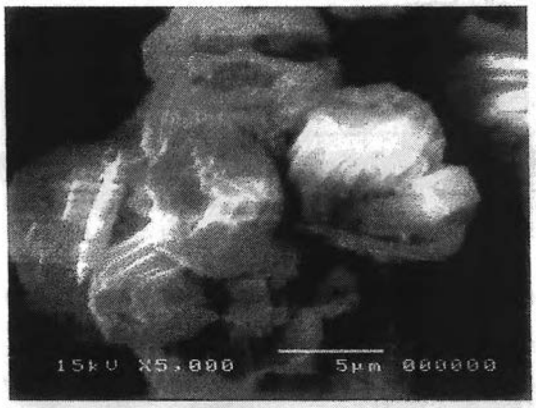
(c) 3.5 %Ag-ZSM-5 Si/Al 28



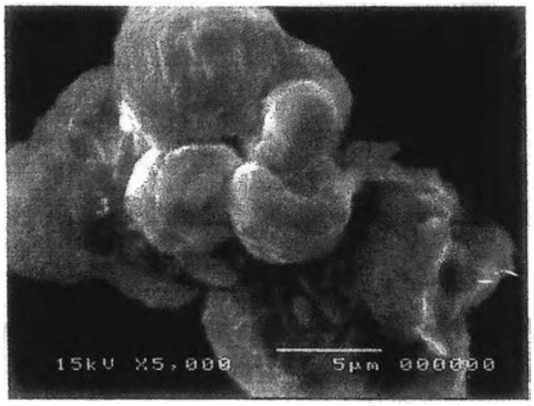
(d) 3.5% Ag-ZSM-5 Si/Al 32



(e) 3.5 %Ag-ZSM-5 Si/Al 60

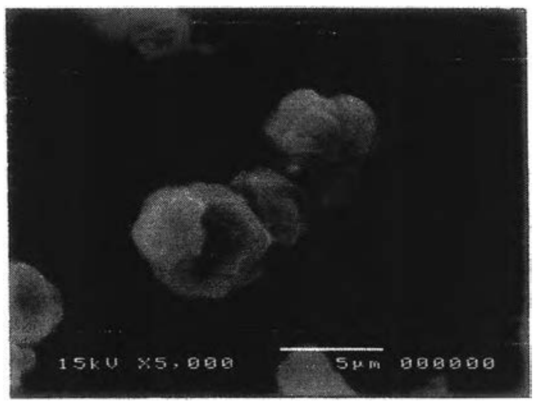


(f) 3.5% Ag-ZSM-5 Si/Al 110



(g) 3.5 %Ag-ZSM-5 Si/Al 150

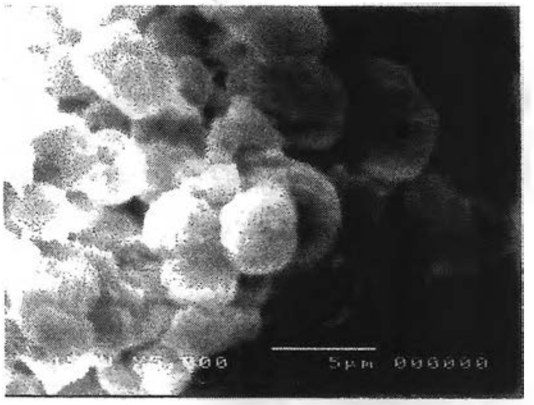
Figure 5.7 SEM photographs of 3.5% Ag-ZSM-5 Si/Al from 20-150



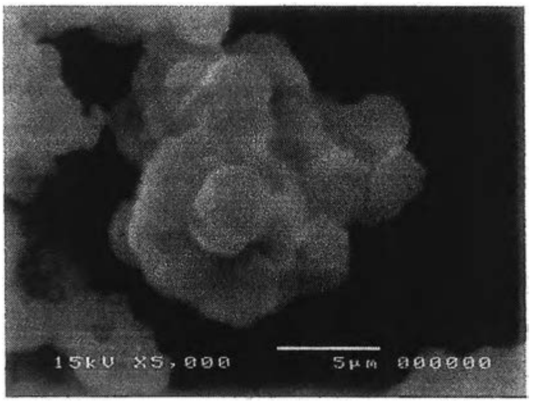
(a) 5 %Ag-ZSM-5 Si/Al 20

(b) 5 % Ag-ZSM-5 Si/Al 22

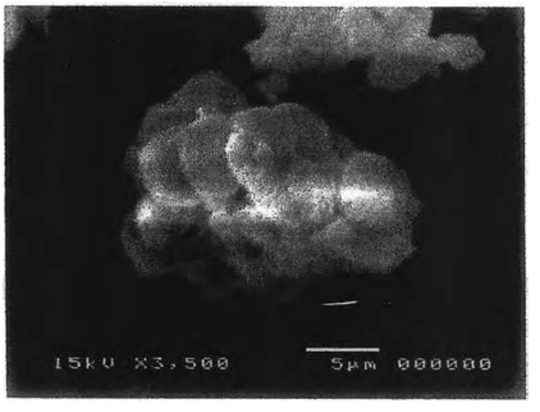
(c) 5 %Ag-ZSM-5 Si/Al 28



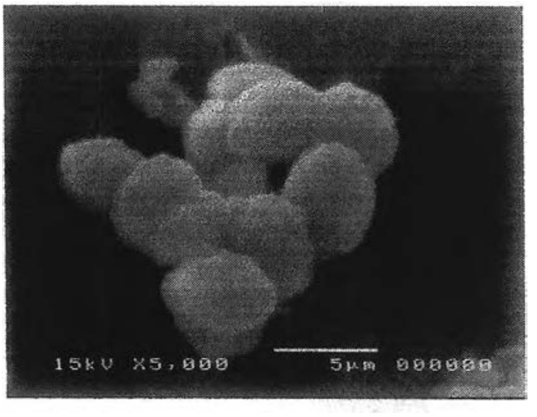
(d) 5 % Ag-ZSM-5 Si/Al 32



(e) 5 %Ag-ZSM-5 Si/Al 60



(f) 5 % Ag-ZSM-5 Si/Al 110



(g) 5 %Ag-ZSM-5 Si/Al 150

Figure 5.8 SEM photographs of 5% Ag-ZSM-5 Si/Al from 20-150

5.1.2 Chemical composition

The results of the quantitative analysis of silicon, aluminum and silver in the prepared catalysts are shown in table 5.1-5.2 respectively.

Table 5.1 Si/Al ratio in Ag-ZSM-5 catalysts

Catalysts	Si/Al ratio load	Si/Al ratio observed
3.5% Ag-ZSM-5 (SI/Al 25)	25	20.48
3.5% Ag-ZSM-5 (SI/Al 30)	30	21.89
3.5% Ag-ZSM-5 (SI/Al 40)	40	27.95
3.5% Ag-ZSM-5 (SI/Al 50)	50	32.12
3.5% Ag-ZSM-5 (SI/Al 100)	100	59.58
3.5% Ag-ZSM-5 (SI/Al 200)	200	109.85
3.5% Ag-ZSM-5 (SI/Al 400)	400	150.19

Catalysts	Si/Al ratio load	Si/Al ratio observed
5% Ag-ZSM-5 (Si/Al 25)	25	20.32
5% Ag-ZSM-5 (Si/Al 30)	30	21.87
5% Ag-ZSM-5 (Si/Al 40)	40	27.89
5% Ag-ZSM-5 (Si/Al 50)	50	32.23
5% Ag-ZSM-5 (Si/Al 100)	100	59.67
5% Ag-ZSM-5 (Si/Al 200)	200	109.74
5% Ag-ZSM-5 (Si/Al 400)	400	150.23

Table 5.2 Ag contents in Ag-ZSM-5 catalysts

Catalysts	% Ag load	% Ag observed
3.5% Ag-ZSM-5 (SI/Al 25)	3.5	2.32
3.5% Ag-ZSM-5 (SI/Al 30)	3.5	3.18
3.5% Ag-ZSM-5 (SI/Al 40)	3.5	2.28
3.5% Ag-ZSM-5 (SI/Al 50)	3.5	2.38
3.5% Ag-ZSM-5 (SI/Al 100)	3.5	3.04
3.5% Ag-ZSM-5 (SI/Al 200)	3.5	1.17
3.5% Ag-ZSM-5 (SI/Al 400)	3.5	0.87

Catalysts	% Ag load	% Ag observed
5% Ag-ZSM-5 (Si/Al 25)	5	4.37
5% Ag-ZSM-5 (Si/Al 30)	5	5.32
5% Ag-ZSM-5 (Si/Al 40)	5	4.32
5% Ag-ZSM-5 (Si/Al 50)	5	4.35
5% Ag-ZSM-5 (Si/Al 100)	5	3.25
5% Ag-ZSM-5 (Si/Al 200)	5	1.72
5% Ag-ZSM-5 (Si/Al 400)	5	1.01

5.1.3 Temperature Programmed Desorption of Ammonia (NH_3-TPD)

The amount of acid and acid strength of the 3.5 wt % Ag- ZSM- 5 and 5wt% Ag-ZSM-5 in the different Si/Al ratios from 20 to 150 were analyzed by Temperature Programmed Desorption of Ammonia (NH_3-TPD) [8,17].

The TPD profiles of all catalysts are shown in figure 5.9 and 5.10. The results indicated that TPD profiles of Ag -ZSM-5 are composed of two peaks. The low temperature peak of weak acid sites is about 166-203 °C and the high temperature of strong acid sites is about 388-455°C

The amount of acid of the 3.5 wt % Ag- ZSM- 5 and 5wt% Ag-ZSM-5 in the different Si/Al ratios from 20 to 150 are showed in table 5.3 and 5.4 respectively.

The results of NH_3-TPD indicated that the amounts of acid of Ag-ZSM-5 catalysts were decreased with the increase of Si/Al ratio. These results corresponded well with many reports in literature [8, 17].

Figure 5.9 TPD profiles of 3.5% Ag-ZSM-5 Si/Al from 20-150

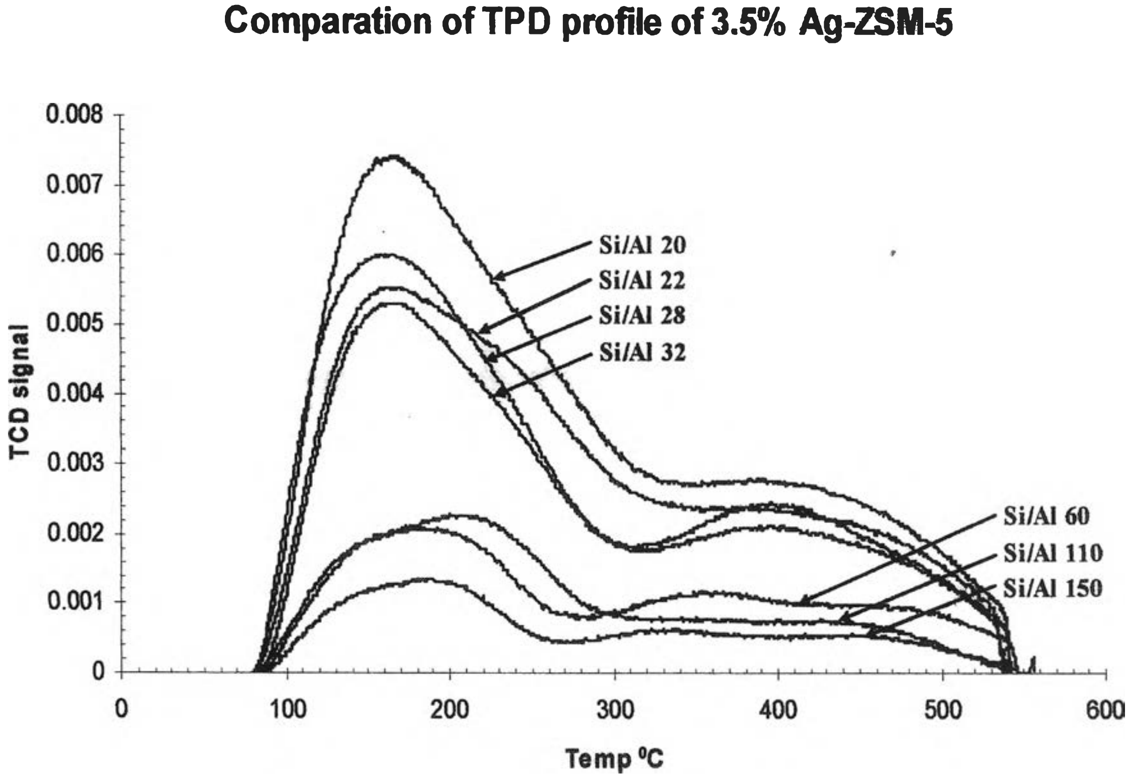


Figure 5.10 TPD profiles of 5% Ag-ZSM-5 Si/Al from 20-150

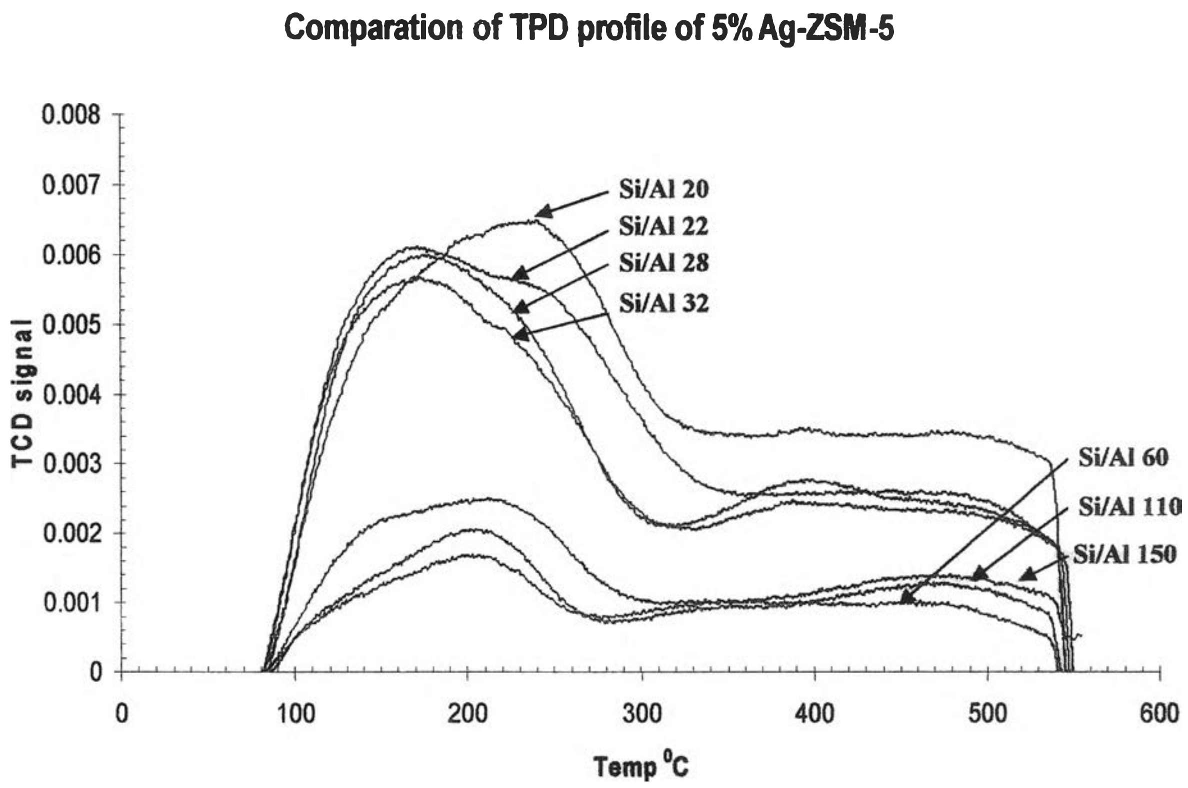


Table 5.3 The amount of acid of the 3.5 wt % Ag-ZSM-5 in the different Si/Al ratio from 20 to 150

Catalyst	Temp at 1st peak °C	Amount of acid at 1st peak μ mol/g cat.	Temp at 2nd peak °C	Amount of acid at 2nd peak μ mol/g cat.
3.5% Ag-ZSM-5 (SI/Al 20)	166	638.05	442	208.62
3.5% Ag-ZSM-5 (SI/Al 22)	171	545.76	451	163.46
3.5% Ag-ZSM-5 (SI/Al 28)	159	545.05	417	152.14
3.5% Ag-ZSM-5 (SI/Al 32)	168	472.93	427	135.33
3.5% Ag-ZSM-5 (SI/Al 60)	185	201.77	428	53.72
3.5% Ag-ZSM-5 (SI/Al 110)	163	116.23	398	114.98
3.5% Ag-ZSM-5 (SI/Al 150)	172	71.52	388	81.57

Table 5.4 The amount of acid of the 5 wt % Ag-ZSM-5 in the different Si/Al ratio from 20 to 150

Catalyst	Temp at 1st peak °C	Amount of acid at 1st peak μ mol/g cat.	Temp at 2nd peak °C	Amount of acid at 2nd peak μ mol/g cat.
5% Ag-ZSM-5 (SI/Al 20)	203	811.24	496	229.73
5% Ag-ZSM-5 (SI/Al 22)	177	739.39	495	150.14
5% Ag-ZSM-5 (SI/Al 28)	171	588.56	483	209.60
5% Ag-ZSM-5 (SI/Al 32)	164	519.44	448	244.73
5% Ag-ZSM-5 (SI/Al 60)	193	252.71	438	204.79
5% Ag-ZSM-5 (SI/Al 110)	194	101.27	464	180.64
5% Ag-ZSM-5 (SI/Al 150)	190	128.65	441	186.89

5.2. UV-Vis spectroscopy

In consideration of Ag cluster in catalysts, we will investigate by UV-Vis spectroscopy[2,3,5,9,10,11,12,20,21,29,30]. UV-Vis spectra of 3.5% Ag ZSM-5 and 5% Ag-ZSM-5 which have the ratio Si/Al from 20-150 will be shown in the figure 5.11 and 5.12 respectively.

Figure 5.11 UV-Vis spectra of 3.5% Ag-ZSM-5 Si/Al from 20-150

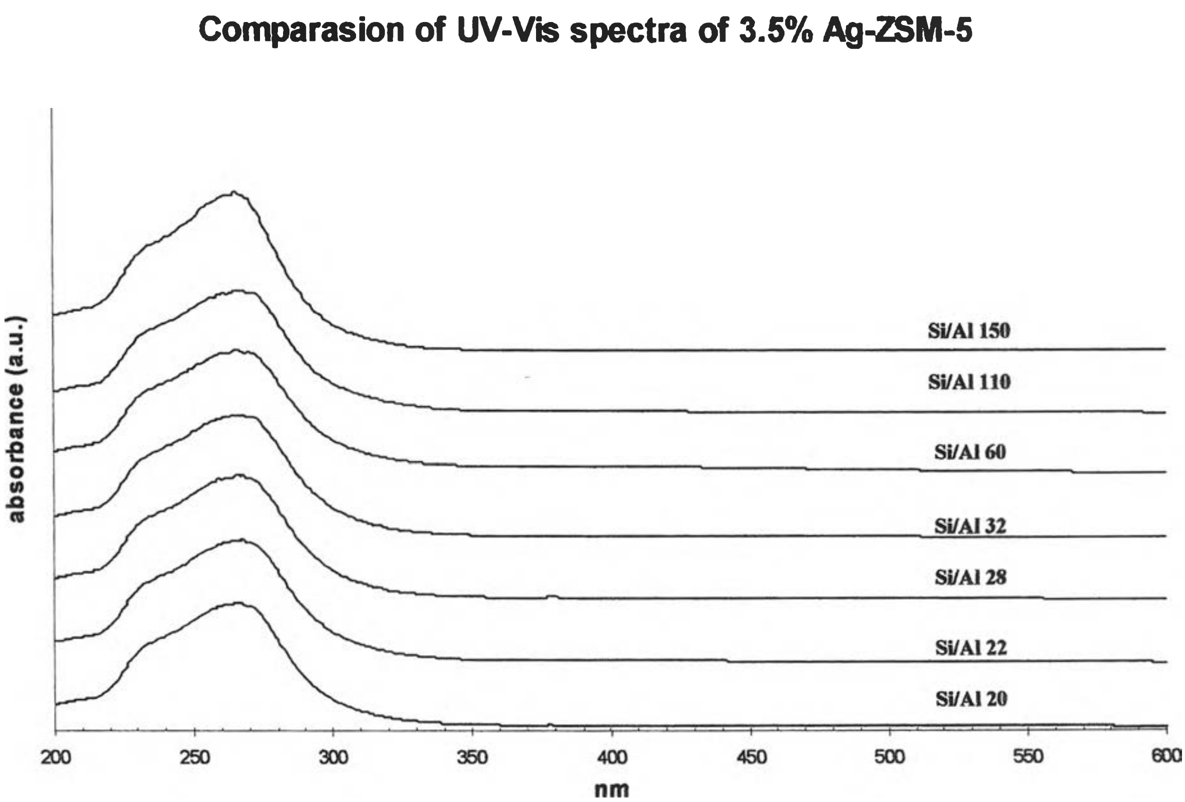
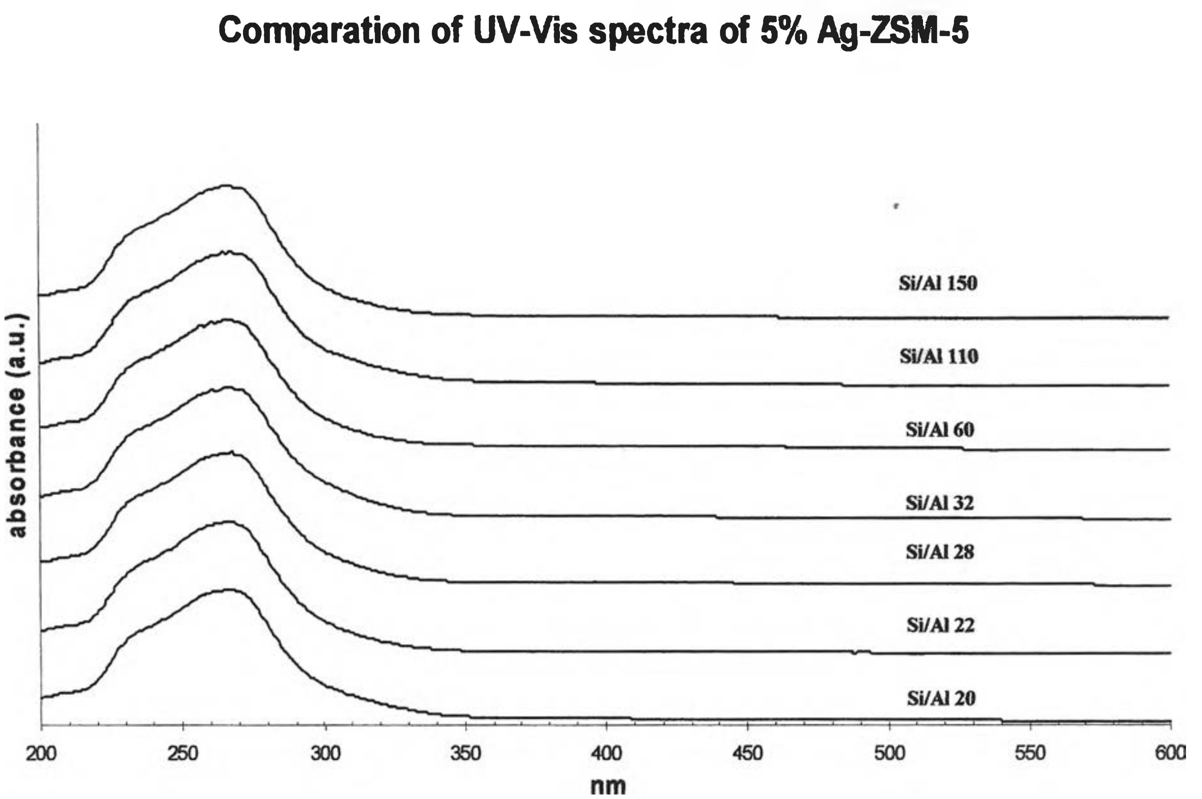


Figure 5.12 UV-Vis spectra of 5% Ag-ZSM-5 Si/Al from 20-150



From the figure 5.11 and figure 5.12, it is found that 3.5% Ag-ZSM-5 and 5% Ag-ZSM-5 at the different Si/Al have the same characterization of UV-Vis spectra by the occurring bands at 210 and 235 nm. From recent researches, [3,5,16,20,21,29,30] bands at 210 and 235 nm, Ag in catalysts will occur in Ag^{+}ion . In conclusion, after the ion exchange, Ag in catalysts will occur in Ag^{+} ion [3,5,16,20,21,29,30]

5.2.1 The study of the effect of Si/Al of Ag ZSM-5 to the silver cluster formation

The silver cluster on Ag ZSM-5 will be prepared by the hydrogen reduction at 300 °C. The result of the reduction of 3.5% Ag ZSM-5 at different Si/Al ratio will be shown in the figure 5.13 and 5.14 respectively.

Figure 5.13 Comparison of UV-Vis spectra of 3.5%Ag-ZSM-5 after reduced with 3%Hydrogen at 300 °C

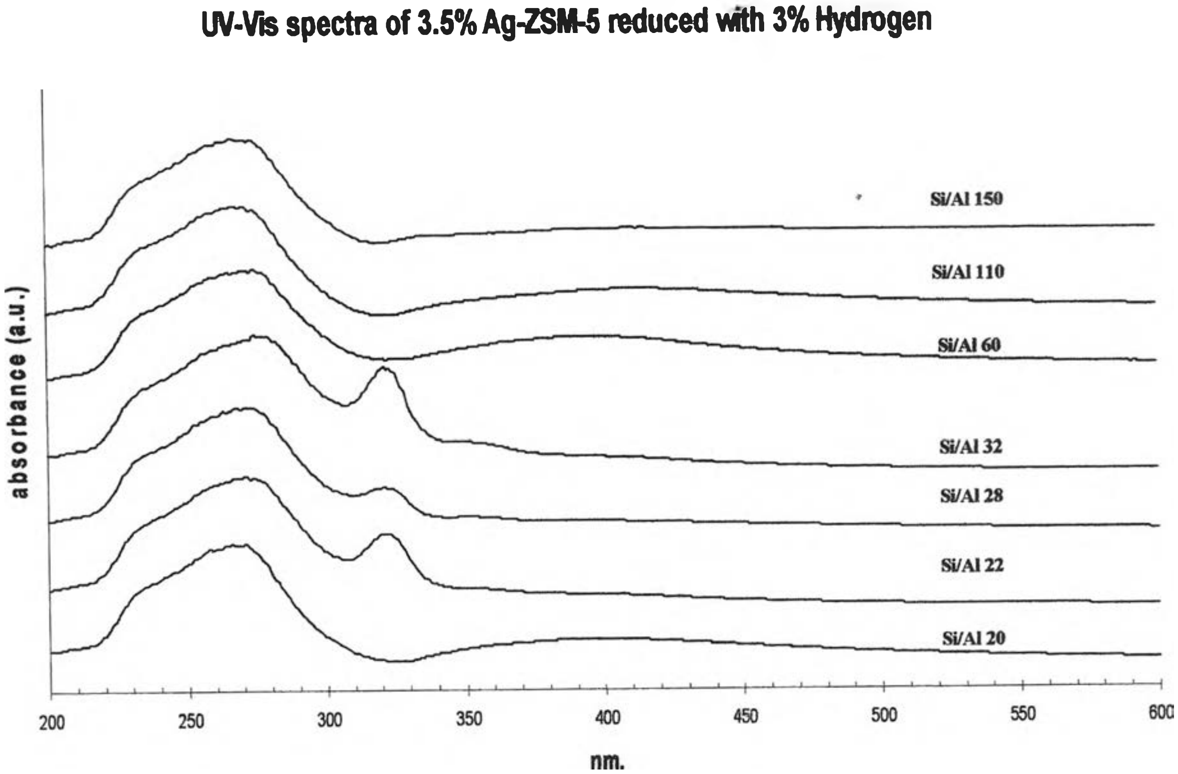
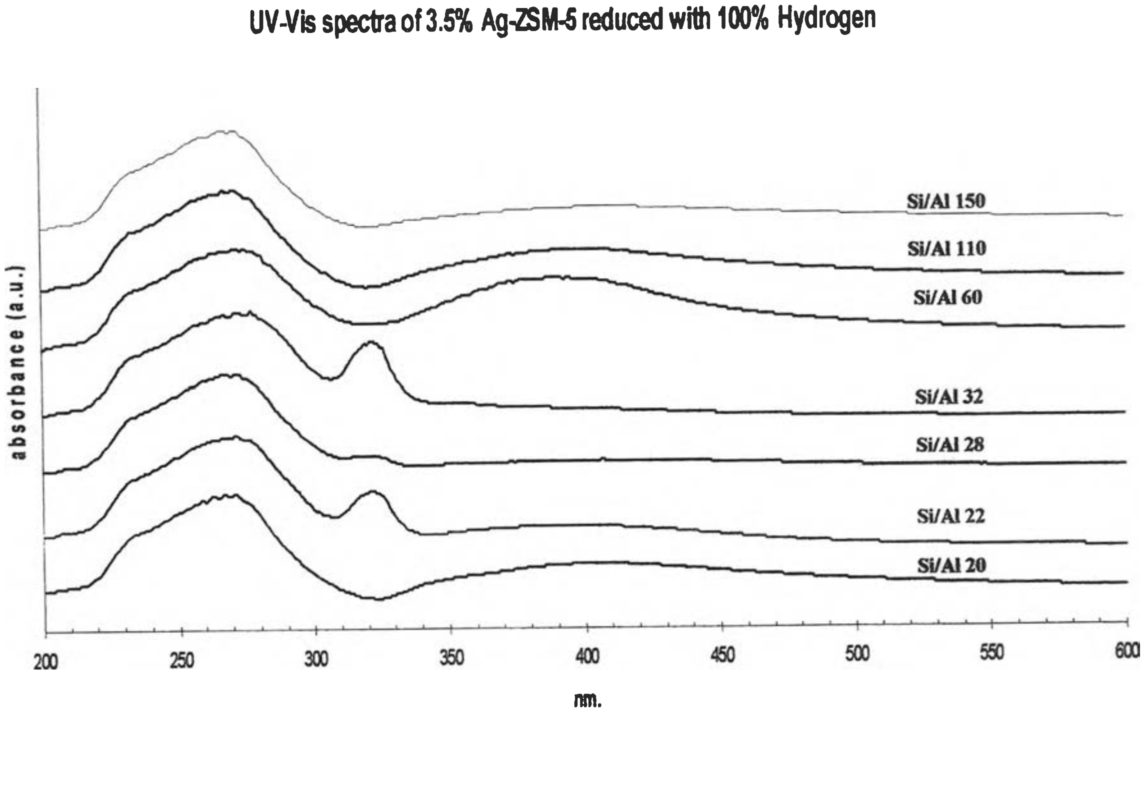


Figure 5.14 Comparison of UV-Vis spectra of 3.5%Ag-ZSM-5 after reduced with 100%Hydrogen at 300 °C



The figure 5.13 and 5.14 show the reduction of 3.5% Ag ZSM-5 at the ratio of 20-150 with 3% of H_2/Ar and with 100% of H_2 at 300°C respectively.

After the reduction with hydrogen, it is found that the broad band will occur between 310-340 nm. at Si/Al of 22, 28, 32. Moreover, the broad band will also occur between 350-380 nm. at Si/Al of 20, 60,110 and 150

The recent researches limited the broad band between 310-340ńm.to be Ag_4^{2+} cluster [20] which increased the conversation of NO to N_2 in the reaction of selective catalytic reduction with C_3H_8 [3,20,21]. In the recent researches, the board band between 350-480 will occur to be Ag metal which will be measured by the peak at 2θ of XRD at 38.1°, 44.5° and 64.5°[20]. The result of XRD of 3.5% Ag-ZSM-5 at Si/Ai 20 to 150 after the reduction with Hydrogen at 3% and 100% (the figure 5.4) show that there is no peak at 2θ = 38.1°,44.5° and 64.5°. So in consideration of the Ag cluster status in the range of the broad band between 350-480 nm [3,21]. , we cannot conclude that there is Ag metal in catalysts after the reduction with H_2. The Ag clusters status in the range of the broad band between 350-480 nm. So we suggested that we should have investigated and identified the species of Ag clusters at the broad band.

Juniji Shibata *et.al.* [21]studied species of supports , mordenite, MFI, bata and Y to Ag_4^{2+} cluster formation. From the research, it was discovered that the acid amount and acid strength would have a good effect on Ag_4^{2+} cluster formation. Supports having less acid would be better reduced. However, Supports having moderate acid would be more suitable for Ag_4^{2+} cluster formation than supports having less acid or much acid. Supports having less acid would be reduced so well that Ag^+ion would change to Ag metal more than Ag_4^{2+} cluster. On the other hand, supports having more acid would be reduced difficultly. So, after the reduction with hydrogen, the status of silver on catalyst was still Ag^+ion.

N. Bogdanchikova *et.al.* [10] studied the SiO_2/Al_2O_3 ratio of mordenite zeolite catalyst to Ag_8 cluster formation. They discovered that Brønsted acid and Lewis Acid of catalyst would affect the stabilization of Ag_8 cluster. The research would study the ratio of SiO_2/Al_2O_3 between 10-206. It was found out that the stabilization of Ag_8 cluster would occur during SiO_2/Al_2O_3 was in the range between 15-72 . In this range, catalyst would have high concentration of Brønsted acid and low concentration of Lewis Acid.

SiO_2/Al_2O_3 in the range of 10, it was discovered that there was no stabilization to Ag_8 cluster formation. From the study of acid species, it was discovered that in this range ,catalyst had low concentration of Brønsted acid and high concentration of Lewis acid . As the result, it was not suitable for Ag_8 cluster stabilization but Ag metal would appear on catalyst.

SiO_2/Al_2O_3 in the range between 110-206, it was found out that there was no stabilization to Ag cluster formation. From the study of acid species, it was discovered that in this range, the concentration of Brønsted acid was less than the concentration of Lewis acid. So it was not suitable for Ag_8 cluster formation. But Ag metal would form on catalyst. From the research, it can be concluded that catalyst which was suitable for Ag_8 cluster stabilization was catalyst having high concentration of Brønsted acid and low concentration of Lewis acid.

From the result of the reduction of 3.5% Ag-ZSM-5 at different Si/Al ratios with H_2, we concluded that the suitable Si/Al ratio for the Ag_4^{2+}cluster formation were Si/Al 22, 28, and 32. For Si/Al 20 was not suitable for Ag_4^{2+} cluster formation might be because of too much acid in catalysts which decreased the ability in the reduction with H_2 for changing Ag^+ ion in catalysts to Ag_4^{2+}cluster[10,11,14,19,20] and because catalyst would have low concentration of Brønsted acid and high concentration of Lewis acid. After the reduction, there was no Ag_4^{2+}cluster but there was other species of Ag instead of the broad band between 350-480 nm.

In case of Si/Al ratios of 60, 110, and 220, the acid in catalysts would be too little [10,11,14,19,20] that made Ag^+ ion in catalysts reduced with H_2 so much that there was no Ag_4^{2+}cluster but there was other species of Ag instead of the broad band between 350-480 nm. and because the concentration of Brønsted acid would be less than the concentration of Lewis acid.

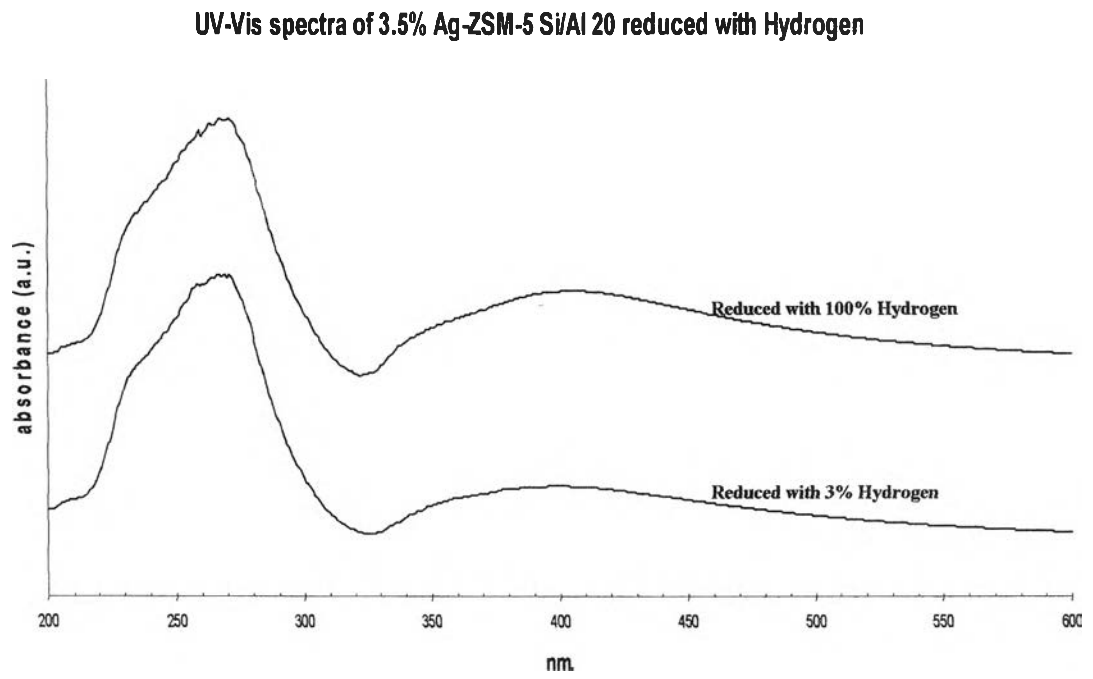
As the result, we suggest that we should study Brønsted acid and Lewis acid on catalyst to study the suitable acid species to Ag_4^{2+} cluster formation.

The preceding results show that the Si/Al ratios of 22, 28, and 32 were suitable for the Ag_4^{2+} cluster formation.

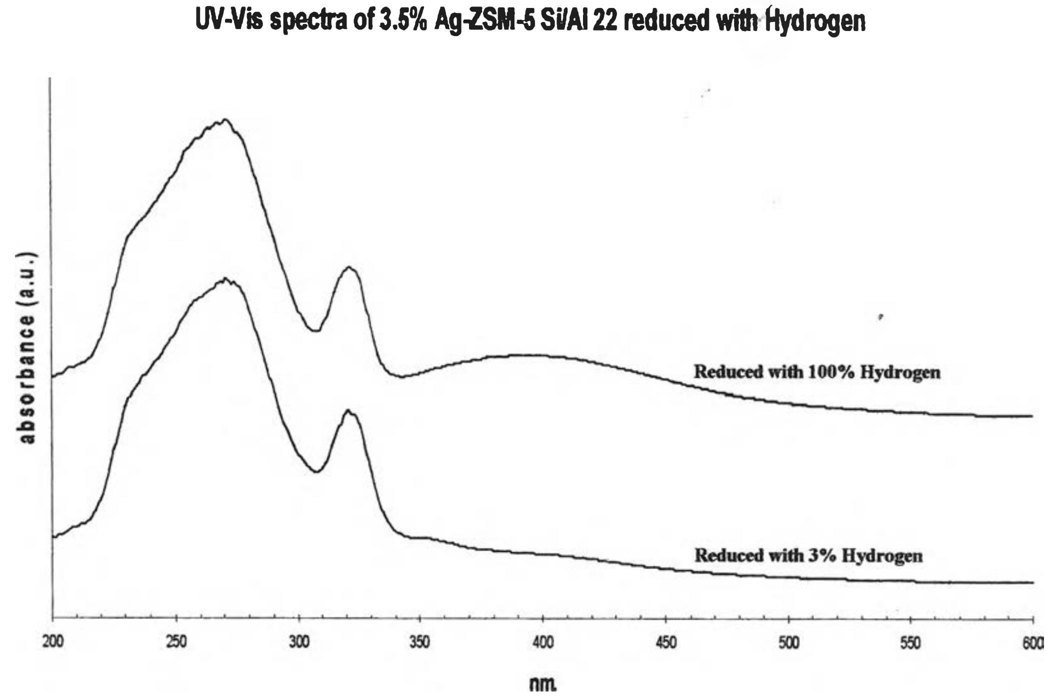
5.2.2 The effect of the concentration of Hydrogen to the silver cluster formation.

UV-Vis spectra of 3.5% Ag ZSM-5 at Si/Al ratios of 20,22,28,32 and 60 which was reduced with 3% of H_2 and with 100% H_2 shown in the figure 5.15

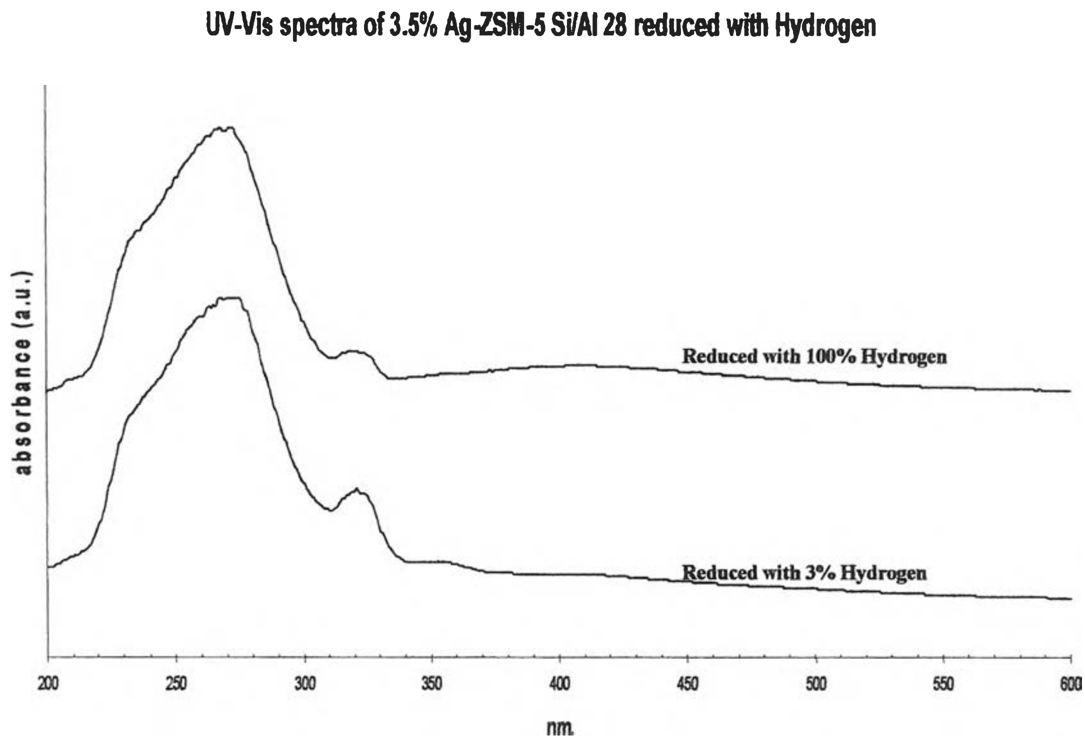
Figure 5.15 Comparison of UV-Vis spectra of 3.5% Ag-ZSM-5 Si/Al from 20-60 after the reduction 3% and 100%



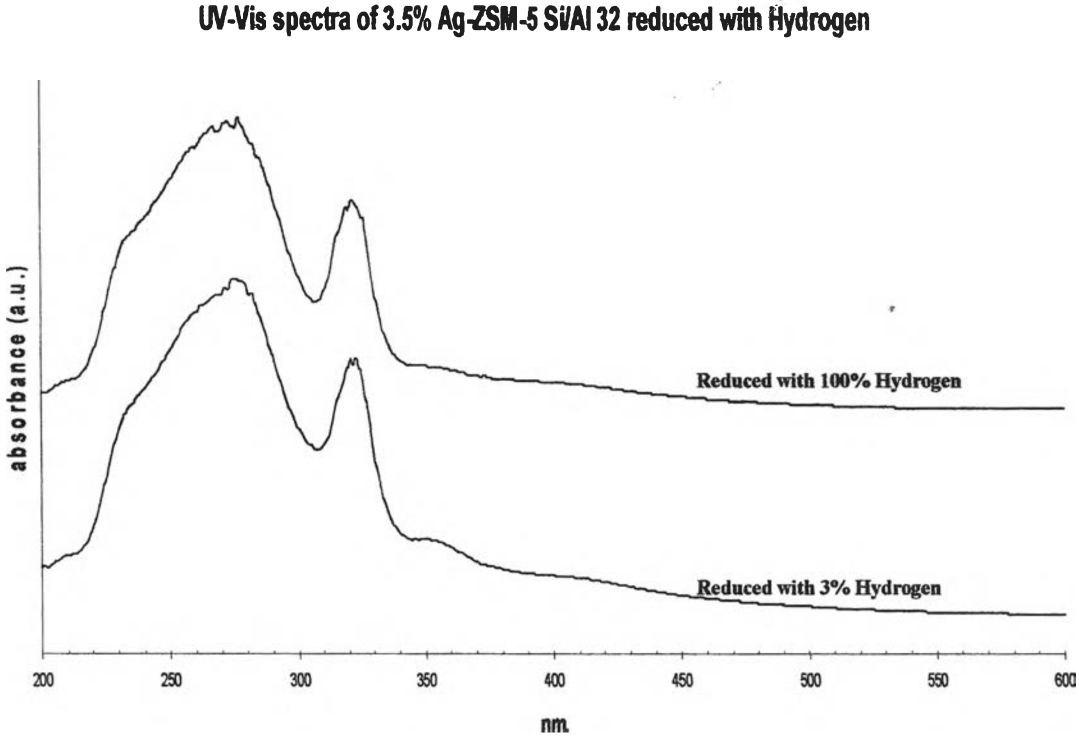
(a) Comparison of UV-Vis spectra of 3.5% Ag-ZSM-5 Si/Al 20 after reduced with 3% and 100% Hydrogen at 300°C



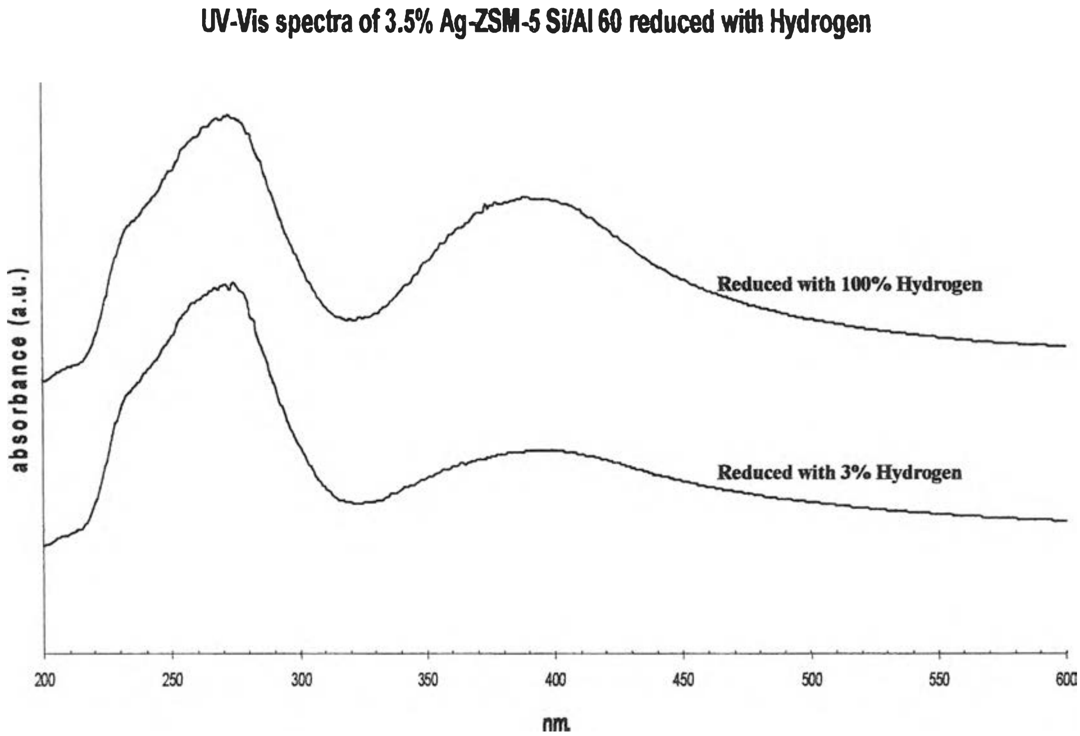
(b) Comparison of UV-Vis spectra of 3.5% Ag-ZSM-5 Si/Al 22 after reduced with 3% and 100% Hydrogen at 300°C



(c) Comparison of UV-Vis spectra of 3.5% Ag-ZSM-5 Si/Al 28 after reduced with 3% and 100% Hydrogen at 300°C



(d) Comparison of UV-Vis spectra of 3.5% Ag-ZSM-5 Si/Al 32 after reduced with 3% and 100% Hydrogen at 300°C



(e) Comparison of UV-Vis spectra of 3.5% Ag-ZSM-5 Si/Al 60 after reduced with 3% and 100% Hydrogen at 300°C

The figure 5.15 is the comparison of the reduction condition of 3.5% Ag ZSM-5 with H_2 to the Ag_4^{2+} cluster formation. In case of Si/Al ratios of 22, 28 and 32, it is found that when there was more amount of H_2 concentration, the amount of Ag_4^{2+}cluster would be decrease by measuring the intensity of the broad band between 310-340 nm.[20]. Meanwhile, the amount of other Ag species at the broad band between 350-480 nm. would increase. In case of Si/Al ratios of 20 and 60, it is found that the increasing of the H_2 concentration in the reduction condition would not form Ag_4^{2+}cluster in catalysts. However, Ag species in the range of the broad band between 350-480 was increased which was considered by the increasing intensity of the broad band in the range of 350-480 nm. From the result, it is concluded that when increasing H_2 concentration in the reduction would decrease Ag_4^{2+}cluster. On the other hand, Ag species at the broad band between 350-480nm. was increased.

5.2.3 The effect of Ag loading for the Ag cluster formation.

In consideration of the effect of the amount of Ag loading to the Ag cluster formation, we will consider it by using Ag-ZSM-5 which has Si/Al ratios of 22 and 28 having Ag loading at 3.5 wt% and 5wt% after the reduction with 3% of H_2/Ar at 300 °C. UV-Vis spectra of the comparison of the amount of Ag loading between 3.5 wt% and 5 wt% of Ag-ZSM-5 at Si/Al ratios of 22 and 28 will shown in the figure 5.16 and 5.17 respectively.

Figure 5.16 Comparison of Ag loading for Ag-ZSM-5 Si/Al 22 reduced with 3% Hydrogen at 300 °C

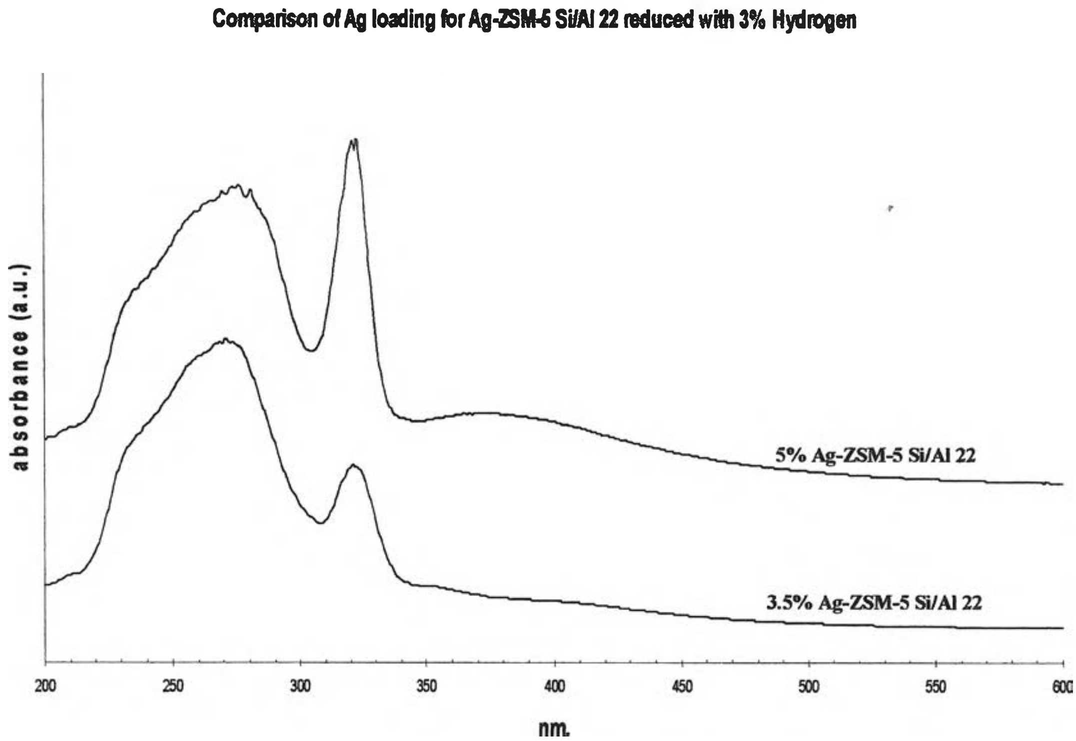
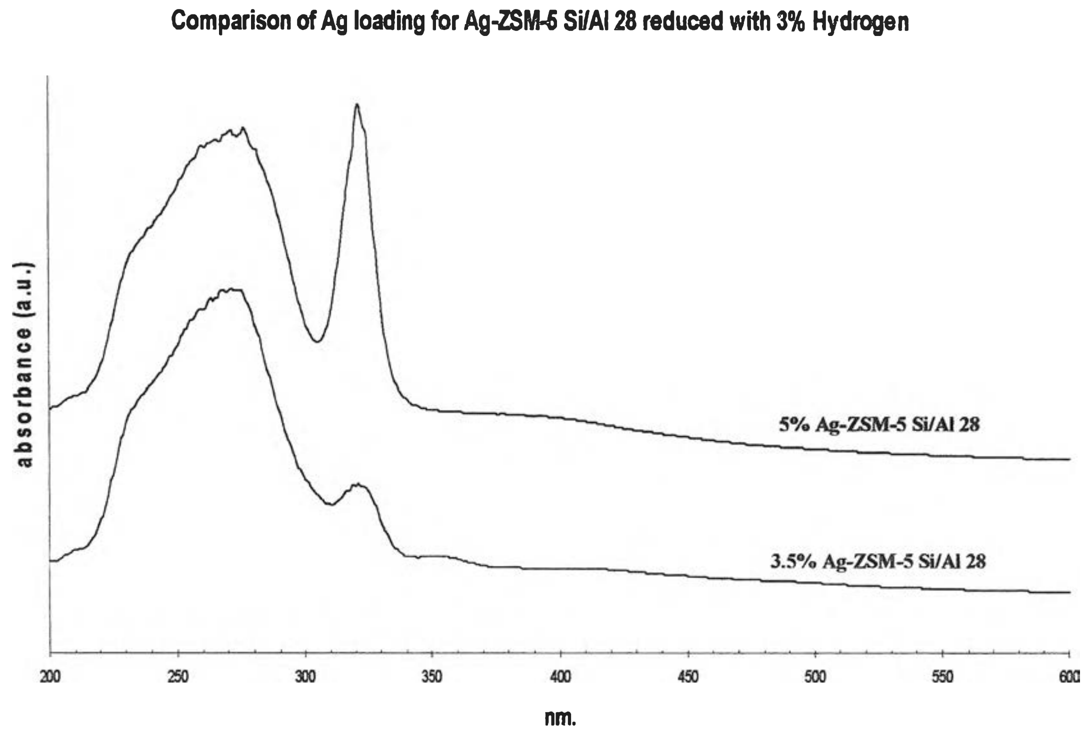


Figure 5.17 Comparison of Ag loading for Ag-ZSM-5 Si/Al 28 reduced with 3% Hydrogen at 300 °C



From the figure 5.16 and 5.17 show that when increasing the amount of Ag loading in catalyst, the intensity of the peak at the broad band between 310-340 nm. will increase; On the other hand, it is shown that the amount of Ag_4^{2+} clusters will increase. The result corresponds well with the recent researches [3, 20, 21].

In conclusion, Ag_4^{2+} clusters will increase when Ag loading is increased in catalysts.