

CHAPTER IV
RESULTS AND DISCUSSION

4.1 Adsorbent Characteristics

Table 4.1 Notations of clinoptilolite used in this work.

Modification technique	Modification condition	Adsorbent
		Pretreated clino
Thermal treatment	300°C, 2 hrs	Clino (300)
	400°C, 2 hrs	Clino (400)
	500°C, 2 hrs	Clino (500)
Acid treatment	0.1 M HNO ₃ , 80°C 5 hrs	H-clino (0.1)
	1 M HNO ₃ , 80°C 5 hrs	H-clino (1)
	3 M HNO ₃ , 80°C 5 hrs	H-clino (3)
Ion exchange	1 M NaCl, 80°C 5 hrs	Na-clino
	1 M KCl, 80°C 5 hrs	K-clino
	1 M Mg, 80°C 5 hrs	Mg-clino
	1 M Ca, 80°C 5 hrs	Ca-clino
Acid treatment prior to ion exchange	1 M HNO ₃ , 80°C 7 hrs + 1 M NaCl, 80°C 7 hrs	Acid-Na-clino
	1 M HNO ₃ , 80°C 7 hrs + 1 M KCl, 80°C 7 hrs	Acid-K-clino
	1 M HNO ₃ , 80°C 7 hrs + 1 M MgCl ₂ , 80°C 7 hrs	Acid-Mg-clino
	1 M HNO ₃ , 80°C 7 hrs + 1 M CaCl ₂ , 80°C 7 hrs	Acid-Ca-clino

4.1.1 BET Surface Areas of Clinoptilolites

Surface areas and pore volumes of the pretreated clinoptilolite and modified clinoptilolites are reported in Table 4.2. The results show that the surface area and pore volumes of clinoptilolites modified by the thermal treatment and ion exchange are rather constant. It indicates that the framework does not collapse with heating up to 500°C, which coincides with the study by Armbruster (1993). The results from the ion exchange treatment implies that at the studied conditions, the amount, type, and size of the cations in the channels of the zeolite have very little effect on the surface area and pore volume.

Interestingly, for clinoptilolite modified by the acid treatment and acid treatment prior to ion exchange, significant increases of both the surface area and pore volume were observed. This is due to the acid effect that cause the decationization and dealumination. With the former technique, the increase in the acid concentration results in the higher surface area and lower pore volume.

Table 4.2 BET surface area and pore volume of the pretreated clinoptilolite and modified clinoptilolite.

Modification technique	Adsorbent	Surface area (m²/g)	Pore volume (cc/g)
	Pretreated clino	10.18	0.0328
Thermal treatment	Clino (300)	10.51	0.0395
	Clino (400)	10.92	0.0402
	Clino (500)	10.95	0.0483
Acid treatment	H-clino (0.1)	99.12	0.1162
	H-clino (1)	139.4	0.1309
	H-clino (3)	160.8	0.1414
Ion exchange	Na-clino	15.41	0.0438
	K-clino	12.07	0.0404
	Mg-clino	10.40	0.0295
	Ca-clino	10.55	0.0365
Acid treatment prior to ion exchange	Acid-Na-clino	121.5	0.1097
	Acid-K-clino	118.9	0.1083
	Acid-Mg-clino	133.6	0.1168
	Acid-Ca-clino	113.2	0.1035

4.1.2 X-Ray Diffraction Results of Clinoptilolites

Figures 4.1-4.4 illustrate the XRD patterns of clinoptilolites modified by the thermal treatment, acid treatment, ion exchange, and acid treatment prior to ion exchange, respectively. The results show that the modified and unmodified zeolites used are clinoptilolite. This can further imply that all modification techniques used in this work do not alter the clinoptilolite framework.

The degree of crystallinity was estimated from the relative intensities of the most characteristic reflections of clinoptilolite at 2 theta equal 9.92° , 22.43° , and 30.50° . The pretreated clinoptilolite are taken as the reference. A progressive decrease of the intensities at 2 theta equal 9.92° , 22.43° , and 30.50° occurs for clinoptilolite modified by the thermal treatment at the calcination temperature above 300°C and also for clinoptilolite modified by the acid treatment with the nitric acid concentration higher than 0.1 M. These changes indicate that a partial loss of the crystallinity takes place.

The XRD patterns of clinoptilolite modified by the ion exchange are similar to that of the pretreated clinoptilolite. It implies that the cation exchange does not significantly change the diffraction pattern of clinoptilolite. This is consistent with the results reported by Arcoya *et al.* (1996). On the other hand, the acid treatment prior to ion exchange technique causes the peak intensities at 2 theta equal 9.92° , 22.43° , and 30.50° decrease slightly, but the peak intensities at 2 theta equal 20.84° , 26.58° and 27.68° increase. This may be the result from the difference in the chemical composition of the modified and unmodified zeolites.

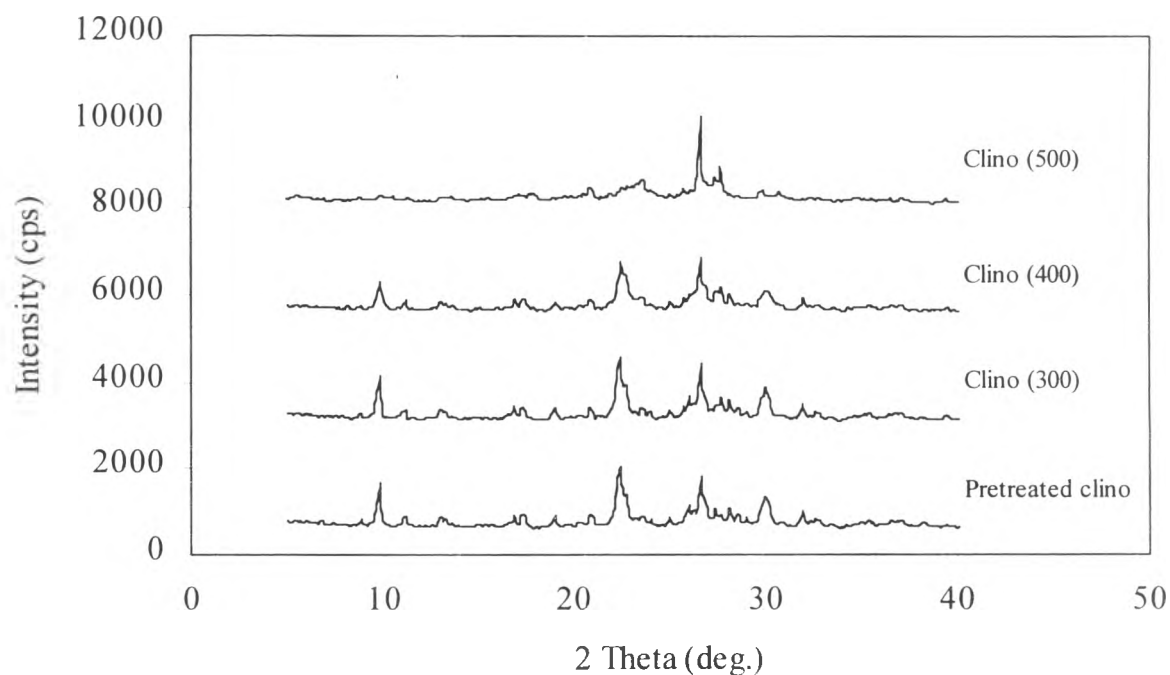


Figure 4.1 XRD diffractograms of clinoptilolite modified by the thermal treatment with different calcination temperatures.

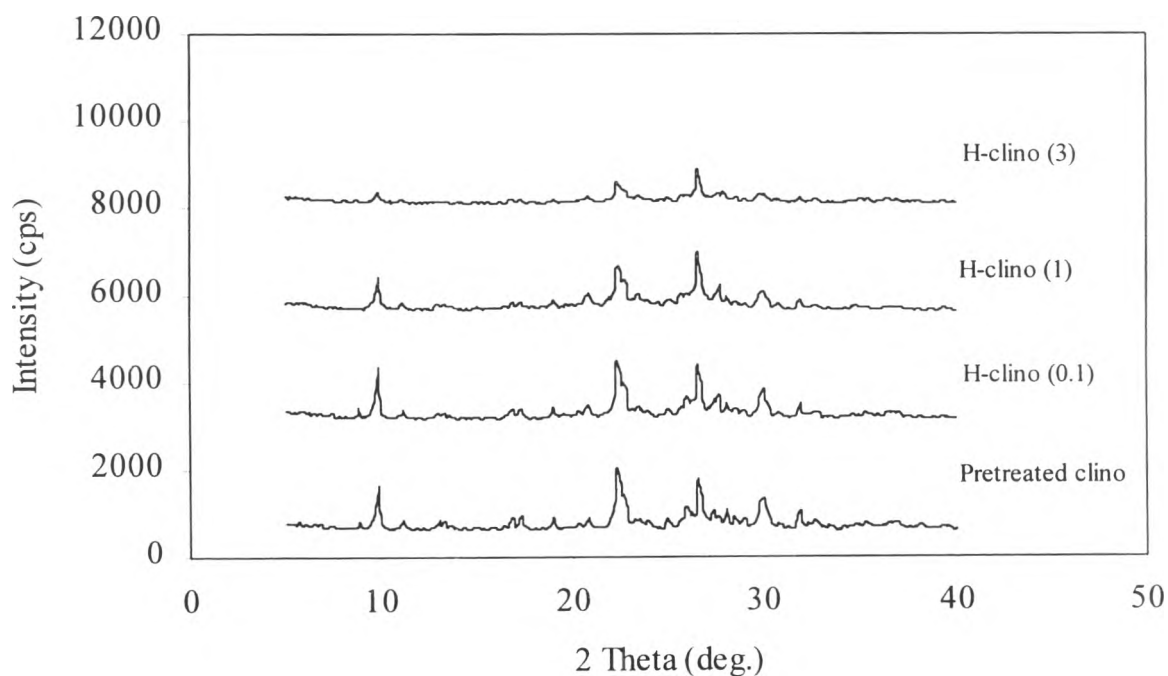


Figure 4.2 XRD diffractograms of clinoptilolite modified by the acid treatment with different nitric acid concentrations.

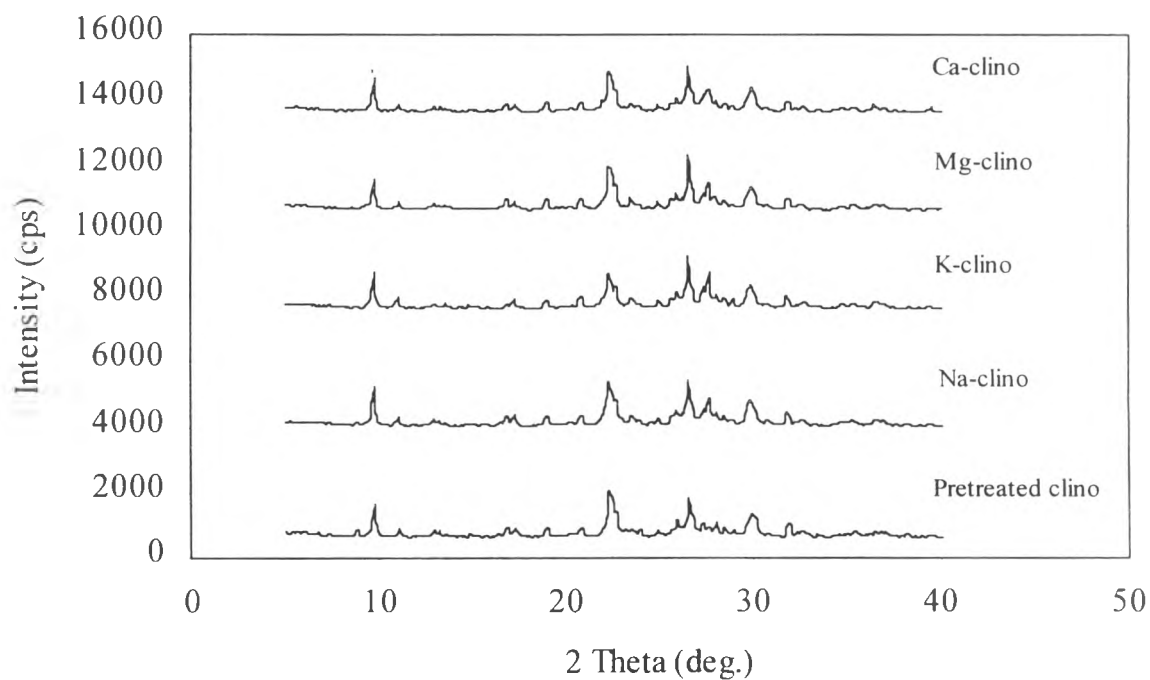


Figure 4.3 XRD diffractograms of clinoptilolite modified by the ion exchange with different cations.

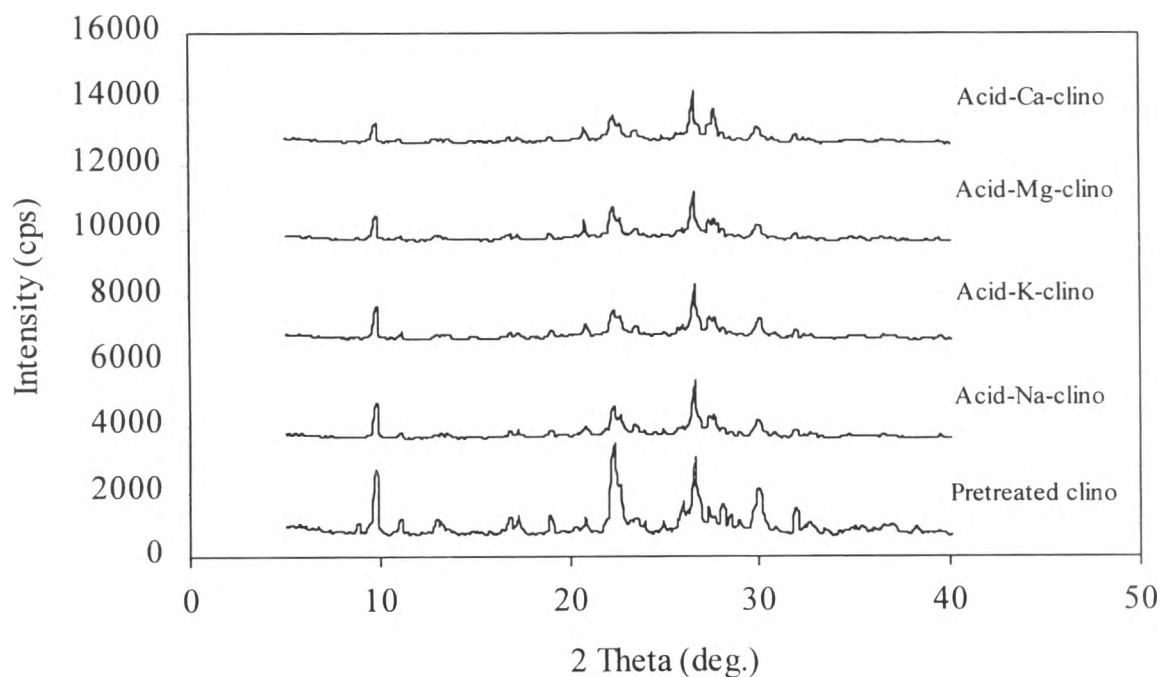


Figure 4.4 XRD diffractograms of clinoptilolite modified by the acid treatment prior to ion exchange with different cations.

4.1.3 Fourier Transform Infrared Spectroscopy

Results of the FTIR are shown in Figures 4.5-4.8 for the modified and unmodified clinoptilolites. The absorption bands at 456-465, 587-606, 795-797, 1059-1081 cm^{-1} indicate the vibrations of Si-O(Al) and Al-O(Si) bonds in the aluminosilicate oxygen framework. The most intense band was observed at 1059-1081 cm^{-1} . The band at 795-797 cm^{-1} is caused by symmetric vibration of the Si-O bond. The absorption band at 587-606 cm^{-1} is related to oscillations of chains of aluminosilicate oxygen tetrahedra. The band at 1632-1642 cm^{-1} indicates adsorbed water on the modified and unmodified clinoptilolite. The 3627-3630 cm^{-1} band shows the water OH group interacting with other water OH groups. Analysis of these data shows that the cations and the calcination temperature less than 500°C do not significantly alter the spectra of clinoptilolite.

Similarly, the acid treatment and acid treatment prior to ion exchange have little effect except for the band at 1059-1081 cm^{-1} . For the acid treatment, the band at 1059 cm^{-1} shifted to 1067, 1076, and 1080 cm^{-1} for clinoptilolite modified with 0.1, 1, and 3 M, respectively. In case of the acid treatment prior to ion exchange, the band at 1059 cm^{-1} shifted to 1079, 1081, 1080, and 1079 cm^{-1} for the clinoptilolite modified in the forms of Na, K, Mg, and Ca, respectively. These are the results from the change in the Si/Al ratio of clinoptilolite.

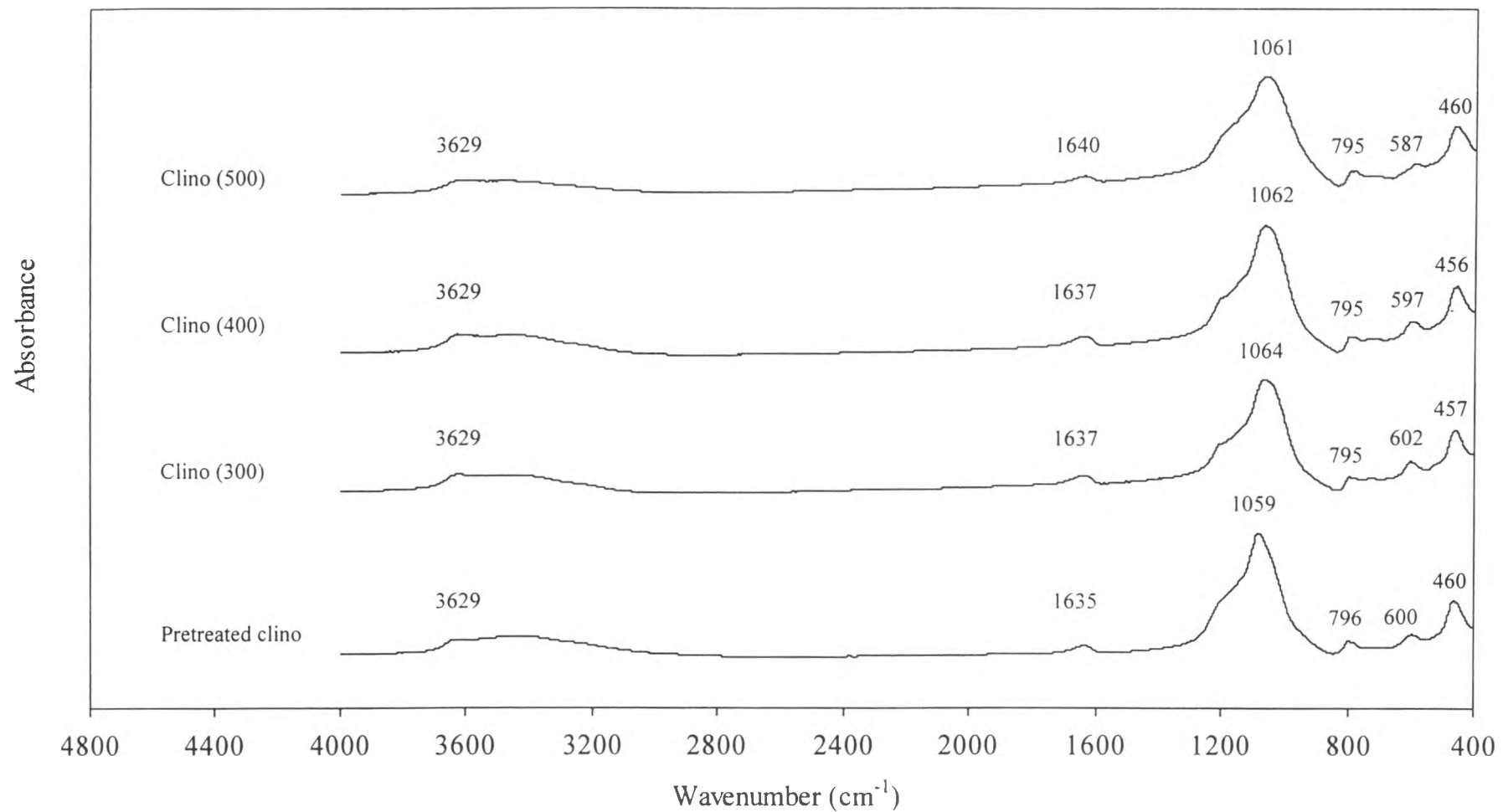


Figure 4.5 Infrared spectra of clinoptililite modified by the thermal treatment with different calcination temperatures.

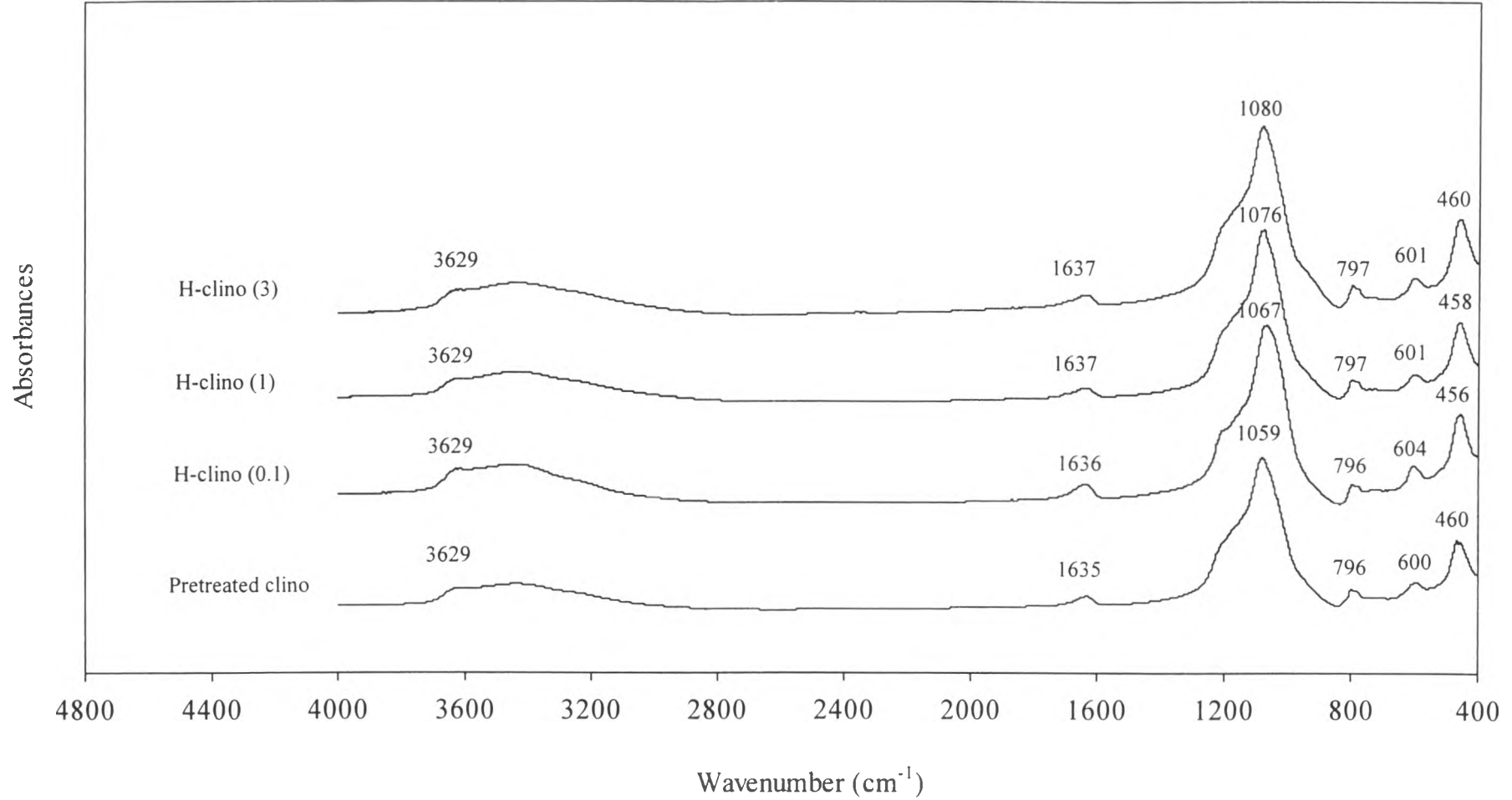


Figure 4.6 Infrared spectra of clinoptilolite modified by the acid treatment with different nitric acid concentrations.

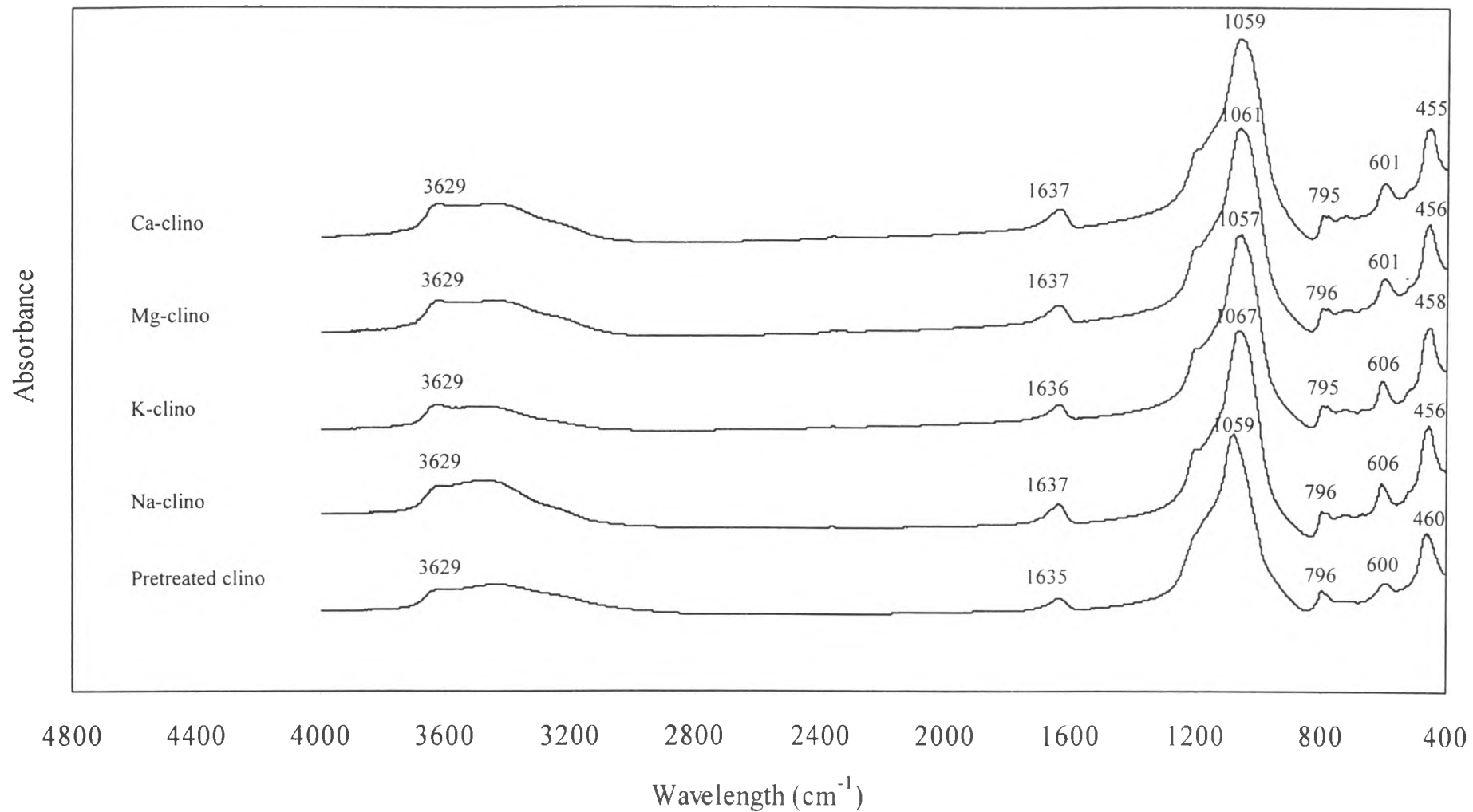


figure 4.7 Infrared spectra of clinoptilolite modified by the ion exchange with different cations.

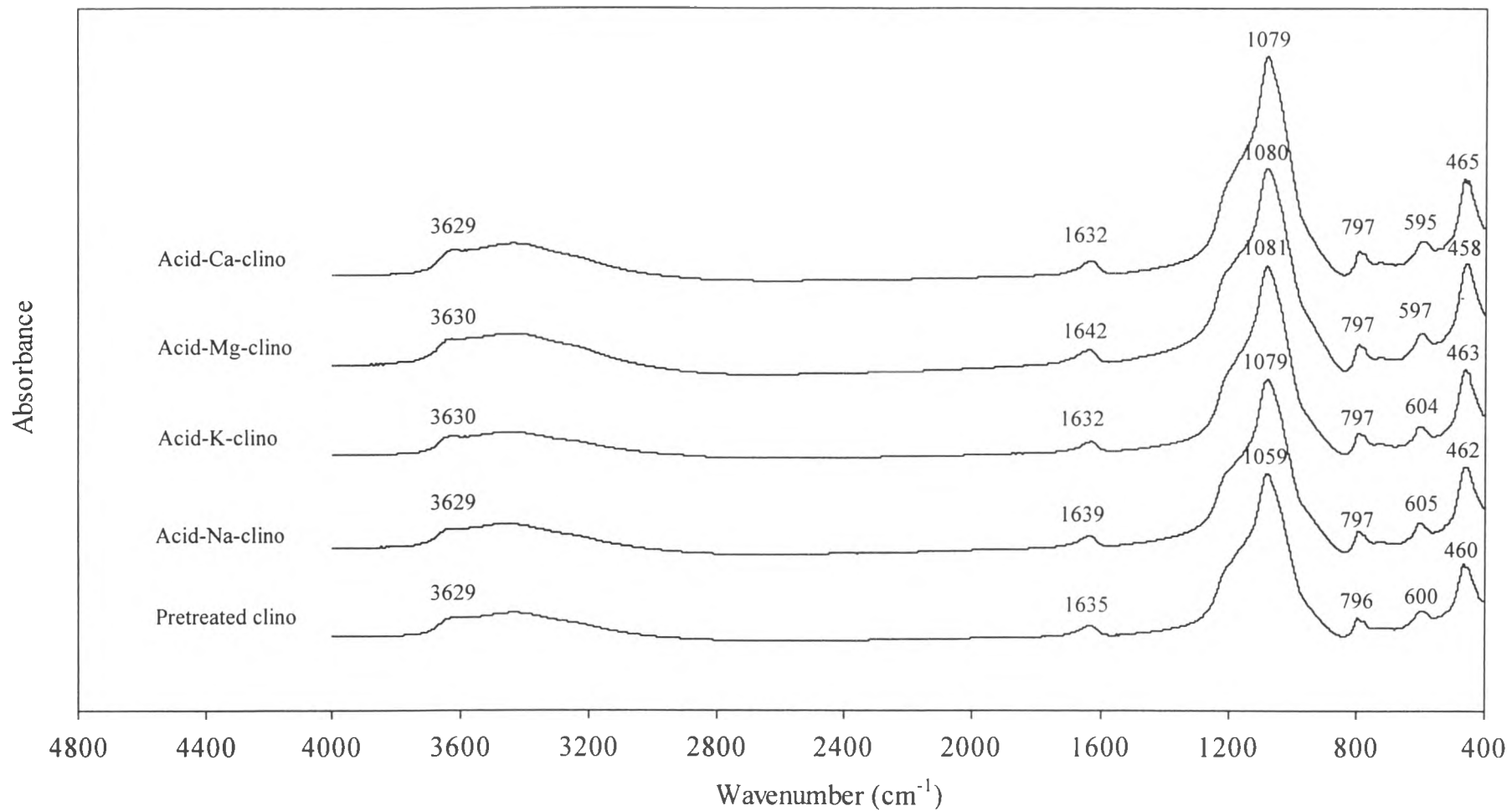


Figure 4.8 Infrared spectra of clinoptilolite modified by the acid treatment prior to ion exchange with different cations.

4.1.4 Compositions of Clinoptilolites

In this part, the energy dispersive x-ray spectrometer was used to determine the compositions of modified and unmodified clinoptilolites. The results are reported in Tables 4.3. According to the data, the zeolite used in this work composes 70.98%wt Si, and K and Ca are present in the comparably significant amount. The Si/Al ratio of the pretreated clinoptilolite is 5.19:1 compared to 5:1 of the origin clinoptilolite.

The results show that only thermal treatment technique does not change the composition of clinoptilolite. On the other hand, the significant change in composition was observed for the other three techniques. Nevertheless, the Si content of clinoptilolite modified by all techniques is rather constant. In other words, all modification techniques used here do not affect significantly the Si content of the zeolites. But the concentrations of cations and Al contents did change with the acid treatment and acid treatment prior to ion exchange because of the dealumination. In case of the acid treatment, the decationization and dealumination increase as the nitric acid concentration increases.

For the ion exchange technique, the amount of cation of the modified clinoptilolite increases with the specific ion used in the treatment. However, this is valid for the Na and K modified forms. This is the result from the difference in selectivity of cation used. Tsitsishvili *et al.* (1992) reported that the selectivity for Na and K is higher than that of Mg and Ca. That explains why the zeolite treated with Mg or Ca still has the relatively same amounts of cations of Mg and Ca as that of the pretreated clinoptilolite. The compositions of clinoptilolites modified by the ion exchange and acid treatment prior to ion exchange techniques shows that clinoptilolite modified by the former technique has higher cation content than that by the latter technique. This is due to the latter technique causes a decrease of Al content of clinoptilolite.

Table 4.3 Composition of the pretreated clinoptilolite and modified clinoptilolites.

Adsorbent	Si (%wt)	Al (%wt)	Na (%wt)	K (%wt)	Mg (%wt)	Ca (%wt)	Si/Al
Pretreated clino	70.98	13.67	0.93	7.16	1.42	5.85	5.19
Clino (300)	71.40	15.68	1.68	6.43	0.94	3.86	4.55
Clino (400)	71.36	14.50	0.99	7.76	1.23	4.15	4.92
Clino (500)	71.37	15.01	0.97	7.05	1.21	4.40	4.75
H-clino (0.1)	72.66	13.84	1.42	7.62	0.92	3.55	5.25
H-clino (1)	79.69	11.56	1.04	5.76	0.59	1.38	6.89
H-clino (3)	80.65	11.81	0.35	5.54	0.57	1.09	6.83
Na-clino	65.85	12.74	<u>12.74</u>	5.56	1.67	1.44	5.17
K-clino	64.47	12.14	2.08	<u>19.48</u>	1.08	0.75	5.31
Mg-clino	70.61	13.39	2.07	7.60	<u>1.98</u>	4.35	5.27
Ca-clino	69.91	12.89	3.54	6.44	1.55	<u>5.84</u>	5.42
Acid-Na-clino	76.47	10.51	<u>6.47</u>	5.29	0.63	0.64	7.28
Acid-K-clino	71.06	8.59	4.84	<u>13.62</u>	1.14	0.74	8.27
Acid-Mg-clino	77.79	9.47	4.51	5.39	<u>1.18</u>	1.67	8.21
Acid-Ca-clino	77.06	9.72	3.02	6.29	0.92	<u>2.99</u>	7.98

4.1.5 Water Adsorption Capacity of Clinoptilolite

The static adsorption was used to measure the water adsorption capacity of modified and unmodified clinoptilolites. The results are shown in Table 4.4. The water adsorption capacity is directly related to the zeolite crystallinity because the active surface for the adsorption is located inside the crystal structure. Therefore, a zeolite with higher crystallinity has high water adsorption capacity. From the XRD results, the zeolite crystallinity decreases as the calcination temperature increases. Consequently, increasing the calcination temperature from 300 to 400 and 500°C reduces the water adsorption capacity.

With the acid treatment, using 0.1 M HNO₃, the water adsorption capacity increases from 0.0828 to 0.1019 g adsorbed water/g clinoptilolite because impurities are removed from the zeolite structure. That consequently increases the void volume. On the contrary, treating the zeolite with 1 M or 3 M HNO₃ does not significantly increase the water adsorption capacity. That is because, as the acid concentration increases, the extent to which the dealumination takes place is also higher.

With the ion exchange technique the water adsorption capacity is not significantly altered compared to the pretreated clinoptilolite although Tsitsishvili *et al.* (1992) reported that for Na and K forms of clinoptilolites, the water adsorption capacity increased about 18 to 28%. Unfortunately, comparison cannot be easily made because the conditions used in the author's work were not clearly stated.

Compared to the pretreated clinoptilolite and the zeolite modified with 1 M HNO₃, the zeolite modified with the combination of acid treatment and ion exchange is comparable except Acid-K-clino. It was found that the ion exchange with K followed the acid treatment does change the water adsorption capacity, but this is not the case with the ion exchange alone. A possible explanation is the time used for the ion exchange for this exchange

is two hours longer than the ion exchange treatment alone. Thus, the effect was only observed with Acid-K-clino but not with the other three zeolites because the amount of K present in Acid-K-clino is much higher than Na, Mg, and Ca in Acid-Na-clino, Acid-Mg-clino, and Acid-Ca-clino, respectively.

Table 4.4 Water adsorption capacity of the pretreated clinoptilolite and modified clinoptilolites.

Modification technique	Adsorbent	Water adsorption capacity (g adsorbed water/g adsorbent)
	Pretreated clino	0.0828
Treatment treatment	Clino (300)	0.0749
	Clino (400)	0.0656
	Clino (500)	0.0510
Acid treatment	H-clino (0.1)	0.1019
	H-clino (1)	0.0948
	H-clino (3)	0.0885
Ion exchange	Na-clino	0.0788
	K-clino	0.0735
	Mg-clino	0.0779
	Ca-clino	0.0727
Acid treatment prior to ion exchange	Acid-Na-clino	0.0873
	Acid-K-clino	0.0685
	Acid-Mg-clino	0.0733
	Acid-Ca-clino	0.0853

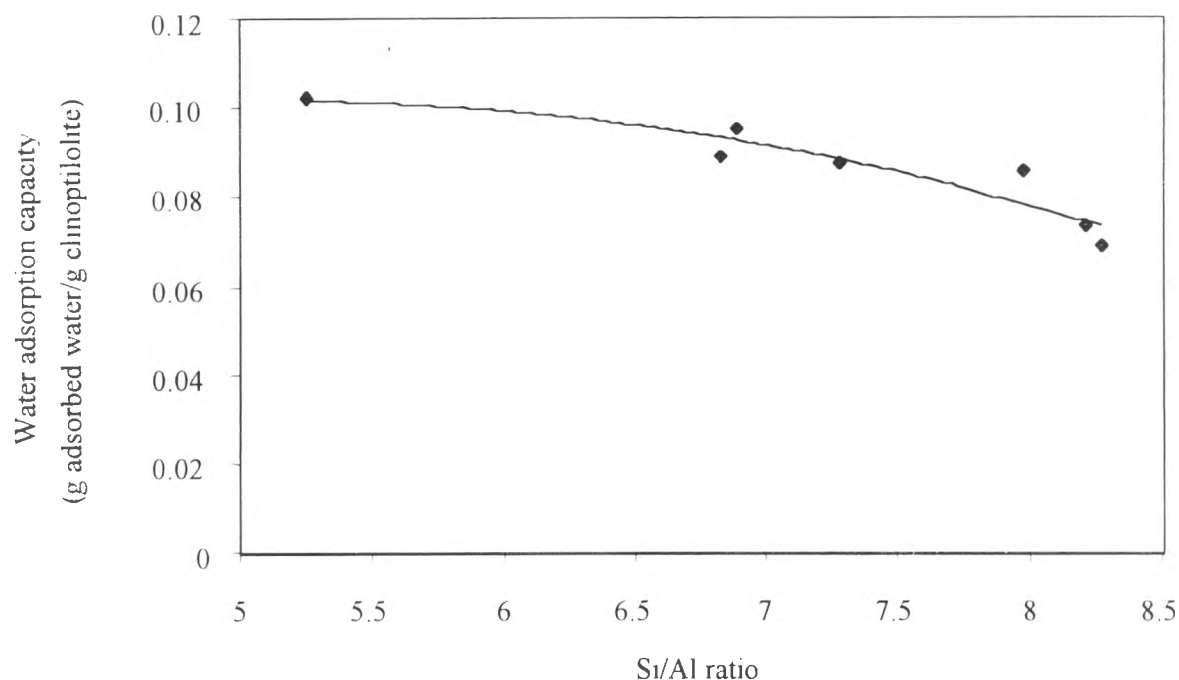


Figure 4.9 Water adsorption capacity of clinoptilolite with different Si/Al ratios.

The relationship between the water adsorption capacity of clinoptilolite and Si/Al ratio is shown in Figure 4.9. The higher Si/Al ratio or lower in Al content causes the decrease in the water adsorption capacity because all water molecules are associated with exchangeable cations that bound to the channel wall at the anion site or AlO_4 -tetrahedra on one side and to a water molecule on the other (Tsitsishvili *et al.*, 1992).

4.1.6 Desorption Temperature of Clinoptilolite

The desorption temperature of clinoptilolite was determined through static thermogravimetry (TG) and differential thermogravimetric curves (DTG). Figure 4.10 shows the derivatograms of the pretreated clinoptilolite. The maximum peak is around 115°C , where the desorption can easily take place.

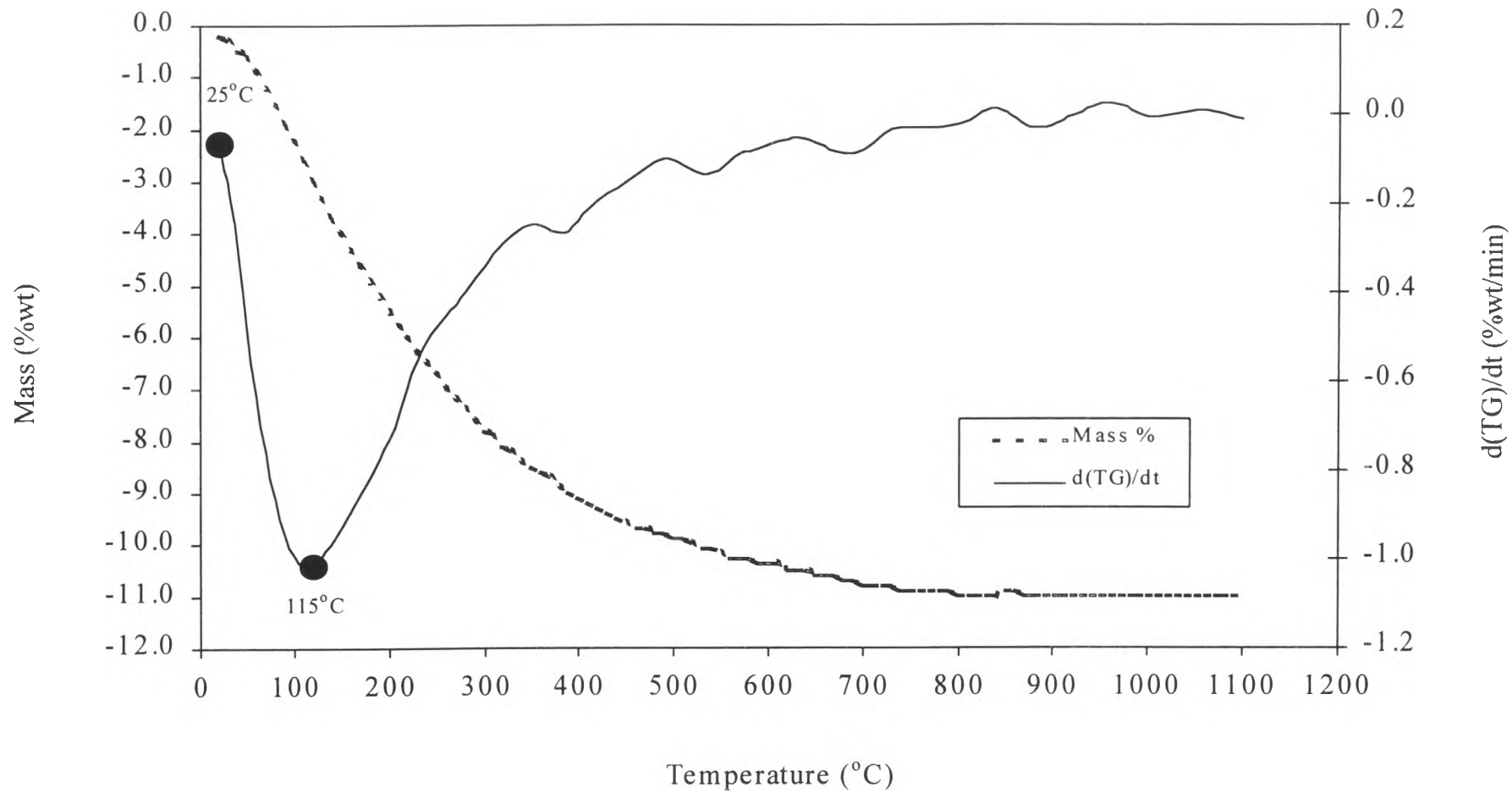


Figure 4.10 The thermogram of water-saturated pretreated clinoptilolite, showing the desorption temperature.

4.2 Competitive Adsorption of Water and Hydrocarbons in the Simulated Natural Gas System

In this part, the focus shifts to the adsorption mechanism of gases, both water and hydrocarbons, on the modified and unmodified clinoptilolites. The selective adsorption between hydrocarbons and water on clinoptilolite was studied. The multicomponent adsorption experiments were carried out on the pretreated clinoptilolite and only a few modified clinoptilolite with high water adsorption capacity. The natural gas used in this study consisted of methane (CH_4), ethane (C_2H_6), propane (C_3H_8), iso- and n-butane (C_4H_{10}). Pentane was added to represent heavy hydrocarbons.

The competitive adsorption behavior of water and hydrocarbons can be explained from a breakthrough curve as shown in Figures 4.11-4.14 for the pretreated clinoptilolite and the clinoptilolite modified by the acid treatment, H-clino (0.1), ion exchange, Na-clino, and acid treatment prior to ion exchange, Acid-Na-clino. At the very beginning of the adsorption process, hydrocarbon molecules are adsorbed onto the clinoptilolite surface, but dramatically desorbed out later. That is indicated by the concentration ratio rises above unity. Ruthven (1984) has described that this phenomenon occurs via the replacement of low molecular weight molecules by higher molecular weight molecules or the replacement of low affinity molecules by molecules with higher affinity. Figures 4.15-4.18 show the adsorption of hydrocarbons on the pretreated clinoptilolite, H-clino (0.1), Na-clino, and Acid-Na-clino. Again, the replacement of the low molecular weight molecules by the high molecular weight molecules was observed.

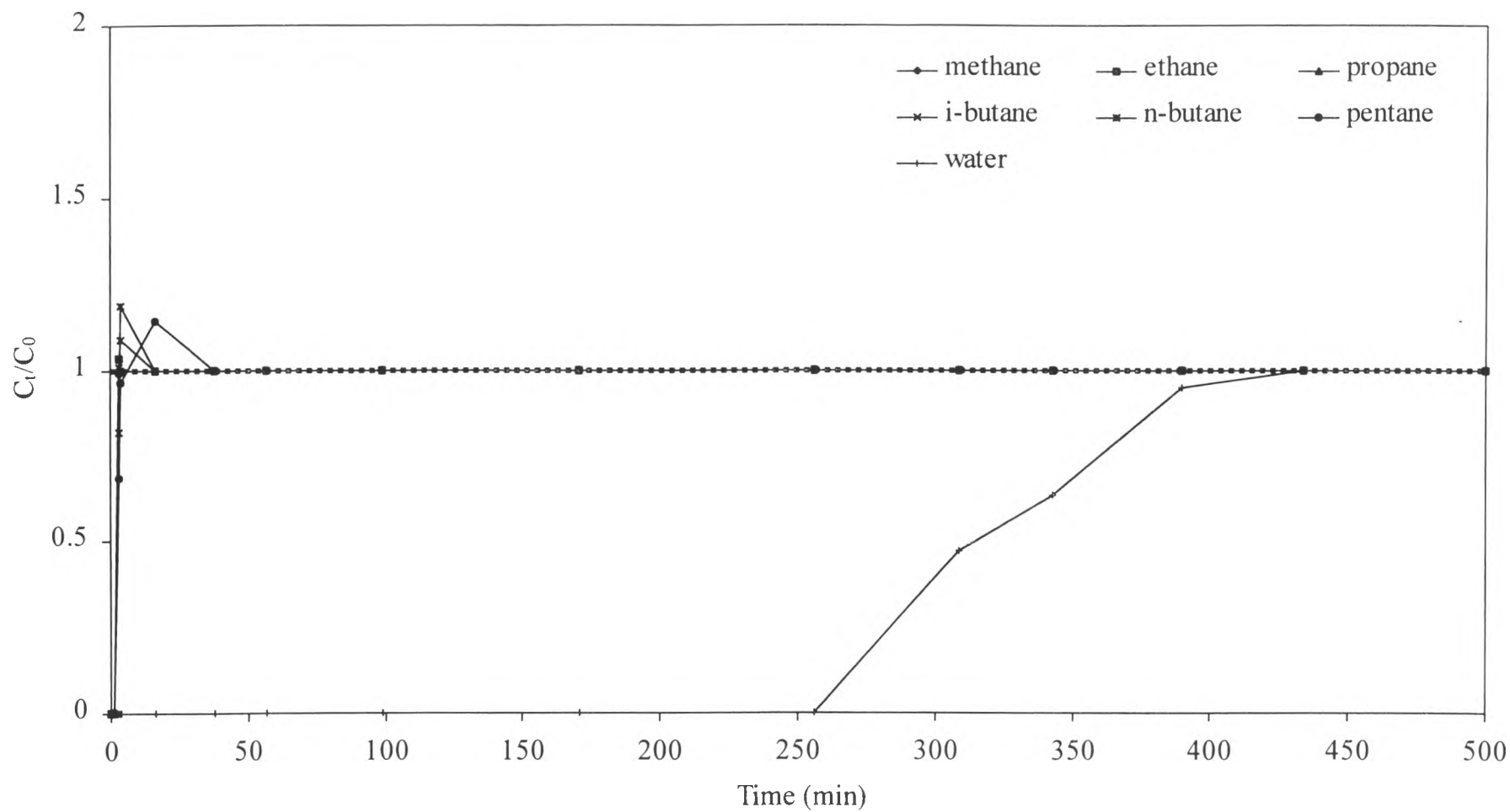


Figure 4.11 Breakthrough curves from the adsorption of humidified natural gas with a mixture of 6.44%vol methane, 1.26%vol ethane, 1.16%vol propane, 0.29%vol n-butane, 0.42%vol iso-butane, 1.35%vol n-pentane, and 1.12%vol water vapor in N_2 at the total flow rate of 25 ml/min on the pretreated clinoptilolite.

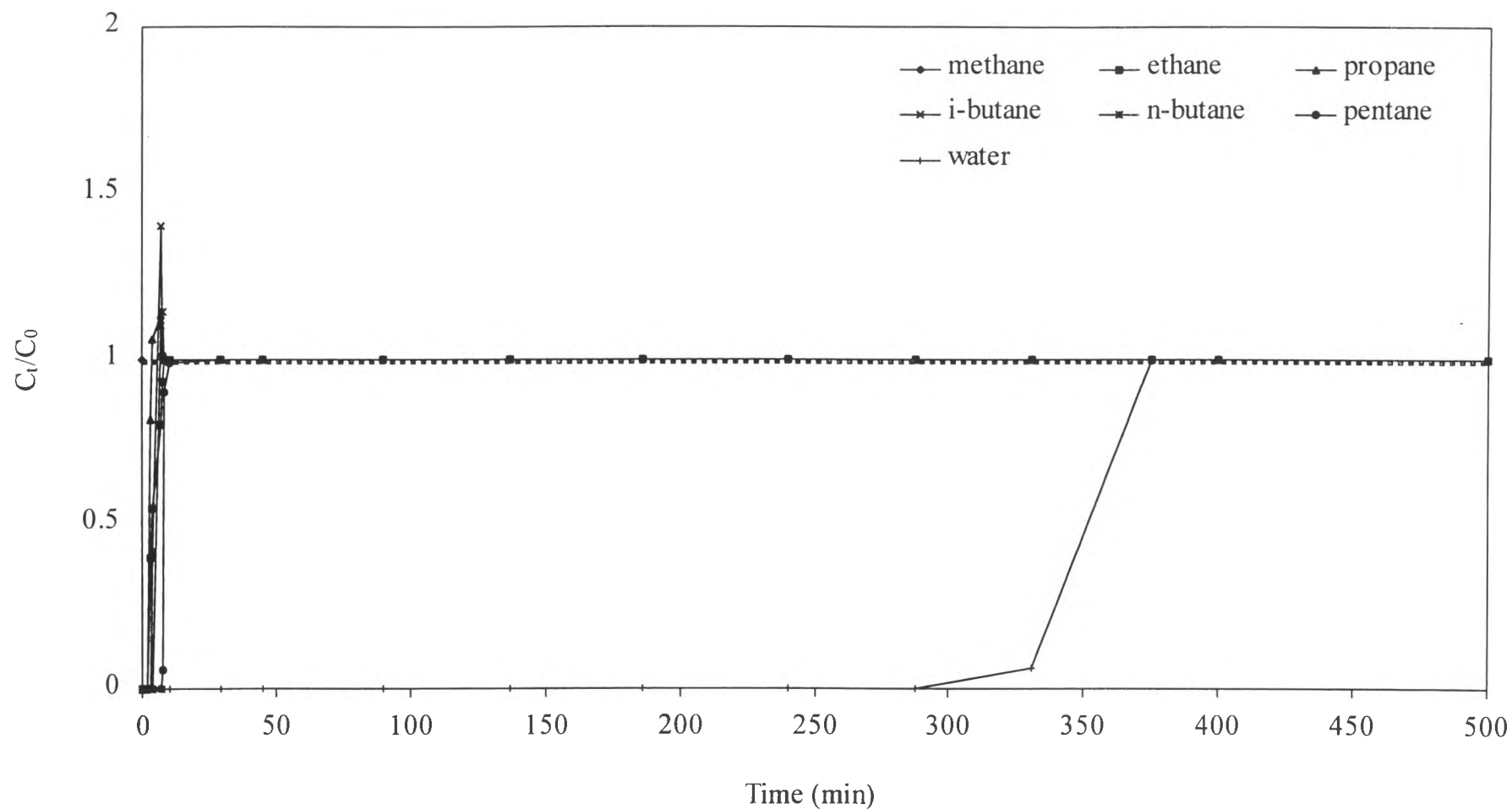


Figure 4.12 Breakthrough curves from the adsorption of humidified natural gas with a mixture of 6.44%vol methane, 1.26%vol ethane, 1.16%vol propane, 0.29%vol n-butane, 0.42%vol iso-butane, 1.35%vol n-pentane, and 1.12%vol water vapor in N_2 at the total flow rate of 25 ml/min on the H-clino (0.1).

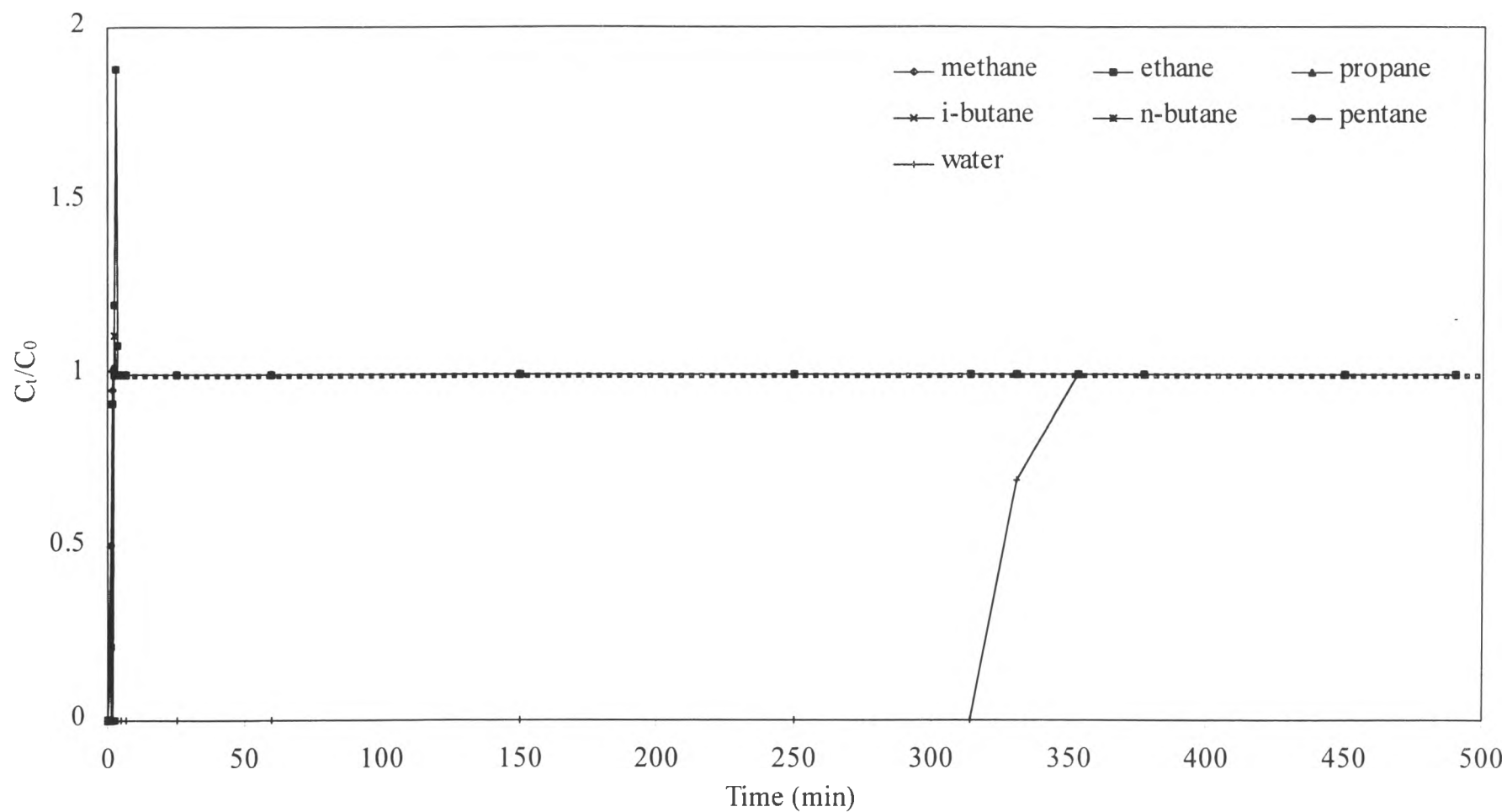


Figure 4.13 Breakthrough curves from the adsorption of humidified natural gas with a mixture of 6.44%vol methane, 1.26%vol ethane, 1.16%vol propane, 0.29%vol n-butane, 0.42%vol iso-butane, 1.35%vol n-pentane, and 1.12%vol water vapor in N_2 at the total flow rate of 25 ml/min on the Na-clino.

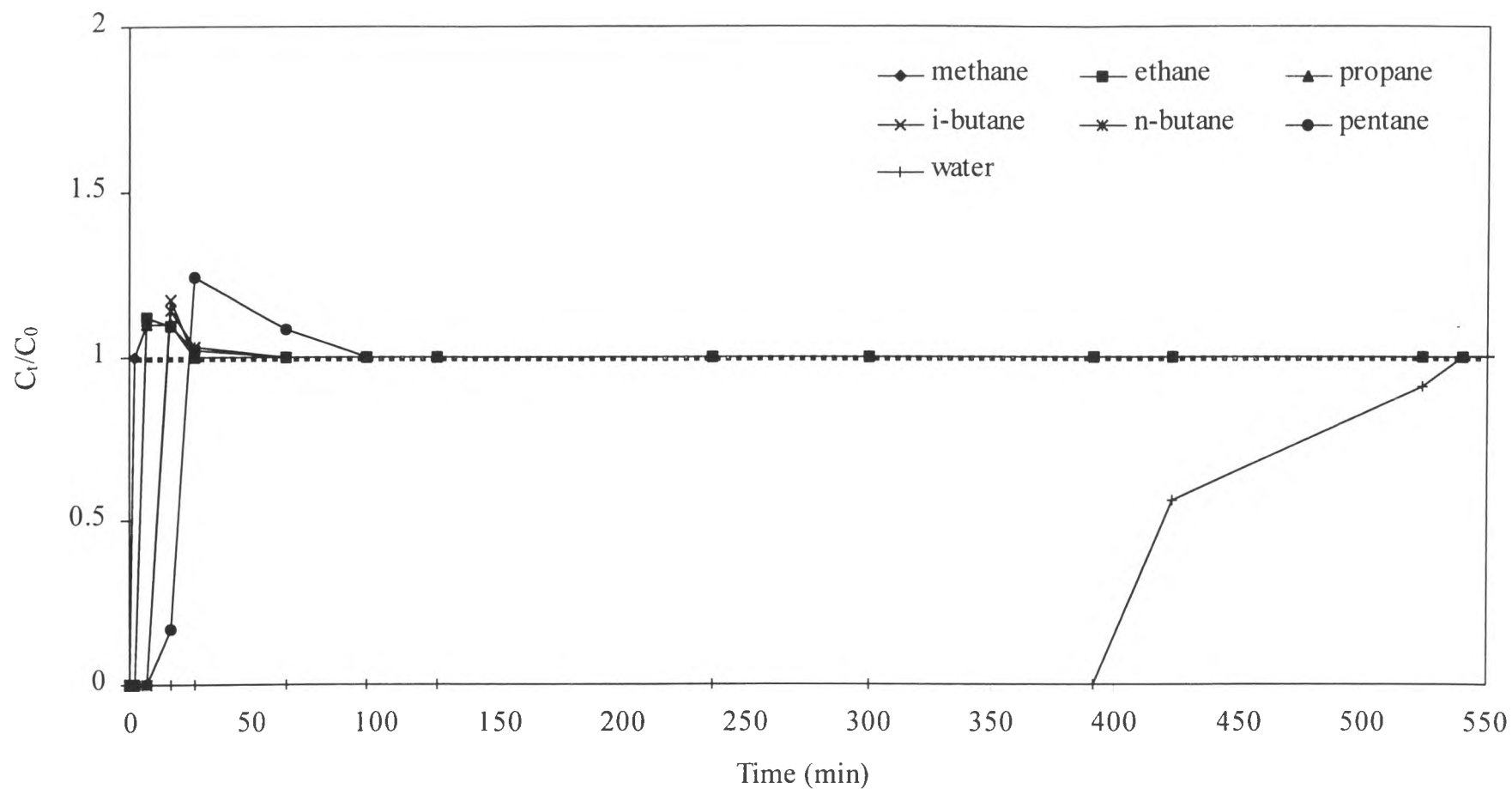


Figure 4.14 Breakthrough curves from the adsorption of humidified natural gas with a mixture of 6.44%vol methane, 1.26%vol ethane, 1.16%vol propane, 0.29%vol n-butane, 0.42%vol iso-butane, 1.35%vol n-pentane, and 1.12%vol water vapor in N₂ at the total flow rate of 25 ml/min on the Acid-Na-clino.

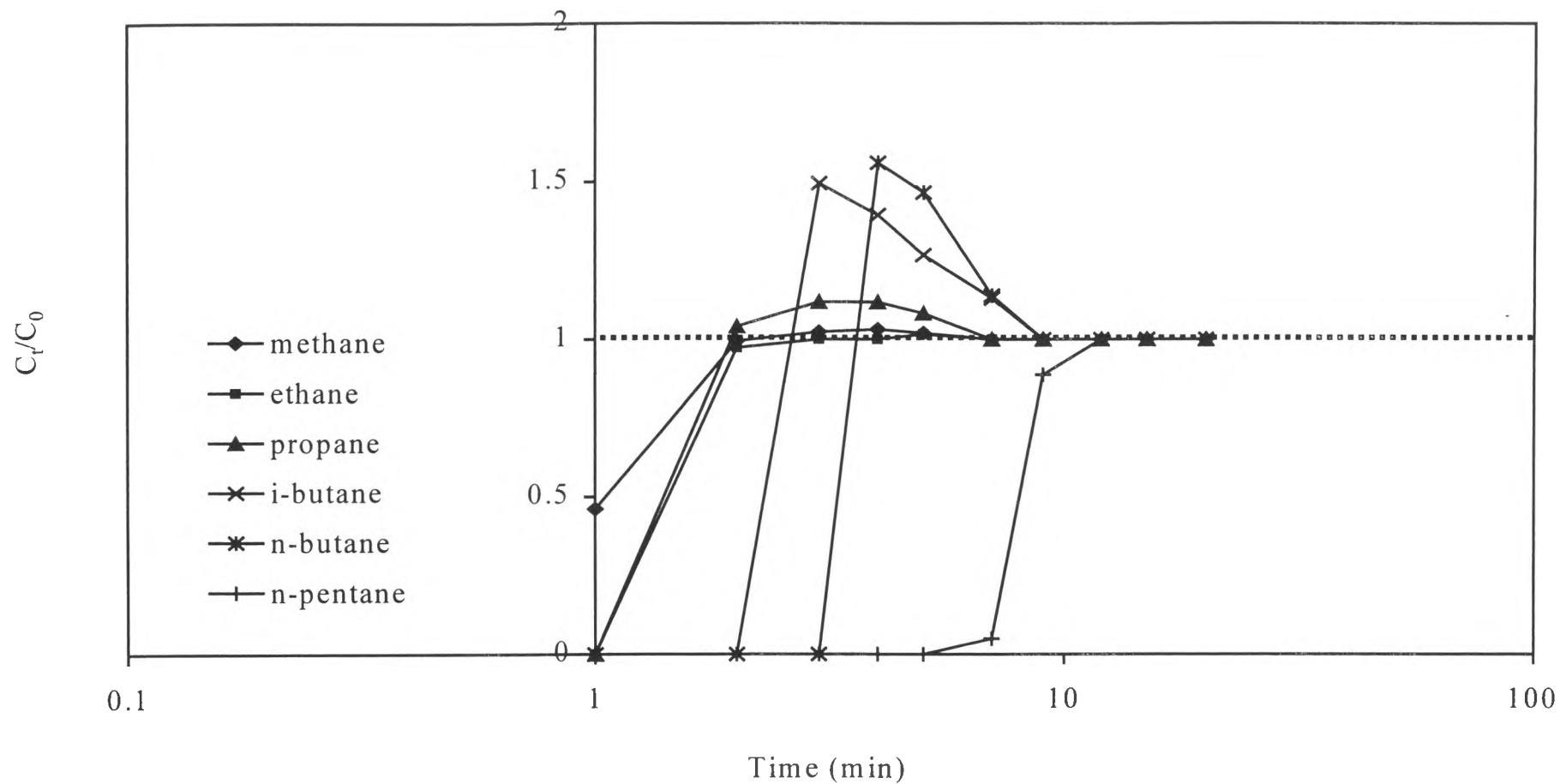


Figure 4.15 Breakthrough curves of hydrocarbons in the presence of 1.20%vol water on the pretreated clinoptilolite.

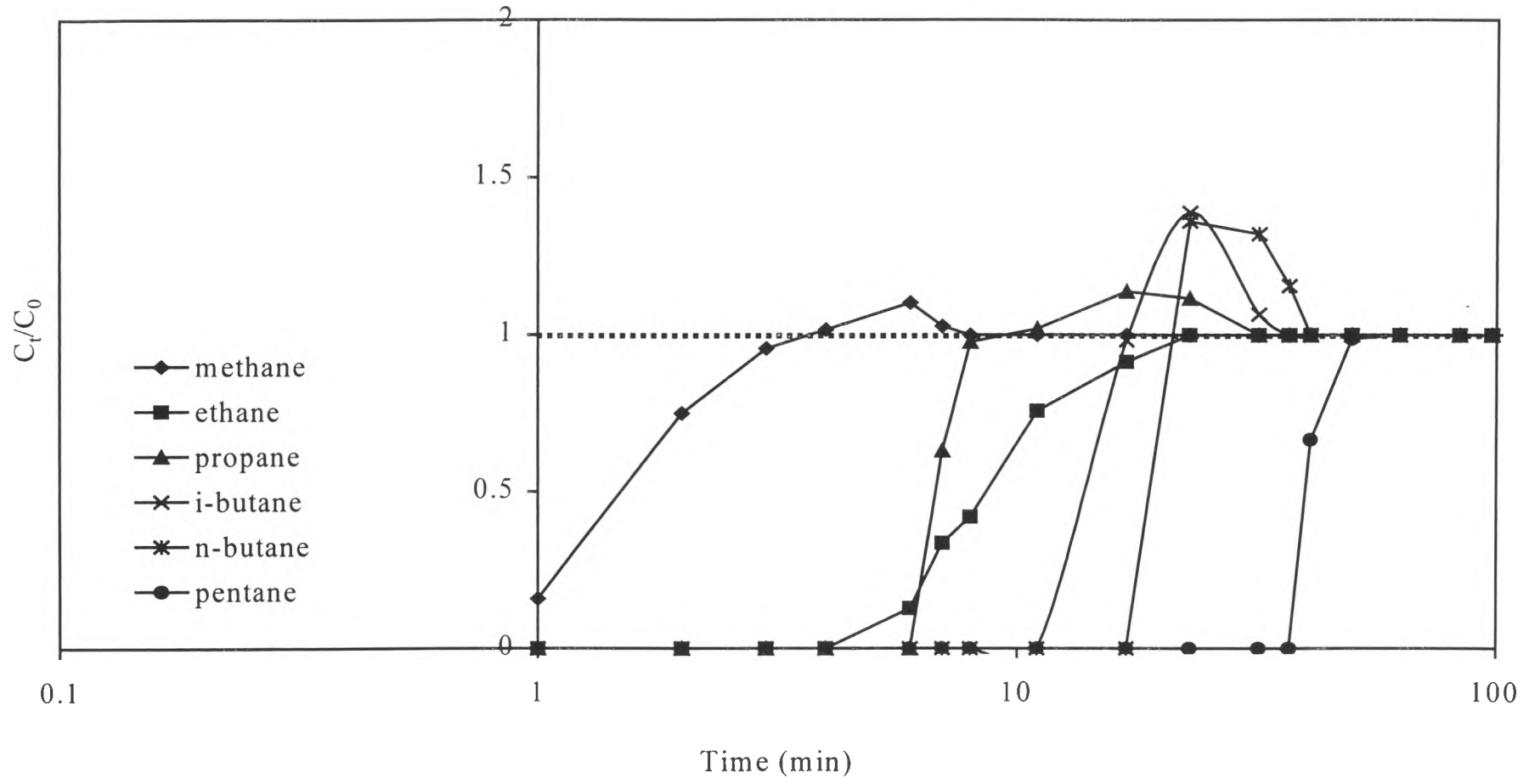


Figure 4.16 Breakthrough curves of hydrocarbons in the presence of 1.20%vol water on the H-clino (0.1).

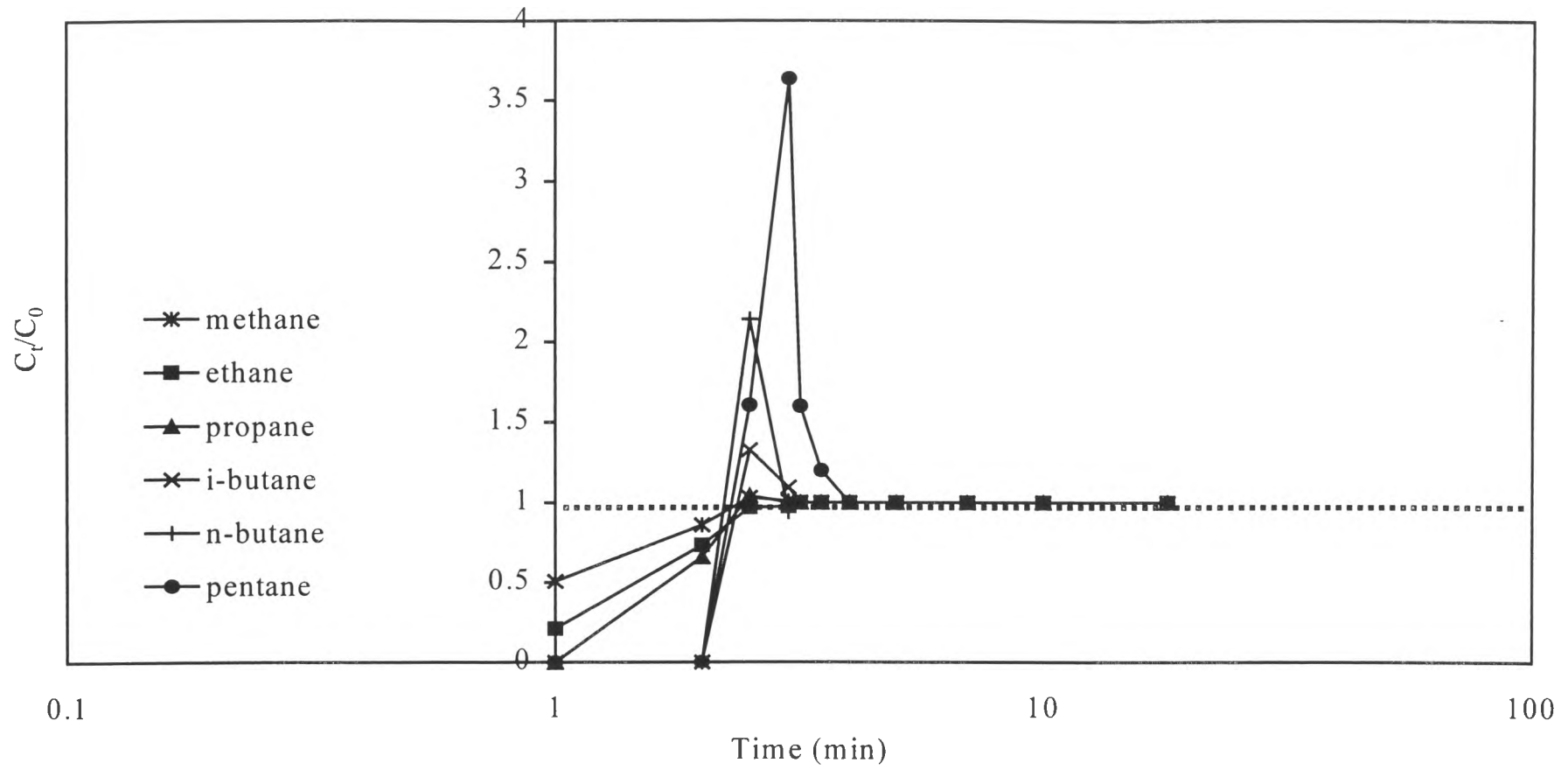


Figure 4.17 Breakthrough curves of hydrocarbons in the presence of 1.20%vol water on the Na-clino.

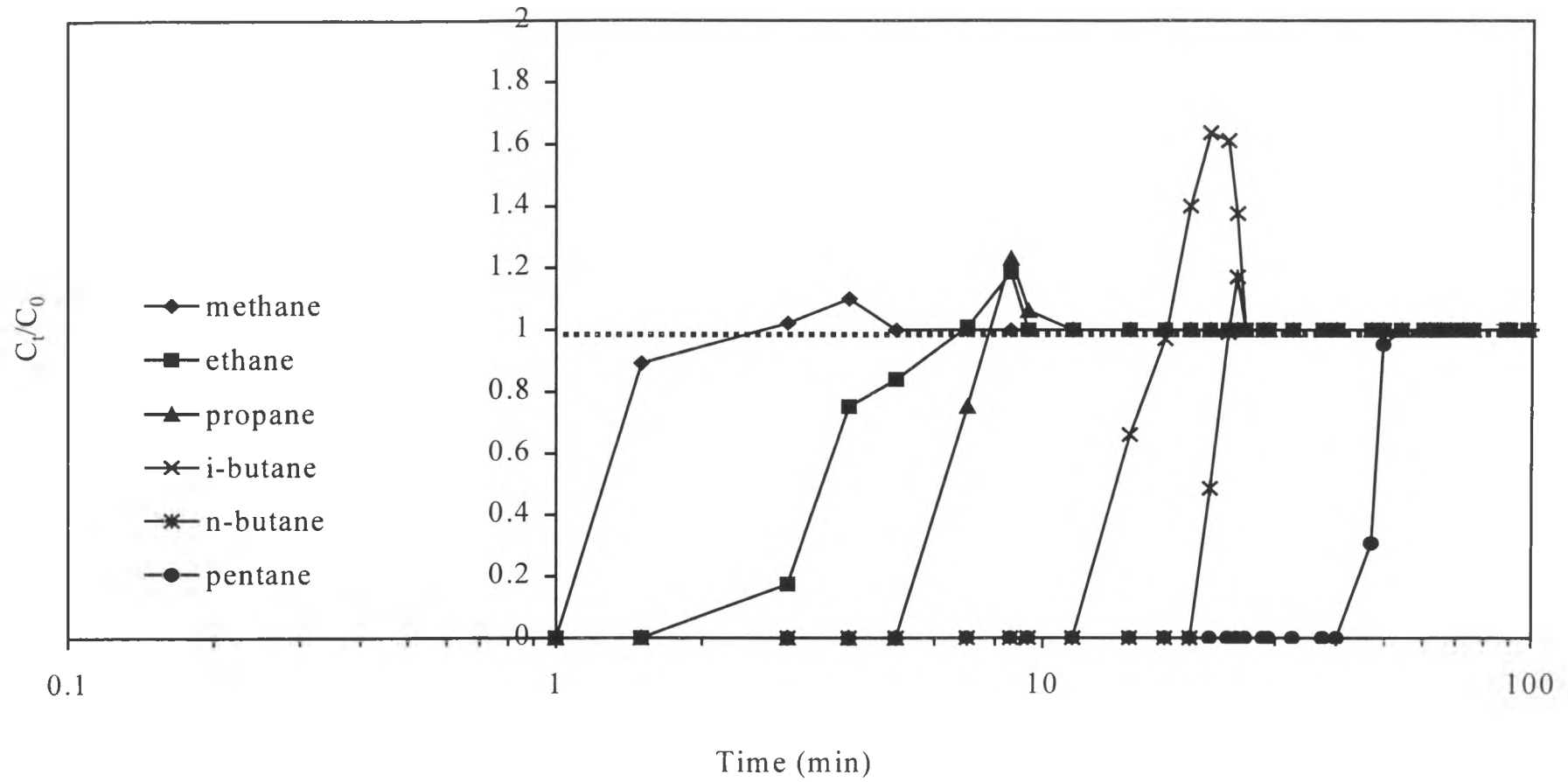


Figure 4.18 Breakthrough curves of hydrocarbons in the presence of 1.20%vol water on the Acid-Na-clino.

The breakthrough times of all hydrocarbons and water of the pretreated clinoptilolite and modified clinoptilolites are shown in Table 4.5. The results show that the breakthrough times of all hydrocarbons are significantly less than that of water. It indicates that the zeolite preferentially adsorbs water to the hydrocarbons.

Table 4.5 The breakthrough time comparison between hydrocarbons and water on one gram of the pretreated clinoptilolite and modified clinoptilolite.

Adsorbent	Breakthrough time (min)						
	Methane	Ethane	Propane	i-butane	n-butane	Pentane	Water
Pretreated clino	1	1-3	1-3	1-3	1-3	1-3	256-309
H-clino (0.1)	0-1	2-3	2-3	3-4	4-7	7.5	331
Na-clino	0-1	0-1	1-2	2-2.5	2-2.5	2-2.5	314-331
Acid-Na-clino	1	4.5	12	12	12	12	407

The comparison of hydrocarbon and water adsorption capacities of the pretreated clino, H-clino (0.1), Na-clino, and Acid-Na-clino in the natural gas is shown in Table 4.6. The amount of water adsorbed in clinoptilolite is directly related to the amount of Al in the zeolite framework. The pretreated clinoptilolite adsorbs small amount of each hydrocarbon. On the other hand, the clinoptilolite modified by the acid treatment and acid treatment prior to ion exchange has higher hydrocarbon adsorption capacity especially for pentane. The water adsorption capacity of Na-clino and Acid-Na-clino drastically increases from 0.0734 to 0.0783 and 0.1004 g adsorbed water/g clinoptilolite, respectively. Their pentane adsorption capacity also increases from 0.0036 to

0.0219 and 0.0452 g adsorbed pentane/g clinoptilolite. In other words, the phobicity of H-clino (0.1) and Acid-Na-clino increases.

Table 4.6 The selective adsorption capacity of hydrocarbons and water of the simulated natural gas on the pretreated clinoptilolite and modified clinoptilolite.

Adsorbent	Adsorption Capacity (g adsorbed gas/g clinoptilolite)						
	Methane	Ethane	Propane	i-butane	n-butane	Pentane	Water
Pretreated clino	0.0025	0.0003	0.0003	8E-05	5E-05	<u>0.0036</u>	<u>0.0734</u>
H-clino (0.1)	0.0044	0.0026	0.0016	0.0006	0.0004	<u>0.0219</u>	<u>0.0783</u>
Na-clino	0.0025	0.0002	0.0003	8E-05	5E-05	<u>0.0009</u>	<u>0.0746</u>
Acid-Na- clino	0.0049	0.0011	0.0027	0.0009	0.0007	<u>0.0452</u>	<u>0.1004</u>