



CHAPTER IV RESULTS AND DISCUSSION

4.1 Molecular Sieve Preparation

4.1.1 Initial Amount of Sodium on Zeolite 4A (NaA)

The amount of the original sodium ions on zeolite 4A was found by dissolution of zeolite 4A with acid (10% volume of conc HNO₃ in water) and then the analysis of the acid solution for sodium ions concentration was done by AAS. The amount of sodium was found to be 5.2 mmole per 1 g of zeolite 4A. From this result, the level of exchange between sodium and divalent cation can be calculated as a percent sodium ions replaced by divalent metal.

4.1.2 Calcium Exchanged on Zeolite 4A (NaA)

4.1.2.1 *Equilibrium Time of Ca Exchanged*

Three initial concentrations of calcium chloride solution prepared from calcium chloride stock solution were used to find equilibrium time of calcium exchanged on zeolite NaA and the results are shown in Table 4.1.

Table 4.1 Final concentration of Ca solution after various contact times between the solid and the solution

Initial concn of Ca solution (ppm)	Ca solution concn after 48 hr. (ppm)	Ca solution concn after 72 hr. (ppm)	Ca solution concn after 96 hr. (ppm)
540	6	4	4
1080	92	70	65
1620	285	295	300

The result shows that the system reached its equilibrium after 72 hours of the contact time between zeolite and the calcium chloride solution.

4.1.2.2 Calcium Exchanged Isotherm

Six initial concentrations of calcium chloride solution were used in order to get six points in the isotherm of the calcium exchanged on zeolite NaA and the results are shown in Table 4.2 and Figure 4.1.

Table 4.2 Calcium exchanged results at 30°C

Initial concn (ppm)	540	810	1080	1620	2160	2700
Final concn (ppm)	4.6	20	65	300	760	1200
difference (ppm)	535.4	790	1015	1320	1400	1500
Ca exchanged (g)	0.027	0.040	0.051	0.066	0.070	0.075
Ca exchanged (mmole)	0.668	0.986	1.266	1.647	1.747	1.871
% Na replaced	25.69	37.90	48.70	63.33	67.17	71.97

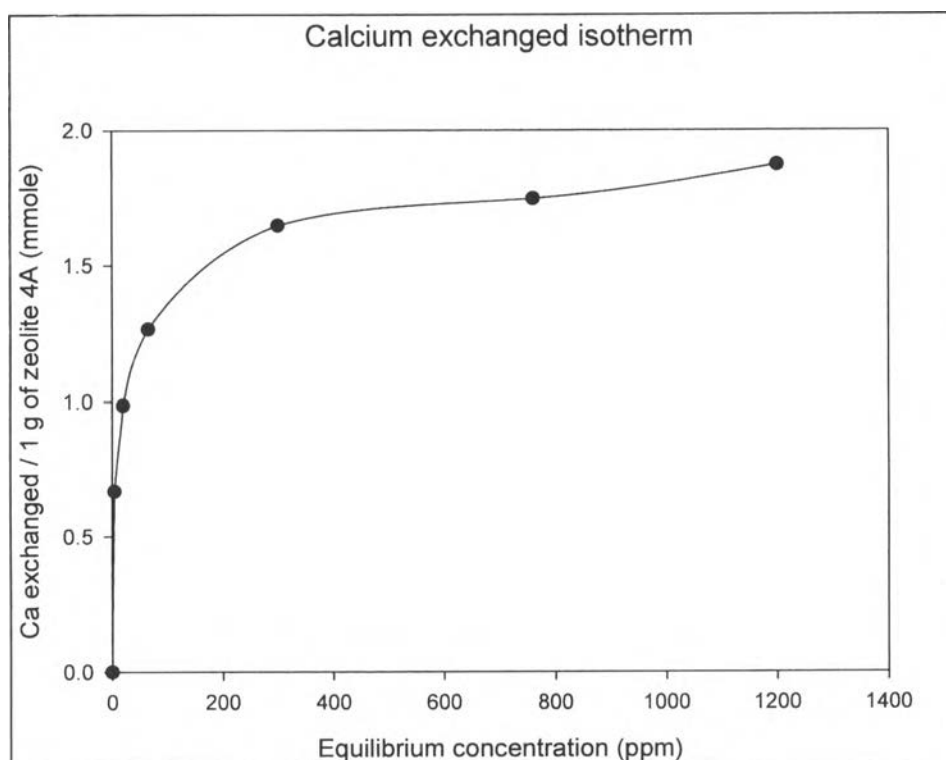


Figure 4.1 Calcium exchanged isotherm at 30°C.

4.1.3 Strontium Exchanged on Zeolite 4A (NaA)

4.1.3.1 *Equilibrium Time of Sr Exchanged*

Three initial concentrations with different contact time of the solid and solution were used to find equilibrium time of strontium exchanged on zeolite NaA. The results are shown in Table 4.3.

The system reached its equilibrium after 72 hours of contact time between the solid and the solution. So, this period of time was used to find strontium exchanged isotherm.

Table 4.3 Final concentration of Sr solution after various contact time of the solid and solution

Initial concn of Sr solution (ppm)	Sr solution concn after 48 hr. (ppm)	Sr solution concn after 72 hr. (ppm)	Sr solution concn after 96 hr. (ppm)
1140	5	2	3
2280	120	50	40
3800	800	700	700

4.1.3.2 *Strontium Exchanged Isotherm*

Five points of strontium exchanged isotherm were obtained from five initial concentrations and the results are shown in Table 4.4 and Figure 4.2.

Table 4.4 Strontium exchanged results at 30°C

Initial concn (ppm)	1140	1900	2280	3040	3800
Final concn (ppm)	2	19	40	230	700
difference (ppm)	1138	1881	2240	2810	3100
Sr exchanged (g)	0.057	0.094	0.112	0.141	0.155
Sr exchanged (mmole)	0.649	1.073	1.278	1.603	1.769
%Na replaced	24.97	41.28	49.16	61.67	68.03

4.1.4 Magnesium Exchanged on Zeolite 4A (NaA)

4.1.4.1 Equilibrium Time of Mg Exchanged

The same method as the calcium and stontium exchanged was used to find equilibrium time of magnesium exchanged on zeolite NaA and the results are shown in Table 4.5.

Table 4.5 Final concentration of Mg solution after various contact time of the solid and solution

Initial concn of Mg solution (ppm)	Mg solution concn after 24 hr. (ppm)	Mg solution concn after 48 hr. (ppm)	Mg solution concn after 96 hr. (ppm)
360	55	27	17
720	290	250	250
1080	600	600	600

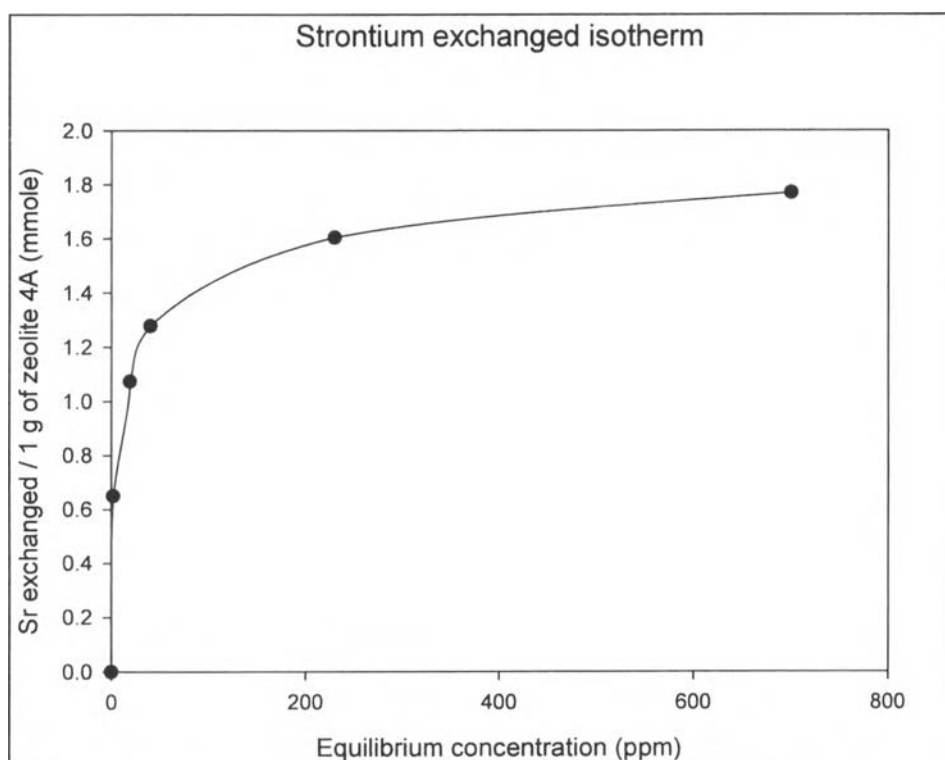


Figure 4.2 Strontium exchanged isotherm at 30°C.

The results in Table 4.5 show that the system reached its equilibrium after 48 hours contact time between the solid and the solution in high

initial concentration systems (720 ppm and 1080) but not in the low initial concentration system. As high level of exchange is needed for effective separation of normal paraffin, low initial concentration equilibrium time would be ignored and the 96 hours contact time of the solid and solution was chosen and assumed to be the appropriate contact time between the solid and the solution of the system.

4.1.4.2 Mg Exchanged Isotherm at 30°C

After the appropriate contact time was found, seven initial concentrations of magnesium chloride solutions were used to find seven points in the magnesium exchanged isotherm and the results are shown in Table 4.6 and Figure 4.3.

4.1.4.3 Mg Exchanged Isotherm at 90°C

Since the level of exchange in magnesium proceeded at 30°C was low comparing to calcium and strontium exchanged due to lower exchanging selectivity of magnesium in zeolite 4A, the ion exchange experiment of magnesium was rerun at 90°C. The maximum level of exchange was found to be higher at this temperature. The results of the experiment are shown in Table 4.7 and Figure 4.4.

Table 4.6 Magnesium exchanged results at 30°C

Initial concn (ppm)	190	380	570	760	950	1520	1900
Final concn (ppm)	1	22	115	270	430	950	1300
difference (ppm)	189	358	455	490	520	570	600
Mg exchanged (g)	0.009	0.017	0.023	0.025	0.026	0.029	0.030
Mg exchanged (mmole)	0.389	0.716	0.936	1.020	1.070	1.172	1.234
% Na replaced	14.95	27.53	35.99	39.24	41.14	45.09	47.46

Table 4.7 Magnesium exchanged results at 90°C

Initial concn (ppm)	270	540	810	1350	1890	2430
Final concn (ppm)	0.8	55	240	750	1200	1700
difference (ppm)	269.2	485	570	600	690	730
Mg exchanged (g)	0.013	0.024	0.029	0.030	0.035	0.037
Mg exchanged (mmole)	0.554	0.998	1.172	1.234	1.419	1.501
% Na replaced	21.30	38.37	45.09	47.46	54.58	57.75

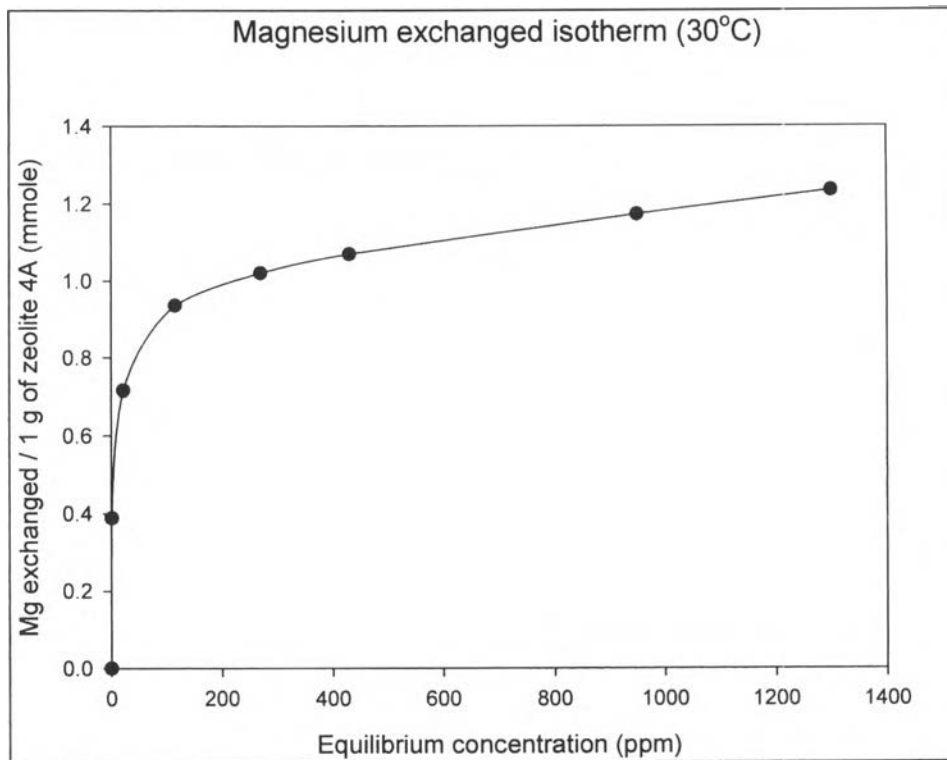


Figure 4.3 Magnesium exchanged isotherm at 30°C.

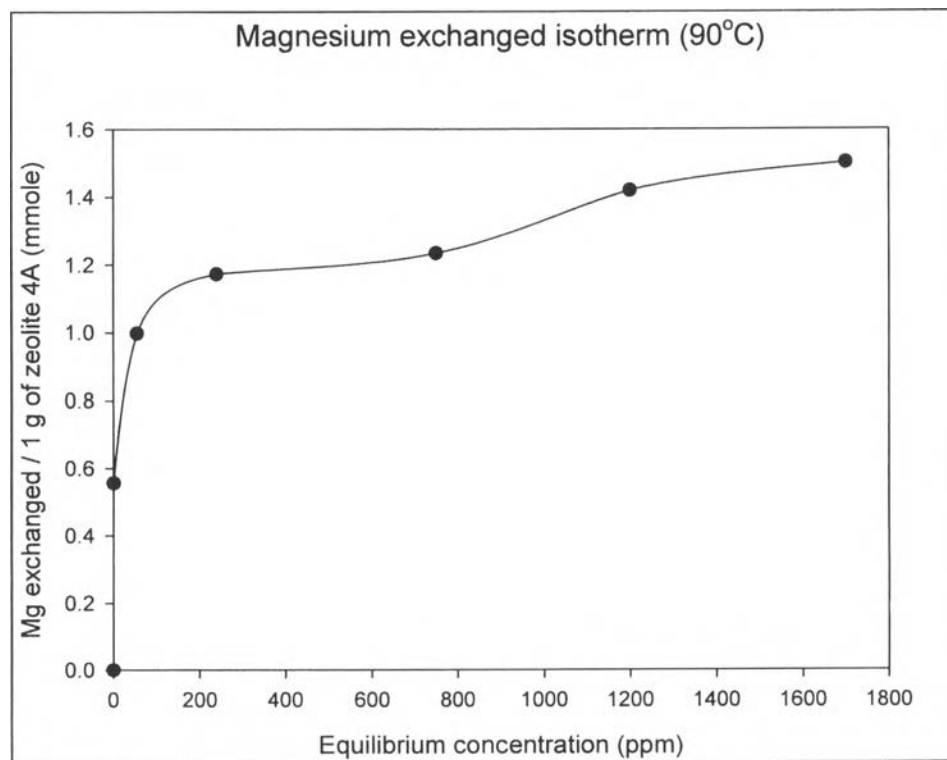


Figure 4.4 Magnesium exchanged isotherm at 90°C.

4.1.5 Level of Exchange Chosen for Paraffin Adsorption

From literature (Milton, 1963), it has been disclosed that higher level of exchange is possible and yields higher capacity of zeolite A for normal paraffin adsorption. However, due to the limitation of magnesium exchanged which is quite low in this experiment, only around 60 percent exchanged on extrudate zeolite 4A was chosen for all three divalent metal cations for normal paraffin adsorption.

4.2 Paraffin Adsorption

4.2.1 Thermogravimetric Analyses

4.2.1.1 *Temperature Program Desorption of Water*

Water desorption curve of strontium and magnesium exchanged form of zeolite A was studied first using zeolite in powder form. These two samples were prepared employing the method invented by earlier work at IFP (Paoli, 2002), not from the isotherm experiments reported above. The procedure used to obtain water desorption profile was quite similar to the one used for normal decane desorption but the temperature was increased directly from ambient temperature to 800°C without stopping at 120°C and the samples were saturated with water instead of normal decane. The results are shown in Figure 4.5.

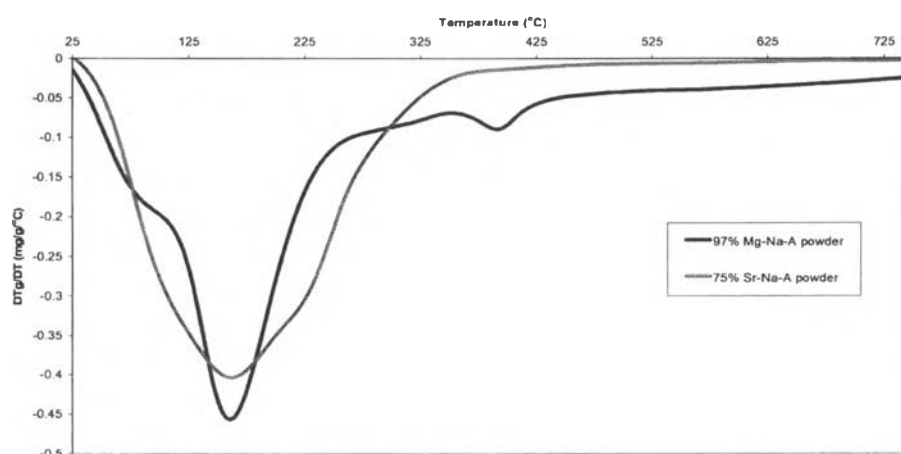


Figure 4.5 Water desorption curve of 97% Mg-Na-A powder form and 75% Sr-Na-A powder form.

From Figure 4.5, the position of the first peak from the two samples was found to be quite the same. However, for Mg-Na-A, the small second peak was observed at around 400°C. This may be due to the destruction of zeolite structure as previously observed in Ba-Na-A (Sherry and Walton, 1966).

4.2.1.2 Temperature Program Desorption of Normal Decane

Temperature program desorption (TPD) thermograms of normal decane in each sample (extrudate) are shown in Figures 4.6, 4.7 and 4.8 for calcium, magnesium and strontium respectively. The comparison of TPD profiles of these three samples is also shown in Figure 4.9. The procedure used to obtain these thermograms was to heat up the sample to 120°C and maintain this temperature for 2 hours in order to purge out normal decane which did not adsorb in the micropore of the molecular sieve. Then the temperature was increased again to 800°C in order to study desorption of normal decane from each solid samples. The dTg/dT curves given in Figures 4.6, 4.7 and 4.8 show several peaks of desorption indicating that the nature of the interaction between adsorbed paraffins and zeolite varies. The normal decane desorption occurs at two ranges of temperature: 120°C-280°C and 280°C-520°C.

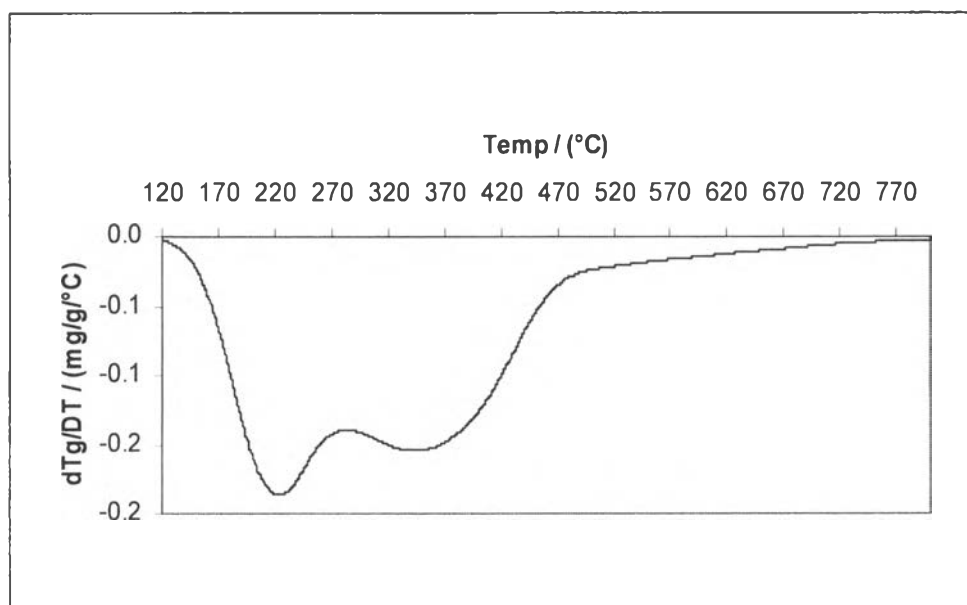


Figure 4.6 TPD thermogram of n-C10 on 53% Ca-Na-A.

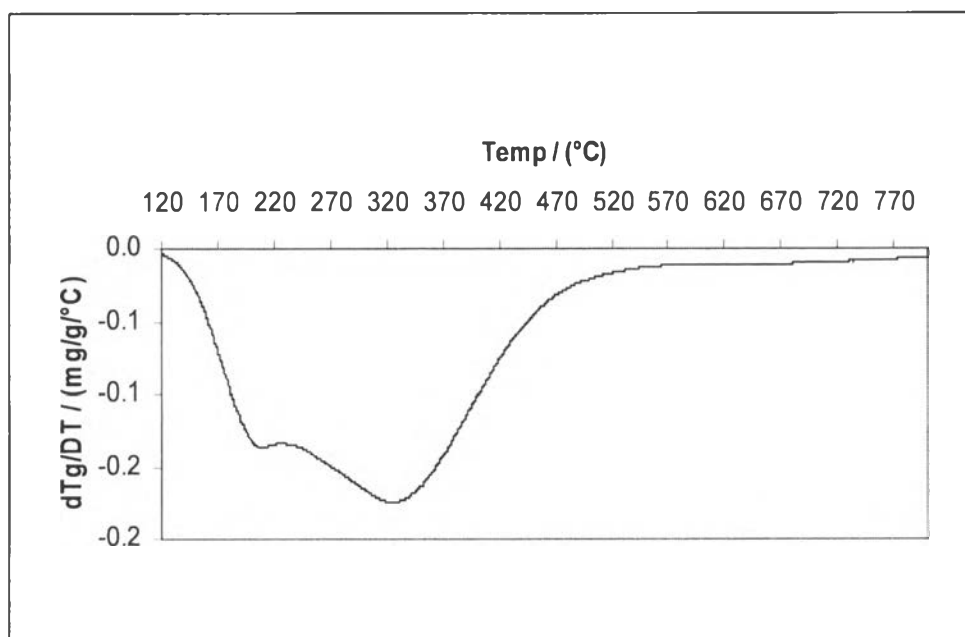


Figure 4.7 TPD thermogram of n-C10 on 57% Mg-Na-A.

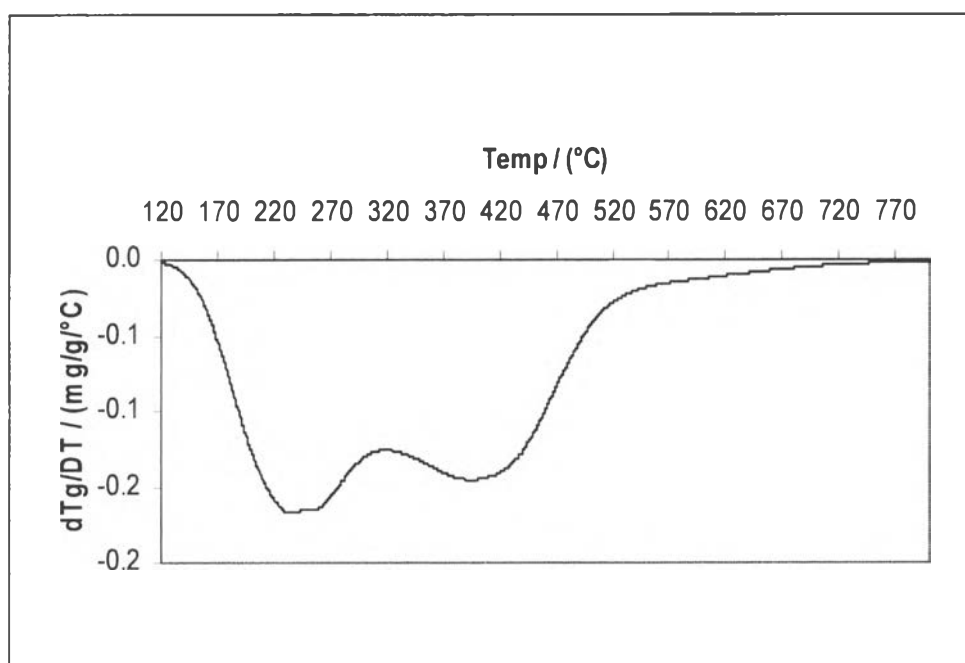


Figure 4.8 TPD thermogram of n-C10 on 54% Sr-Na-A.

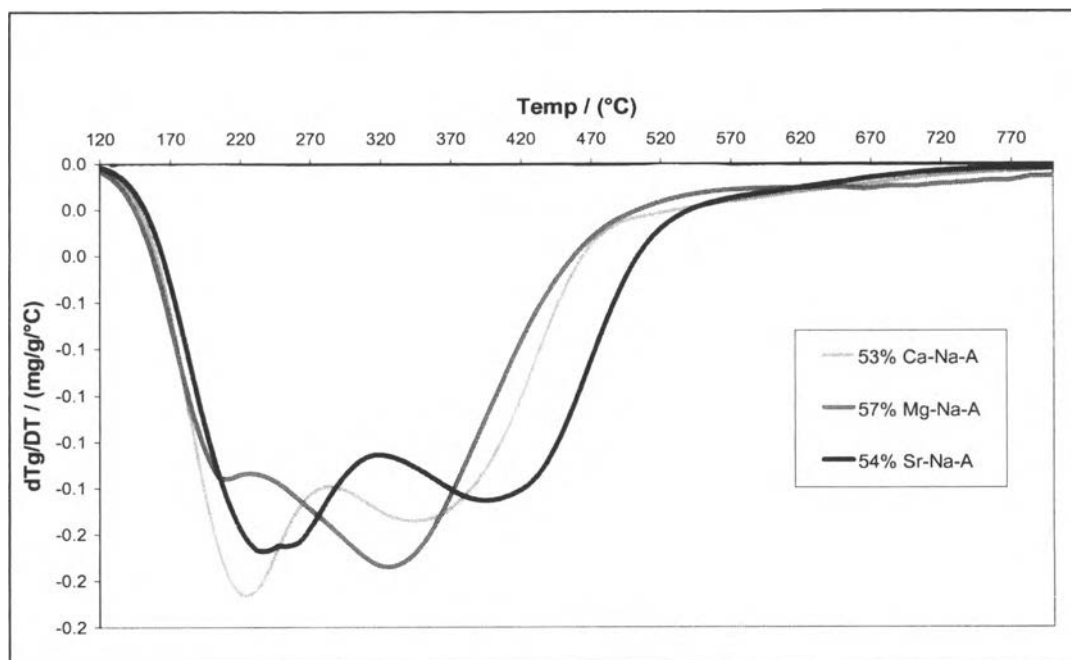


Figure 4.9 Comparison of TPD curves between 53% Ca-Na-A, 57% Mg-Na-A, and 54% Sr-Na-A, all in extrudate form.

It was also observed from Figure 4.9 that as the size of cation increases from magnesium to calcium and strontium the position of peak shifts to the higher temperature. This is due to confinement effect, as when the size of metal increases the cavity of the zeolite decreases, which increases the van der Waal force between adsorbed paraffins and cation. Temperature of the peak positions and number of n-C10 molecules desorbed per unit cell of each sample are shown in Table 4.8 (see calculation in Appendix A).

Table 4.8 Peak position and amount of normal decane desorbed

Metal form	Peak position (°C)		Number of n-C10 molecules desorbed per unit cell
	No.1	No.2	
Ca	227	345	1.5
Mg	213	327	1.3
Sr	239	397	1.4

4.2.2 Breakthrough Curve Experiment

In this part of the study, several conditions were tested with the calcium exchanged zeolite A in order to find the best condition which gives the good profile of the breakthrough curve. Breakthrough curve is a plot of the outlet concentration of the adsorbate divided by the inlet concentration (normalized concentration) as a function of time. For ideal breakthrough curve, normalized concentration would be essentially zero at the beginning, gradually increases and finally reaches unity. The best conditions for the breakthrough experiment are shown in Table 4.9.

Table 4.9 Conditions chosen for breakthrough curve experiment

Column diameter (cm)	1
Column length (cm)	10
Amount of solids loaded (g)	1.5
Adsorption temperature (°C)	300
N ₂ flowrate (liter / hour)	0.5

Using the above conditions, the magnesium and strontium exchanged forms of zeolite 4A samples were used in the experiment in order to compare with the calcium one. Breakthrough curves are shown in Figures 4.10, 4.11 and 4.12 for calcium, magnesium and strontium, respectively.

From the breakthrough curves, the first moment or average time, which is the area on the left side of the breakthrough curve, can be calculated for all divalent metal-exchanged zeolite samples. The results are shown in Table 4.10.

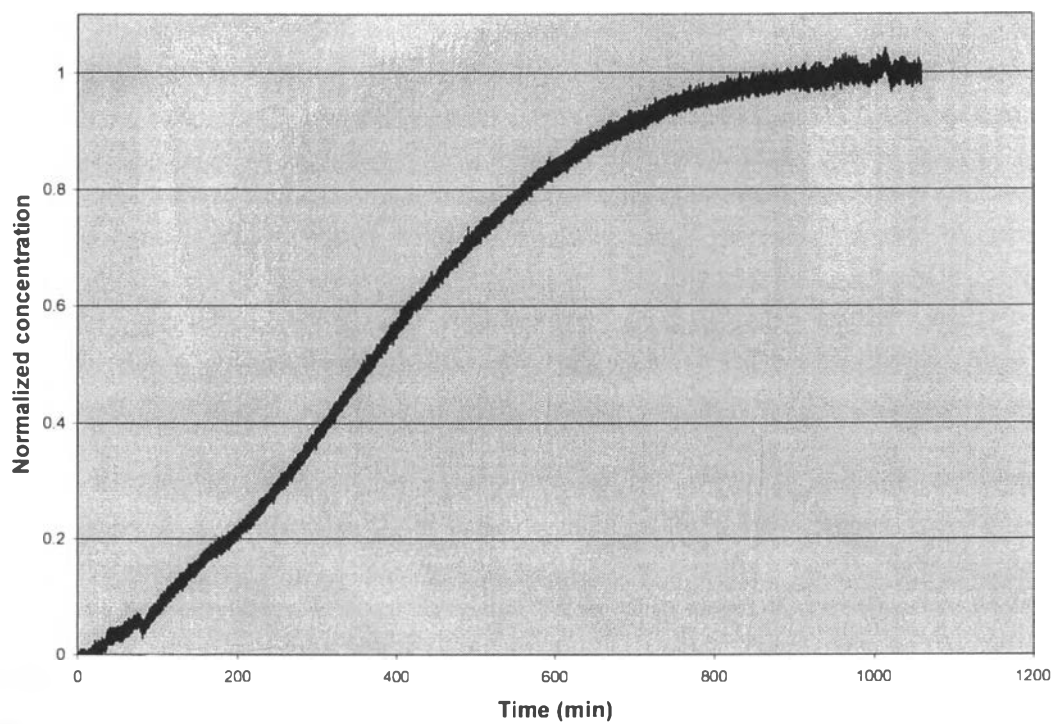


Figure 4.10 53% Ca-Na-A Breakthrough curve at 300°C.

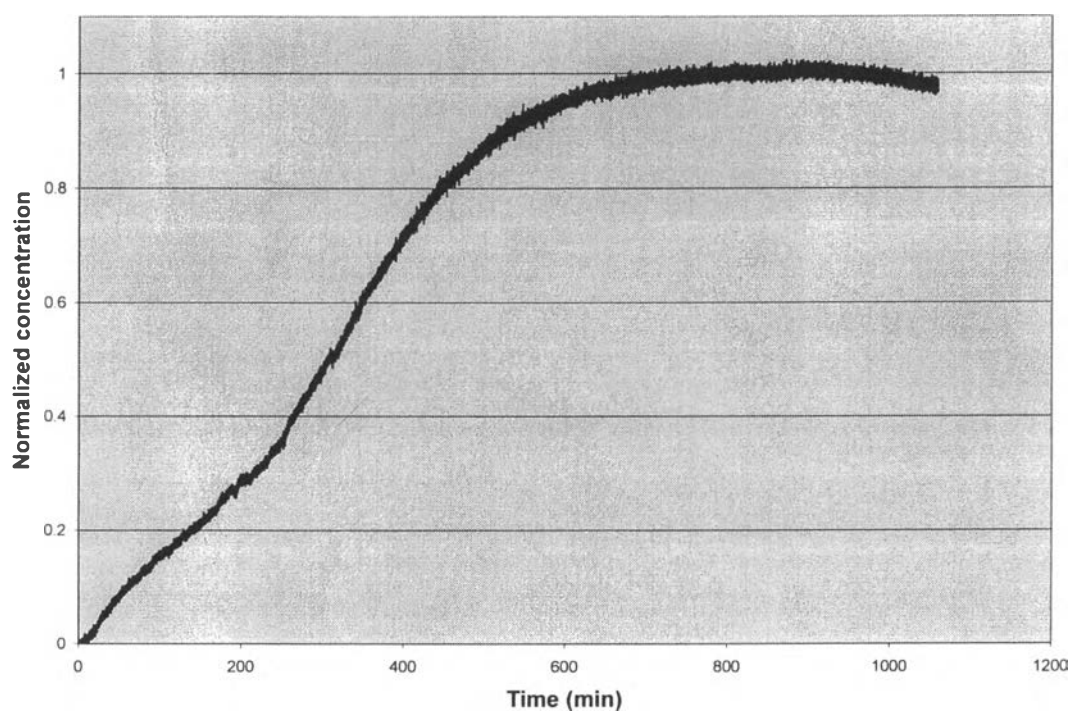


Figure 4.11 57% Mg-Na-A Breakthrough curve at 300°C.

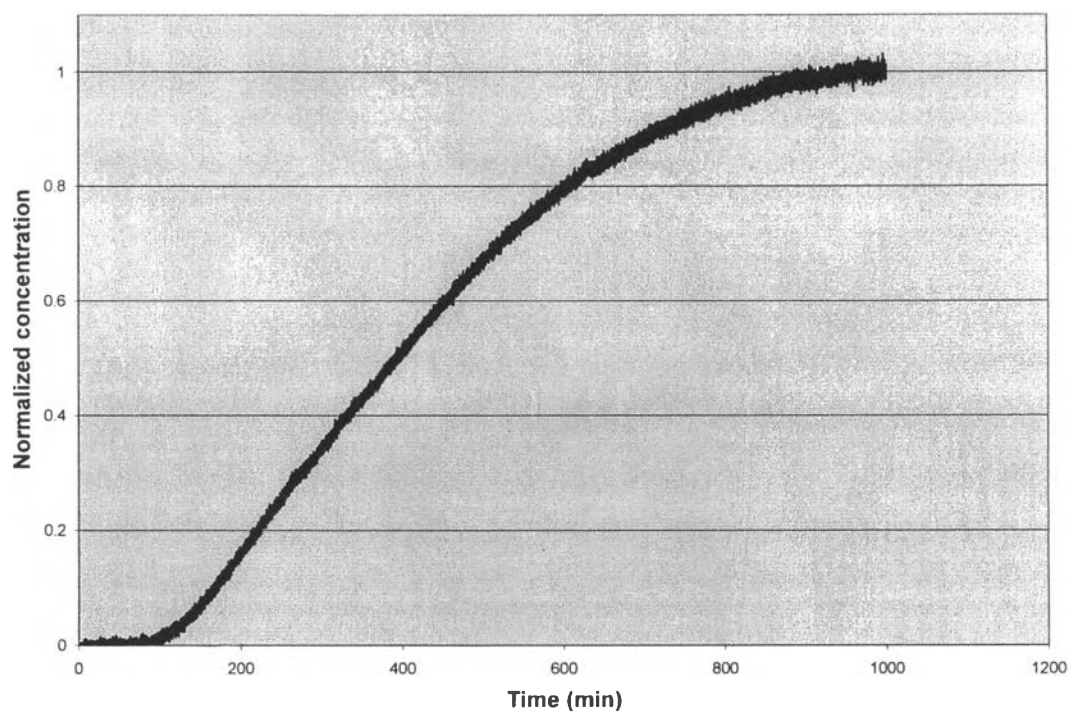


Figure 4.12 54% Sr-Na-A Breakthrough curve at 300°C.

Table 4.10 Average times obtained from breakthrough curve experiment

Metal exchanged on zeolite	Average time (min)
Magnesium	303
Calcium	383
Strontium	420

From the average times shown in Table 4.10, magnesium form zeolite has the lowest average time of 303 minutes, while those of calcium and strontium are higher and the values are not quite different (383 and 420 minutes, respectively). This observation seems to support the hypothesis that the crystal structure of the magnesium exchanged form of zeolite A was collapsed during dehydration when the solid was heated up to 400°C. This kind of phenomena was also found in barium form of zeolite A (Sherry and Walton, 1966). The reason of the disruption of the crystal structure in barium form of zeolite A is due to the large internuclear distances between the proton and the oxygen atom of the lattice that

must be expected in large size cation. However, this explanation may not be used for magnesium since the magnesium is the small size cation. The instability of Mg-Na-A structure is probably due to low selectivity of the magnesium ion for the structure of zeolite A type.