

## CHAPTER V

### RESULTS AND DISCUSSION

In this research the investigation of surface basicity of catalysts by pyrrole adsorption had been carried out. The results are divided into two sections. The measurement of basicity of catalysts by infrared spectroscopy is reported in section 5.1. Section 5.2 shows the results of pyrrole and CO<sub>2</sub> adsorption on catalysts .

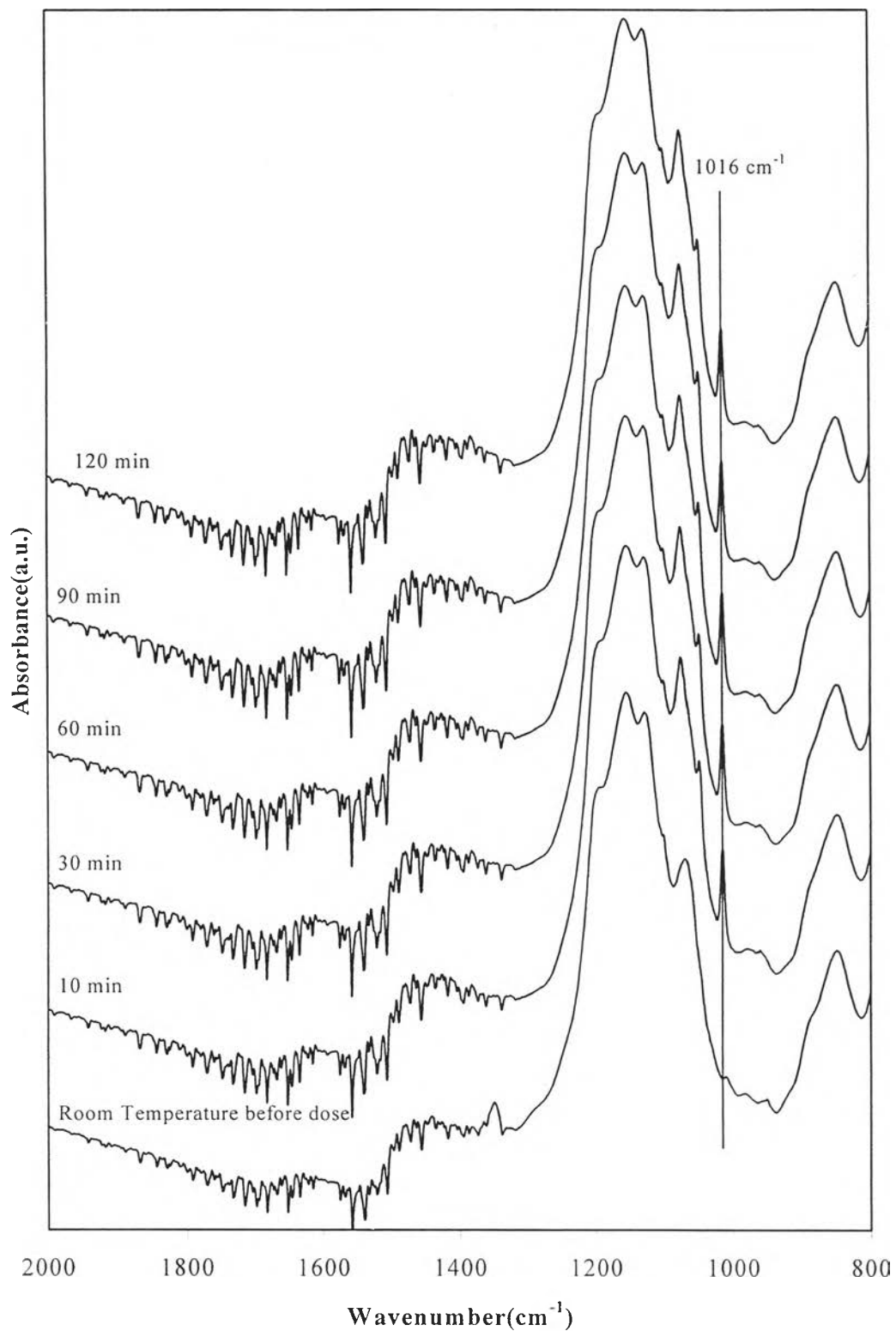
#### 5.1 Characterization of basicity by FTIR

##### 5.1.1 Effect of time for introducing pyrrole vapour.

In this section, the basicity measurement of the MgO by IR technique is carried out using pyrrole as probe molecule. Some papers reported that adsorption band of trace water in pyrrole (3400 -3600 cm<sup>-1</sup>) can interfere the adsorbed pyrrole band (3200-3400 cm<sup>-1</sup>) on the basic sites of the sample. Thus, in this study the trace water was removed from the pyrrole by molecular sieve before use. The clearness of IR adsorption band is affected by time for introducing pyrrole vapour. If pyrrole vapour is introduced onto surface of catalysts for too long time, signal of noise appears in the IR adsorption band. This signal of noise occurred from residual water which cannot be removed by molecular sieve. Too short time results in unsaturate adsorption of pyrrole vapour on catalyst surface.

IR spectra of adsorbed pyrrole on pure MgO at various time are shown in figures 5.1 and 5.2 in the range of wavenumber 800-2000 cm<sup>-1</sup> and 3000-3500 cm<sup>-1</sup>, respectively. From figure 5.1 the sharp peak at 1016 cm<sup>-1</sup> assigns ring stretching signal of pyrrole molecule on the surface of metal oxide. The ring stretching vibration of pyrrole is used to confirm the appearance of adsorption. Figure 5.2 indicates broad band of NH stretching between 3000-3500 cm<sup>-1</sup> relates with adsorption of pyrrole on basic sites. Peak height of IR adsorption band at wavenumber 1016 cm<sup>-1</sup> is shown in figure 5.3(A). And the figure of peak height in

the region of NH stretching shown in figure 5.3(B), the maximum band at  $3386\text{ cm}^{-1}$  was decreased with increasing the time of introducing the pyrrole vapour from 10 to 120 minutes. From figure 5.3(A) and 5.3(B), it showed well correlated of decreasing of peak height at various time. The maximum band at  $3386\text{ cm}^{-1}$  was attributed to the position of pyrrole adsorbed on the basic sites, which contact to the pyrrole vapour for different time period of introducing pyrrole vapour. It is reasonable to explain that the decline of maximum band is affected by the hindrance of baseline of  $\text{H}_2\text{O}$  band which cannot be absolutely removed with the molecular sieve and the base line of the maximum band at  $3386\text{ cm}^{-1}$  will be changed. Therefore, the suitable time for introducing pyrrole vapour is about 10 minutes to investigate the pyrrole adsorption by FTIR technique. Hence, the optimum time for introducing pyrrole vapour as discussed in this section was used in the subsequent experiment.



**Figure 5.1** IR spectra of ring stretching region of pyrrole adsorption on pure MgO at various time for introducing pyrrole vapour

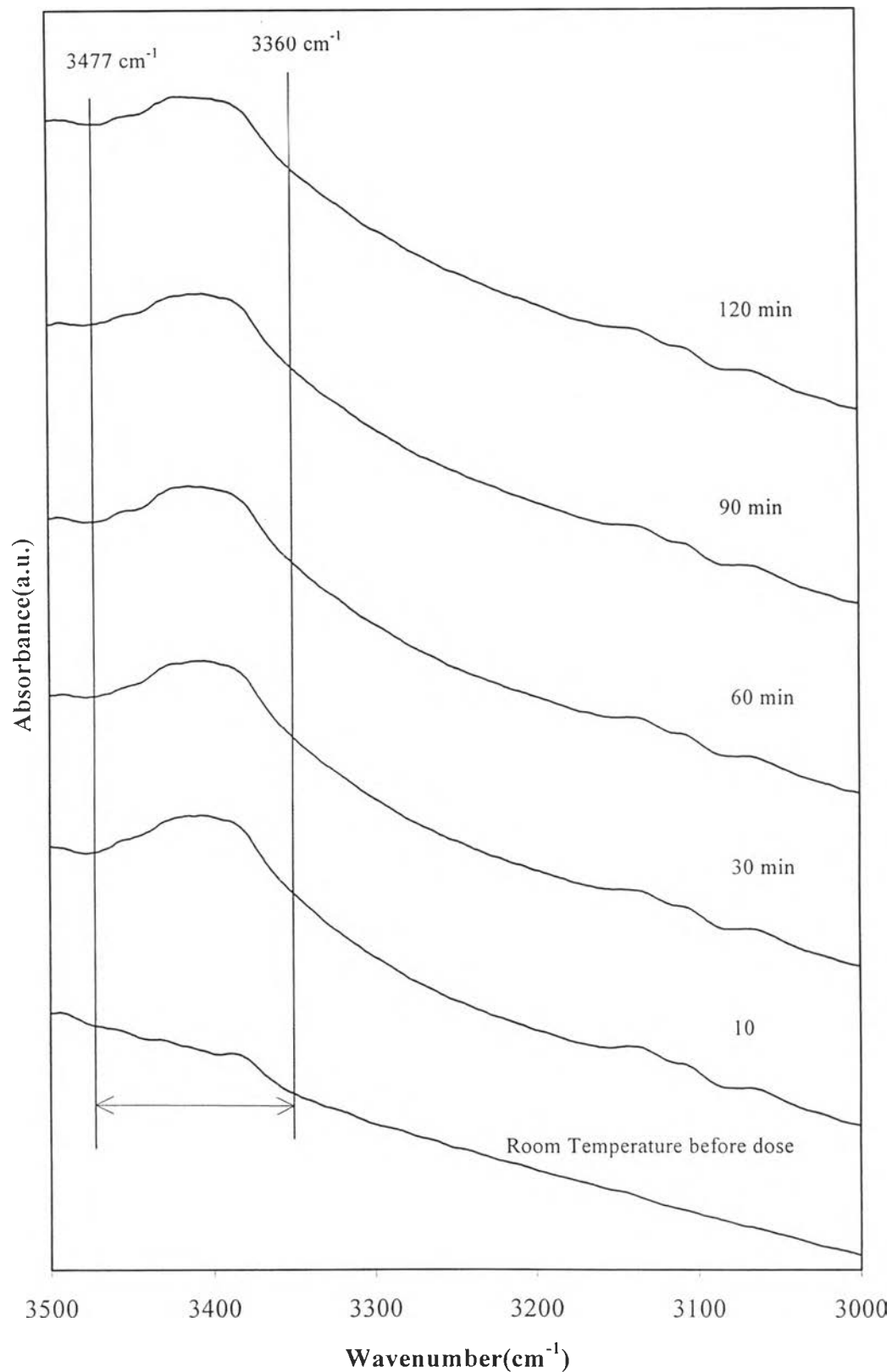
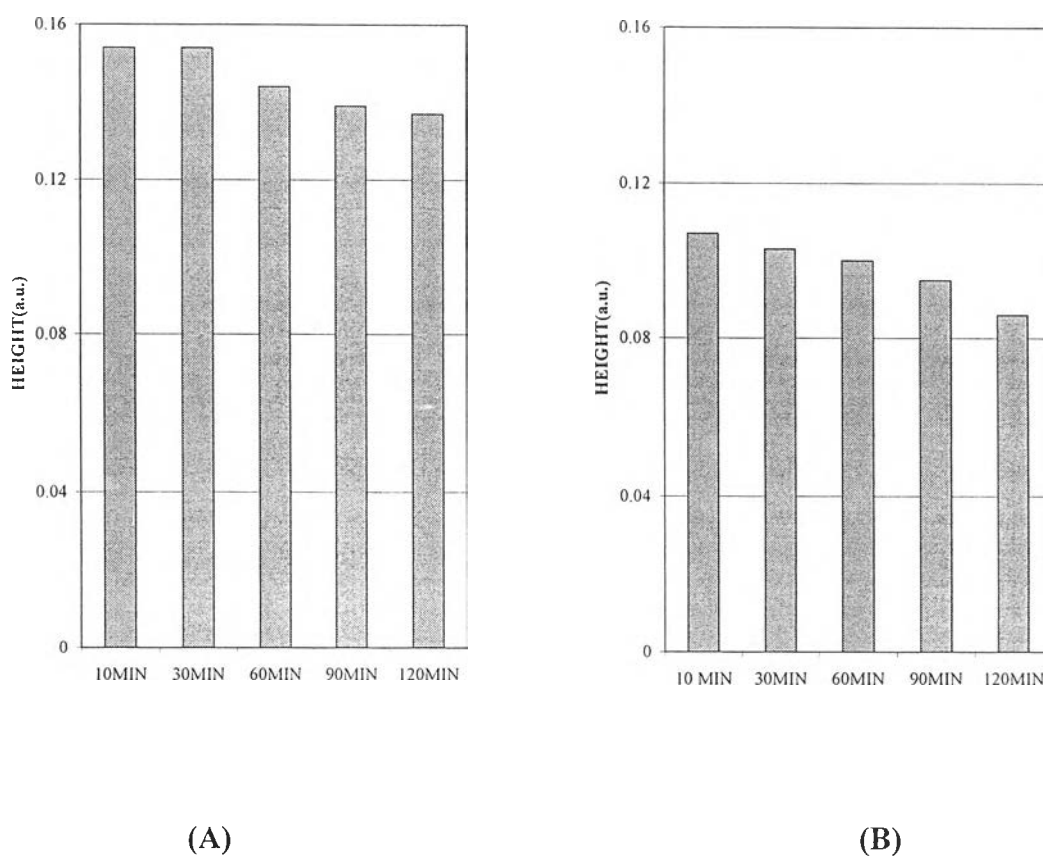


Figure 5.2 IR spectra of NH stretching region of pyrrole adsorption on pure MgO at

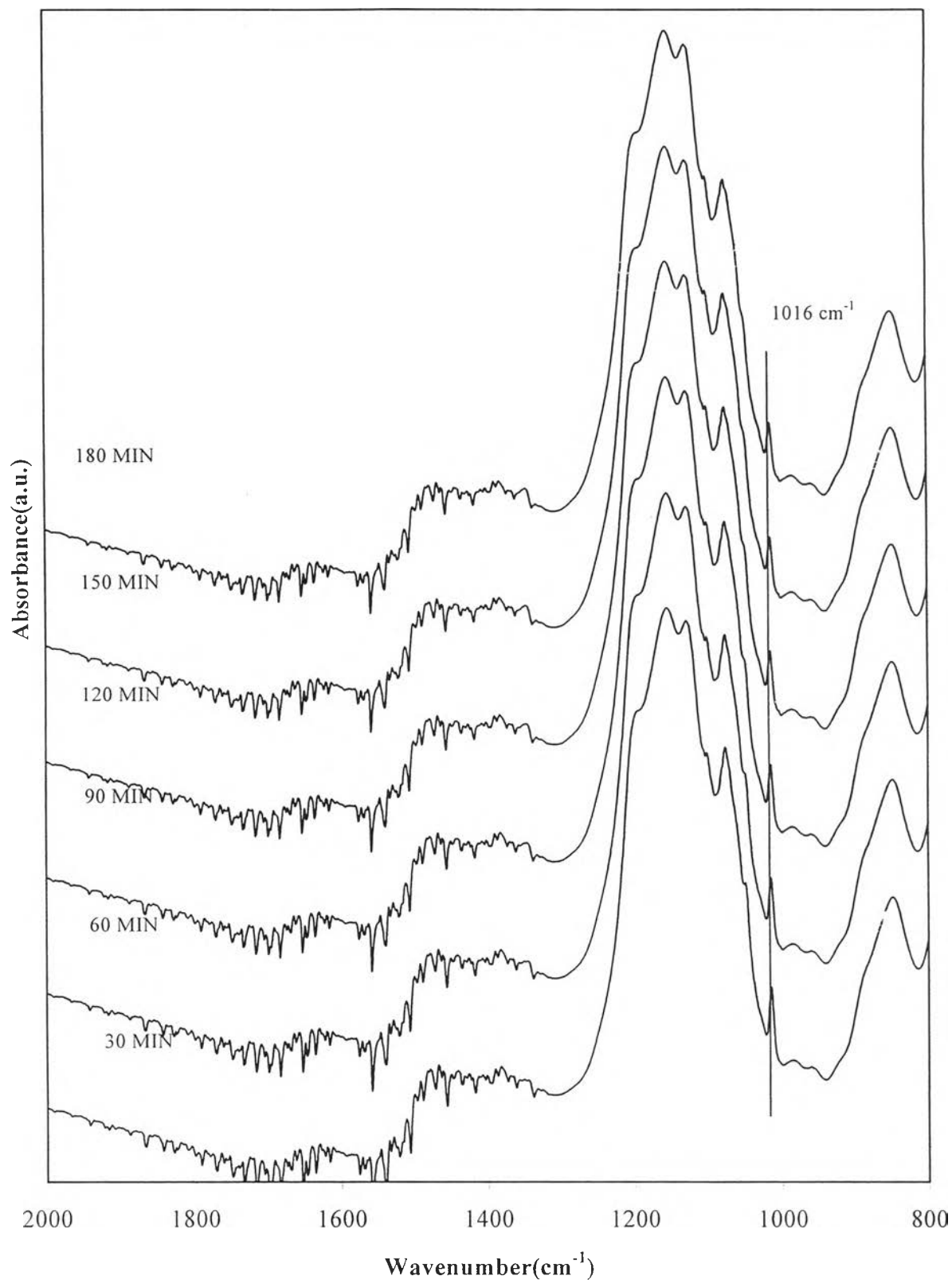


**Figure 5.3(A)** Peak height of IR spectra of ring stretching region of pyrrole adsorption on pure MgO(wavenumber 1016 cm<sup>-1</sup>) at various time for introducing pyrrole vapour

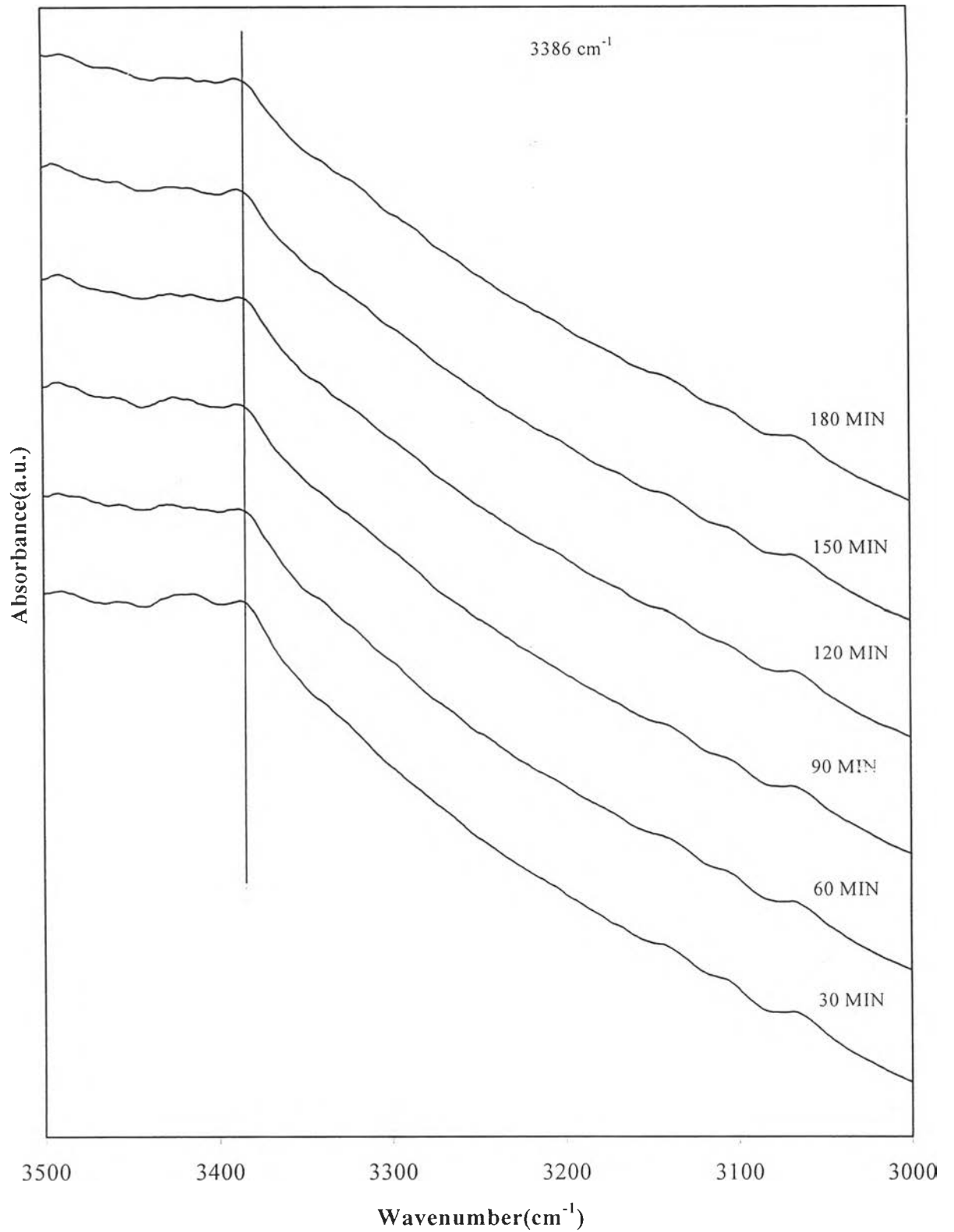
**(B)** Peak height of IR spectra of NH stretching region of pyrrole adsorption on pure MgO(wavenumber 3386 cm<sup>-1</sup>) at various time for introducing pyrrole vapour

### 5.1.2 Effect of time for evacuation after introducing pyrrole vapour.

The gaseous phase and physisorbed pyrrole on the MgO surface was evacuated after the step of dosing pyrrole at room temperature. Because the desorption time of chemisorbed pyrrole from surface of catalysts is still uncertain, evacuation time is the next parameter to be investigated. Too short evacuation time results in residual physisorbed pyrrole. While too long evacuation time results in removing of some chemisorbed pyrrole. In figure 5.5, IR spectra of NH stretching region of the pyrrole, which was adsorbed on the pure MgO, are shown. The maximum band in figure 5.5 was in accordance with the band at  $3386\text{ cm}^{-1}$  in section 5.1.1. Similar to section 5.1.1, the height of maximum peak was measured and correlated to the time for evacuation. It was found that the height of maximum peak tended to decrease with increasing the evacuation time as shown in figure 5.6(A) and 5.6(B). From figure 5.6(B), in order to prevent the effect of residual physisorbed pyrrole and removing of some chemisorbed pyrrole, the time for evacuation after introducing pyrrole vapour was set in the range of time between 60 to 120 min. Hence, in the subsequent experiment was used the time for evacuation after introducing pyrrole vapour was set at 90 min to prevent the effect that mentioned above.

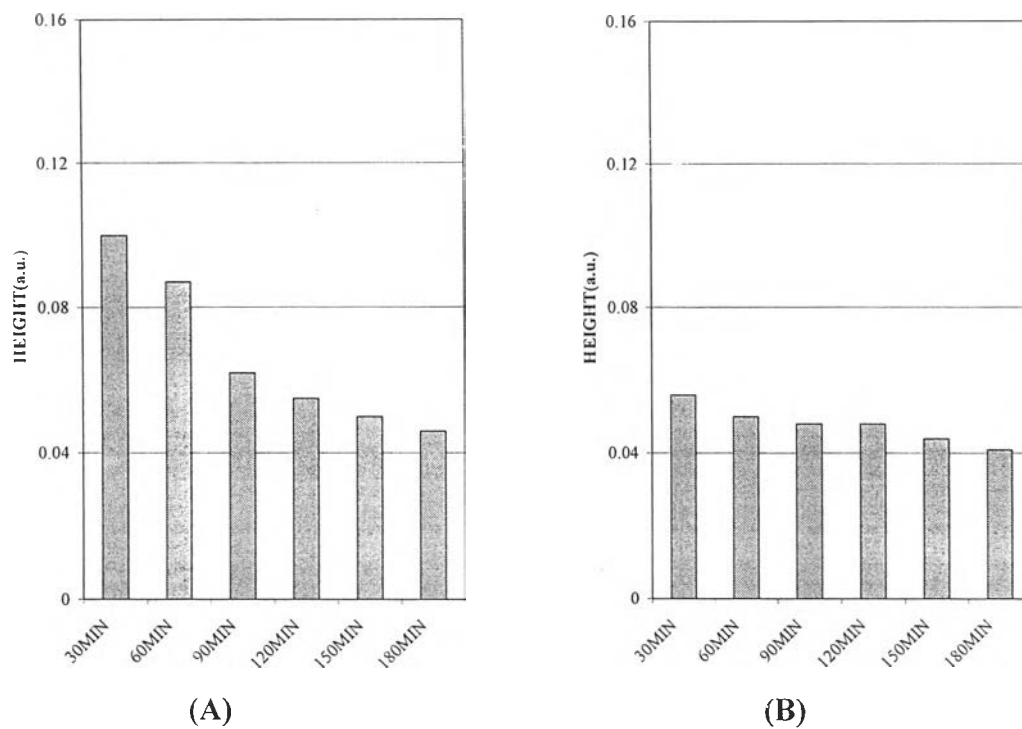


**Figure 5.4** IR spectra of ring stretching region of pyrrole adsorption on pure MgO at various time for evacuation after introducing pyrrole vapour



**Figure 5.5** IR spectra of NH stretching region of pyrrole adsorption on pure MgO at various time for evacuation after introducing pyrrole vapour





**Figure 5.6(A)** Peak height of IR spectra of ring stretching region of pyrrole adsorption on Pure MgO(wavenumber 1016 cm<sup>-1</sup>) at various time for evacuation after introducing pyrrole vapour  
**(B)** Peak height of IR spectra of NH stretching region of pyrrole adsorption on Pure MgO(wavenumber 3386 cm<sup>-1</sup>)at various time for evacuation after introducing pyrrole vapour

### 5.1.3 Characterization of pyrrole adsorption on catalysts

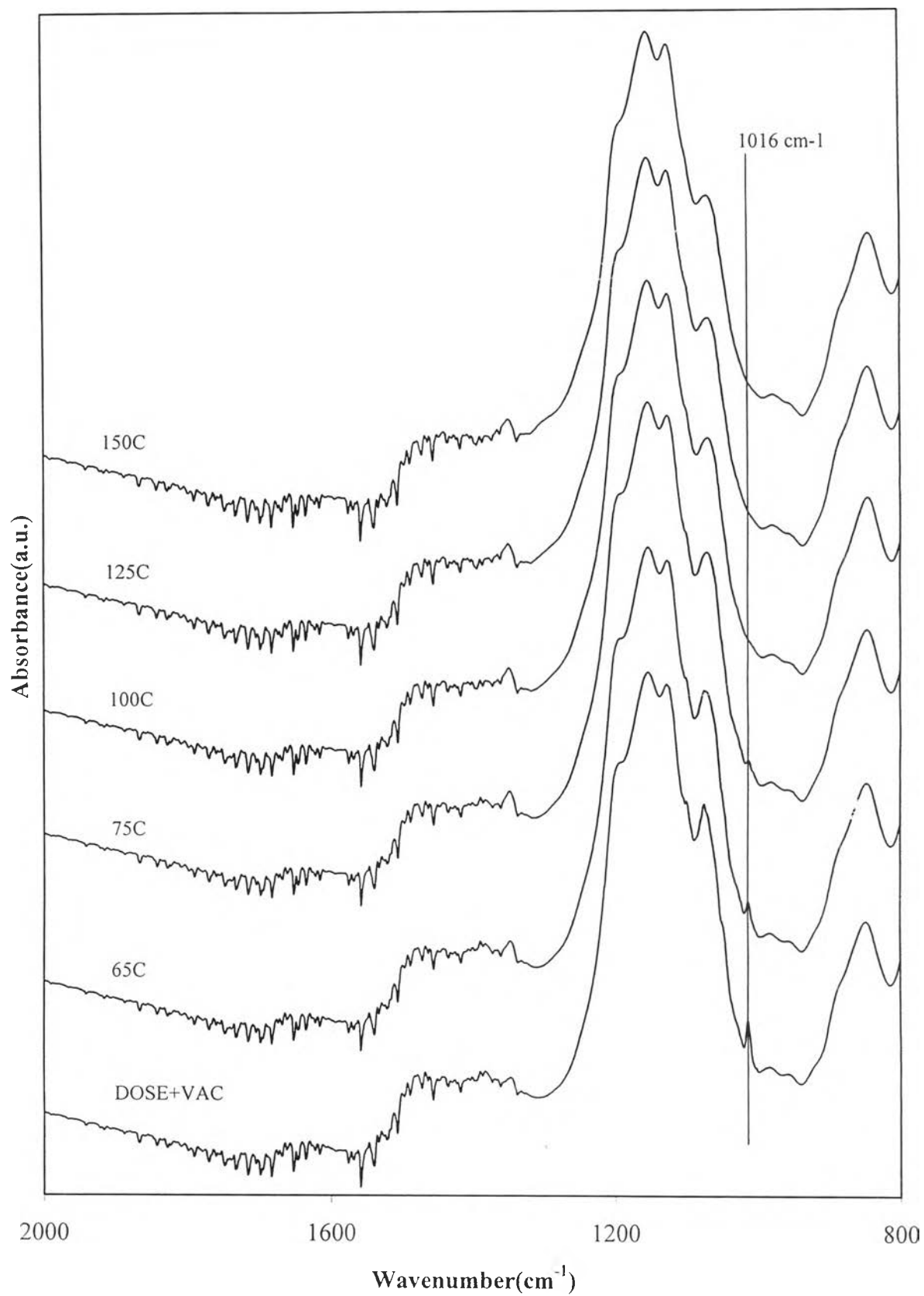
As discussed in sections 5.1.1 and 5.1.2, the procedures of the previous two sections are used for discussion in this section.

#### 5.1.3.1 Pure MgO

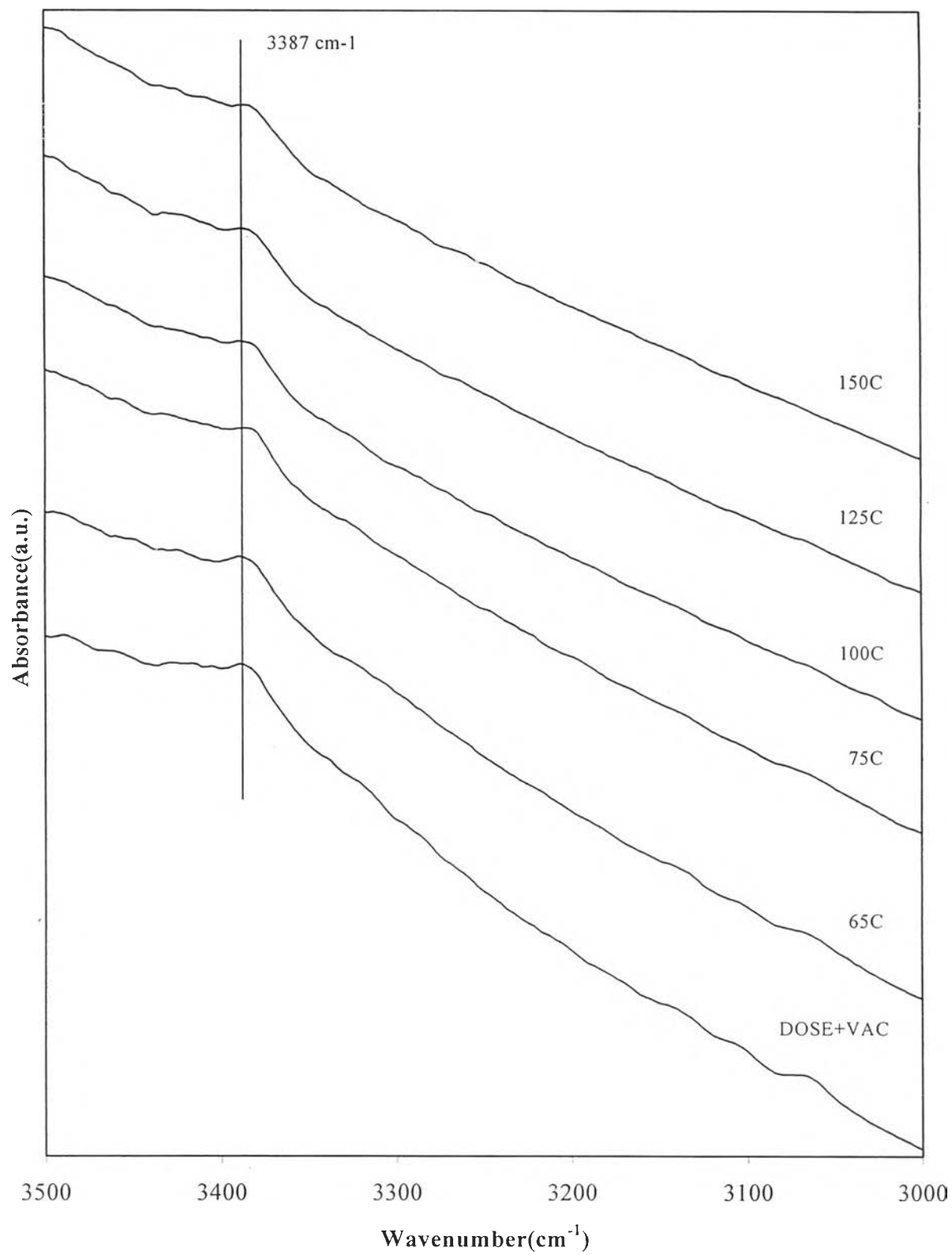
Figure 5.7 shows the IR spectra obtained from adsorbed pyrrole on pure MgO in the wavenumber range of 800-2000  $\text{cm}^{-1}$  at room temperature to 100°C. The spectra recorded between room temperature to 100°C were collected. Pyrrole dosing was performed after the background of MgO was recorded. After evacuation at room temperature, it is found that the peak appearing at 1016  $\text{cm}^{-1}$  belongs to CH in plane deformation species of pyrrole molecule[Scokart and Rouxhet (1980)]. This result can be used to confirm the appearing of adsorption of pyrrole molecule on MgO catalyst. Figure 5.9(A) and figure 5.9(B) are the peak height at 1016  $\text{cm}^{-1}$  and 3386  $\text{cm}^{-1}$  respectively. After evacuating, the peak height at 3386  $\text{cm}^{-1}$  is decreased with increasing time for evacuation as shown in figure 5.9(B) because the gas phase pyrrole is eliminated. In addition, the sign at 1016  $\text{cm}^{-1}$  of spectrum of evacuated peak at 65°C is decreasing to be at least sharp peak. Increasing temperature to 75°C can eliminate this peak completely. The decreasing of the peak height at 1016  $\text{cm}^{-1}$  and 3386  $\text{cm}^{-1}$  is well correlated as shown in figure 5.9(A) and figure 5.9(B), respectively. This result agrees with the research work of Scokart and Rouxhet(1980) which showed that the adsorption peak of adsorption of pyrrole on surface basic site of MgO catalyst will be fully eliminated at 80°C.

Another regime of pyrrole adsorption spectrum appears in the range of 3000 - 3500  $\text{cm}^{-1}$  as shown in figure 5.8. A broad band in the range of 3300 - 3450  $\text{cm}^{-1}$  occurs, because of the adsorption of pyrrole on basic site, intermolecular bonds of pyrrole molecules and gaseous phase of pyrrole. After evacuation at room temperature, it can be observed that the broad band is narrow because of the lacking of pyrrole gaseous phase. Physically adsorbed pyrrole is eliminated if MgO is evacuated at 65°C. Scokart and Rouxhet(1980) has attributed the band at 3386  $\text{cm}^{-1}$

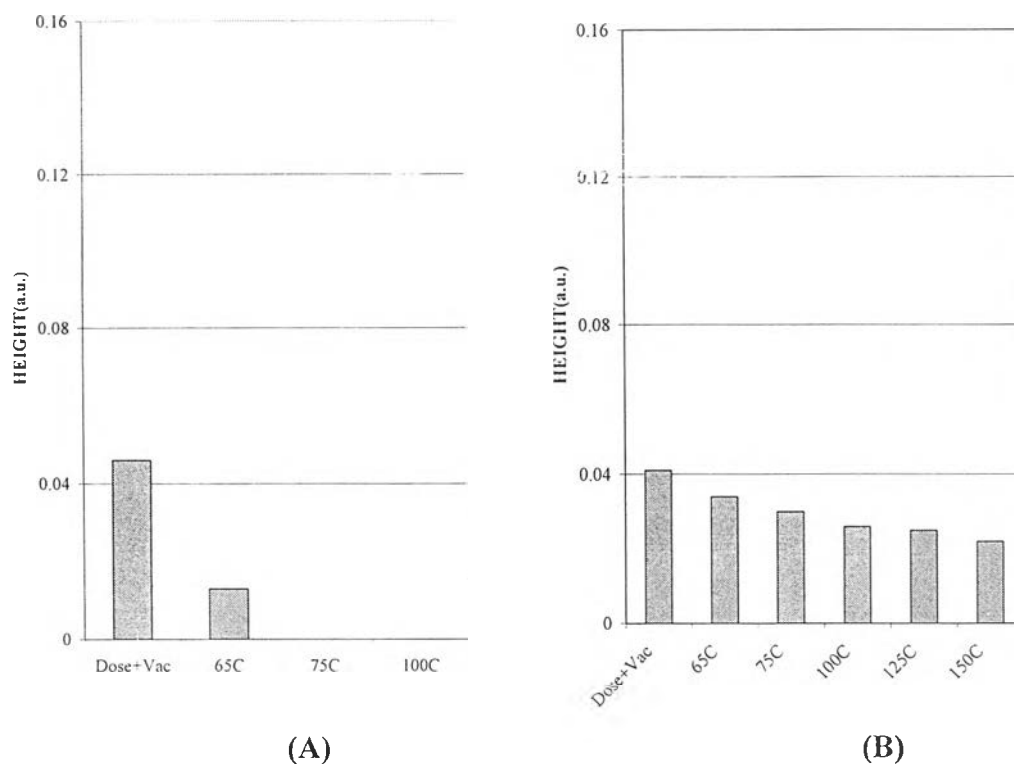
to species interacting with basic sites on the surface acting as a preferential adsorption center. They reported that the shift of the band at  $3386\text{ cm}^{-1}$  and the frequency of the free N-H reflected the strength of the basic sites. Therefore, a broad band observed may reflect a distribution in basic strength of the basic centers on the surface.



**Figure 5.7** IR spectra of ring stretching region of pyrrole adsorption on pure MgO at various temperature



**Figure 5.8** IR spectra of NH stretching region of pyrrole adsorption on pure MgO at various temperature



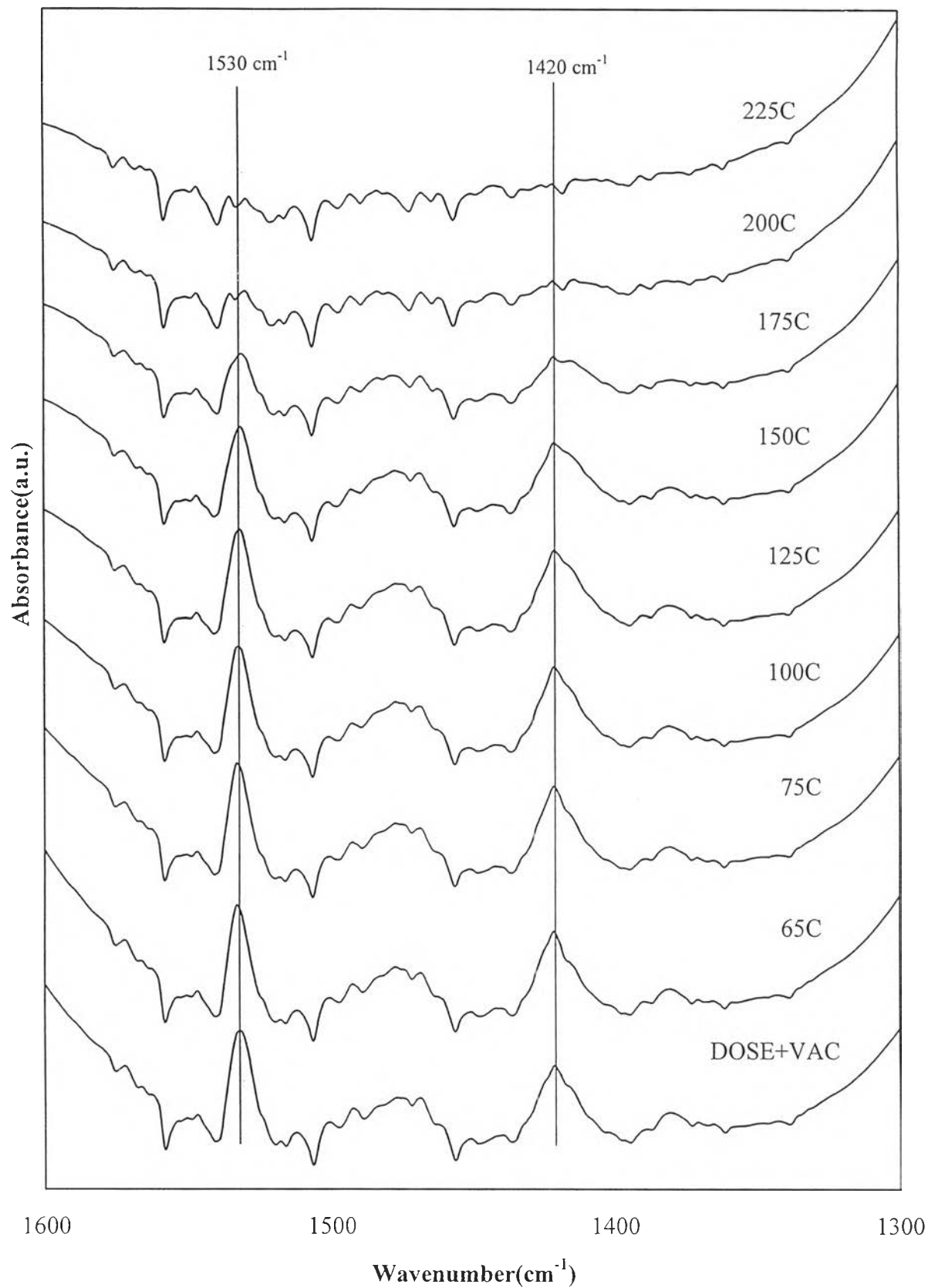
**Figure 5.9 (A)** Peak height of IR spectra of ring stretching region of pyrrole adsorption on pure MgO(wavenumber 1016 cm<sup>-1</sup>) at various temperature

**(B)** Peak height of IR spectra of NH stretching region of pyrrole adsorption on pure MgO(wavenumber 3386 cm<sup>-1</sup>) at various temperature

### 5.1.3.2 NaY catalyst

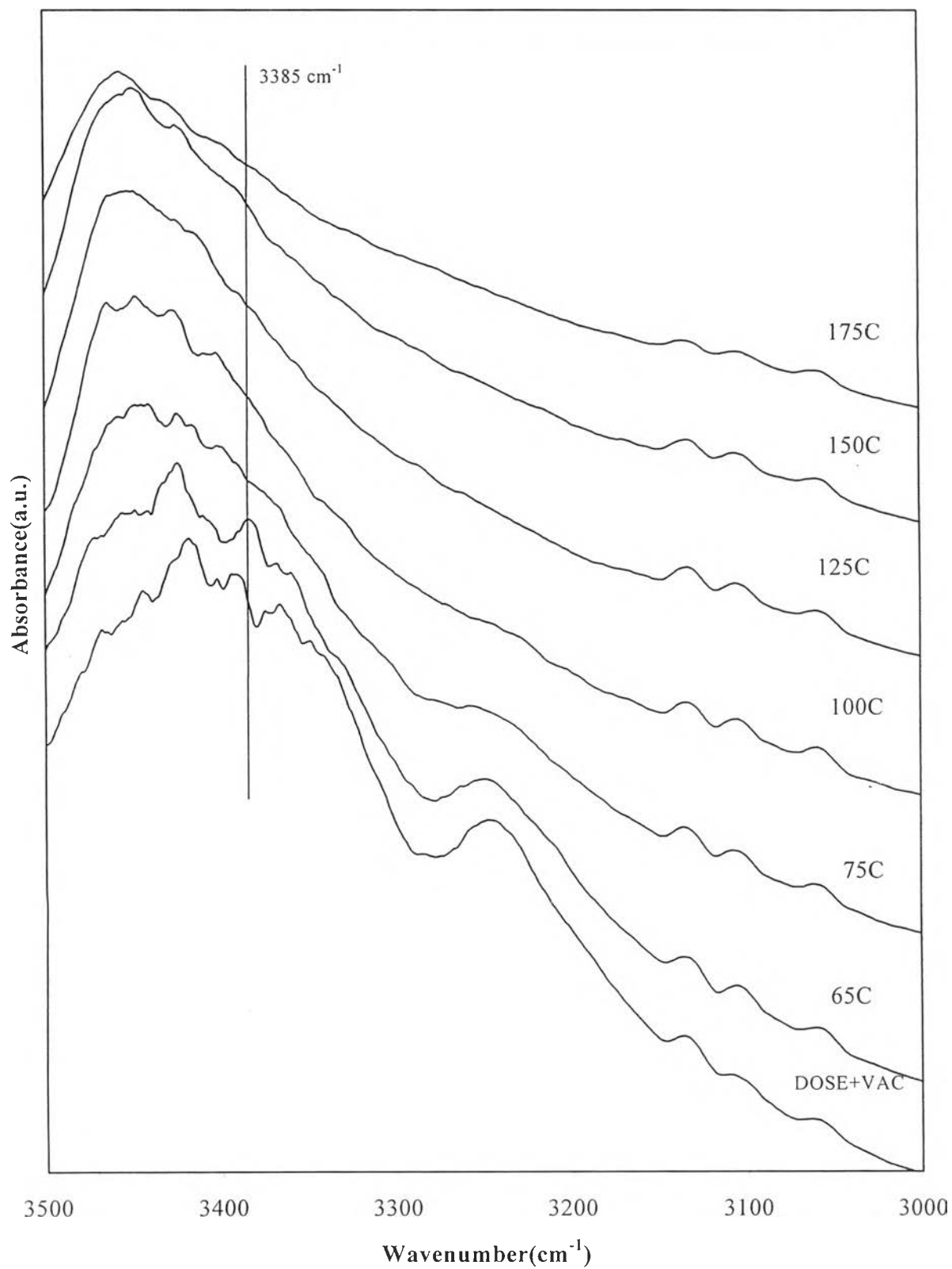
The IR spectra of pyrrole adsorption on NaY catalyst are shown in figure 5.10 and 5.11 for the region of wavenumber 1300 - 1600  $\text{cm}^{-1}$  and 3000 - 3500  $\text{cm}^{-1}$  respectively. Figure 5.10 shows IR spectra of pyrrole adsorption in the ring stretching region 1300 - 1600  $\text{cm}^{-1}$ . The IR spectra of pyrrole ring-stretching region can be observed on NaY zeolite located at 1533 and 1420  $\text{cm}^{-1}$ . These bands are attributed to the stretching vibration. The work of Huang and Kaliaguine(1992) also showed the same IR spectra for Y zeolite.

Figure 5.11 shows that after dosing pyrrole and following by vacuum at 65°C, the spectra show the broad bands at 3381-3400  $\text{cm}^{-1}$  and 3410-3440  $\text{cm}^{-1}$ . The broad band between 3410 - 3440  $\text{cm}^{-1}$  belongs to species of intermolecular of pyrrole molecule and the other band at 3381 - 3400  $\text{cm}^{-1}$  is attributed to pyrrole molecule adsorb on basic site of NaY catalyst. The increasing temperature from room temperature up to 100°C decreases the peak height of adsorption peak at 3385  $\text{cm}^{-1}$  until it is completely removed at 100°C. From the work of Huang and Kaliaguine (1992) the broad band at 3390  $\text{cm}^{-1}$  can be assigned to the main NH band of pyrrole molecule adsorption on basic site of NaY .



**Figure 5.10** IR spectra of ring stretching region of pyrrole adsorption on NaY at various temperature

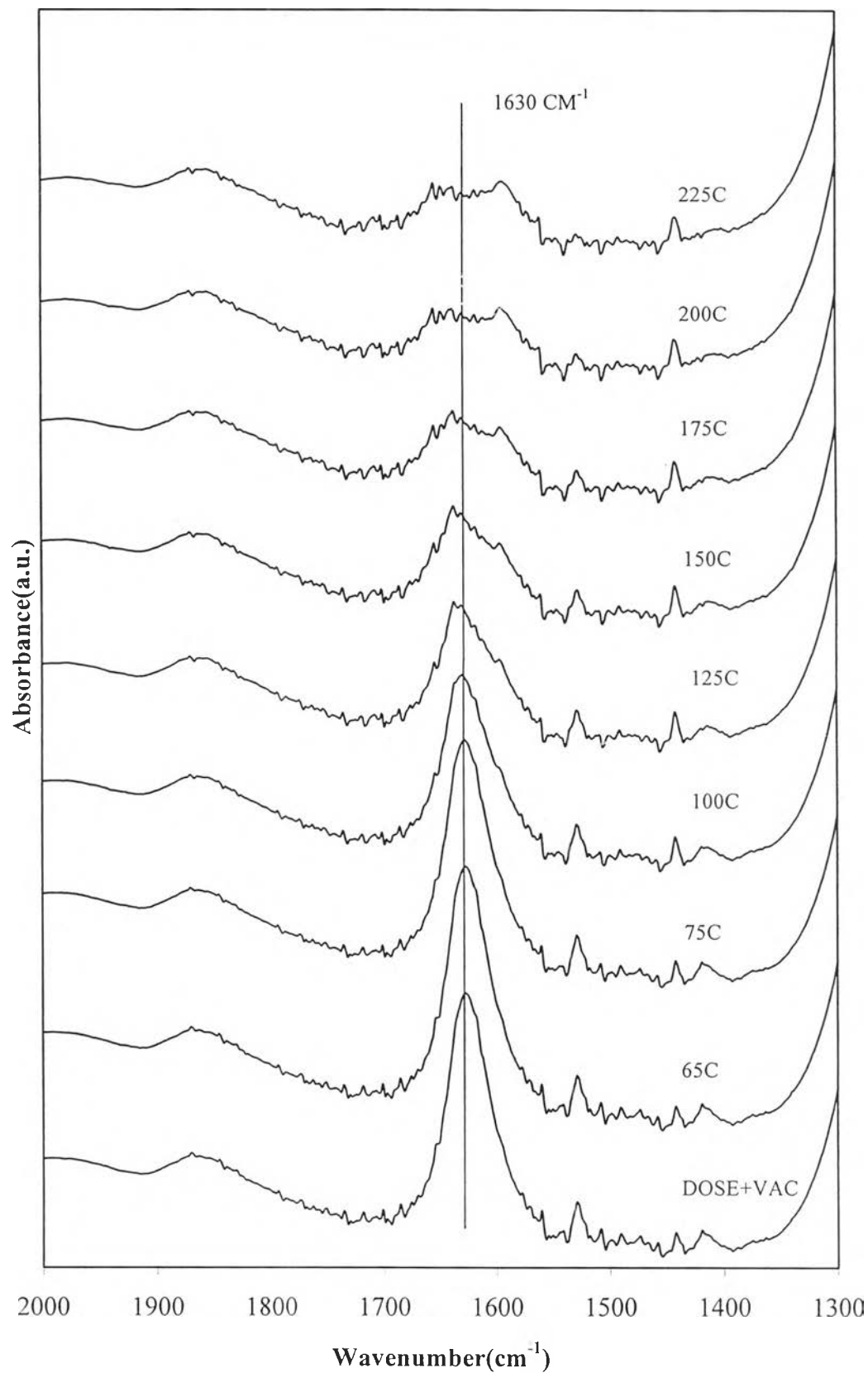




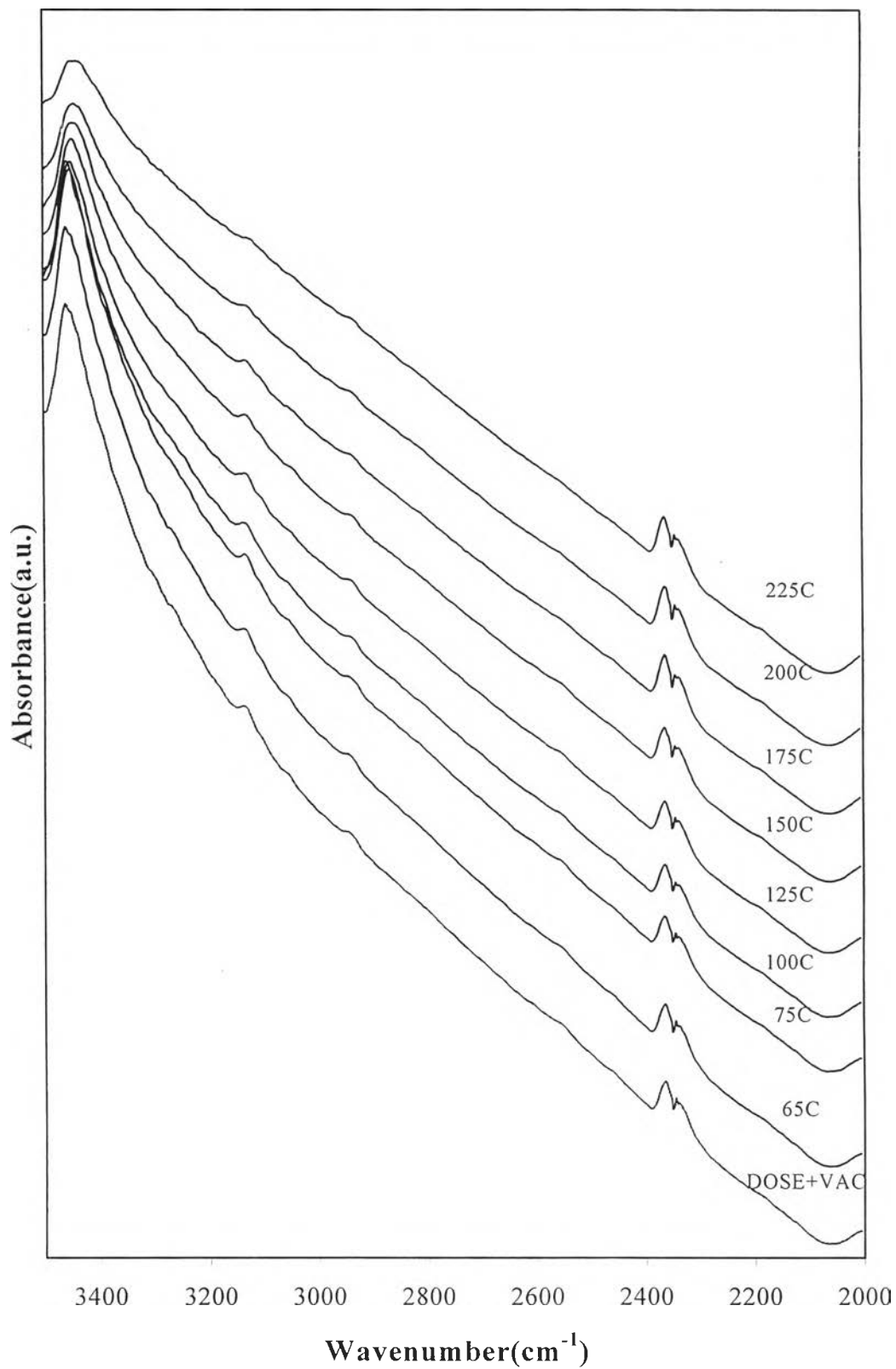
**Figure 5.11** IR spectra of NH stretching region of pyrrole adsorption on NaY at various temperature

### 5.1.3.3 Na-mordenite

IR adsorption band of Na-mordenite (ratio Si/Al = 20) is shown in figures 5.12 and 5.13. Figure 5.12 shows the adsorption band of IR ring stretching band of pyrrole at  $1630\text{ cm}^{-1}$ , which is the vibration of pyrrole ring. Figure 5.13 shows that there is no signal of NH stretching band, which is pyrrole species adsorbed on basic sites of Na-mordenite catalyst. The results indicate that pyrrole is adsorbed on surface of Na-mordenite. Basically both basic sites and acidic sites can be detected by pyrrole. Huang and Kaliaguine (1992) reported that the basicity in higher Si zeolites becomes weaker both in basic strength and the density of basic sites, as indicated by the high NH-stretching frequency and the weak band intensity. Therefore, in this present work it can be concluded that adsorption of pyrrole on Na-mordenite is maybe occur on acidic sites.



**Figure 5.12** IR spectra of ring stretching region of pyrrole adsorption on Na-mordenite at various temperature



**Figure 5.13** IR spectra of NH stretching region of pyrrole adsorption on Na-mordenite at various temperature

#### 5.1.3.4 Brönsted Base

The basic site of catalyst that containing OH<sup>-</sup> group (Brönsted basic) is also tested by pyrrole adsorption in this thesis. Commercial calcium hydroxide (Ca(OH)<sub>2</sub>) is used for testing Brönsted basic.

Figure 5.14 shows IR spectra of adsorbed pyrrole on Brönsted base. Since the Brönsted base may decompose at high temperature, this sample was evacuated at room temperature before exposure to pyrrole vapour. Before pyrrole adsorption, the spectrum of Ca(OH)<sub>2</sub> shows strong broad band between 3400 to 3700 cm<sup>-1</sup>. A comparison between IR spectra at room temperature of Ca(OH)<sub>2</sub> before and after evacuation shows no change in IR spectrum. After introduction of pyrrole at the same temperature, the IR signal of pyrrole adsorbed species on this sample could not be detected as same as Huang and Kaliaguine(1992) have reported.

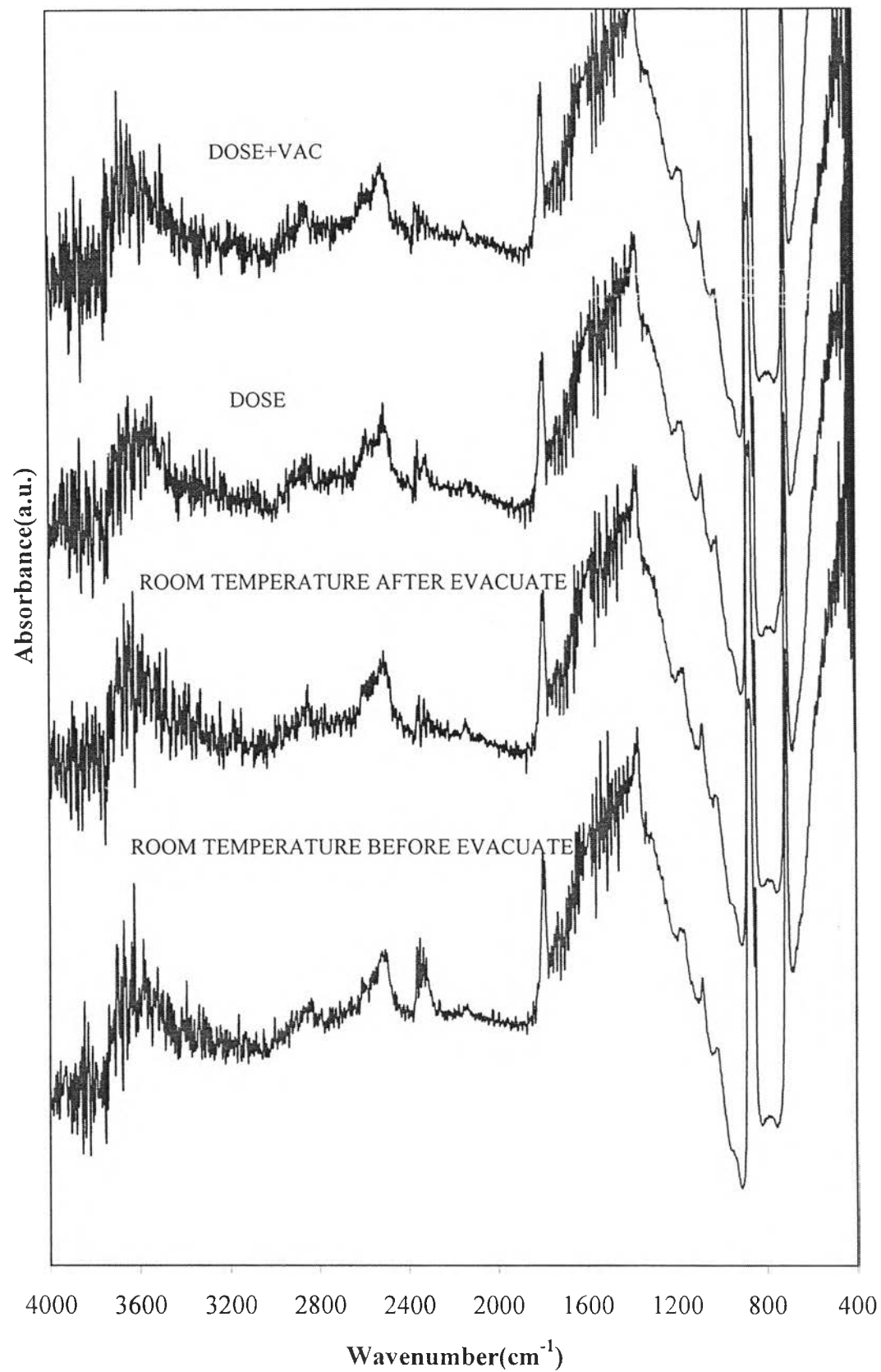


Figure 5.14 IR spectra of pyrrole adsorption on Ca(OH)<sub>2</sub>

## 5.2 Adsorption of Pyrrole and CO<sub>2</sub> by GC

Results in section 5.1 indicate that there are some problems due to the measurement of weak intensities in the pyrrole adsorption band characterized by FTIR technique, In this section, gas chromatography was applied to determine the amount of adsorption of pyrrole on catalyst surface. The results are shown in tables 5.1 and 5.2.

**Table 5.1** Results of pyrrole adsorption on various catalysts

Catalysts	Amount of adsorbed pyrrole ( $\mu\text{mol/gcat}$ )
MgO	1.17
NaY	0.32
Ca(OH) <sub>2</sub>	0.33
Na-mordenite Si/Al = 20	2.74

Table 5.1 showed the amount of adsorbed pyrrole on surface of catalysts. It shows that the amount of pyrrole adsorption on various catalyst can be arranged in the following order: Na-mordenite > MgO > Ca(OH)<sub>2</sub>  $\cong$  NaY. Most results of pyrrole adsorption on catalysts surface are consistent with IR results except Na-mordenite .

**Table 5.2** Results of carbon dioxide adsorption on various catalysts

Catalysts	Amount of adsorbed CO <sub>2</sub> ( $\mu\text{mol/gcat}$ )
MgO	1.75
NaY	0.46
Ca(OH) <sub>2</sub>	0.44
Na-mordenite Si/Al = 20	0.33

Table 5.2 shows the adsorption of carbon dioxide on surface catalysts, it was found that the amount of CO<sub>2</sub> adsorption on various surface catalyst is in the following order: MgO > NaY  $\cong$  Ca(OH)<sub>2</sub> > Na-mordenite.

Comparing the amount of adsorption between these two probe molecules on the sample catalyst (MgO, NaY and Ca(OH)<sub>2</sub>) it is shown that there are more CO<sub>2</sub> adsorption than pyrrole. In contrast on Na-mordenite surface, there is less CO<sub>2</sub> adsorption than pyrrole.

From the above results, it can be explained that since Si/Al ratio of Na-mordenite is twenty, therefore it is a highly acidic catalyst. As mentioned in IR result, for Na-mordenite catalyst IR adsorption band of pyrrole adsorption on basic sites, could not be detected therefore adsorption of pyrrole on Na-mordenite should not occur on basic sites. From the result of CO<sub>2</sub> adsorption on Na-mordenite, it was found that there was less amount of CO<sub>2</sub> adsorption than other catalysts. Because both basic sites and acidic sites can interact with pyrrole. Therefore, it can be concluded that the adsorption of pyrrole on Na-mordenite occurs on acidic sites.

For the case of MgO, NaY and Ca(OH)<sub>2</sub>, it can be explained that the amount of adsorbed CO<sub>2</sub> are more than the amount of adsorbed pyrrole because CO<sub>2</sub> is more acidic than pyrrole. Therefore, CO<sub>2</sub> can detect the weaker basic sites that can not be detected by pyrrole. Consequently, the amount of adsorbed CO<sub>2</sub> is more than adsorbed pyrrole.

IR adsorption band and adsorbed pyrrole of Na-mordenite and NaY, show that IR adsorption band of pyrrole on basic sites of NaY can be seen clearer than Na-mordenite but there is less amount of adsorbed pyrrole than Na-mordenite. The above result can be explained by adsorption on acid sites.