

CHAPTER V

RESULTS AND DISCUSSION

In this chapter, the experimental results are analyzed. The IR spectra of oxide support sample at different temperature are reported in section 5.1. Following by the IR examination of fresh Pt-Sn/ γ -Al₂O₃ catalyst as exhibit in section 5.2. Finally, determination of coked catalyst from a sequence of time on stream by IR spectroscopy are demonstrated in section 5.3.

Pt-Sn/ γ -Al₂O₃ propane dehydrogenation catalyst is a selected model to study deposited carbon by infrared spectroscopy technique in this research as this catalyst is one of the most choice being investigated in many aspects. Several detailed information related to this catalyst have been reported, however, the mechanism of coking remains unclear. It is important to understand how carbon species developed on the catalyst surface. In respect to the structure of coked catalyst, IR spectroscopy technique can provide a significant insight into the functional groups of adsorbed species on catalyst surface.

To study the structure of carbon deposit on catalyst by IR spectroscopy technique is not a simplicity since it does not possess of a pure component. This is a complex system formed by two major components. Coke is an organic compound with hydrocarbon arrangement adsorbed on catalyst surface which is an inorganic compound. The essential problems are generated from oxide support, γ -Al₂O₃. The surface of γ -Al₂O₃ is inherently complicated for IR characterization. γ -Al₂O₃ produced very noisy signal in the region 400-1000 cm⁻¹ and 2000-4000 cm⁻¹, see figure 5.1. The surface hydroxyl group of γ -Al₂O₃ is responsible for the IR absorption bands in region ≥ 2500 cm⁻¹ [7]. In addition, the very strong Al-O stretching band of γ -Al₂O₃ may cause a very low IR transmittance in the region below 1000 cm⁻¹ [21], thus it is also taken into the noisy signal. Since the signal in these regions always noisy, in this thesis the

discussion will not be concentrated on them anymore. The attention is then focused in the range of 1000-2000 cm^{-1} where many organic compounds, including CO_2 and surface water, adsorb IR in this region. Strong bands in the 1000-2000 cm^{-1} region provide a complex background spectrum which makes it difficult to see or measure small bands arising from adsorbed molecules or surface groups of the catalyst [3]. Hence the IR technique is needed to be developed to obtain reasonable good resolved coked catalyst spectra in the interested region.

The basic practice of sampling method in analytical IR transmission mode for powdered solids is the alkali halide pressed disk method. Although it is simple experimentally, this method will probably never be attained in this research, because the alkali halide is likely to pick up moisture during the analysis, and once the sample is pressed in combination with alkali halide, it cannot be subjected to further treatment.

For these reasons, the self-supporting disk method is applied in this work. With this method, the disk sample of coked catalyst is able to be treated by increasing temperature in order to eliminate the interference of IR spectrum from adsorbed CO_2 or adsorbed water. The experiment was operated by in-situ IR as mentioned before. First of all, the spectra of $\gamma\text{-Al}_2\text{O}_3$ as a base or support of coked species were detected, and the following subject considers the experimental treatment effect on $\gamma\text{-Al}_2\text{O}_3$ spectra.

5.1 IR spectra of oxide support sample ($\gamma\text{-Al}_2\text{O}_3$) at different temperature

Figure 5.2, the spectrum of $\gamma\text{-Al}_2\text{O}_3$ at ambient temperature in air, one major broad band is seen between 1640-1650 cm^{-1} . After purging with N_2 the intensity of this peak is minimized as shown in figure 5.3. Further treatment by heating to elevated temperature can remove the adsorbed species which belong to this peak even more as indicated from a decrease in intensity of this peak (figure 5.4). The disappearance of some peaks observed is expected to be the desorption of some species. The IR spectroscopic investigation of $\gamma\text{-Al}_2\text{O}_3$ by Hair [5] reported that the IR absorption band in the region 1650 cm^{-1} is due to a

hydrogen-oxygen band vibration of adsorbed water molecules. The work of Perkins [22] has shown that the band at 1640 cm^{-1} usually exist on the surface of $\gamma\text{-Al}_2\text{O}_3$ at room temperature was produced by CO_2 adsorbed on alumina which was attributed to carbonate surface structure. A recent paper [7] reported that the ambient temperature adsorption of CO_2 on $\gamma\text{-Al}_2\text{O}_3$ had IR absorption band at 1650 cm^{-1} .

Accordingly, the absorption band in the region $1640\text{-}1650\text{ cm}^{-1}$ should be attributed to hydroxyl group from adsorbed water as well as carbonate structure of CO_2 adsorbed on $\gamma\text{-Al}_2\text{O}_3$ at ambient condition. This adsorbed species were nearly completely removed upon further increase sample temperature to 200°C as illustrate in figure 5.5. This is the expected result, it is supposed to be the base (or background) spectrum for the coked catalyst which will generate many interested adsorbed species in the region $1000\text{-}2000\text{ cm}^{-1}$. By this way, after the proper process of treatment in in-situ IR analysis, the interference bands can be eliminated and leave the $\gamma\text{-Al}_2\text{O}_3$ spectrum smooth enough for the possibility to study adsorbed species of coked catalyst. While increasing the sample temperature higher than 200°C ; i.e. 300°C and 400°C as shown in figures 5.6 , and 5.7 ,there is a considerable similarity of these spectra with spectrum at 200°C . This demonstrates that heating temperature higher than 200°C does not alter IR absorption pattern in this study.

Finally, cooling down the sample to room temperature in N_2 atmosphere is the last state of treatment. In case of $\gamma\text{-Al}_2\text{O}_3$, the sample spectrum collected at this condition was shown in figure 5.8. It can be seen that the feature of this spectrum is quite similar to previous spectra which were determined at elevated temperature. This can point out that when the adsorbed species of interference bands were desorbed and displaced from sample surface, it could not able to readsorb once again in this experimental condition.

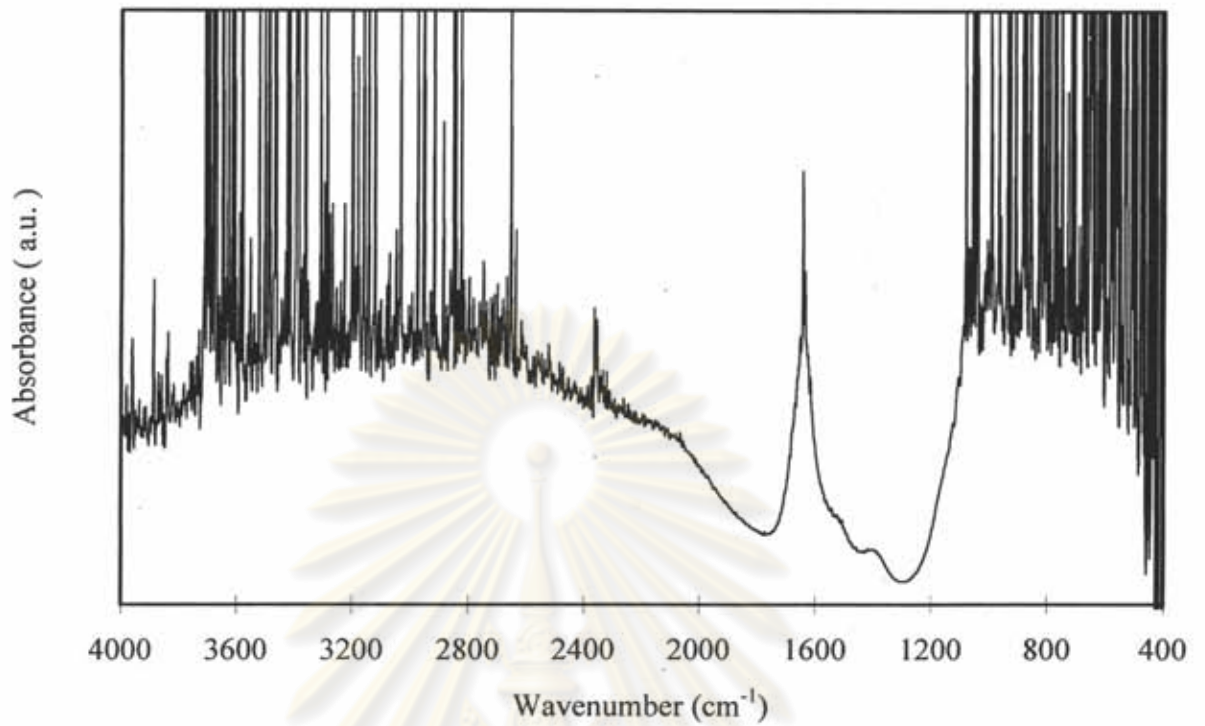


Figure 5.1 IR spectrum of γ -Al₂O₃ at room temperature in ambient air, region 400 - 4000 cm⁻¹

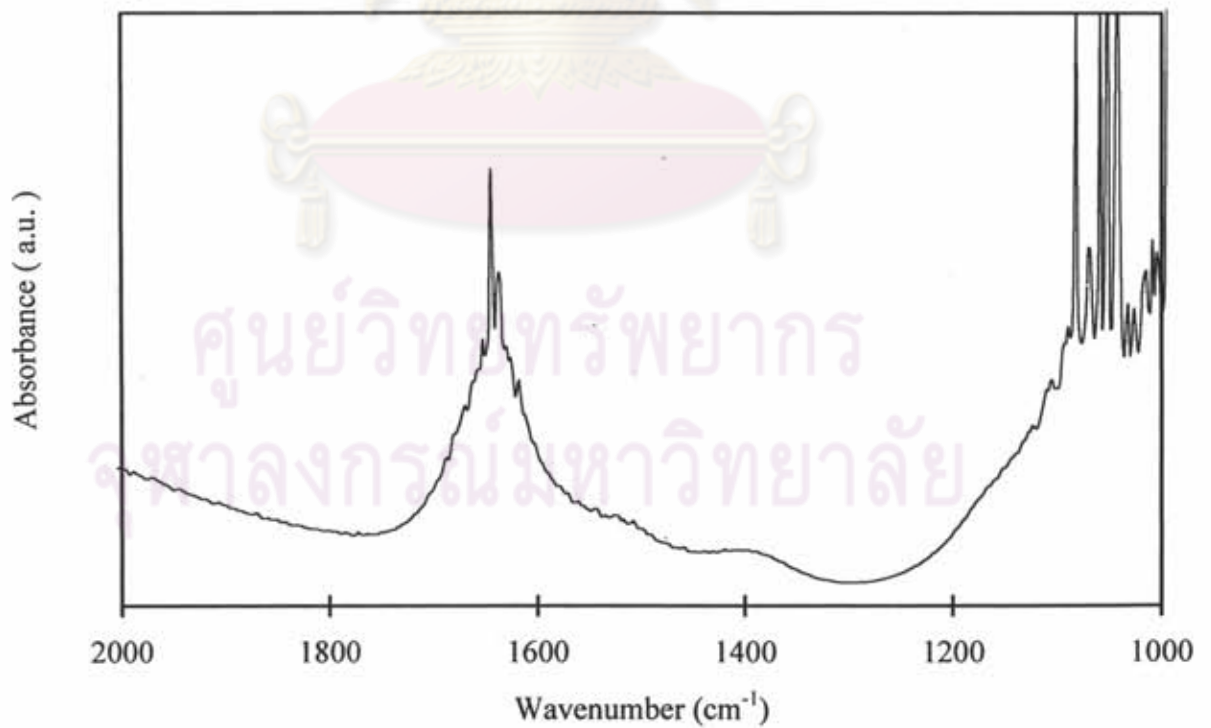


Figure 5.2 IR spectrum of γ -Al₂O₃ at room temperature in ambient air, region 1000 - 2000 cm⁻¹

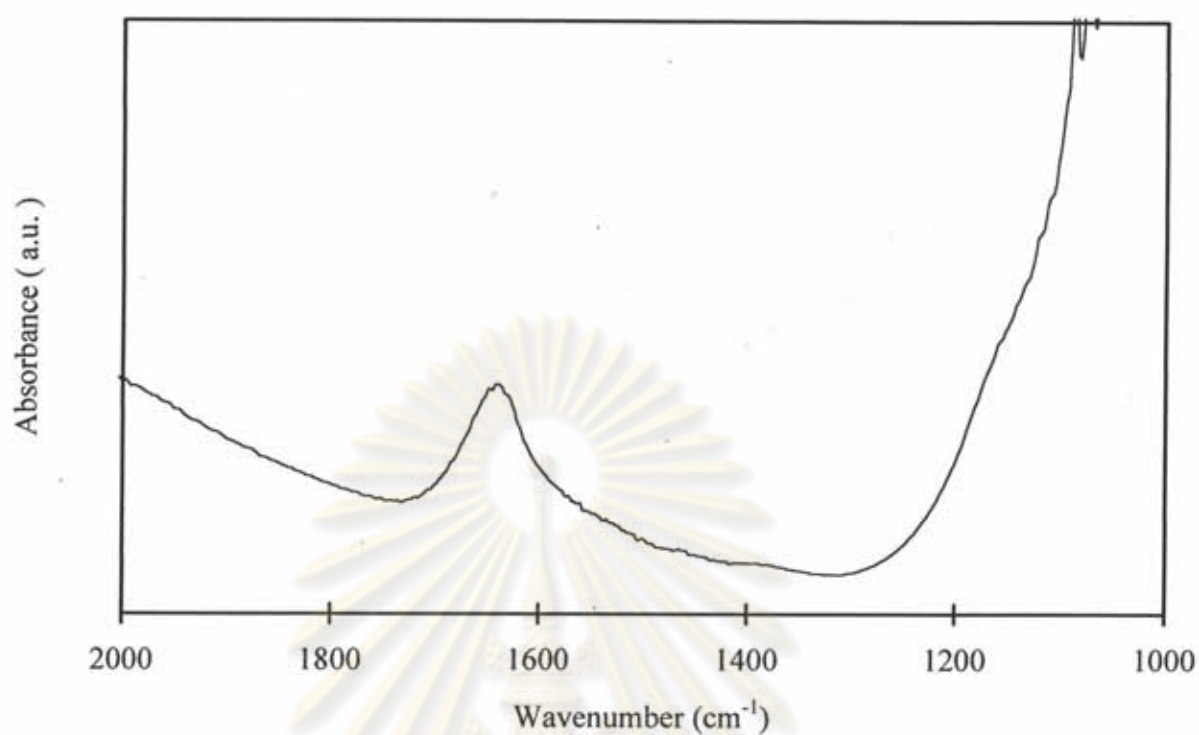


Figure 5.3 IR spectrum of γ -Al₂O₃ at room temperature in N₂ atmosphere

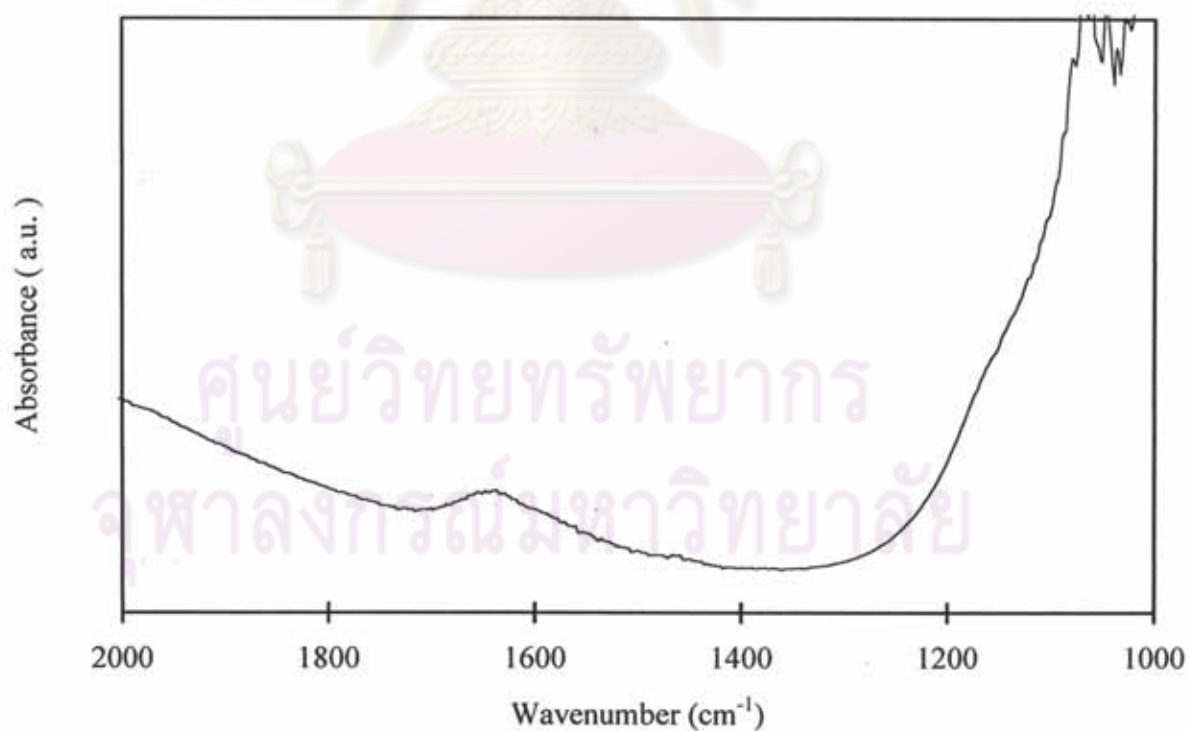


Figure 5.4 IR spectrum of γ -Al₂O₃ at 100°C in N₂ atmosphere

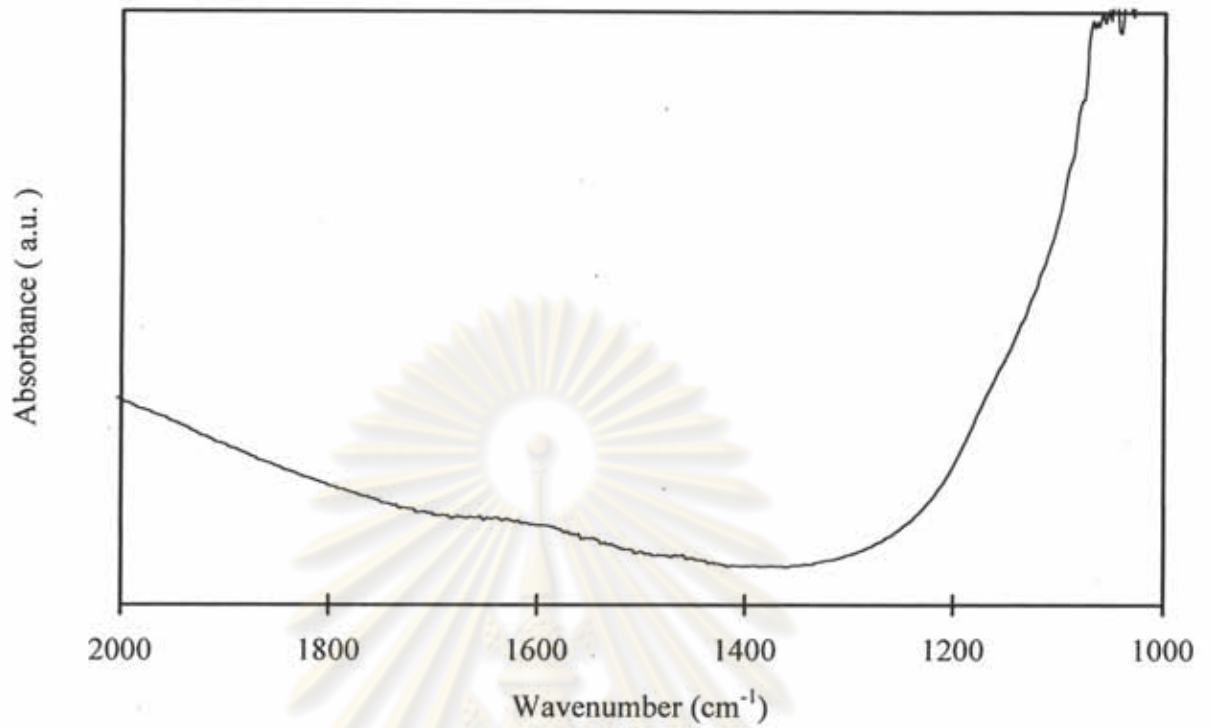


Figure 5.5 IR spectrum of γ -Al₂O₃ at 200°C in N₂ atmosphere

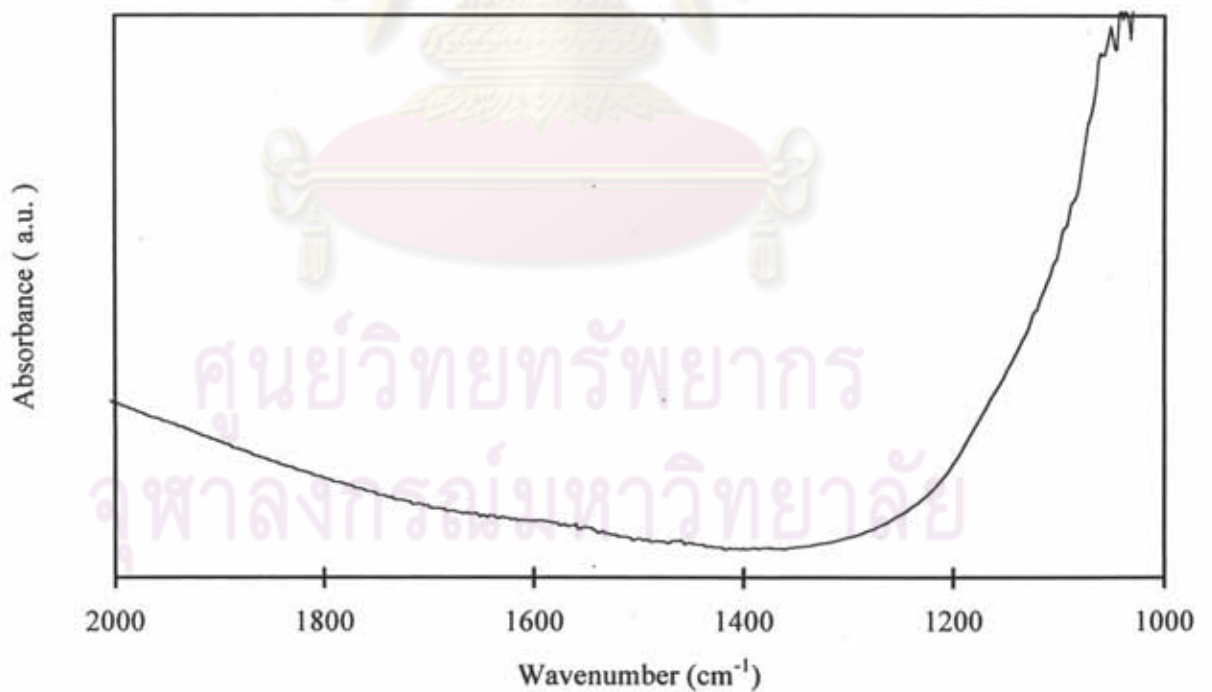


Figure 5.6 IR spectrum of γ -Al₂O₃ at 300°C in N₂ atmosphere

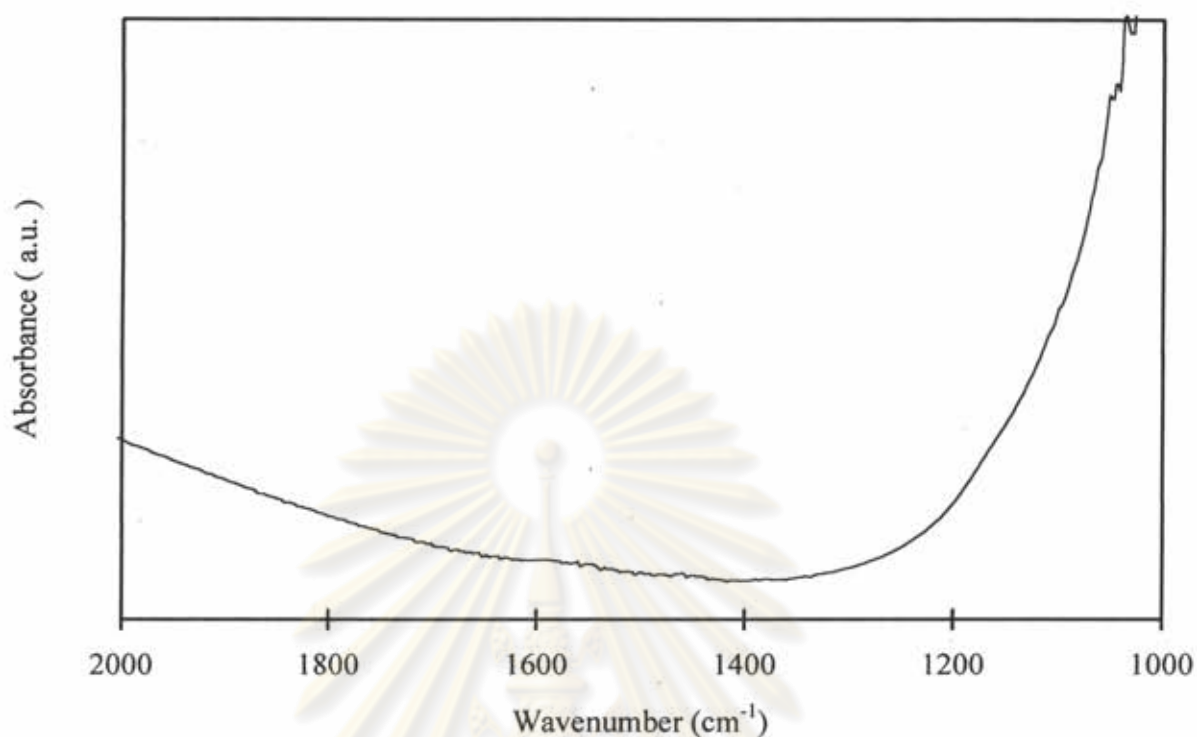


Figure 5.7 IR spectrum of γ -Al₂O₃ at 400°C in N₂ atmosphere

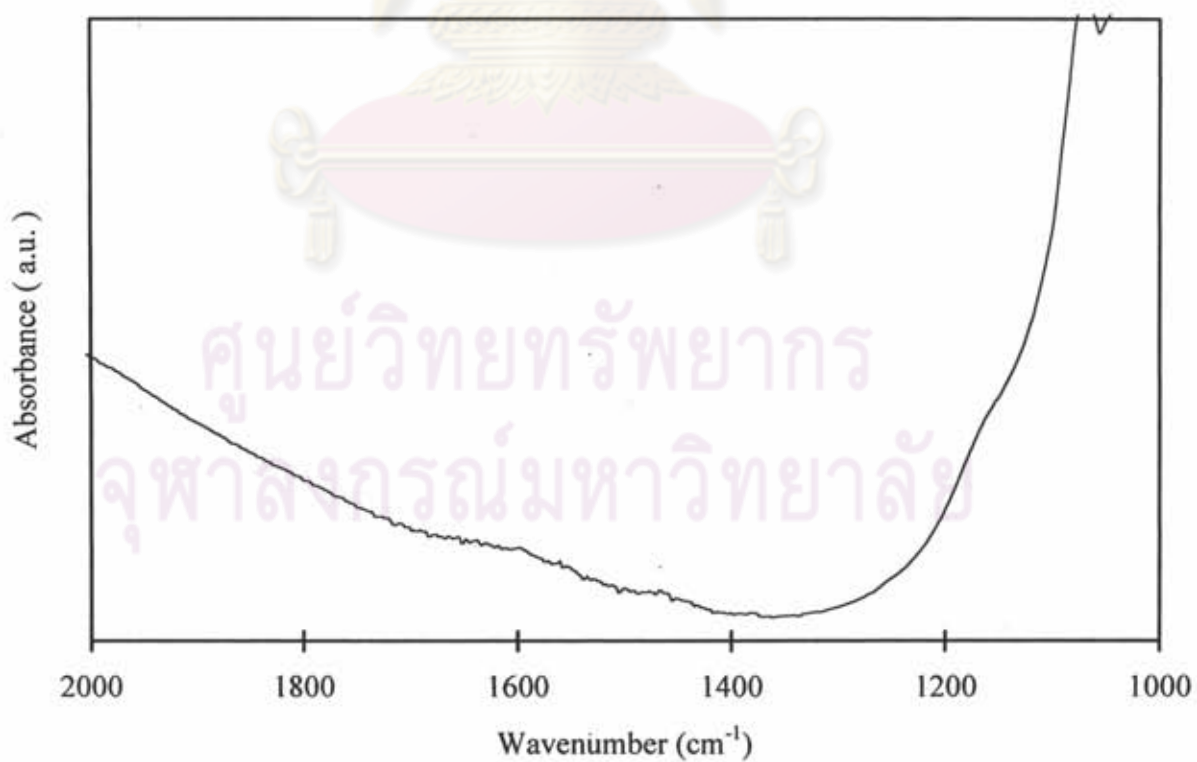


Figure 5.8 IR spectrum of γ -Al₂O₃ cooled down to room temperature in N₂ atmosphere

5.2 IR spectra of fresh Pt-Sn/ γ -Al₂O₃ catalyst

Most of IR absorption bands of inorganic compounds involved in the fresh Pt-Sn/ γ -Al₂O₃ catalyst are localized in the range out of 1000-2000 cm⁻¹. They usually give rise in the IR absorption bands lower than interval of mid-infrared (400-4000 cm⁻¹) such as Pt-Pt vibration appears in region 180-190 cm⁻¹, Pt-Sn shows the IR absorption bands in region 193-210 cm⁻¹, and Sn-Sn gives IR absorption bands in region 190-208 cm⁻¹ [23]. Therefore, in the range of 1000-2000 cm⁻¹ as discussed in this work, there is not any difference noticed between the spectrum of γ -Al₂O₃ support and fresh Pt-Sn/ γ -Al₂O₃ catalyst .

The overall behavior of IR spectra of fresh Pt-Sn/ γ -Al₂O₃ catalyst is comparable to those of γ -Al₂O₃ support. Figures 5.9-5.10 give IR spectra of fresh catalyst in ambient air at room temperature and in N₂ atmosphere at room temperature. Again, after heating the sample in N₂ , some adsorbed species related to CO₂ and adsorbed water were removed which can be noted from a decrease in the peak height (absorbance) of the 1640-1650 cm⁻¹ band.

Increasing the sample temperature up to 200°C is considered since this temperature is analogous to the temperature of heated γ -Al₂O₃ spectrum in which it exhibited a sufficient flat spectrum and it is appropriate to accept the spectrum at this temperature as a base spectrum to compare the difference with coked catalyst spectrum. The spectrum of fresh catalyst at 200°C in N₂ atmosphere in figure 5.12 shown rather smooth spectrum with the absence of interference bands.

As in the same manner of γ -Al₂O₃ , the spectrum of cooled down fresh catalyst in N₂ atmosphere after heating can insist that the readsorption of removed species cannot be detected in this process.

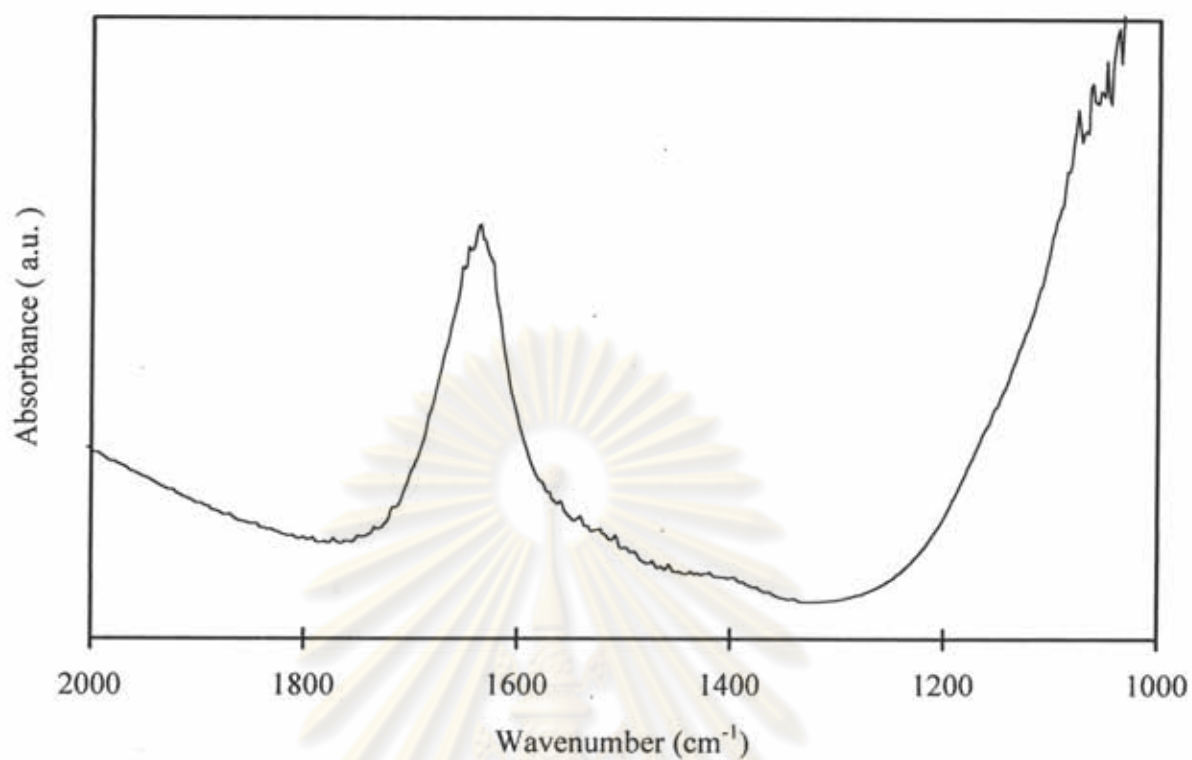


Figure 5.9 IR spectrum of fresh Pt-Sn/ γ -Al₂O₃ catalyst at room temperature in ambient air

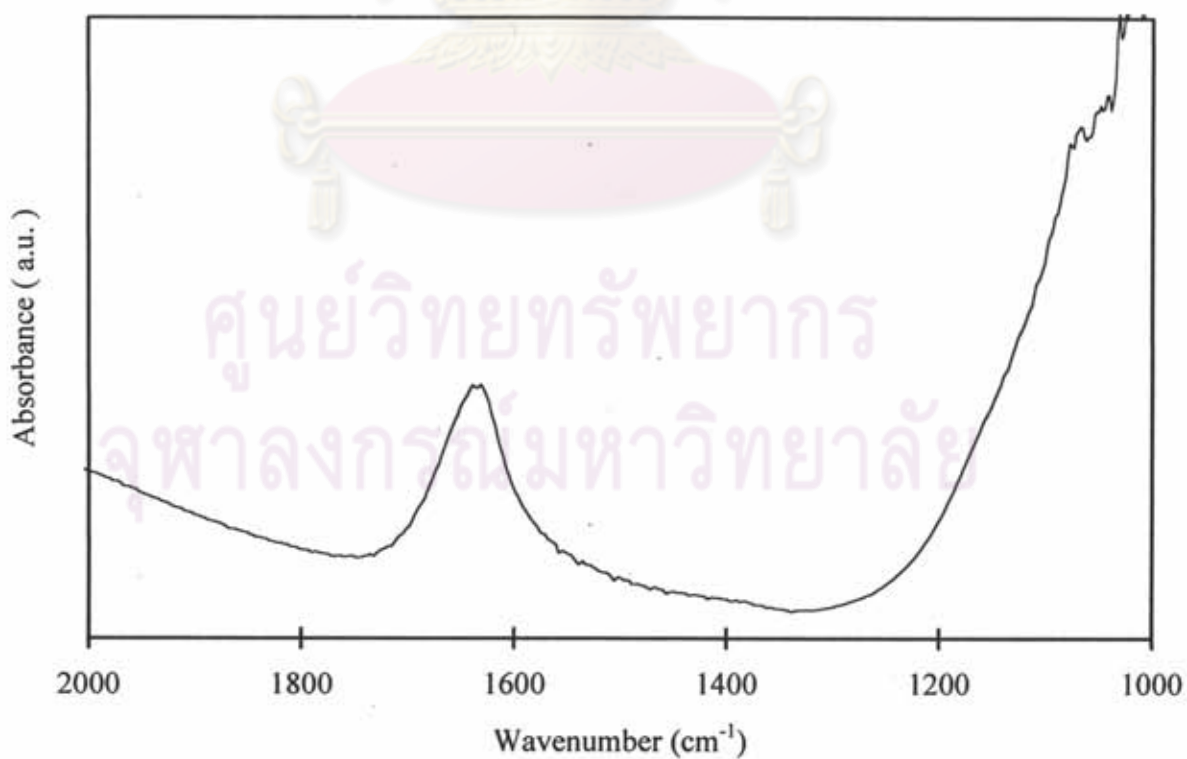


Figure 5.10 IR spectrum of fresh Pt-Sn/ γ -Al₂O₃ catalyst at room temperature in N₂ atmosphere

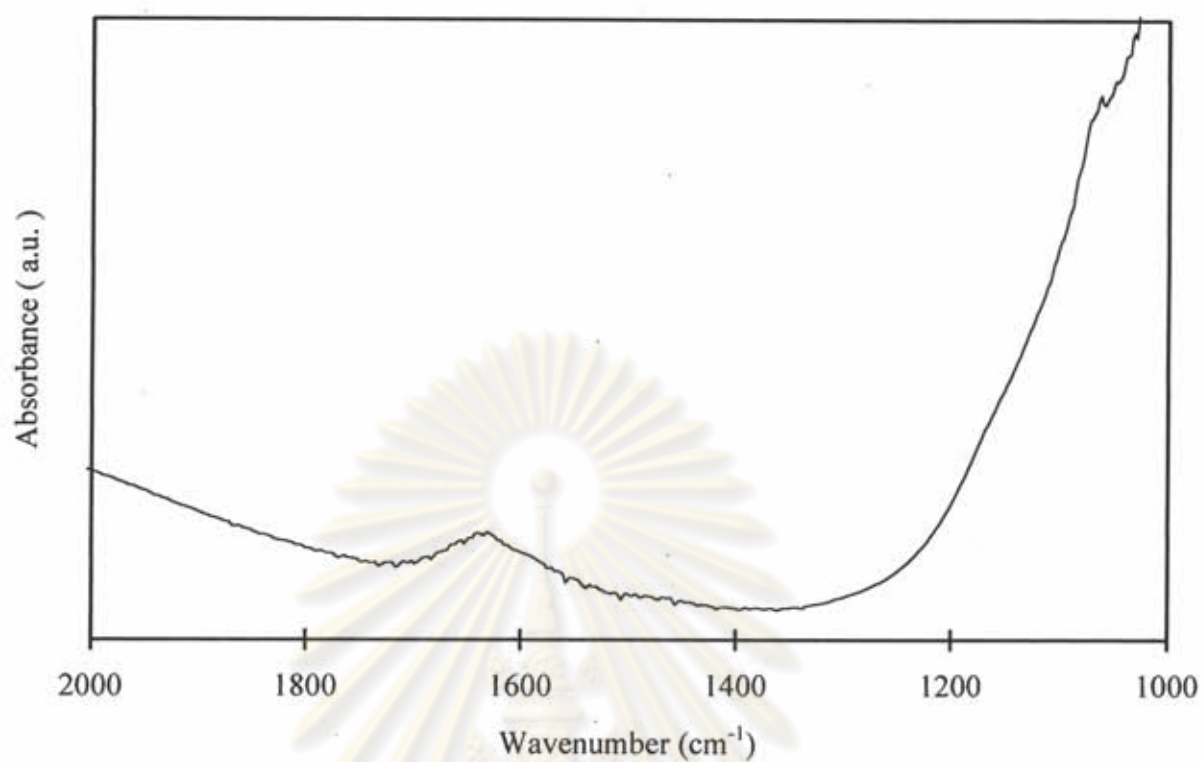


Figure 5.11 IR spectrum of fresh Pt-Sn/ γ -Al₂O₃ catalyst at 100°C in N₂ atmosphere

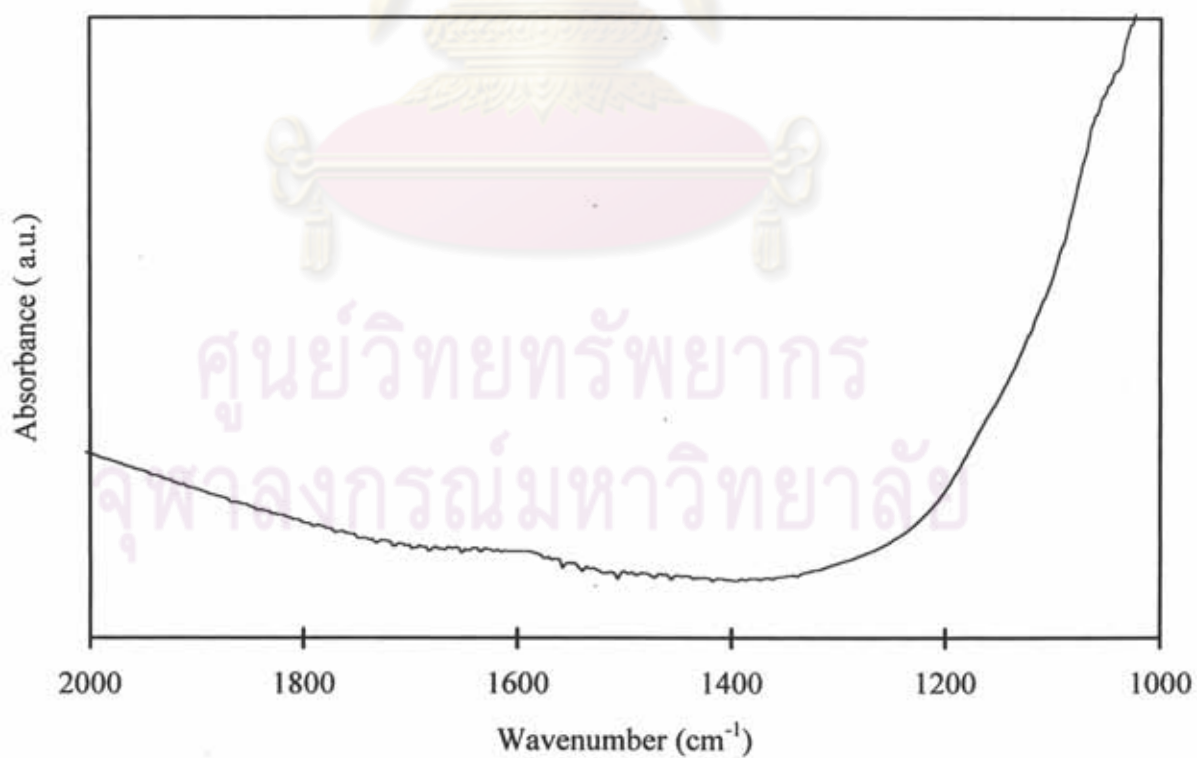


Figure 5.12 IR spectrum of fresh Pt-Sn/ γ -Al₂O₃ catalyst at 200°C in N₂ atmosphere

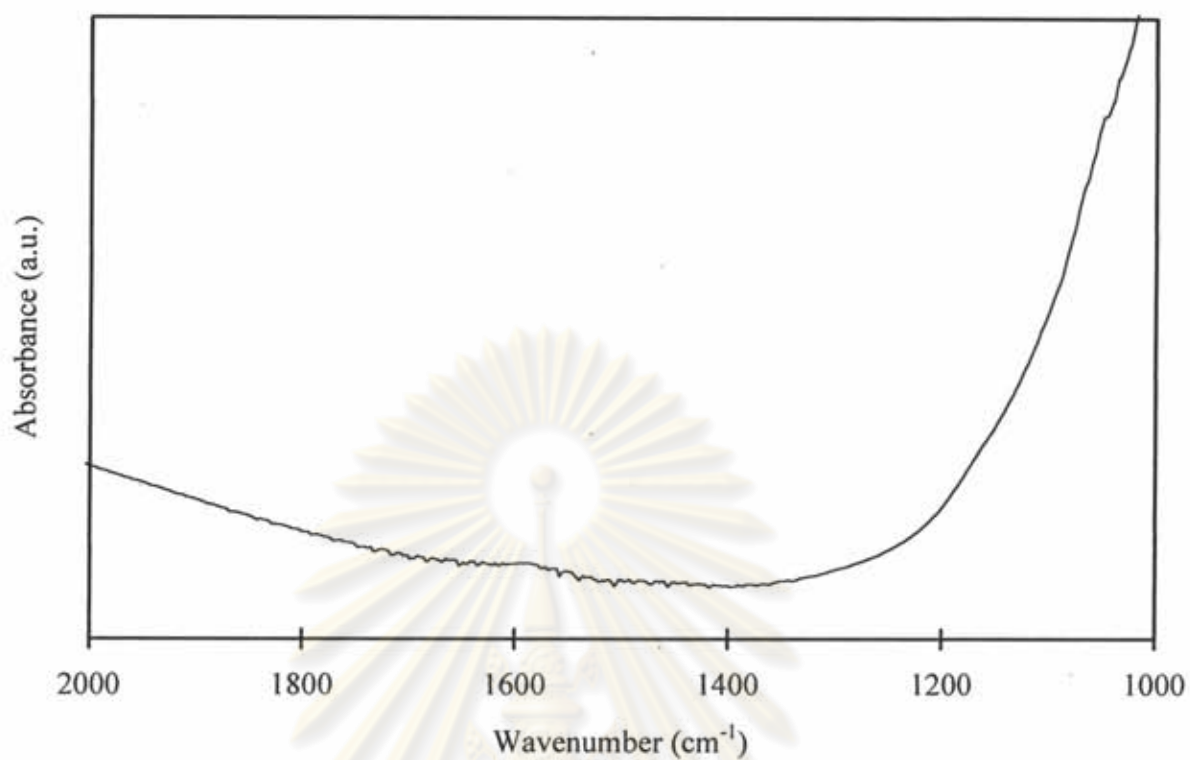


Figure 5.13 IR spectrum of fresh Pt-Sn/ γ -Al₂O₃ catalyst at 300°C in N₂ atmosphere

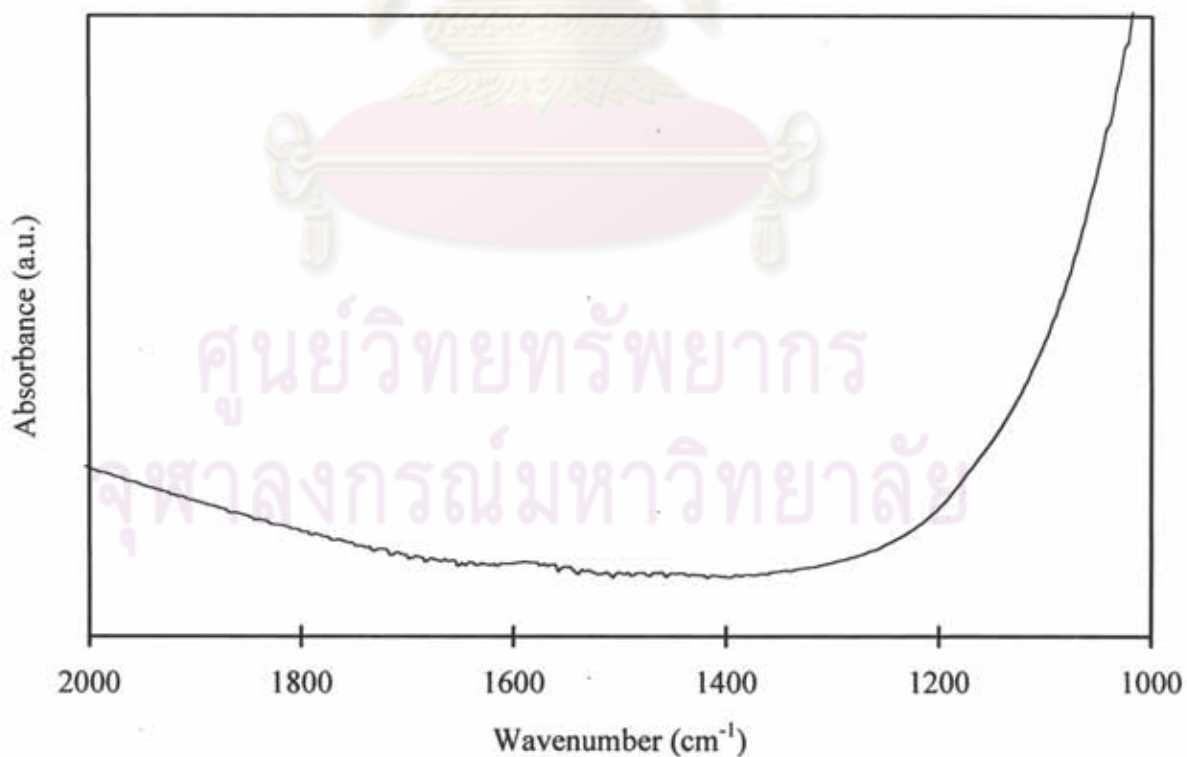


Figure 5.14 IR spectrum of fresh Pt-Sn/ γ -Al₂O₃ catalyst at 400°C in N₂ atmosphere

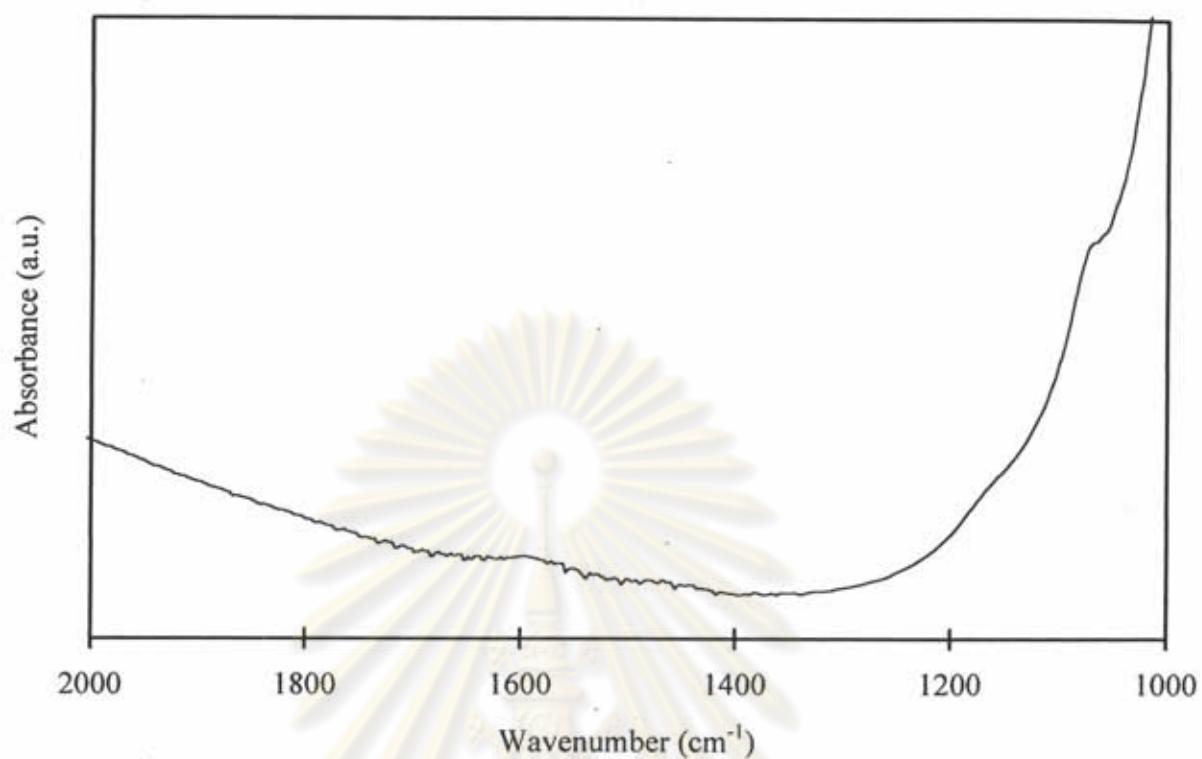


Figure 5.15 IR spectrum of fresh Pt-Sn/ γ -Al₂O₃ catalyst cooled down to room temperature in N₂ atmosphere

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5.3 Determination of coked catalysts by infrared spectroscopy

Since the aim of this study is to develop an IR spectroscopy technique which can be used to characterize adsorbed species of coked catalysts specifically in the earlier coking period, and if possible identify the structure of coke. Therefore the coked catalysts employed in this study are collected from 2min,5min,10min,30min,1hr,2hr,and 4hr on stream. The coked catalysts were prepared by dehydrogenation of propane to propylene at the reaction temperature of 600°C in microreactor as described in the experimental section. The coked catalysts were then ready for IR analysis.

5.3.1 IR spectra of coked catalysts, 2min. on stream.

The evaluation in functional groups of initial coked catalyst in case of this research, 2 min. on stream was chosen as an beginning of initial coked catalyst. This depends on the limitation in the operating system of reaction apparatus available. Since the fraction of carbon content in initial coked catalyst is comparatively lower than entirely part of catalyst that coke occupied. Therefore, to obtain enough coke deposit from a low carbon content of coked catalyst in order to give rise to the appearance of IR absorption bands, the sample disks of initial coked catalyst(2,5,and 10 min. on stream) to be performed in-situ were prepared from the original coked catalyst as directly taken from coking reaction without dilution with γ -Al₂O₃. The essential of coked catalysts at longer time on stream to be diluted with γ -Al₂O₃ for IR analysis has been discussed briefly in the experimental section.

Figure 5.16 shows the IR spectrum of 2min. coked catalyst in ambient air at room temperature. The whole range in this spectrum is superimposed by several adsorbed species which difficult to distinguish between the bands of interest and the bands of interference, otherwise two prominent though broad bands can be observed. The stronger one located in between 1640-1650 cm⁻¹, and the smaller one gives the broad band slopes downward near region 1400-1420 cm⁻¹.

The following state of treatment is purging sample with N₂ ultra high purity grade, 99.999%. It is important to keep coked catalyst samples in inert atmosphere during the course of analysis so as to avoid combustion of coke in presence of O₂ which generally exists in the ambient atmosphere.

Figure 5.17 shows the spectrum of coked Pt-Sn/ γ -Al₂O₃ catalyst (2 min. on stream) in N₂ at room temperature. The spectrum becomes to give 3 main bands. The combination of the first two bands locate in region 1640-1650 cm⁻¹ and 1580-1590 cm⁻¹. The third band locates apart from those two bands in region 1460 cm⁻¹. Upon increasing the sample temperature to 200°C in correspondence with the temperature of base spectrum of γ -Al₂O₃ and fresh catalyst, the CO₂ and H₂O bands at 1640-1650 cm⁻¹ disappear which is consistent with the spectra obtained from γ -Al₂O₃ and fresh catalyst. In contrast, the bands at 1580 cm⁻¹ and 1460 cm⁻¹ are intensified (see figure 5.19). The IR spectra for further treatment of coked catalysts by raising the sample temperature to 300°C and 400°C, and consequently cooling the samples to room temperature in N₂ atmosphere are illustrated in figures 5.20-5.22, respectively. The overall pattern of these spectra are very similar to spectrum at 200°C. This suggests that heating samples higher than 200°C and cool down process does not affect the pattern of IR spectra for coked catalysts. This result is in agreement with those of γ -Al₂O₃ and fresh catalyst. Therefore, the spectra at 300°C, 400°C, and cool down in N₂ atmosphere for coked catalysts at the other times on stream are collected in appendix B. and only spectra at 200°C will be discussed in the subsequent part.

The assignment of bands in the coked catalyst system should base on the fundamental of deposited carbon which constructed from various groups of hydrocarbon compound. Consequently, the characteristic group frequencies of hydrocarbon at 1580 cm⁻¹ is C=C stretching in aromatic ring [18,19], and the band at 1460 cm⁻¹ is associated with methyl or methylene bending [18,19].

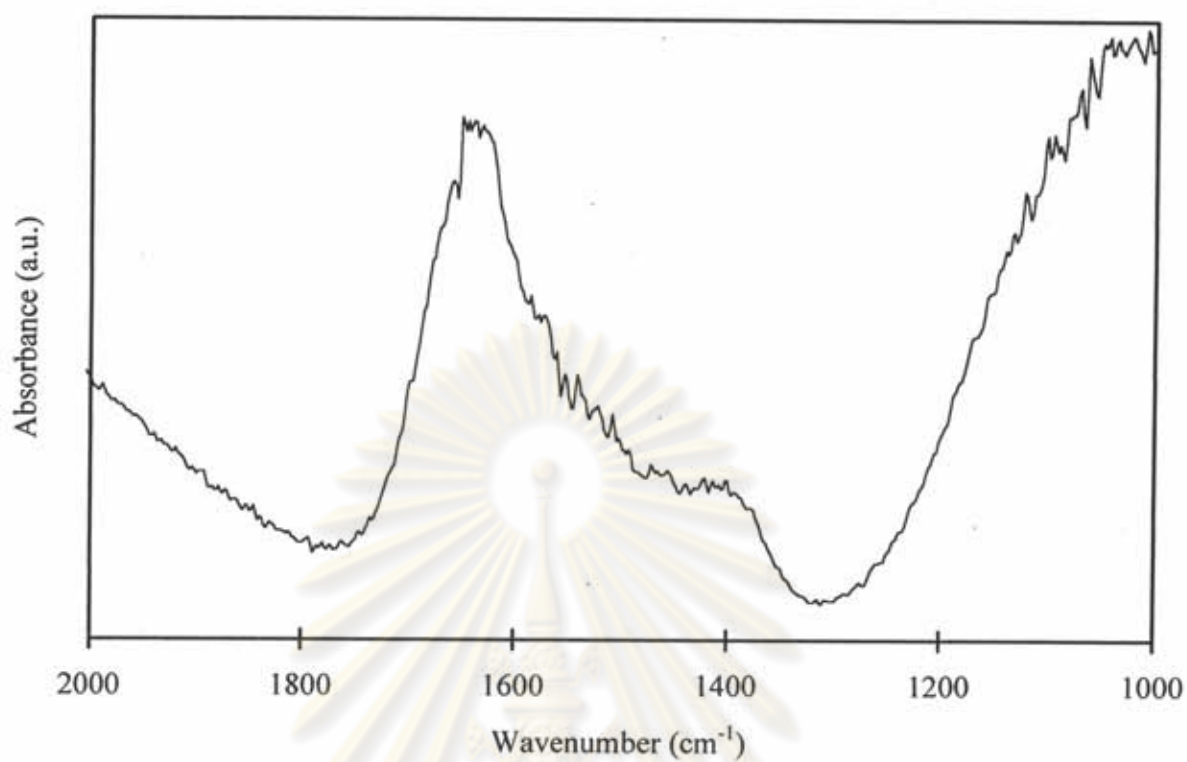


Figure 5.16 IR spectrum of 2 min.coked catalyst at room temperature in ambient air

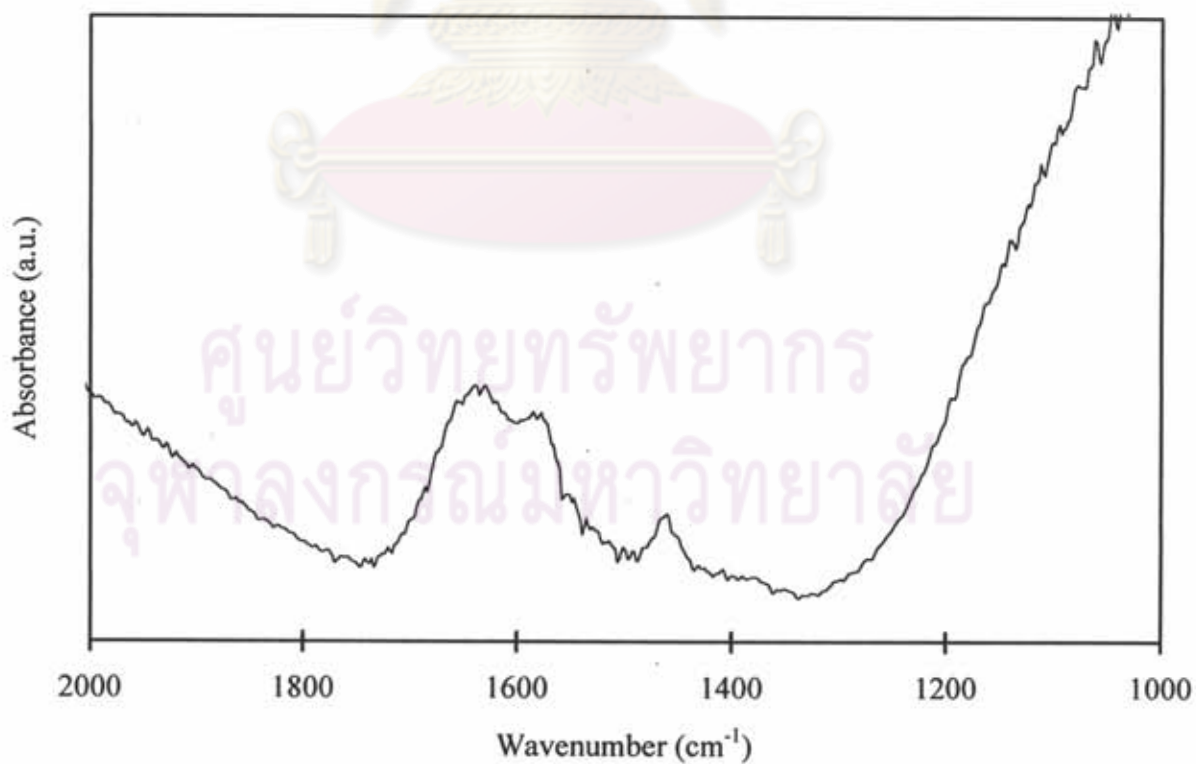


Figure 5.17 IR spectrum of 2 min.coked catalyst at room temperature in N₂ atmosphere

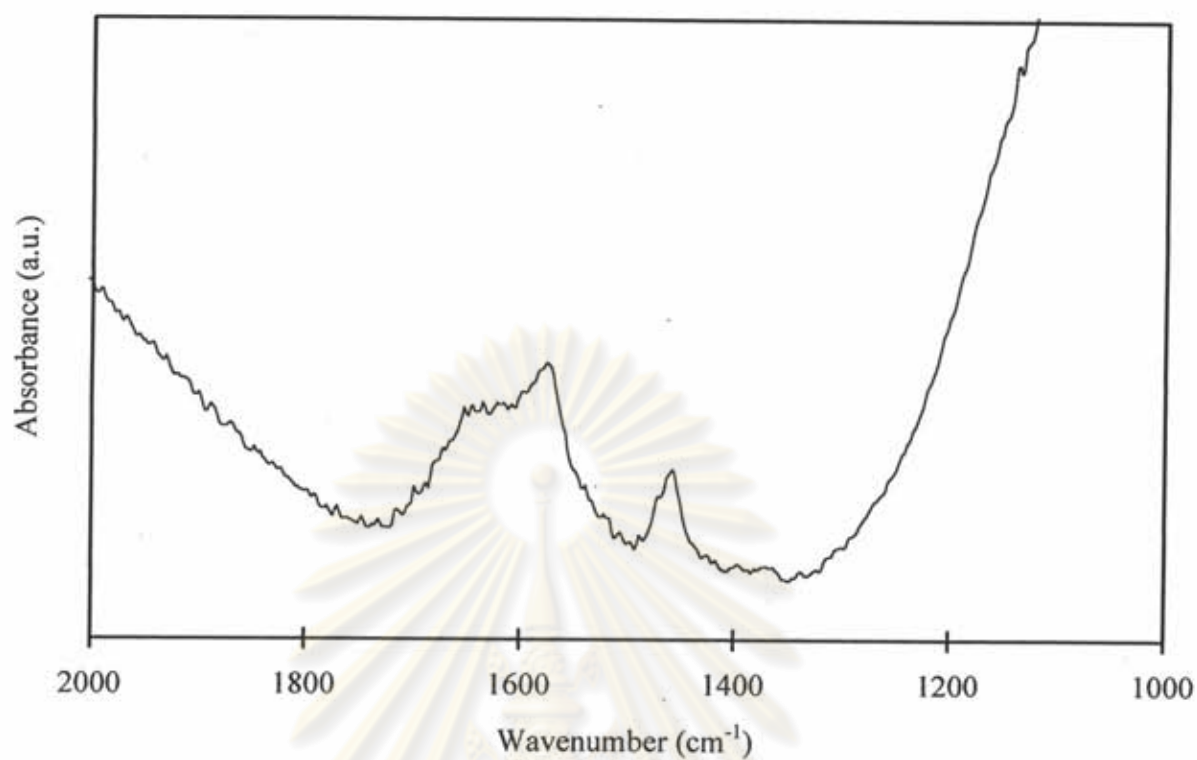


Figure 5.18 IR spectrum of 2 min.coked catalyst at 100°C in N₂ atmosphere

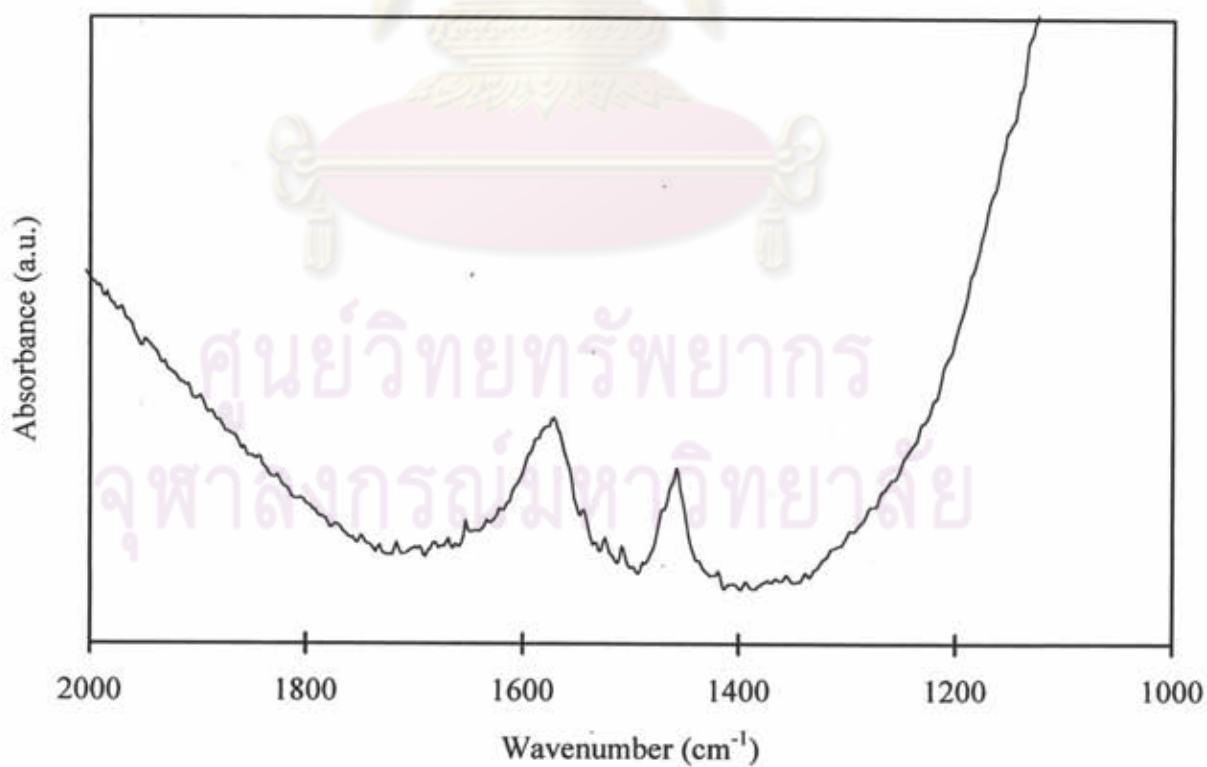


Figure 5.19 IR spectrum of 2 min.coked catalyst at 200°C in N₂ atmosphere

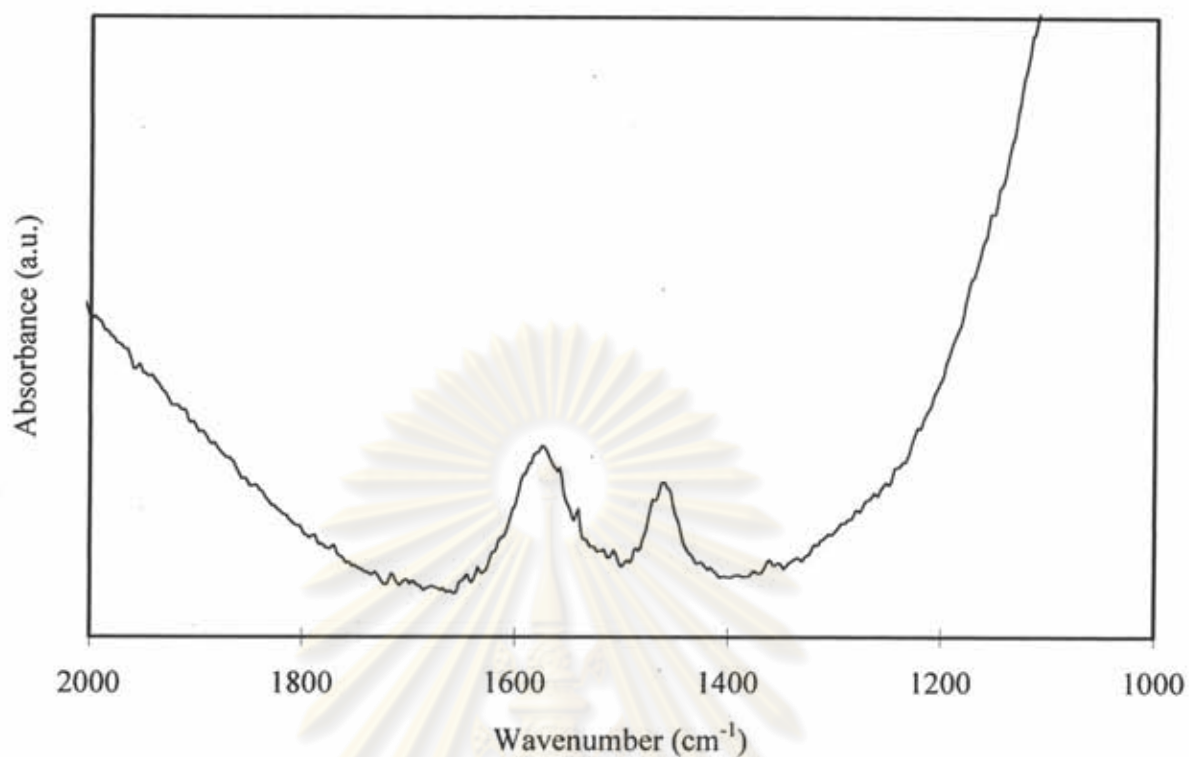


Figure 5.20 IR spectrum of 2 min.coked catalyst at 300°C in N₂ atmosphere

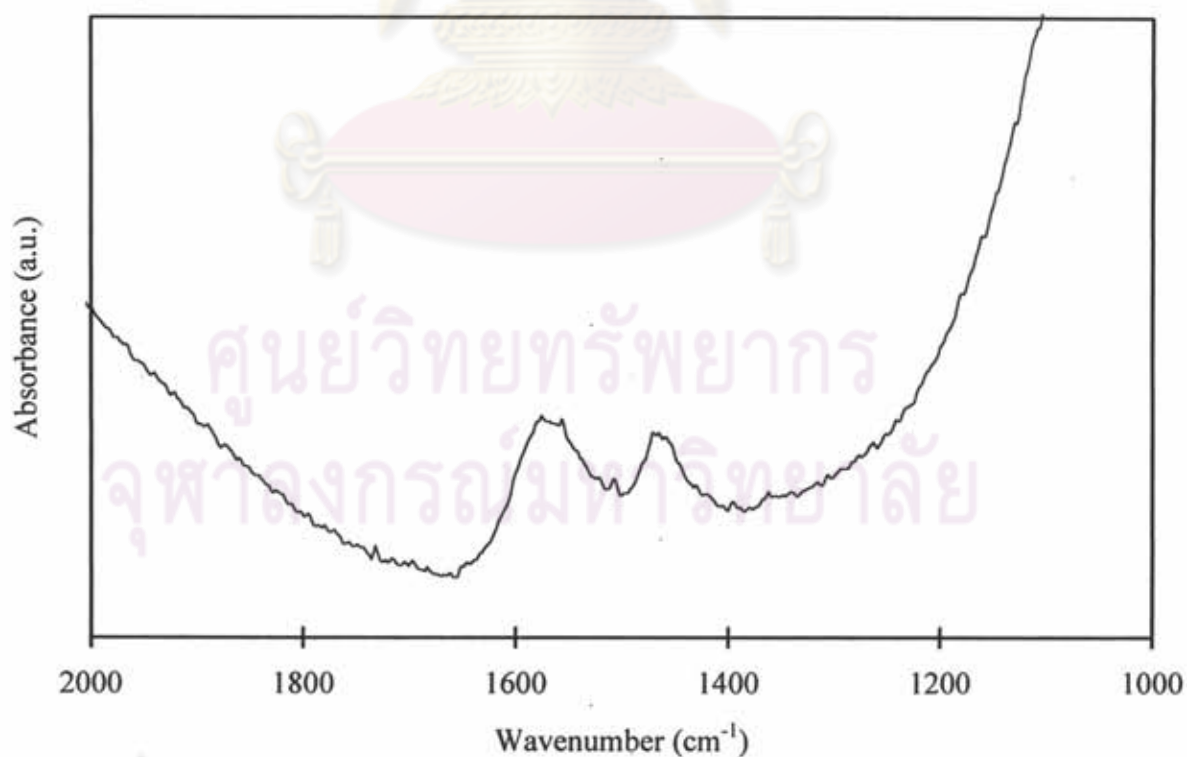


Figure 5.21 IR spectrum of 2 min.coked catalyst at 400°C in N₂ atmosphere

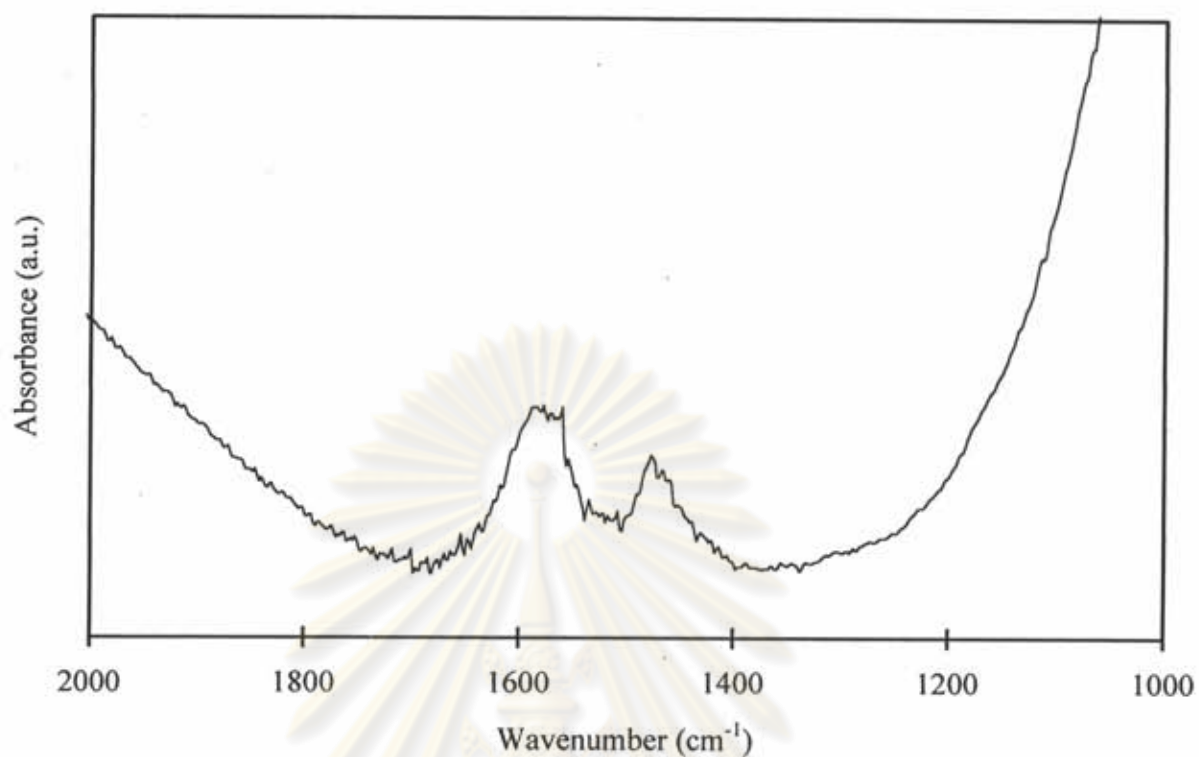


Figure 5.22 IR spectrum of 2 min.coked catalyst cooled down to room temperature in N_2 atmosphere

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5.3.2 IR spectra of coked catalyst, 5min. and 10 min. on stream

IR spectra of 5min. coked catalyst at room temperature in ambient air and in N₂ atmosphere are given in figures 5.23 and 5.24, respectively. Certainly, most deposited carbon bands obscured by adsorbed water and CO₂ in every samples at ambient air are more visible after the progressive heating in N₂ atmosphere as already described (such as at 100°C in figure 5.25). The discussion for every coked catalyst samples is then targeted toward coked catalysts heated to 200°C, the same temperature as being discussed in γ -Al₂O₃ and fresh Pt-Sn/ γ -Al₂O₃ catalyst.

Figure 5.26 is IR spectrum of 5min coked catalyst heated at 200°C. In this spectrum, four intense bands are detected at approximately 1590, 1560, 1490, and 1460 cm⁻¹. Normally, the bands in the region of 1500-1600 cm⁻¹ are very specific to stretching mode of aromatic systems [18,19]. The in-plane bending vibrations of the carbon hydrogen bonds of methyl or methylene groups occur in the region of 1340-1470 cm⁻¹ [18,19]. Thus, this spectrum indicates absorption in these regions, suggesting the presence of aromatic ring and also methyl or methylene groups in this molecule which are already found in the spectrum of 2min. coked catalyst.

Compare with the spectrum of 2min. coked catalyst, the spectrum of 5min. coked catalyst shows slightly lower ratio of methyl/methylene per aromatic, suggesting that coke begins to condense into aromatic ring.

For IR spectrum of 10 min. coked catalyst, the individual spectrum of 10 min. coked catalyst is very coincident to those of 5min. coked catalyst as represent in figures 5.27-5.30. This evidence indicates that there is so little modification in the structure of coked catalyst for the reaction time in the period of 5min.- 10 min.

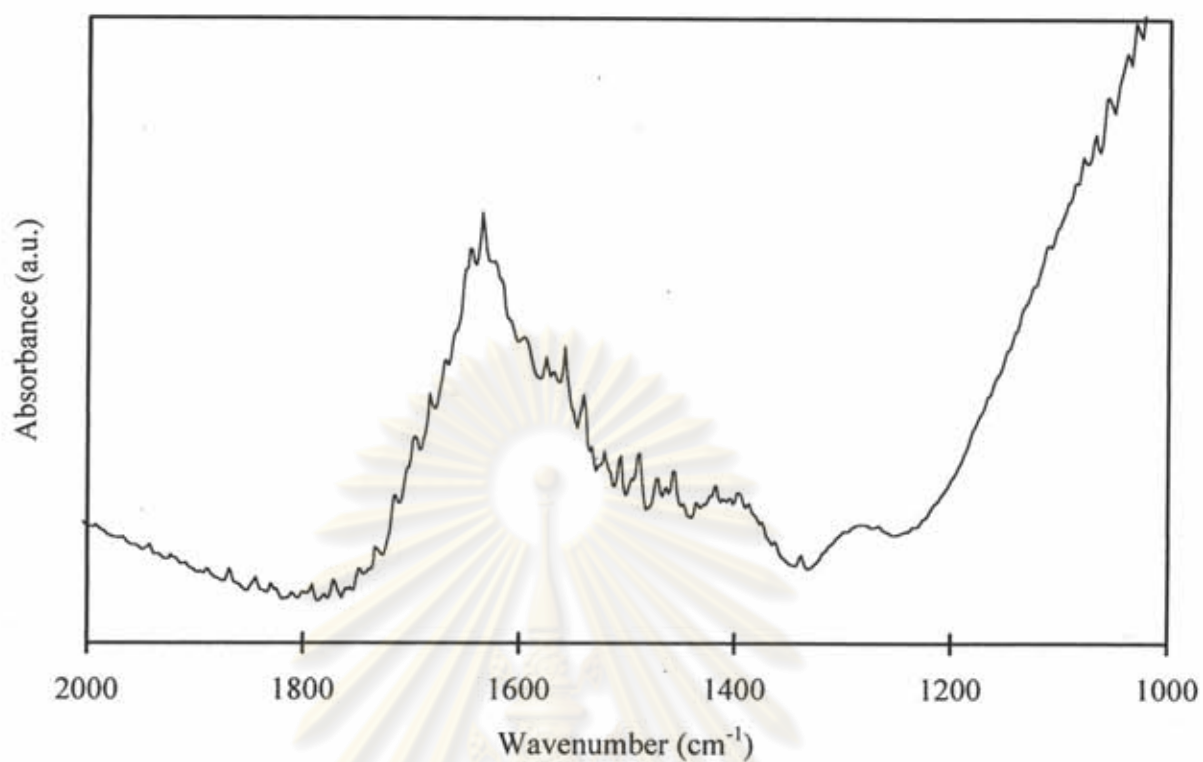


Figure 5.23 IR spectrum of 5 min.coked catalyst at room temperature in ambient air

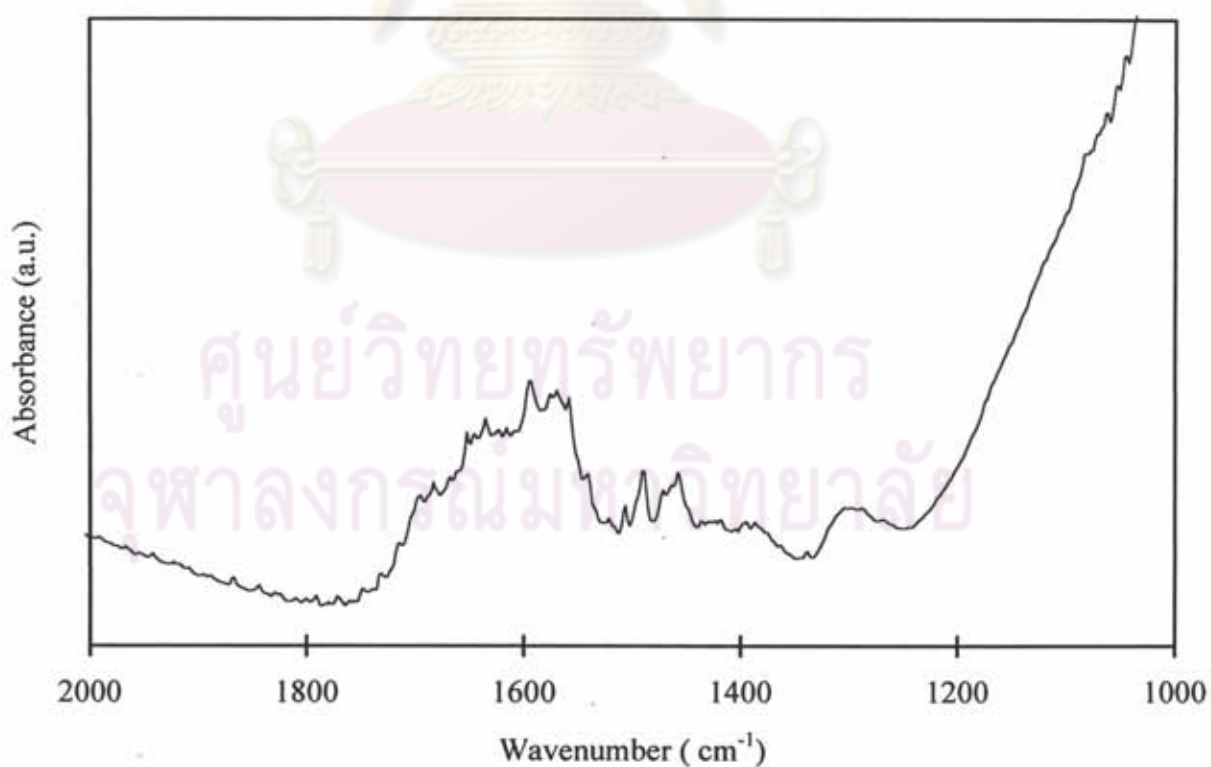


Figure 5.24 IR spectrum of 5 min.coked catalyst at room temperature in N₂ atmosphere

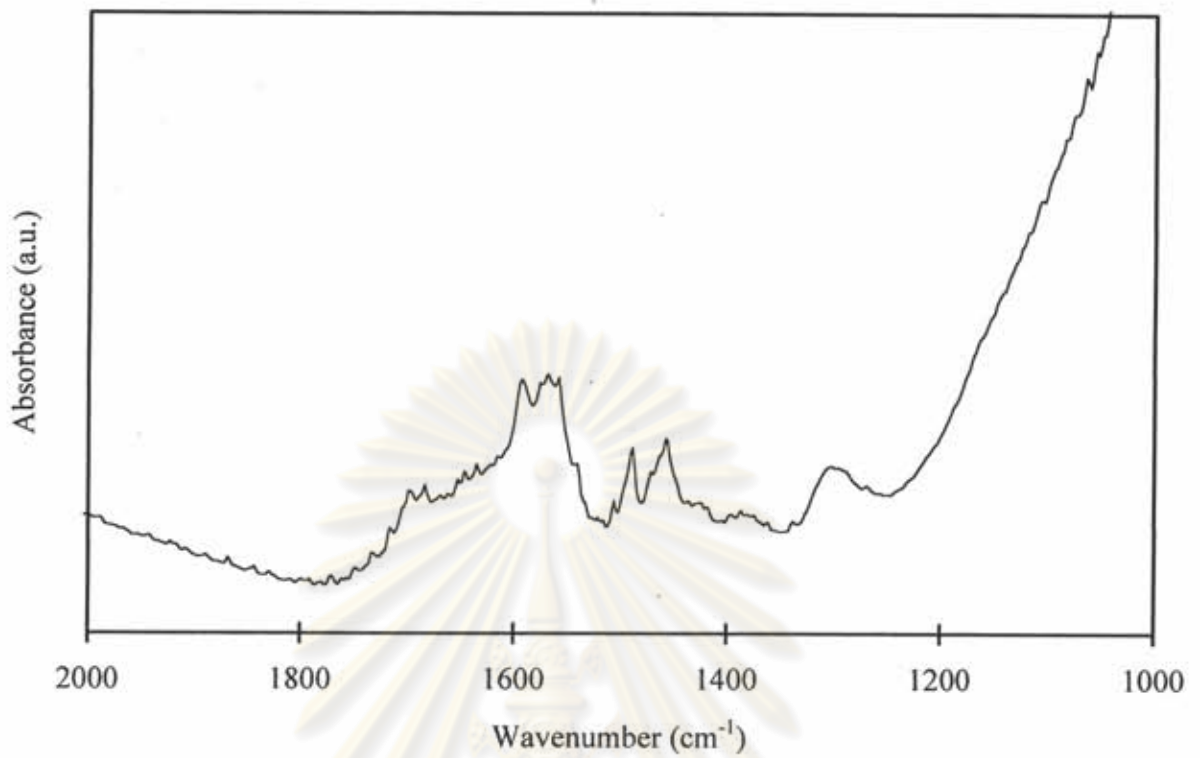


Figure 5.25 IR spectrum of 5 min.coked catalyst at 100°C in N₂ atmosphere

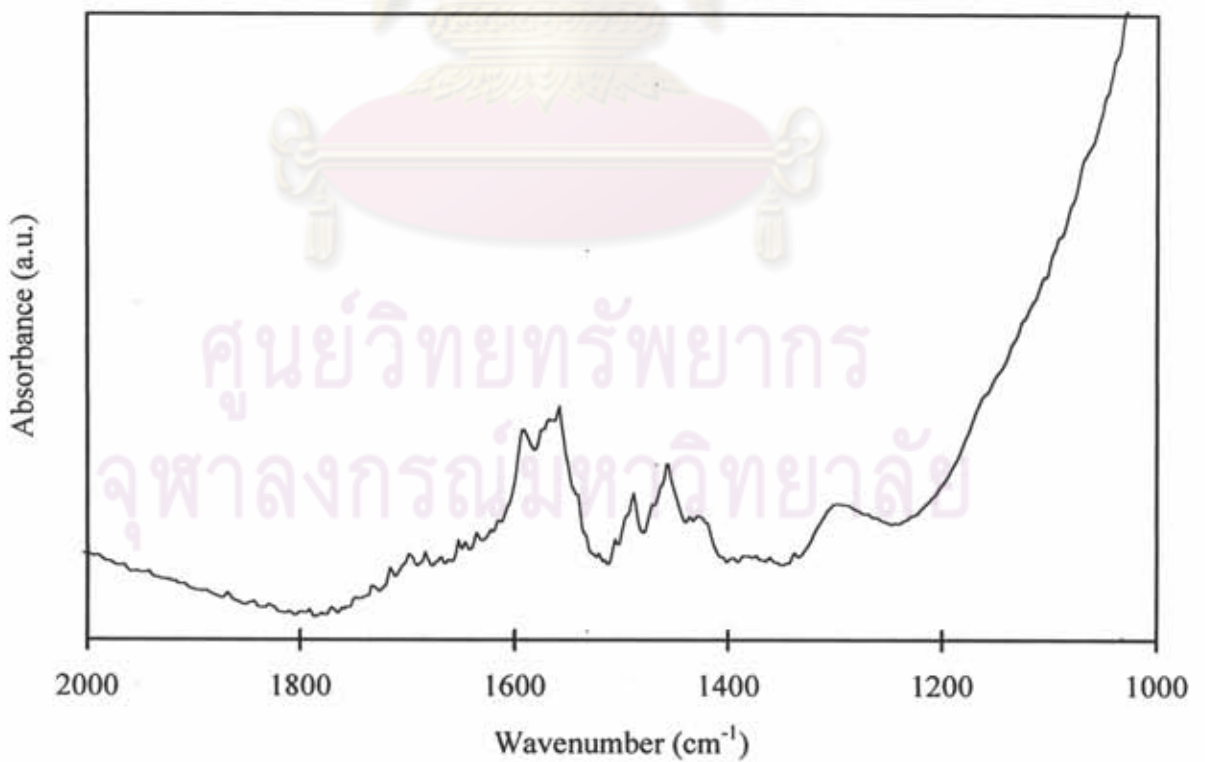


Figure 5.26 IR spectrum of 5 min.coked catalyst at 200°C in N₂ atmosphere

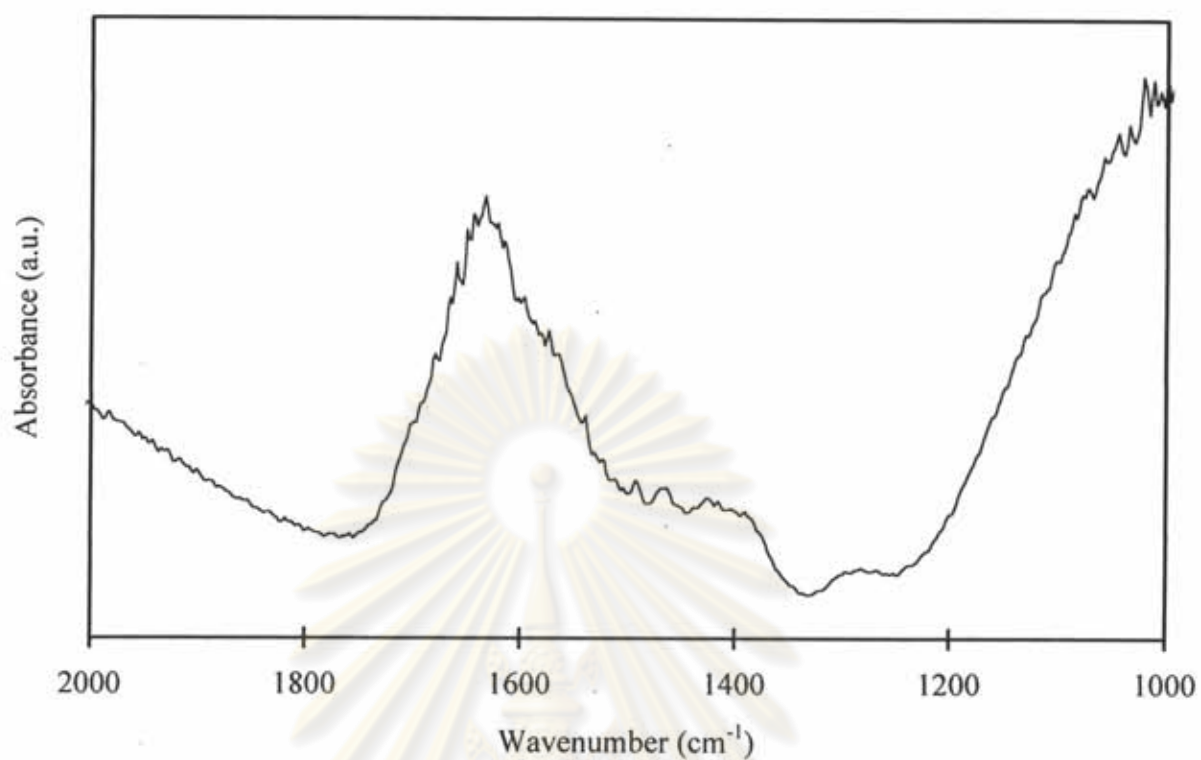


Figure 5.27 IR spectrum of 10 min.coked catalyst at room temperature in ambient air

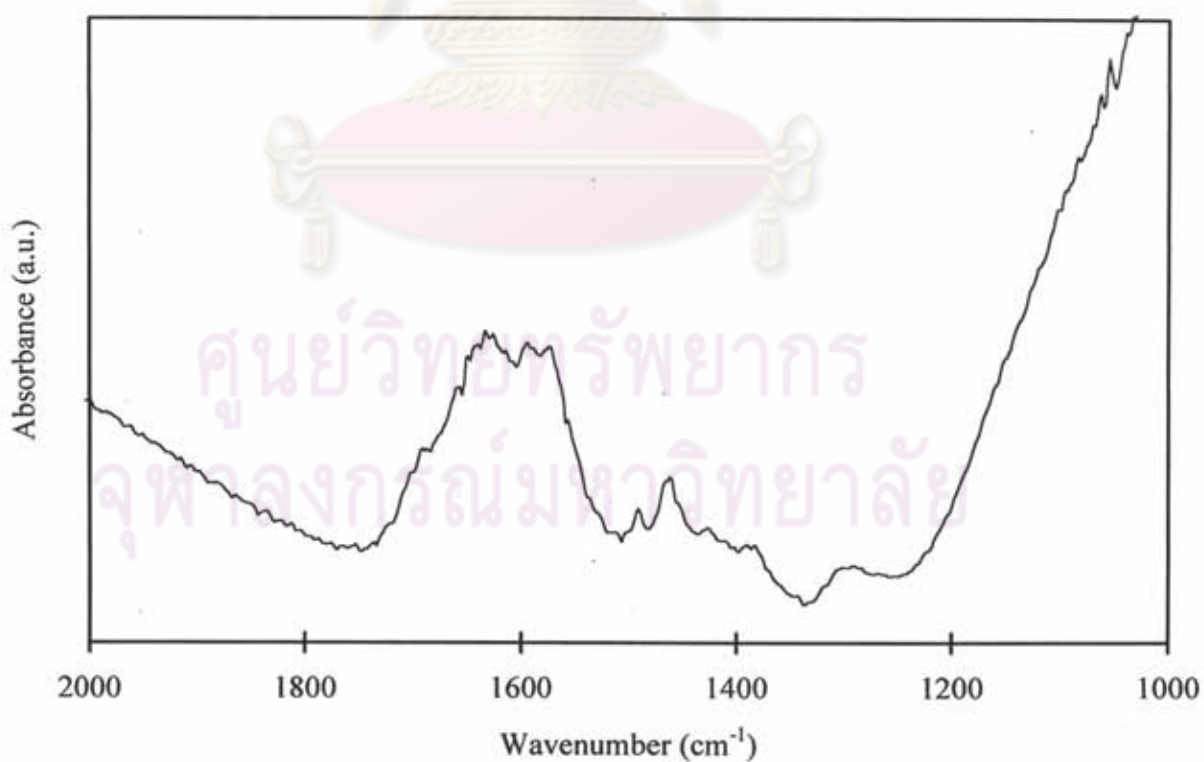


Figure 5.28 IR spectrum of 10 min.coked catalyst at room temperature in N₂ atmosphere

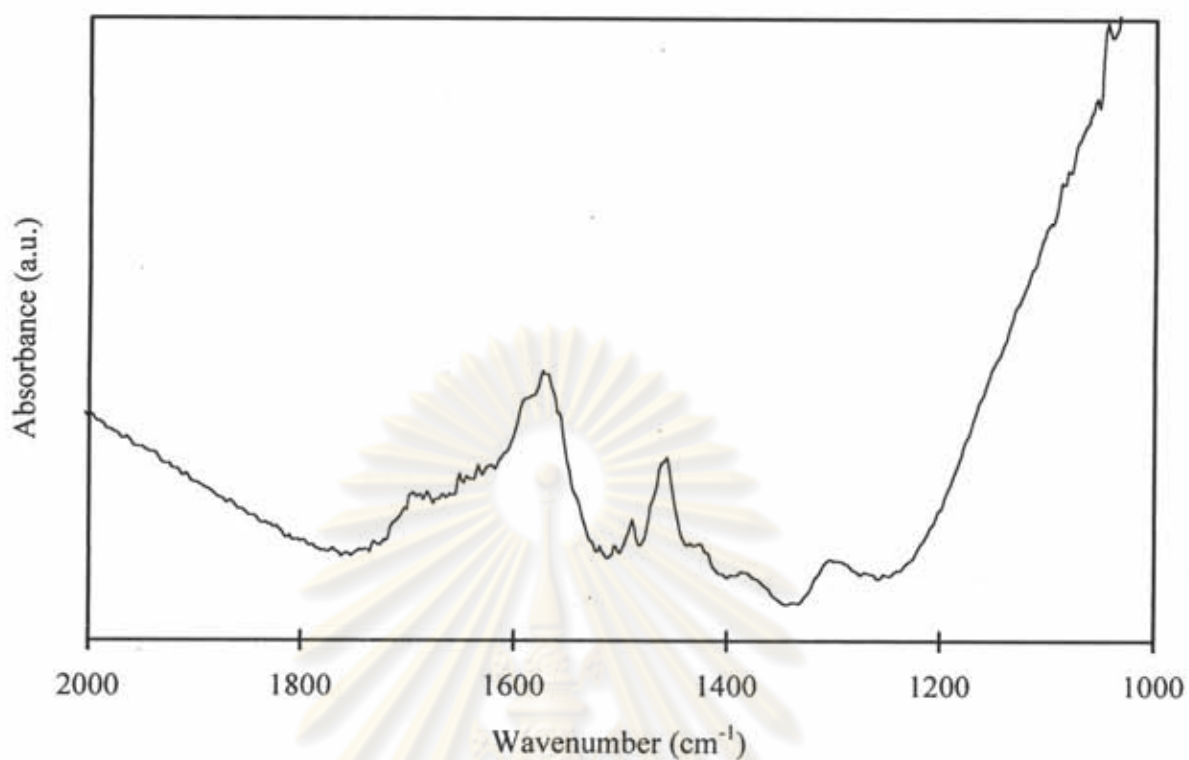


Figure 5.29 IR spectrum of 10 min.coked catalyst at 100°C in N₂ atmosphere

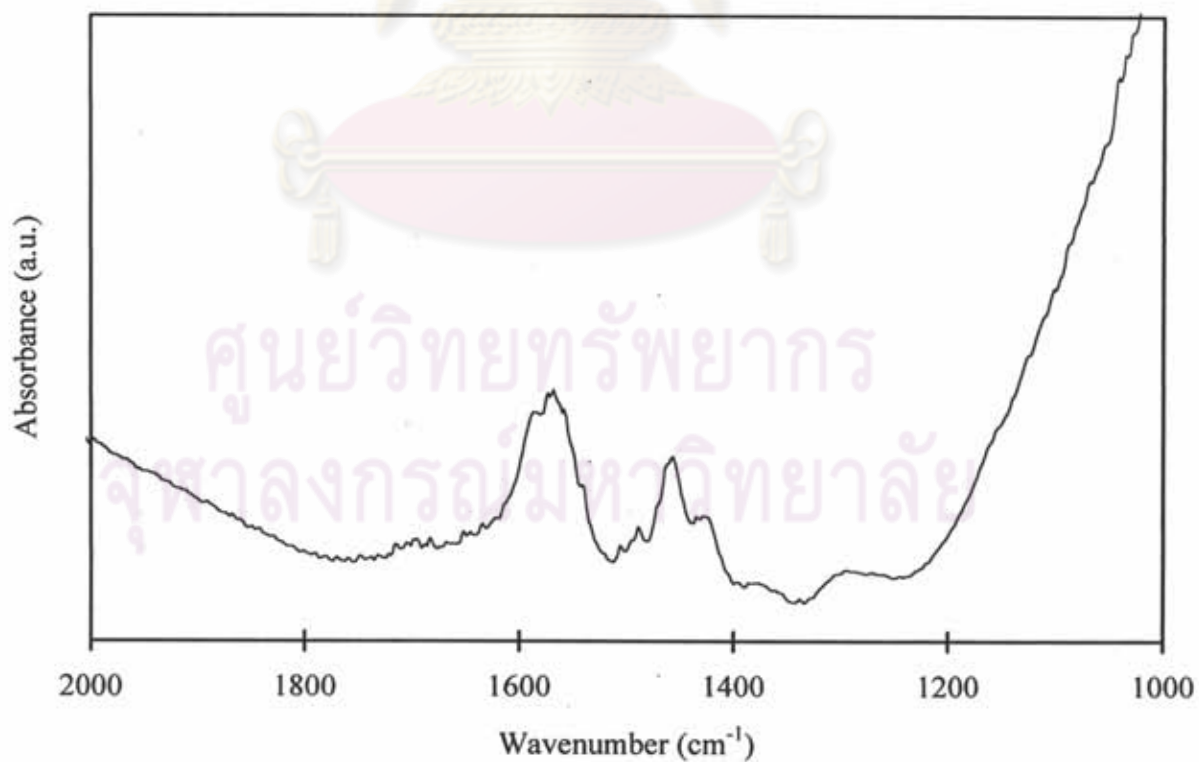


Figure 5.30 IR spectrum of 10 min.coked catalyst at 200°C in N₂ atmosphere

5.3.3 IR spectra of coked catalyst, 30 min. on stream and longer.

In analyzing the spectrum of 30 min. coked catalyst heated to 200°C (figure 5.34), the most intense band is at 1590 cm^{-1} . This absorption region again confirms the identification of aromatic ring bending vibration. It is interesting to note that, as the reaction time proceeds to 30 min., there is an important decrease of methyl or methylene groups which locate near 1460 cm^{-1} . This can be interpreted as a possibility in the decreasing of methyl or methylene structures during the dehydrogenation process which takes place at long reaction time.

The spectra of catalyst collect from longer reaction time (1hr,2hr, and 4hr) are illustrated in figures 5.35-5.46. The spectra obtain from these samples are similar to that at 30 min. coked catalyst. Only aromatic ring structure can be identified. The longer the reaction time the more complicate the spectrum. The spectra of 2hr. and 4hr. coked catalyst shows several new absorption peaks which, at this moment cannot be identified. One hypothesis is they may caused by the formation of bigger polyaromatic rings or more complex substitution groups which disturb the vibration of aromatic ring in the region 1400-1600 cm^{-1} [18,19]. Therefore, to prove this hypothesis, it needs further study in detail.

From this research, we may be able to roughly divide period of coke formation into 2 periods by using their structure. The first period is the period at which methyl / methylene groups exist in a significant amount when compare to aromatic structure. The second period is the period at which structure is dominated by aromatic structure.

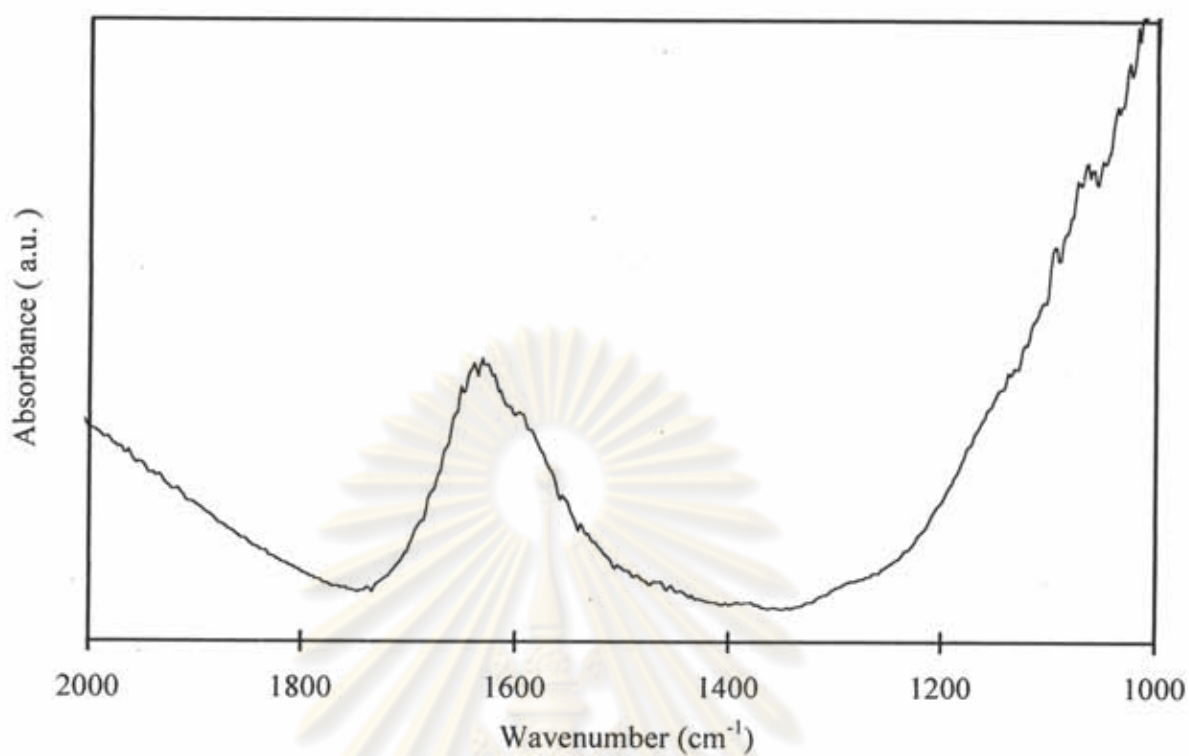


Figure 5.31 IR spectrum of 30 min.coked catalyst at room temperature in ambient air

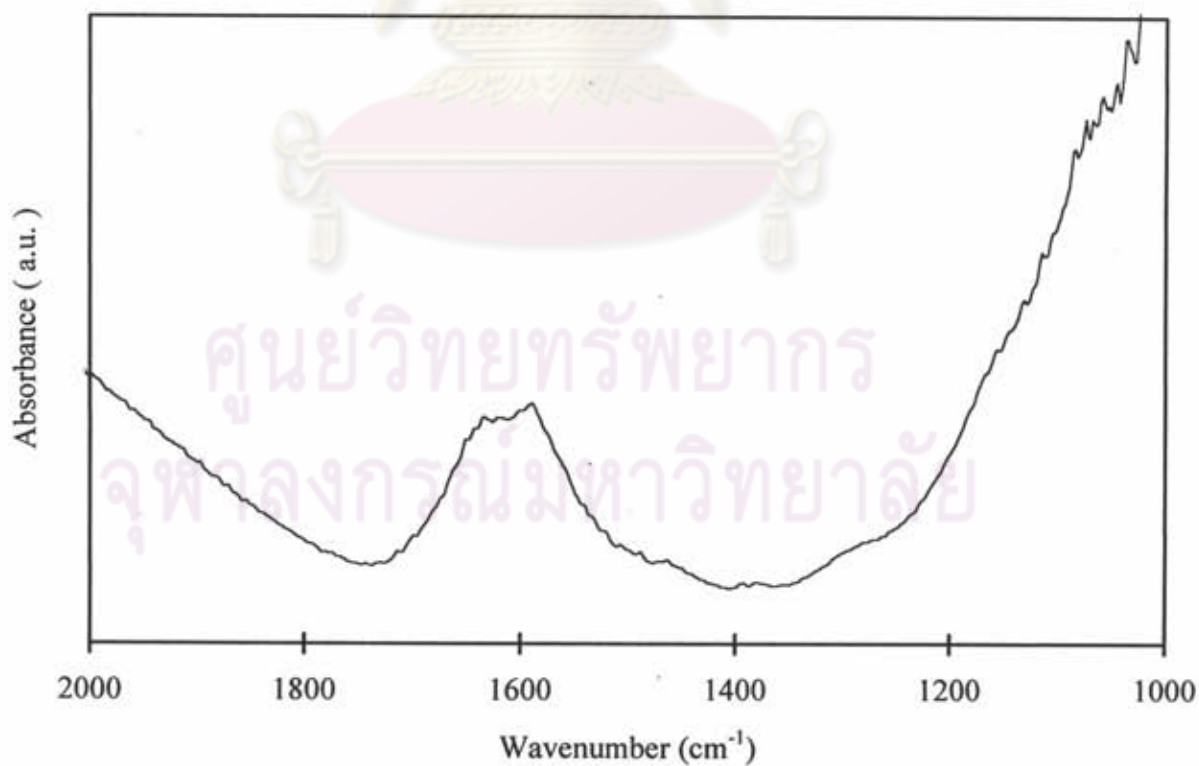


Figure 5.32 IR spectrum of 30 min.coked catalyst at room temperature in N₂ atmosphere

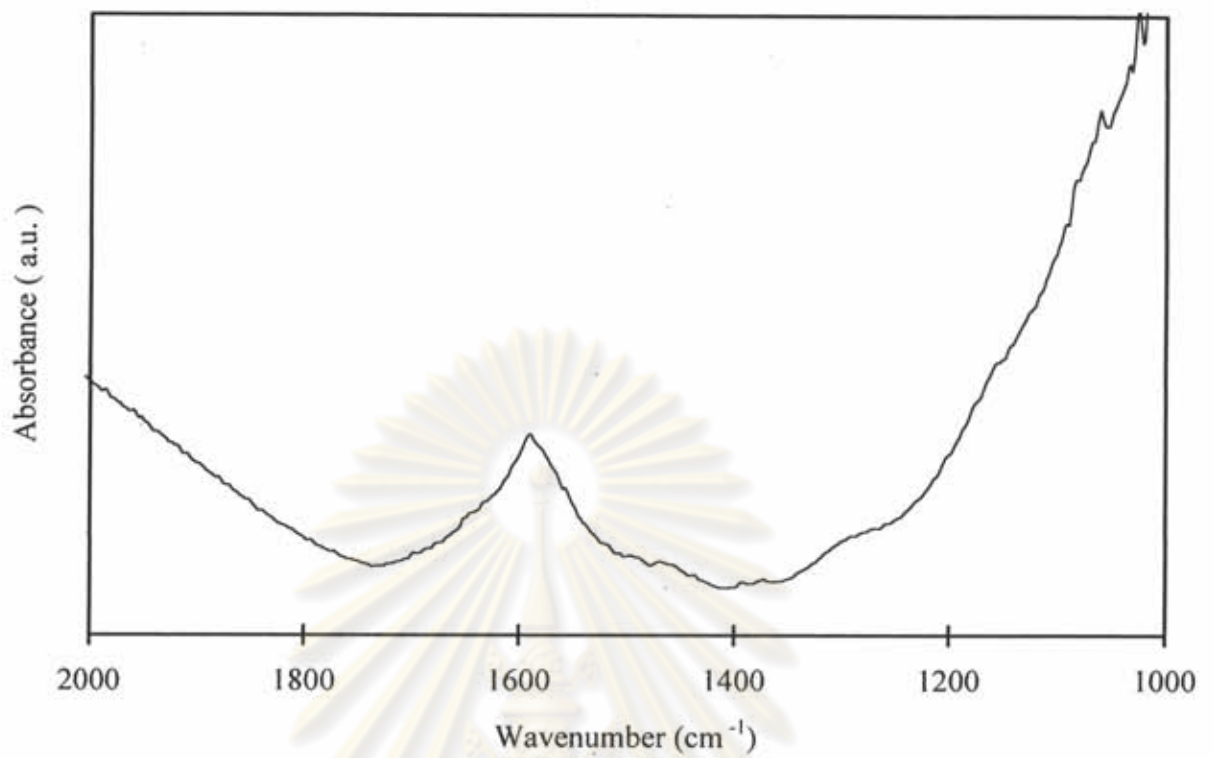


Figure 5.33 IR spectrum of 30 min.coked catalyst at 100°C in N₂ atmosphere

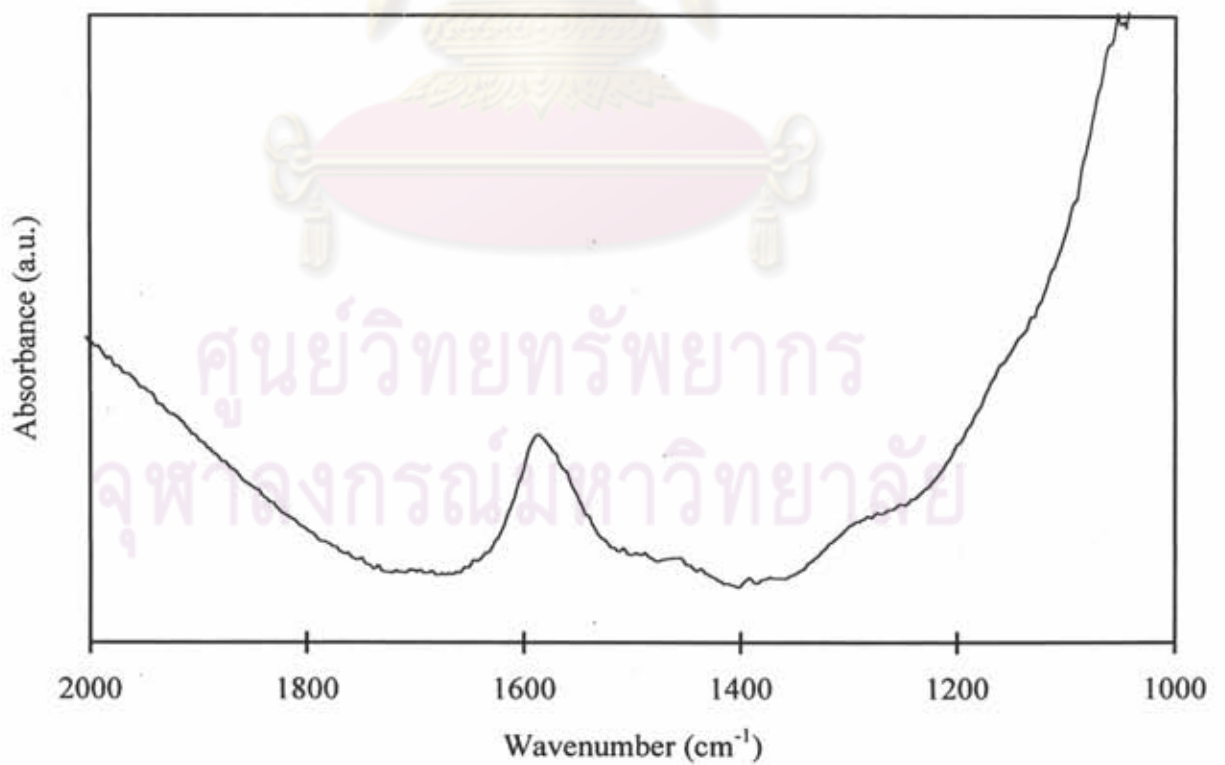


Figure 5.34 IR spectrum of 30 min.coked catalyst at 200°C in N₂ atmosphere

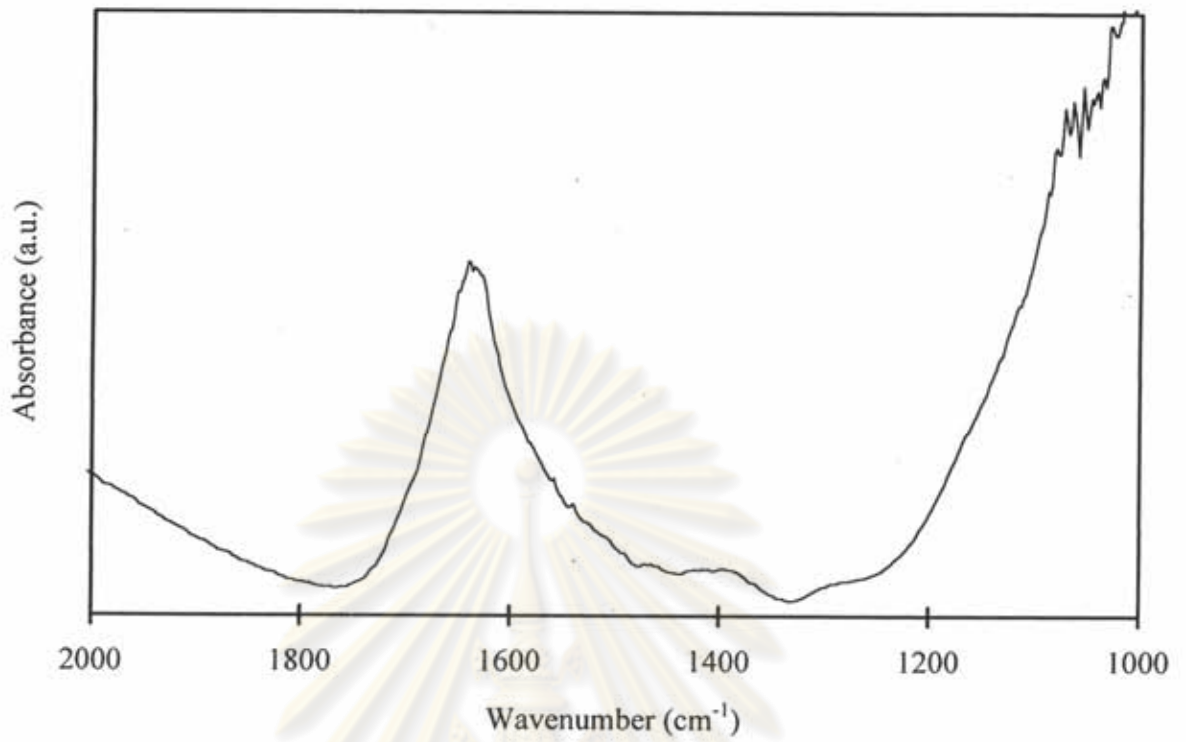


Figure 5.35 IR spectrum of 1 hr.coked catalyst at room temperature in ambient air

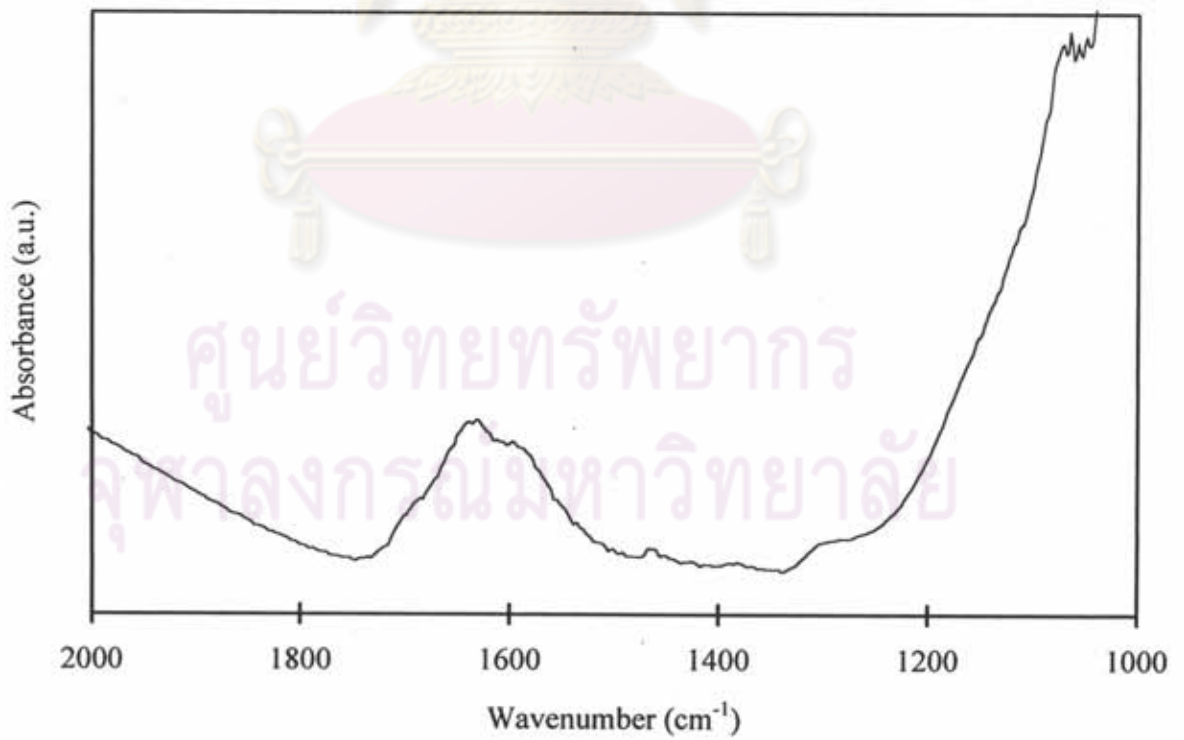


Figure 5.36 IR spectrum of 1 hr.coked catalyst at room temperature in N₂ atmosphere

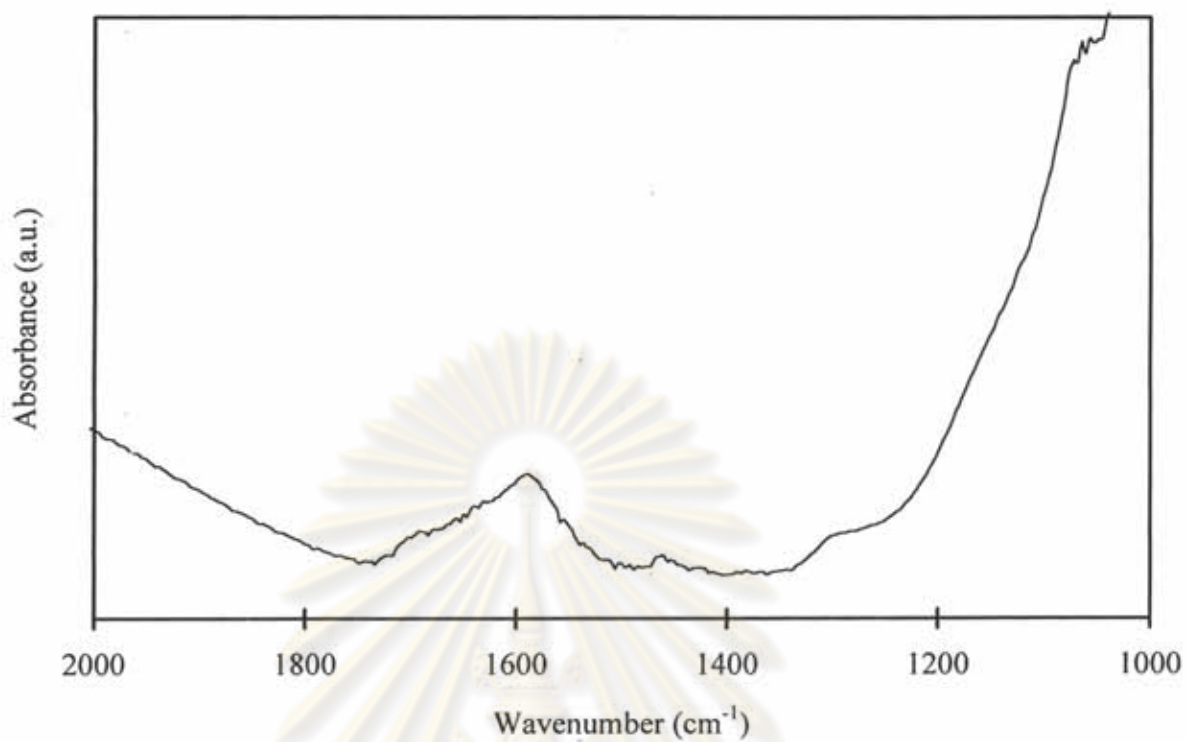


Figure 5.37 IR spectrum of 1 hr.coked catalyst at 100°C in N₂ atmosphere

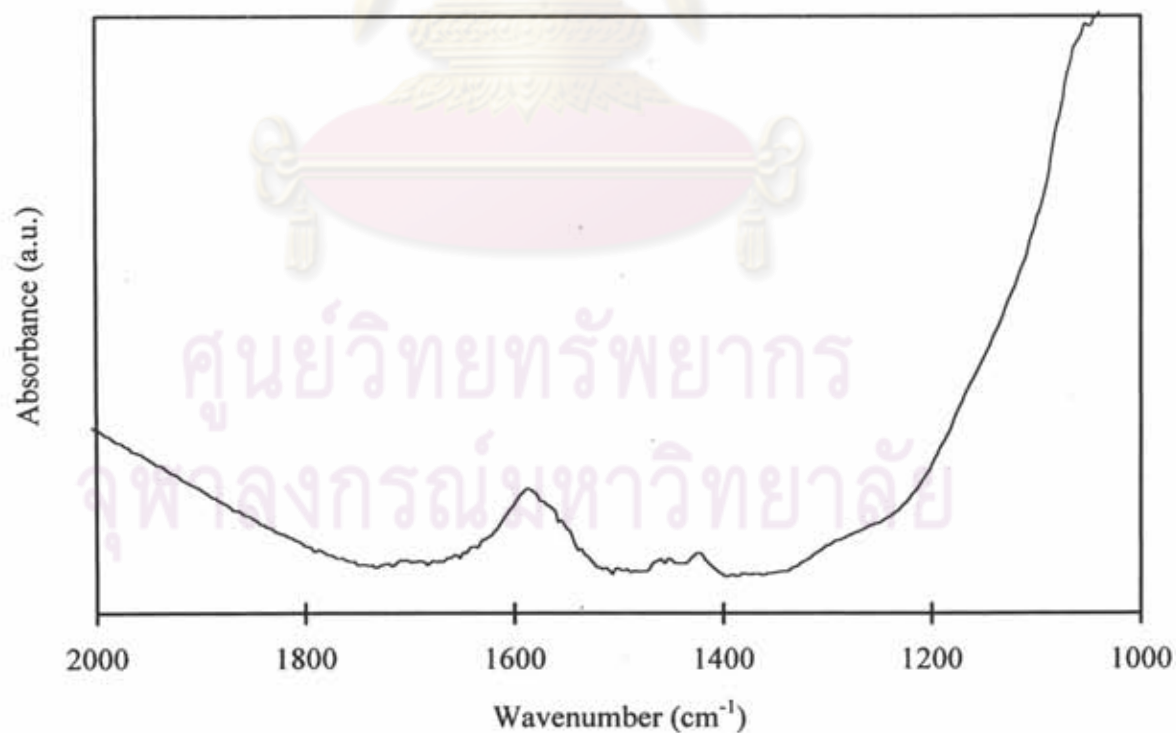


Figure 5.38 IR spectrum of 1 hr.coked catalyst at 200°C in N₂ atmosphere

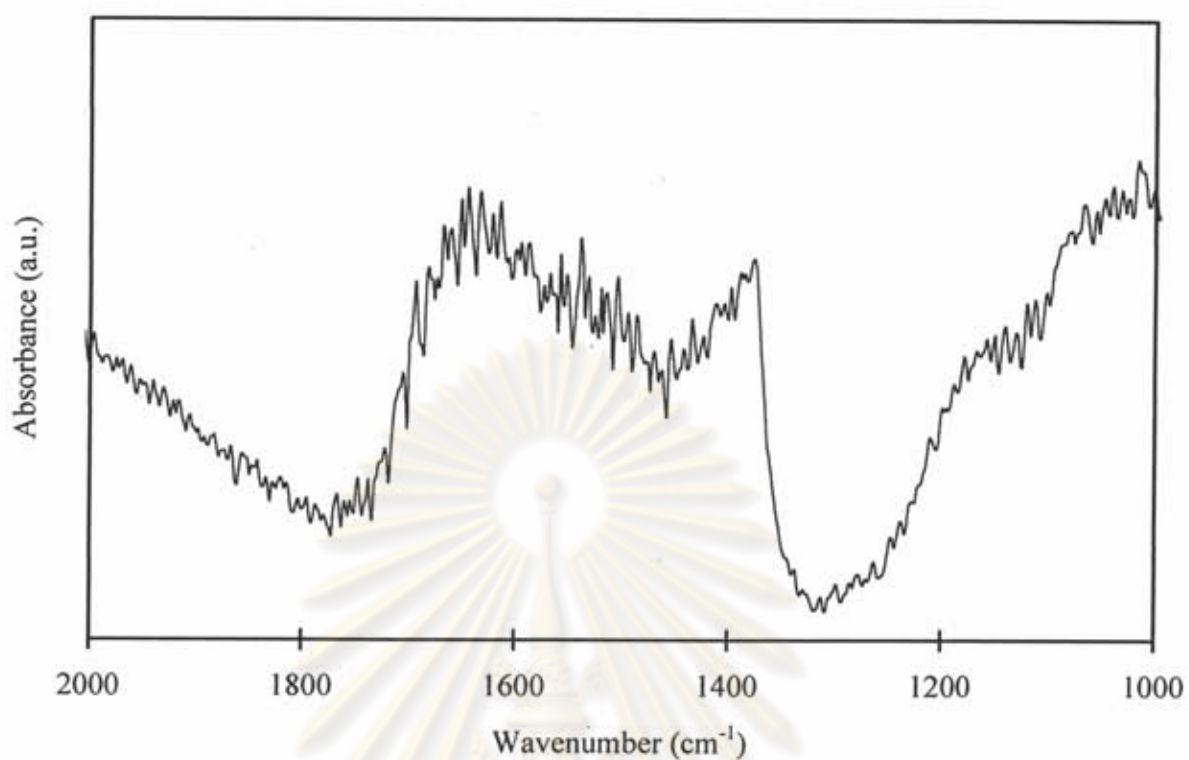


Figure 5.39 IR spectrum of 2 hr.coked catalyst at room temperature in ambient air

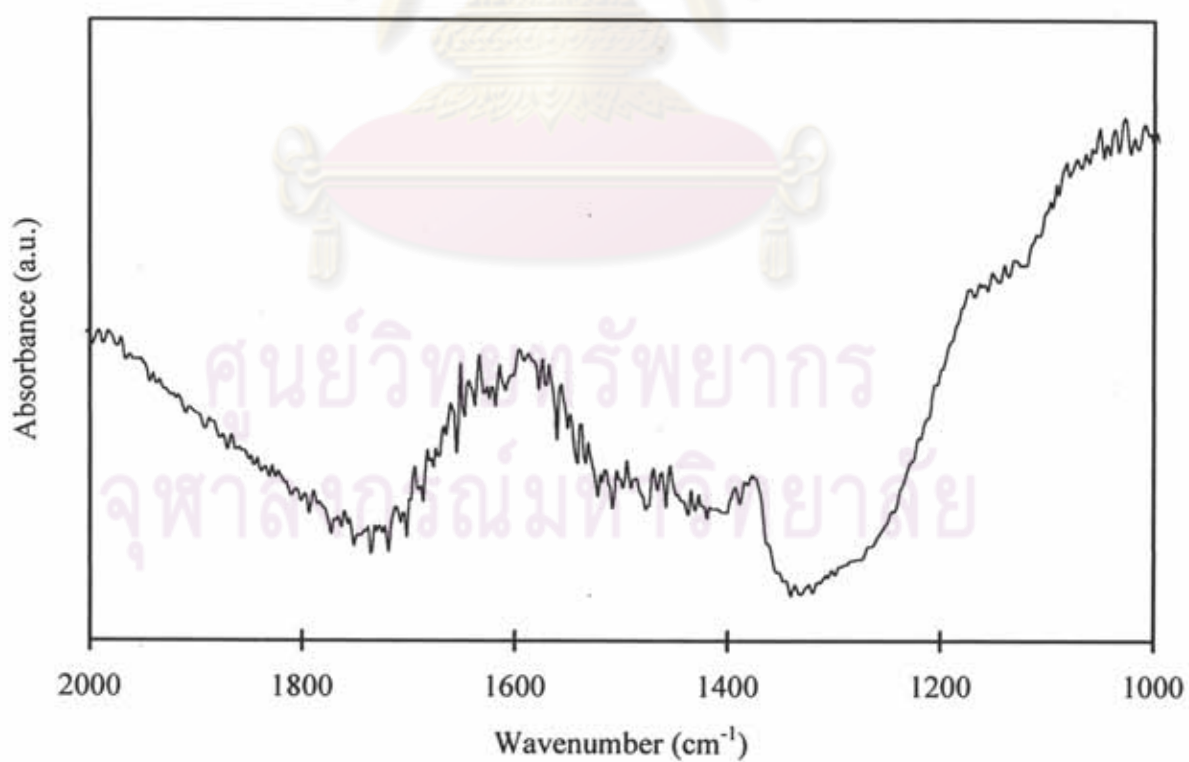


Figure 5.40 IR spectrum of 2 hr.coked catalyst at room temperature in N₂ atmosphere

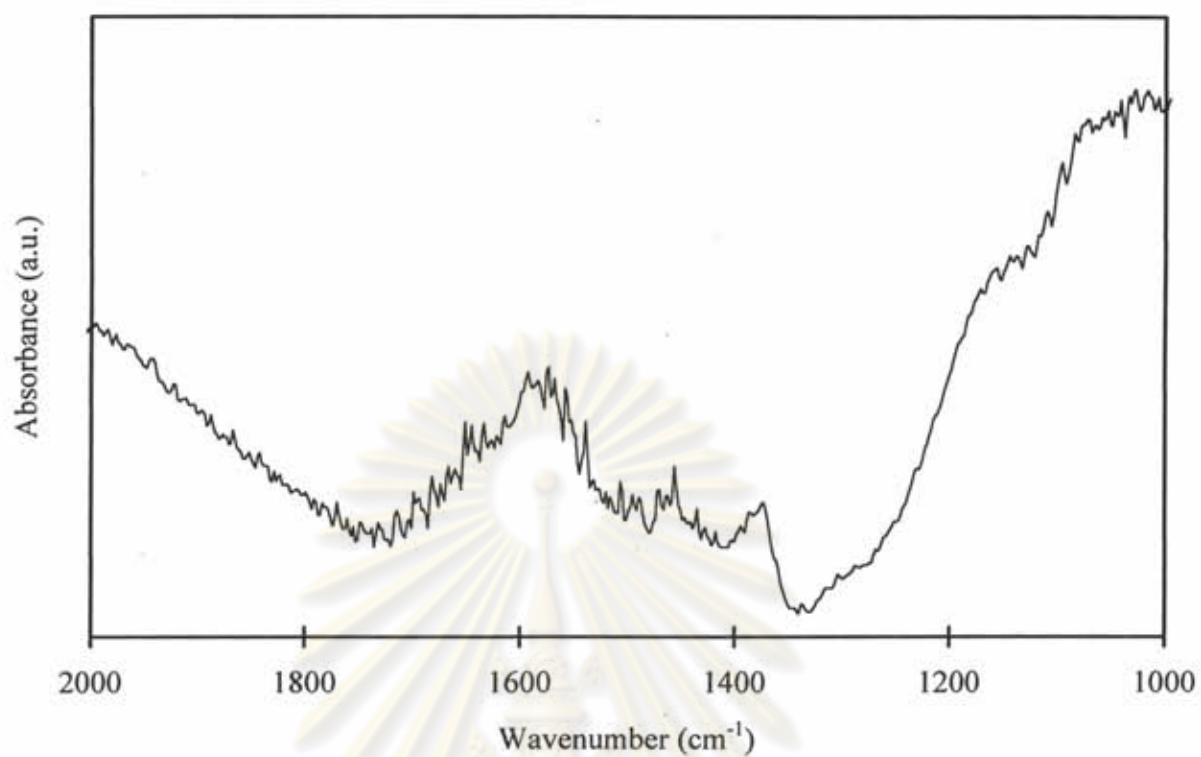


Figure 5.41 IR spectrum of 2 hr.coked catalyst at 100°C in N₂ atmosphere

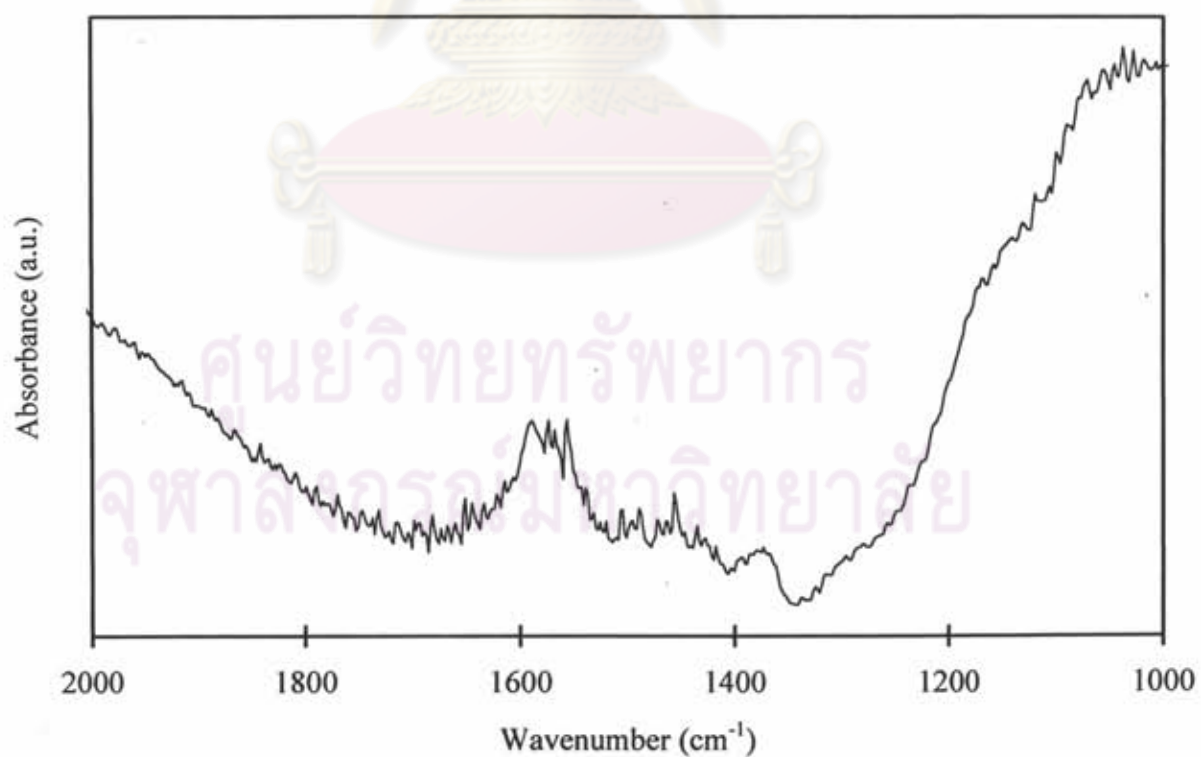


Figure 5.42 IR spectrum of 2 hr.coked catalyst at 200°C in N₂ atmosphere

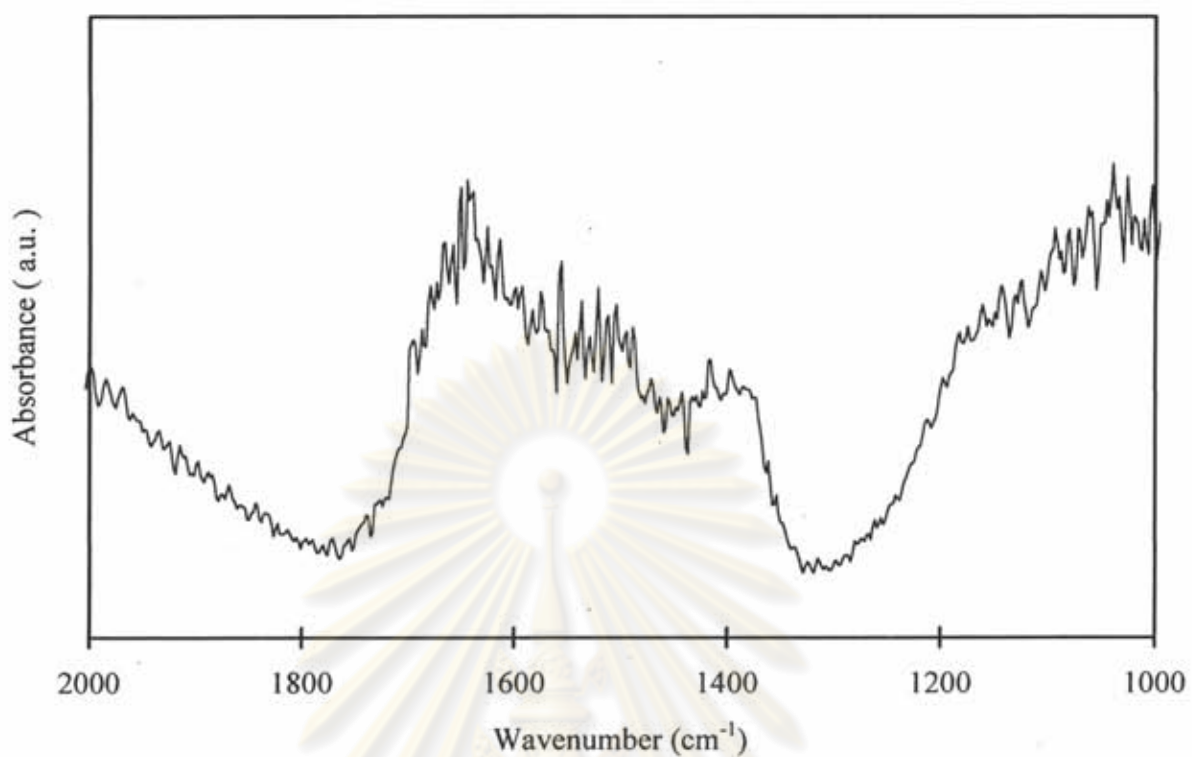


Figure 5.43 IR spectrum of 4 hr.coked catalyst at room temperature in ambient air

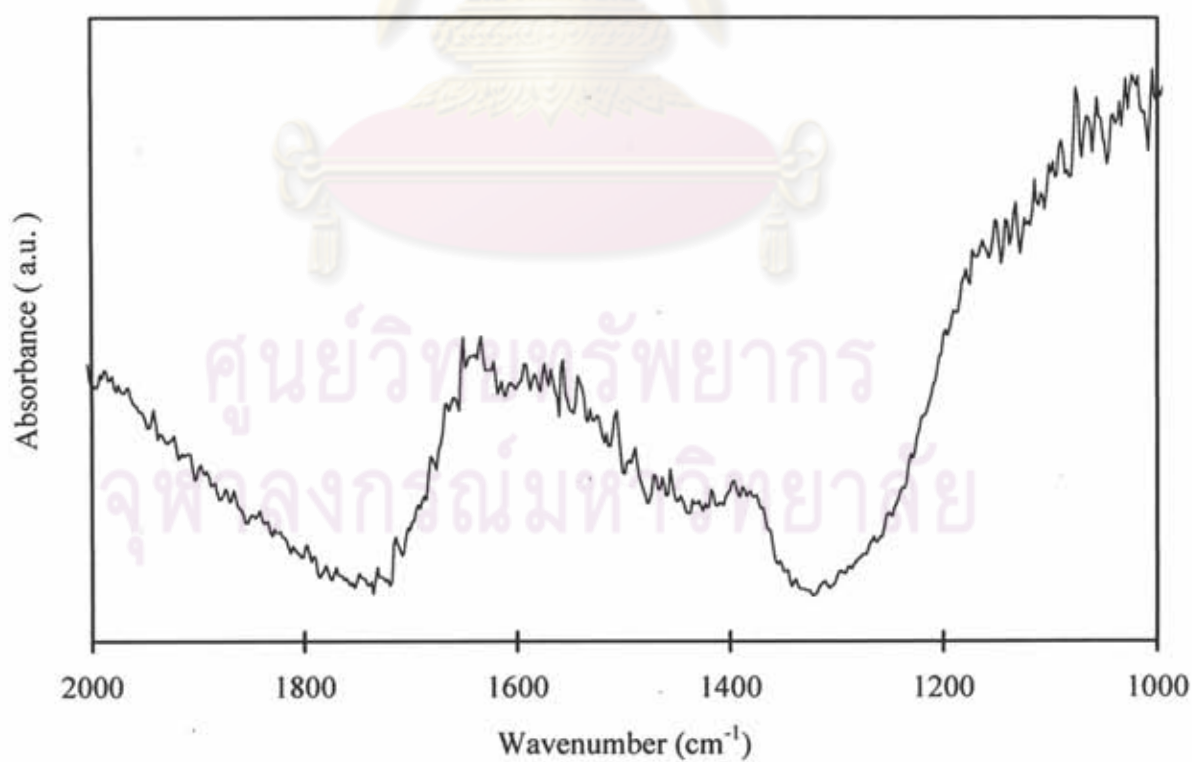


Figure 5.44 IR spectrum of 4 hr.coked catalyst at room temperature in N₂ atmosphere

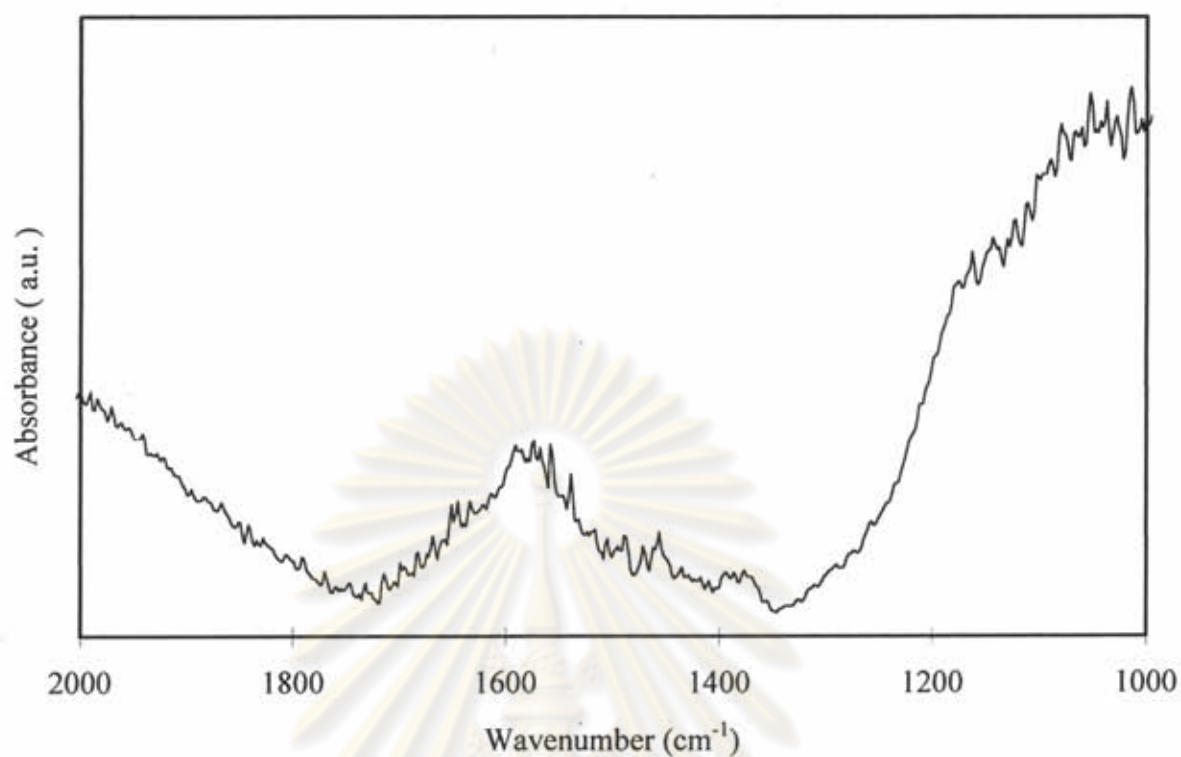


Figure 5.45 IR spectrum of 4 hr.coked catalyst at 100°C in N₂ atmosphere

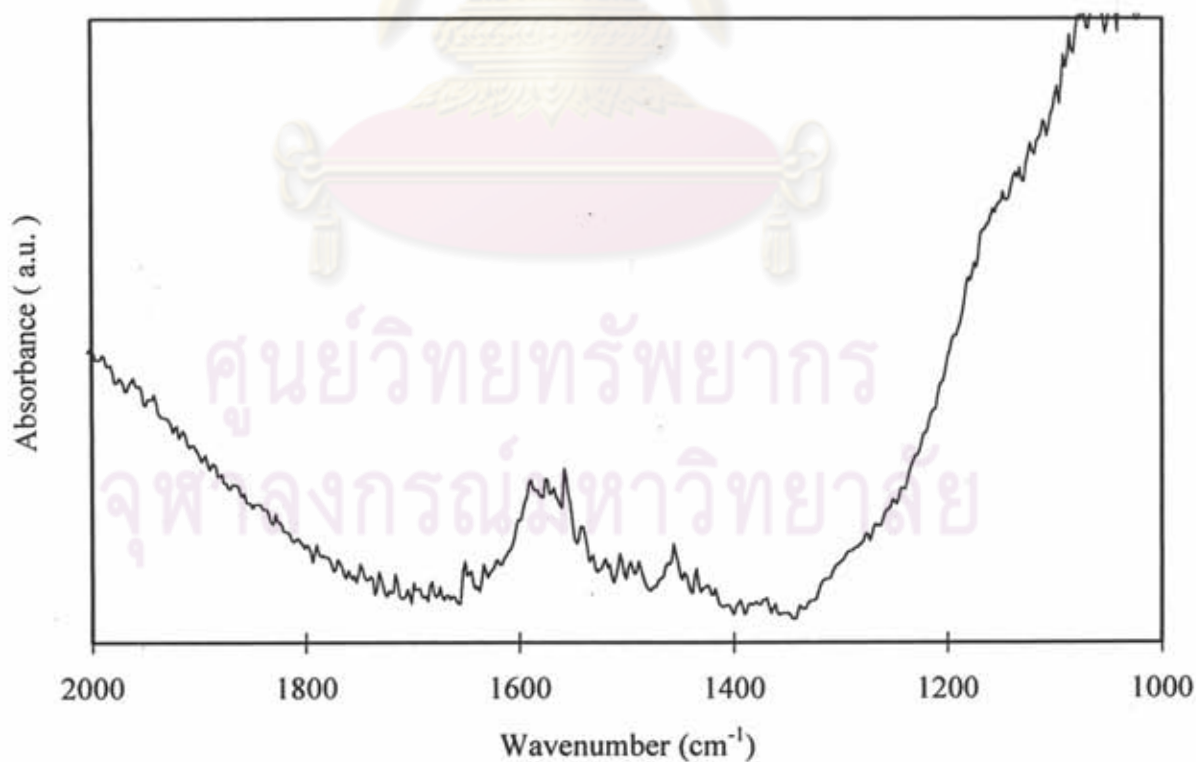


Figure 5.46 IR spectrum of 4 hr.coked catalyst at 200°C in N₂ atmosphere