CHAPTER V

RESULTS AND DISCUSSIONS

In this research, new catalysts, Co,Al-silicate compound group, were prepared and their activity on selective NO reduction with CH_4 in the presence of excess oxygen were investigated and compared to those of Co/ZSM-5s, recently interesting more active catalysts for the same reaction. For the first, characterization of the prepared catalysts were performed to confirm the MFI structure. Second, catalytic reduction activity of Co ion-exchanged ZSM-5 and Co,Al-silicate catalysts on NO removal by CH_4 in an oxidizing atmosphere were examined. And next, comparison of Co-ion exchanged ZSM-5, and Co,Al-silicate catalysts on catalytic activity for NO reduction with CH_4 under an oxidizing condition were conducted. In addition, the change of activity due to the effect of SO_2 on the same reaction and characterization of these catalysts were also measured and determined to show the nature that modifies NO catalytic reduction. Finally, Co-ion exchange Co,Al-silicate catalysts were studied as the same way.

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5.1 Characterization of the catalysts

The prepared Co ion-exchanged ZSM-5, Co,Al-silicate and Co ion-exchanged Co,Al-silicate catalysts were determined the metal content by Atomic Absorption Spectroscopy technique. The parent ZSM-5 and Co,Al-silicate were characterized by XRD patterns and morphology.

5.1.1 X-Ray Diffraction Patterns

The X-ray diffraction patterns for the ZSM-5 structure is shown in Figure 5.1 and used as reference. The XRD pattern of the MFI (ZSM-5) zeolite, prepared in this laboratory is also shown in Figure 5.2 and well corresponding to that reported in the literatures [43.67,68]. This indicated that the prepared MFI catalyst has the same structure as that of the reference. Figures 5.2-5.6 display the XRD patterns of a series of Co,Al-silicate with amount of cobalt vary from 0.32-3.83 wt.%. Again, their patterns of prepared Co,Al-silicates as described in chapter IV agreed with the reference pattern. It indicates that a small amount of cobalt incorporated into the MFI framework does not significantly change the main structure of zeolite.

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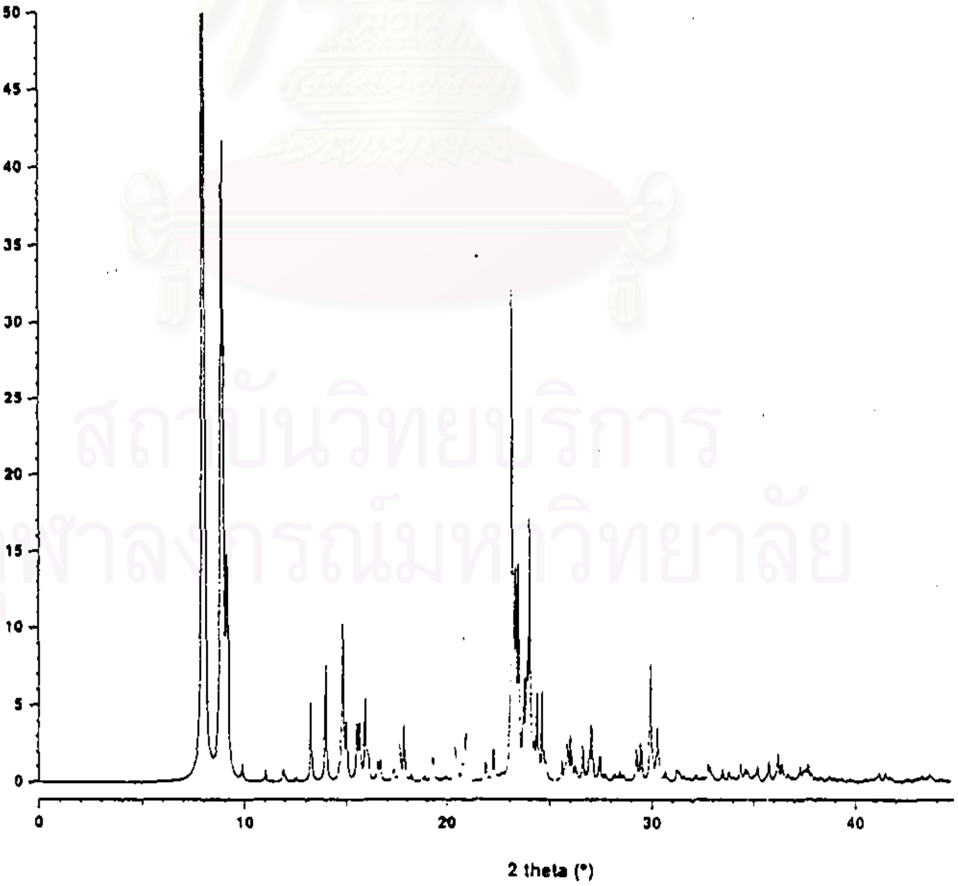

Figure 5.1 X-ray diffraction pattern of ZSM-5 [68]

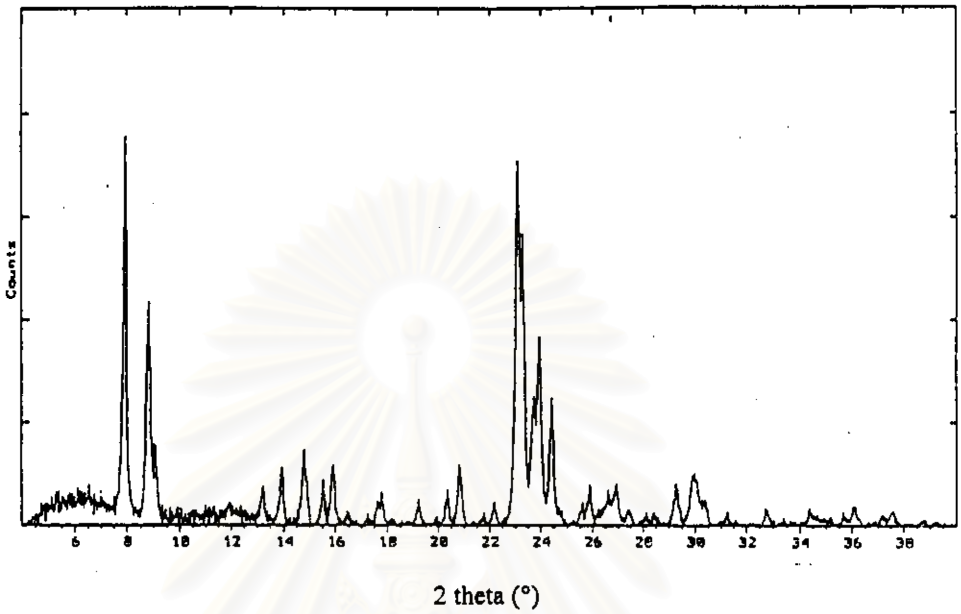

Figure 5.2 X-ray diffraction pattern of prepared ZSM-5

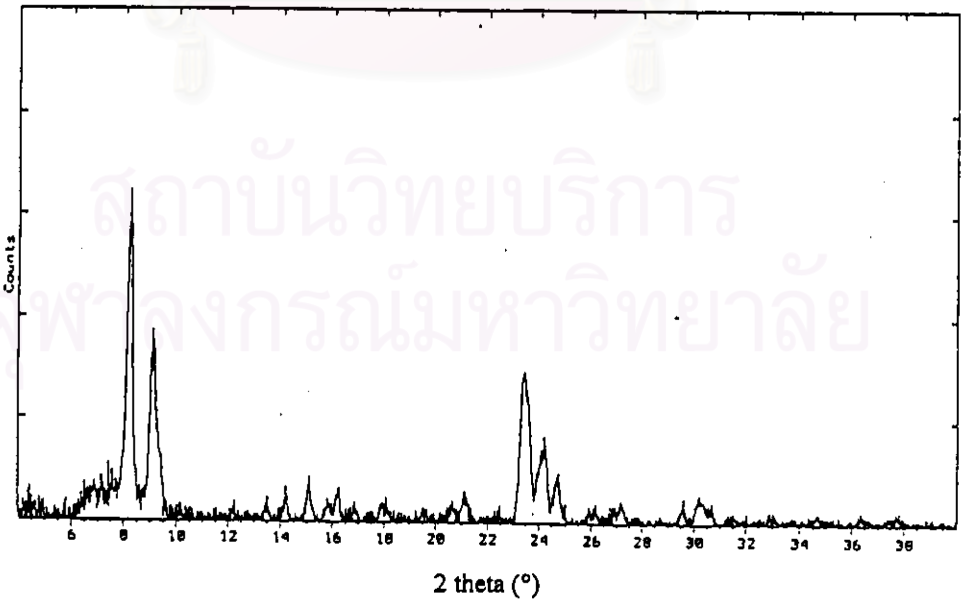

Figure 5.3 X-ray diffraction pattern of prepared Co,Al-silicate (0.32 wt.% Co)

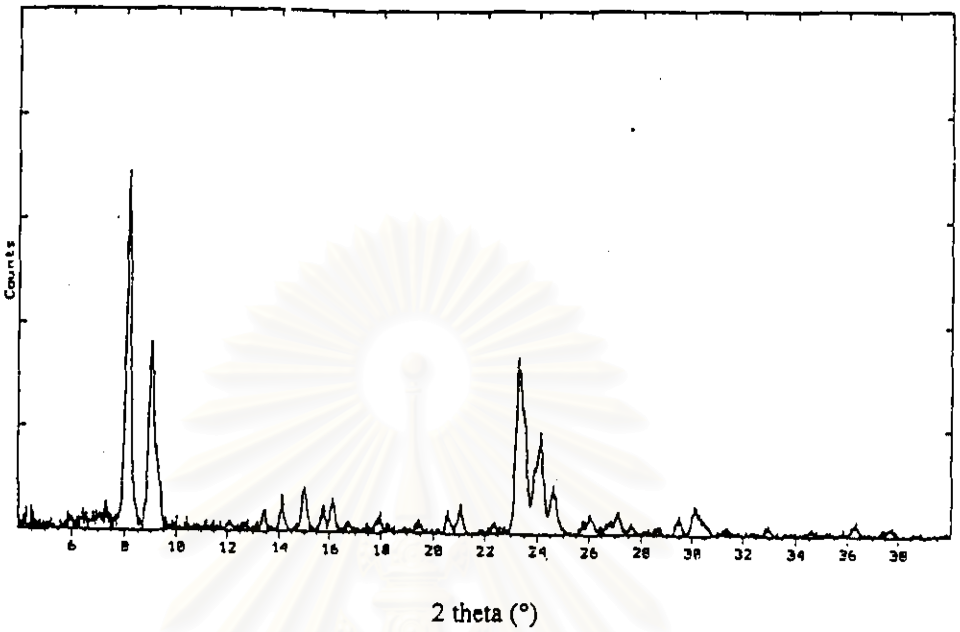

Figure 5.4 X-ray diffraction pattern of prepared Co,Al-silicate (0.98 wt.% Co)

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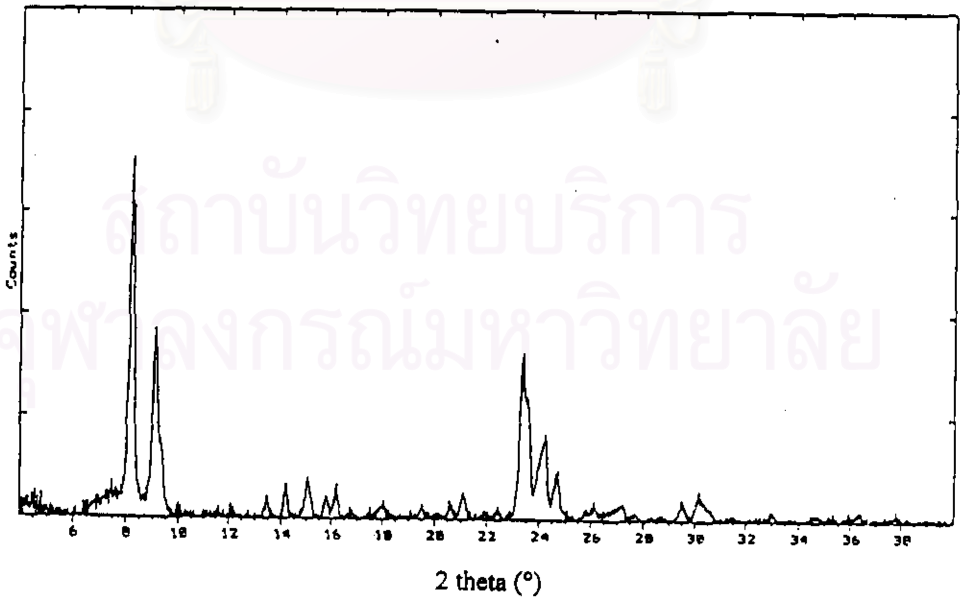

Figure 5.5 X-ray diffraction pattern of prepared Co,Al-silicate (1.99 wt.% Co)

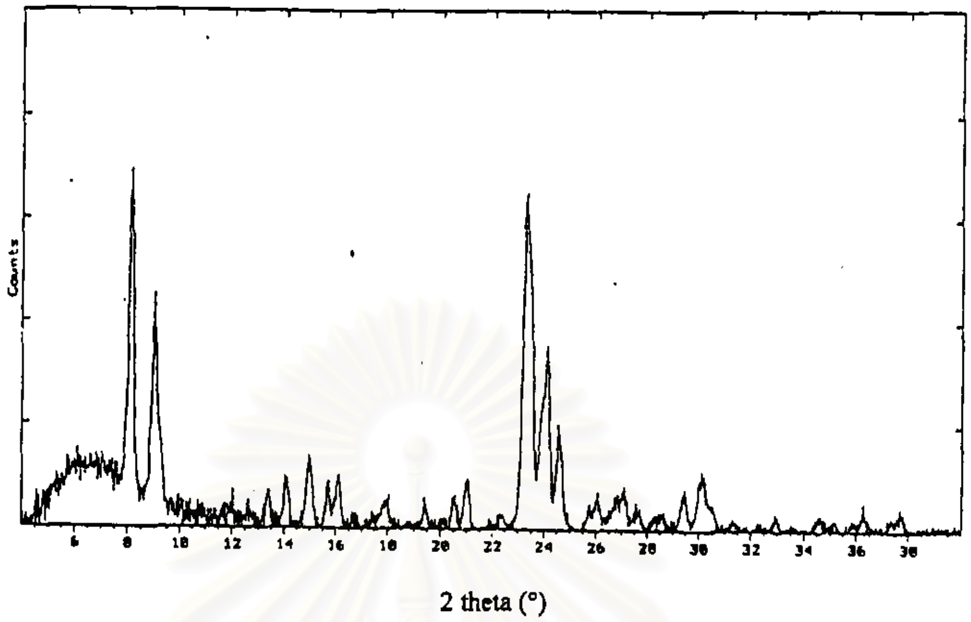

Figure 5.6 X-ray diffraction pattern of prepared Co,Al-silicate (3.83 wt.% Co)

5.1.2 Morphology

Scanning Electron Microscopy (SEM) photographs of the prepared catalysts are shown in Figures 5.7-5.11. As shown, the shape of all catalysts are roughly crystallized spherical particles which are composed of many small regular plates. It was observed that cobalt incorporation does not greatly alter the shape of crystals. And it has no obvious evidence that metal adding into the framework influences the size of zeolite. However, the as-synthesized H-Co-silicate, having MFI structure, prepared by Inui et al. [41] according to the rapid crystallization method, showed an uniform crystallite shape and sizes of about 5 μm but in this study, all catalysts prepared using the same method as above have average size diameter of 8 μm. The difference in size diameter may be occur from the different apparatus used.

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Figure 5.7 SEM photograph (x 10000) of prepared ZSM-5

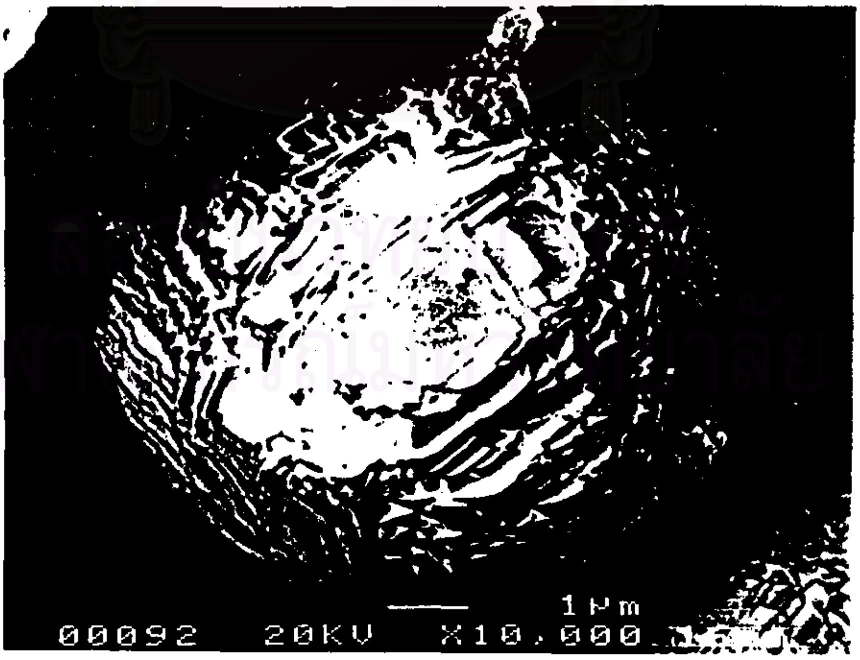

Figure 5.8 SEM photograph (x 10000) of prepared Co,Al-silicate (0.32 wt.% Co)

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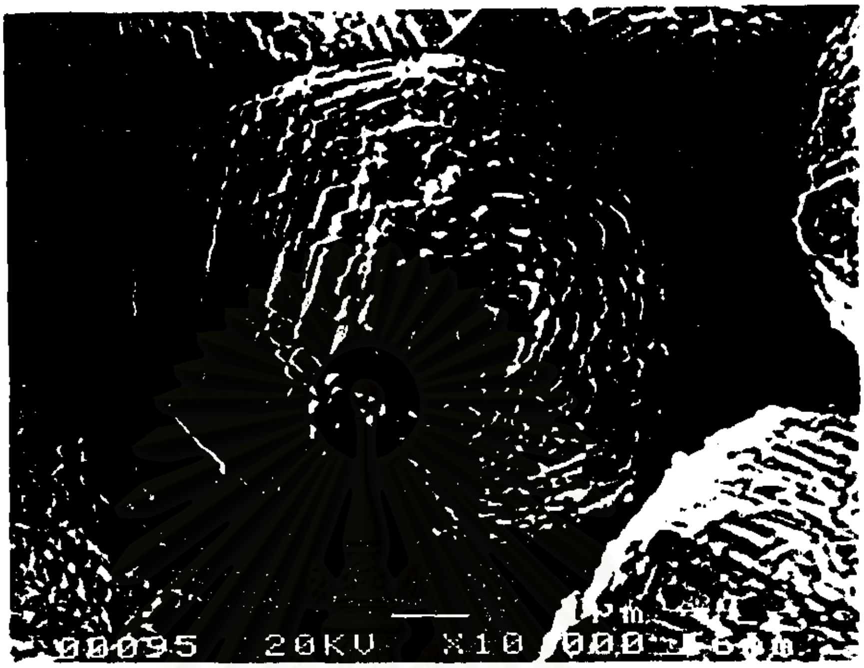

Figure 5.9 SEM photograph (x 10000) of prepared Co,Al-silicate (0.98 wt.% Co)

Figure 5.10 SEM photograph (x 10000) of prepared Co,Al-silicate (1.99 wt.% Co)

Figure 5.11 SEM photograph (x 10000) of prepared Co,Al-silicate (3.83 wt.% Co)

5.2 The effect of cobalt loading by ion-exchange on ZSM-5 catalysts in selective reduction of NO by methane in the presence of an excess oxygen

5.2.1 Co/Na-ZSM-5

Recently Co/ZSM-5 was described as one of the more active catalysts for the reduction of NO with CH_4, and the presence of oxygen greatly enhanced the catalytic activity [2]. Because oxygen is essential to the NO reduction, the stoichiometry of this reaction can be expressed by reaction 5.1. In addition, CH_4 combustion also occurs (reaction 5.2). These two reactions compete for use of CH_4 [3].

$$2\,NO + CH_4 + O_2 \rightarrow N_2 + CO_2 + 2\,H_2O \qquad (5.1)$$

$$CH_4 + 2\,O_2 \rightarrow CO_2 + 2\,H_2O \qquad (5.2)$$

The temperature dependencies of NO and CH_4 conversions were studied on a series of Co/Na-ZSM-5 catalysts. Figure 5.12 shows the temperature dependency of NO to N_2 conversion activity on Co/Na-ZSM-5 by a variety of Co content (1.02 – 3.94 wt.%). For all catalysts, the conversion increases with reaction temperature, but the conversion curve bends down at T > ca. 400 °C. The optimum temperature is dependent on the cobalt content; increasing amount of Co-ion exchanged into MFI framework leads to higher NO conversion activity, in agreement with data of Li and Armor [3], and also broadens temperature window range for both high temperature side and low temperature side. However, this effect conducts to some limit value of cobalt content. As shown in Figure 5.12, the profile of Co/Na-ZSM-5 with 3.94 wt.% Co content exhibits lower activity and narrower reaction temperature window than that of Co/Na-ZSM-5 with 2.53 wt.% Co content. It is noteworthy that, amount of cobalt increased by ion-exchanging Na-ZSM-5 several times enhances the SCR activity of NO by CH_4 and broadens the effective reaction temperature window to the lower range but, conversely, excess cobalt content widens that activity to higher temperature range. However, nitric oxide conversions with methane over Co/Na-ZSM-5 in this study are slightly higher than that reported by Li and Armor [3] with broader reaction temperature window. These differences may be due simply to the lower space velocity used in this work or may be associated with differences in the metal loading, zeolite preparation or the different experimental conditions used [23].

Temperature effect on CH_4 conversion over Co/Na-ZSM-5 catalysts which were varied the amount of cobalt by more time ion-exchange addition does not be

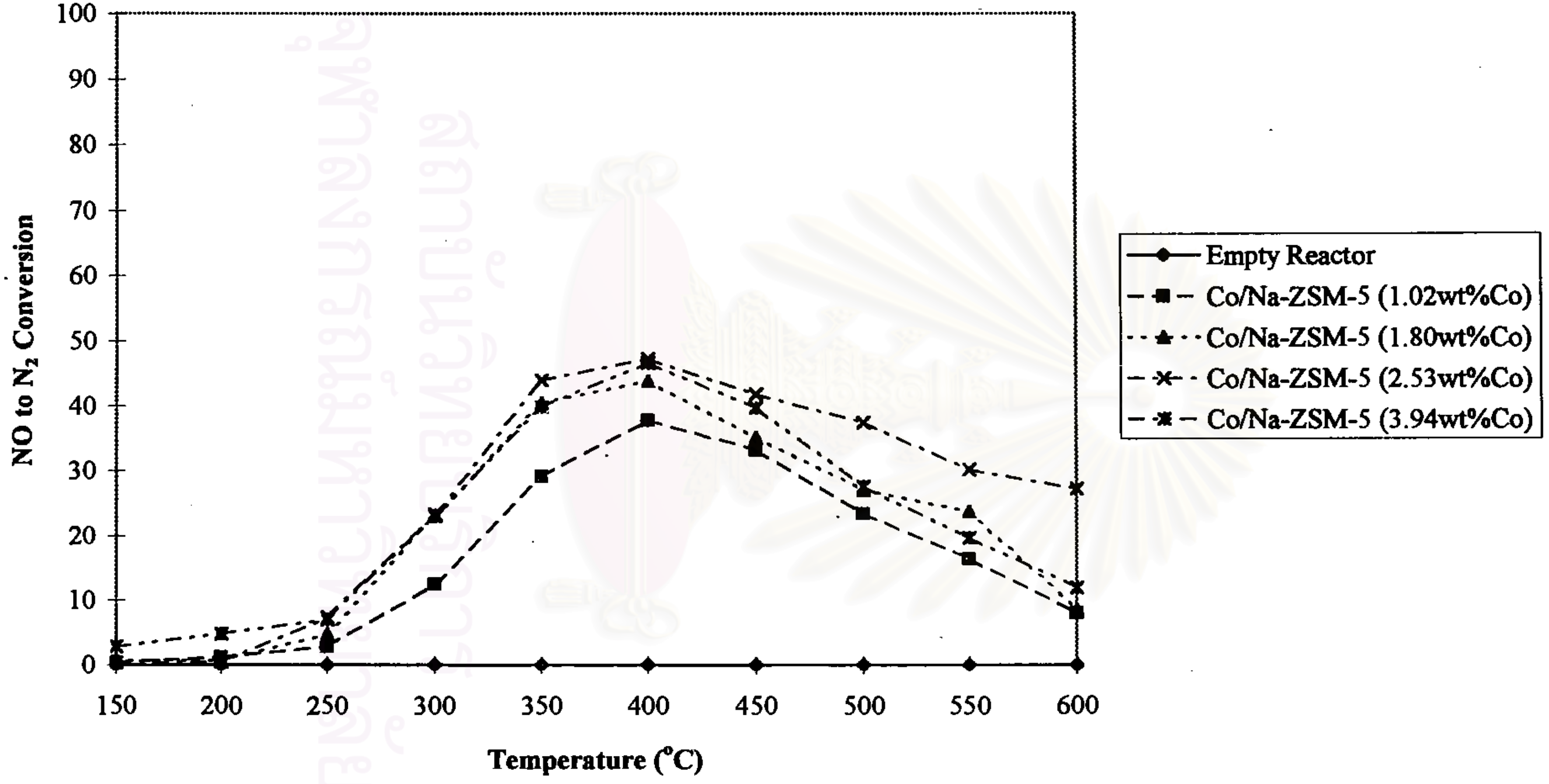

Figure 5.12 Nitric oxide conversion as a function of temperature and cobalt content on Co/Na-ZSM-5 and Empty reactor $[NO] = 1000$ ppm, $[CH_4] = 10000$ ppm, $[O_2] = 10$ %, GHSV = 4000 h^{-1}

similar to that of NO conversion. Figure 5.13 shows the activity of Co/Na-ZSM-5 for methane conversion as a function of reaction temperature. As shown, amount of CH_4 conversion gradually increases at ca. 250 °C and reach 100% conversion at 500 °C. The difference in cobalt content in ZSM-5 does not significantly distinguish CH_4 conversion curve from each other, in the other word, the CH_4 conversion does not show to be a function of cobalt concentration, but can assume that quantity of cobalt may have an affect on CH_4 conversion up to a limit, by that, CH_4 conversion profiles of Co/Na-ZSM-5 which have cobalt content in range of 1.80 – 3.94 wt.% seem to have the same change and have higher activity than that of Co/Na-ZSM-5 which has lower amount of Co (1.02 wt.%).

At low temperature (< 400 °C), methane selectively reacts with NO more than oxygen, thus NO conversion continuously increases. However, at high temperature (> 400 °C) the oxidation of CH_4 by oxygen begins to dominate the oxidation by NO [3,30,36]. This phenomenon decreases NO conversion, while conversion of CH_4 rapidly increases and reaches 100% conversion at 500 °C. For higher temperature, almost CH_4 in the feed reacts with oxygen and leaves only a small portion to react with NO [30,36]. It is known that the NO reduction rate is proportional to the level of methane in the feed [2]. The bending over of NO conversion at higher temperature may be the result of significant lower partial presence of methane in the reactor [3].

Figures 5.12 and 5.13 also show the reaction conversion in empty reactor (Homogeneous reaction). As seen, in the absence of a catalyst, N_2 formation was not observed although the combustion of methane could occur even at higher temperature. It indicated that a catalyst is necessary for the formation of N_2. The result is similar to that observed by Lukyanov et al. [28,36].

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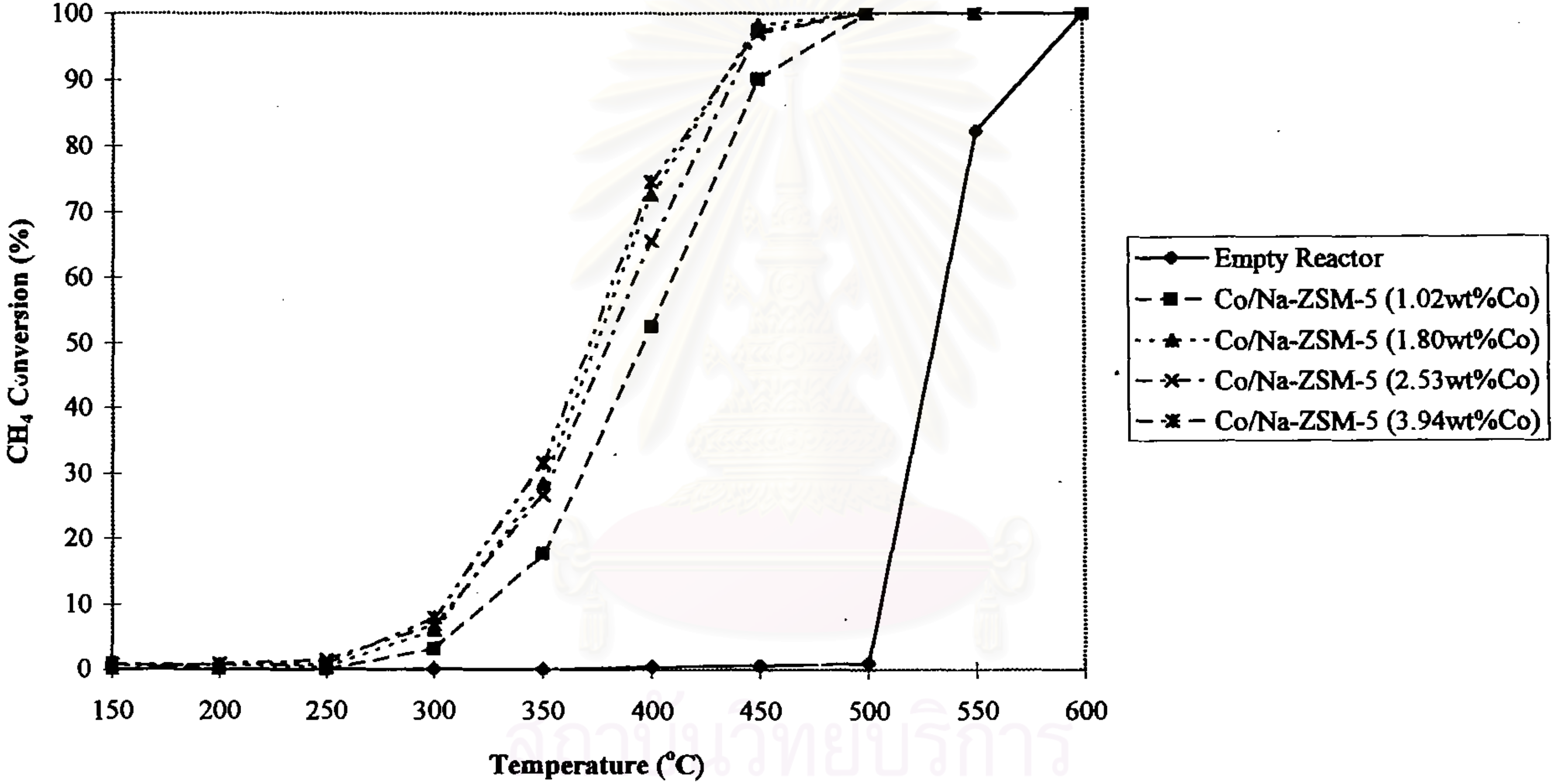

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Figure 5.13 Methane conversion as a function of temperature and cobalt content on Co/Na-ZSM-5 and Empty reactor $[NO] = 1000$ ppm, $[CH_4] = 10000$ ppm, $[O_2] = 10$ %, GHSV = 4000 h^{-1}

5.2.2 Co/H-ZSM-5

Since H-ZSM-5 has moderate activity for the selective catalytic reduction of NO by CH_4 [3] while Na-ZSM-5 is inactive in this reaction [2,3,32,36], expectably, metal ion-exchange into H-ZSM-5 should improve its activity, similarly to Na-ZSM-5 when the metal is cobalt (Co).

Figure 5.14 reveals the results of the reduction of NO over four Co/H-ZSM-5 catalysts having different cobalt concentrations. In general, the temperature dependence of the NO conversion takes a volcanic shape [33] viz. the conversion of NO increases with temperature up to the maximum reach, beyond which it declines with further increasing temperature. The same tendency was also reported on Co/Na-ZSM-5.

Amount of cobalt ion-exchanged into H-ZSM-5 about 1 wt.% can improve NO conversion activity and broaden reaction temperature window range, after more increase the quantity of cobalt into H-ZSM-5 by twice and three times ion-exchange, activity of NO conversion display the tend that increases with cobalt concentration, being close to the result obtained by Campa et al.[32] but the activity at higher temperature declines.

Follows the similar trend of Co/Na-ZSM-5, Co content enhances activity of NO conversion on Co/H-ZSM-5 up to limit value. Excess amount of cobalt appears to suppress activity for NO removal of catalysts, may be due to the formation of cobalt oxide which is known to be active in methane oxidation [32] result in decrease of methane concentration in the system, however, the maximum conversion temperature in this case does not change.

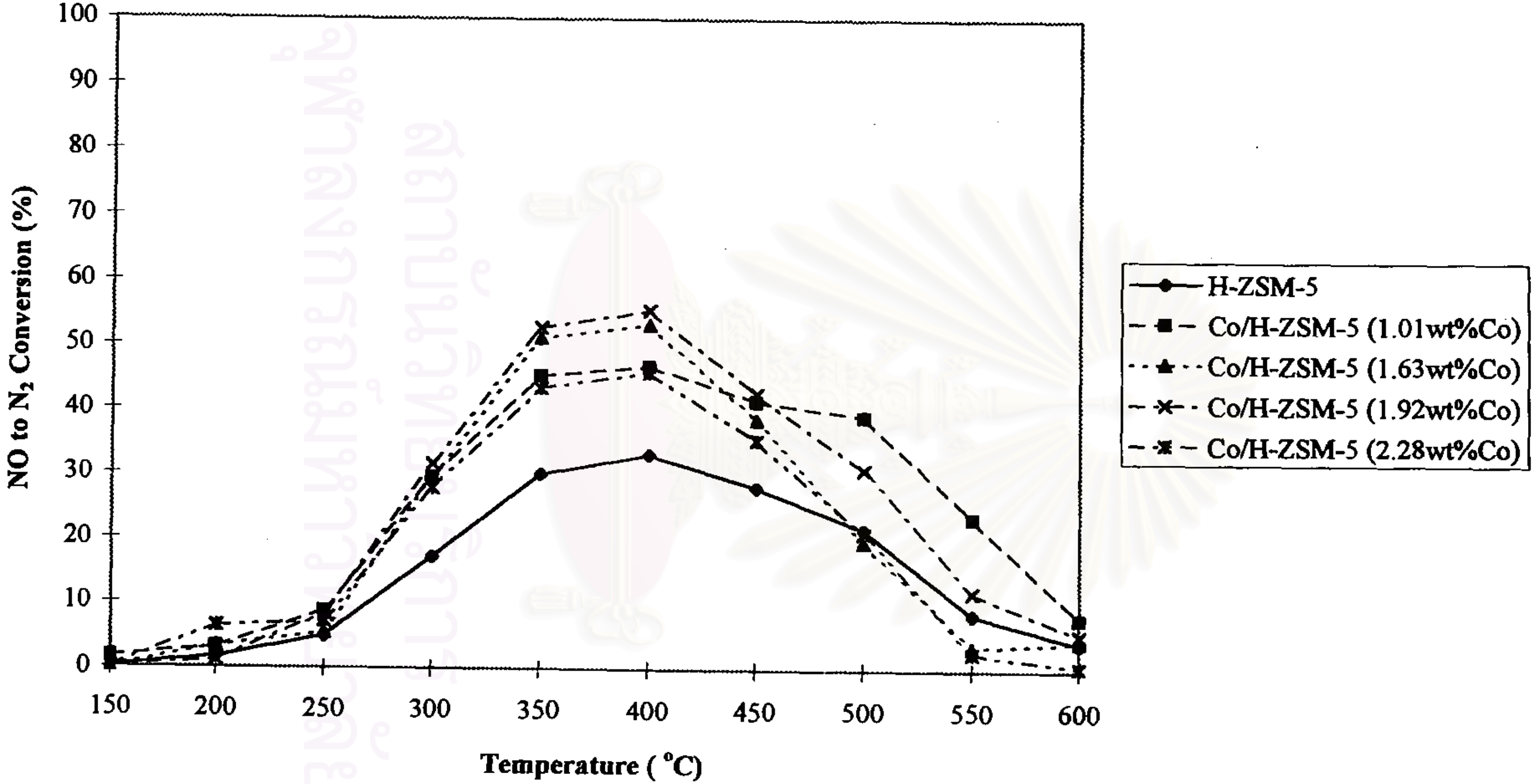

Figure 5.14 Nitric oxide conversion as a function of temperature and cobalt content on H-ZSM-5 and Co/H-ZSM-5 catalysts. [NO] = 1000 ppm, [CH_4] = 10000 ppm, [O_2] = 10 %, GHSV = 4000 h^{-1}

Temperature dependence of CH_4 conversion on Co/H-ZSM-5 is depicted in Figure 5.15. CH_4 conversion curve of H-ZSM-5 shows that this catalyst is less active for CH_4 conversion compared to the other Co/H-ZSM-5 catalysts. It is clear that, once cobalt was ion-exchanged into H-ZSM-5, CH_4 conversion sharply increases. However, more amount of cobalt ion-exchange into H-form of MFI type zeolite, a conversion slightly improves. In earlier evaluation, CH_4 conversion in SCR composed of two parallel reaction, i.e., NO reduction by CH_4 and combustion of CH_4 by oxygen, both occur simultaneously during a reaction run but the latter reaction prefers elevated temperature [30,36]. As illustrated in Figure 5.15, for high temperature region, CH_4 conversion curves of almost catalysts except H-ZSM-5 reach 100 % conversion while NO conversion (Figure 5.14) for the same catalyst gradually decreases. As evidenced, almost CH_4 undergo oxidative reaction. This suggests that H-ZSM-5 catalyst which is indicated to have not high activity for oxidation [51], may be less active for CH_4 combustion than Co/H-ZSM-5 catalysts, on the other hand, cobalt cation introduced into ZSM-5 structure by ion-exchanged activated CH_4 combustion. This conclusion is consistent with the reports of Campa et al. [32] and Lukyanov et al. [30,36] which pointed out that H-ZSM-5 is slightly more selective for methane oxidation by NO (SCR reaction) than Co ion-exchanged ZSM-5 but the latter catalyst abates NO for more efficiently than does the pure H-ZSM-5.

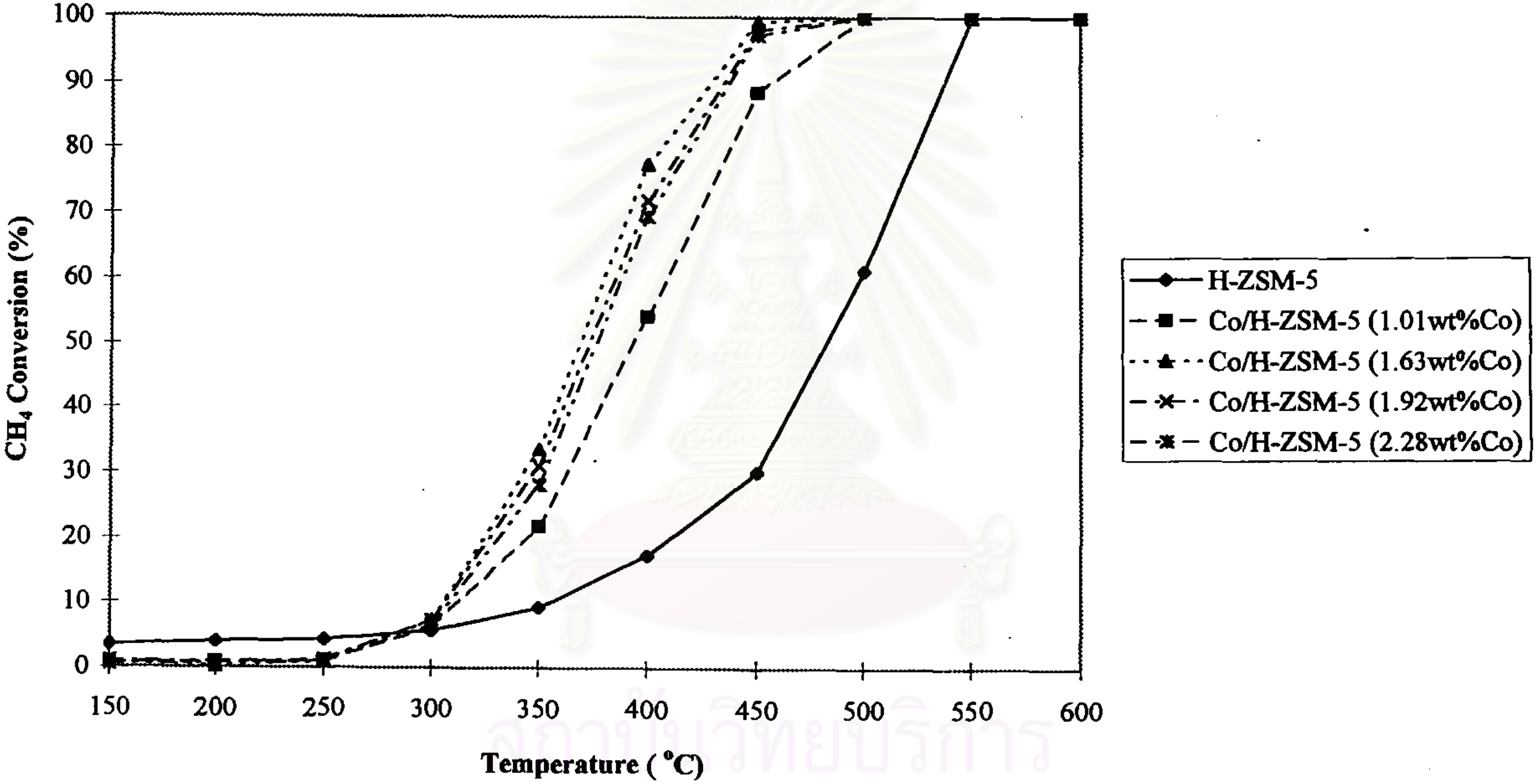

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Figure 5.15 Methane conversion as a function of temperature and cobalt content on H-ZSM-5 and Co/H-ZSM-5 catalysts. [NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

5.3 The effect of cobalt content incorporated into MFI structure of Co,Al-silicate catalysts in selective NO removal with the presence of methane and excess oxygen

5.3.1 Na-Co,Al-silicate

To exhibit the dependencies of MFI structure and metal content on the NO removal in selective catalytic reduction by methane in oxidizing atmosphere, Co,Al-silicate catalysts which have Co incorporated in framework were synthesized using rapid crystalline method developed by Inui [12]. As shown in Figure 5.16, Co,Al-silicates in Na-form have very low activity for NO conversion compared to Co/Na-ZSM-5 (Figure 5.12) even have more amount of cobalt. It is well known that Na-ZSM-5 is not active for SCR of NO by hydrocarbon [2,3,32,36], incorporation of Co into MFI (ZSM-5) structure improve that activity a little and only in high temperature range (> 450 °C).

CH_4 conversion curves of different cobalt concentrations in Na-Co,Al-silicates, as depicted in Figure 5.17 reveal that Na-Co,Al-silicate catalysts are less active for CH_4 conversion, particularly that catalysts with higher Co content. Perhaps, this may be the reason why Na-Co,Al-silicate has little activity for NO conversion. Since C–H bond breaking is the rate determining step [27], if CH_4 can be oxidizing by NO or O_2 at only higher temperature, unquestionably, NO conversion can occur at only higher temperature too. In Figure 5.17, Na-Co,Al-silicate which has 3.83 wt.% Co content, the highest amount of cobalt, shows the lowest CH_4 conversion among another catalysts and exhibits the lowest activity for NO conversion compared to the

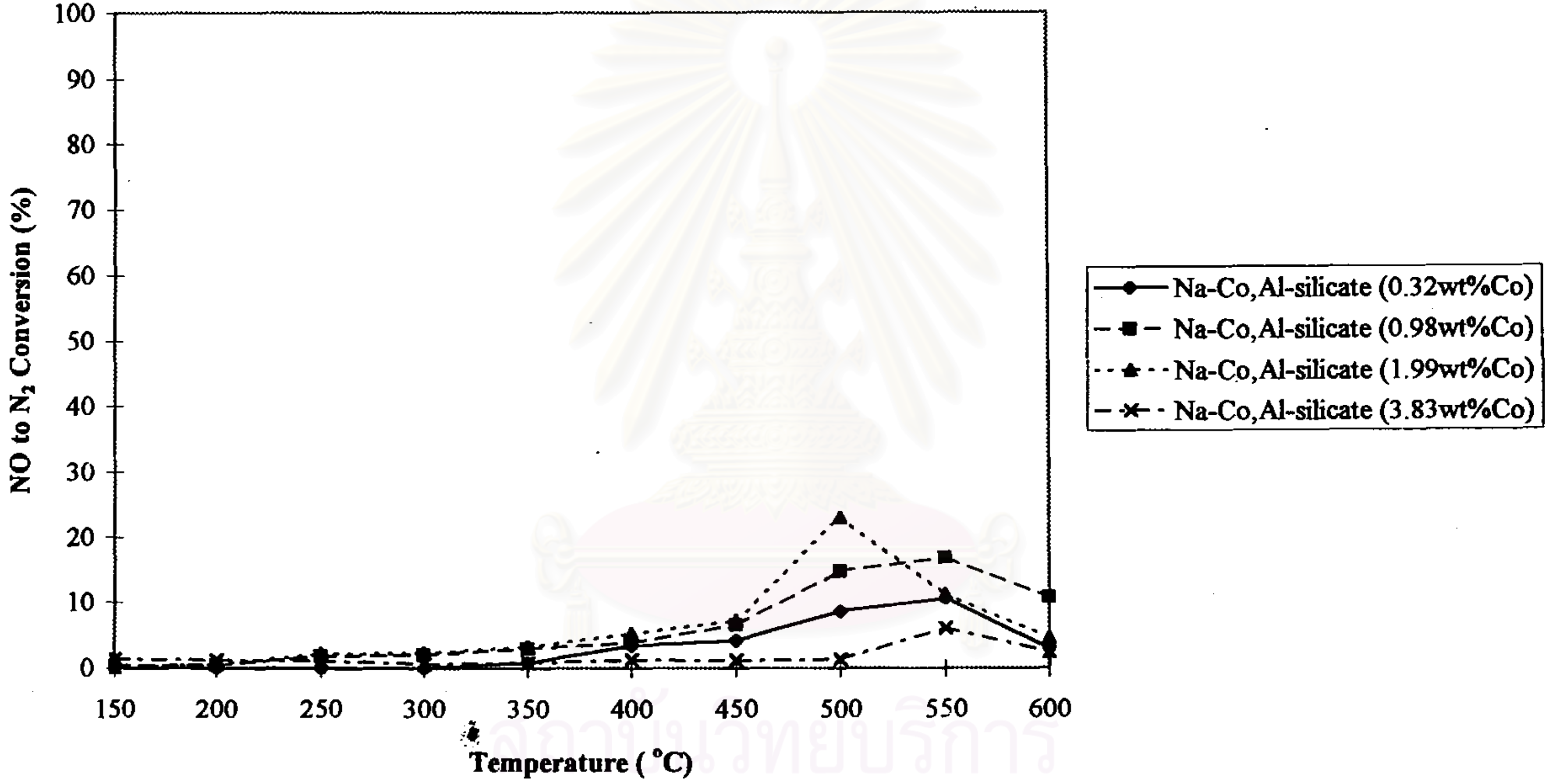

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Figure 5.16 Nitric oxide conversion as a function of temperature and cobalt content on Na-Co,Al-silicate catalysts.
[NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

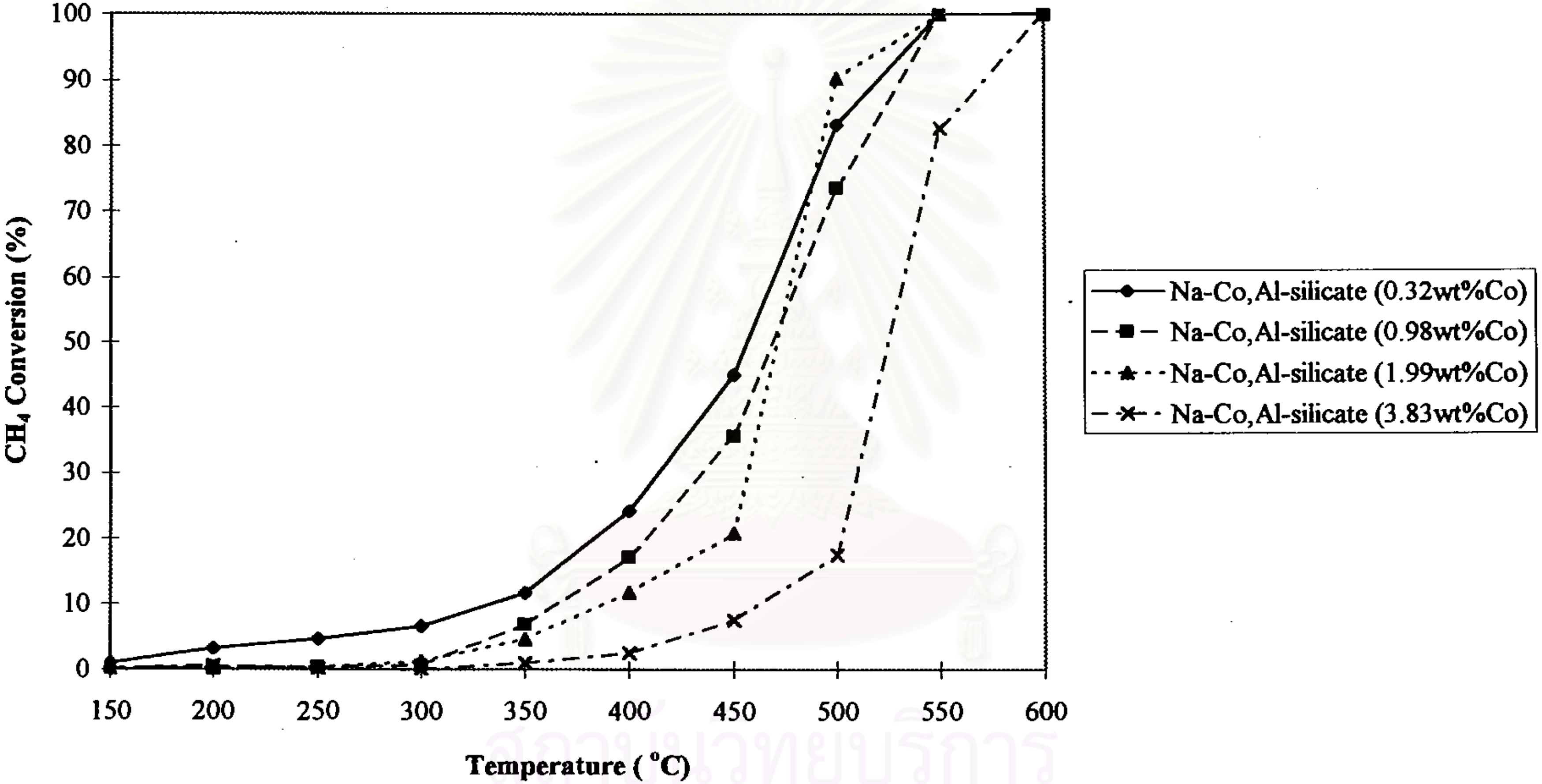

Figure 5.17 Methane conversion as a function of temperature and cobalt content on Na-Co,Al-silicate catalysts. $[NO] = 1000$ ppm, $[CH_4] = 10000$ ppm, $[O_2] = 10$ %, GHSV = 4000 h^{-1}

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other. These results conclusively demonstrates that cobalt incorporated into aluminosilicate, having MFI structure, can hardly activate the conversion of methane and also NO and allows to hypothesize on some aspects that incorporated Co site in Co,Al-silicate is not the active site for reduction or oxidation in SCR reaction, in contrary to Co/Na-ZSM-5 which cobalt cation exchanged site is speculated to be the active center for SCR reaction [31,32,34,50].

5.3.2 H-Co,Al-silicate

Many studies reported that H-ZSM-5 can catalyze NO reduction by CH_4 in excess O_2 with moderate activity [328,30,36]. Figure 5.18 shows NO conversion of H-Co,Al-silicate compared to that of H-ZSM-5. It is evaluated that inputting cobalt into H-form of MFI framework which already has aluminium (Al) and silicon (Si), like the structure and elements composition of H-ZSM-5, by incorporation in stage of gel formation of rapid crystallization method can enhance NO conversion activity.

As demonstrated in Figure 5.18 and 5.19, NO and CH_4 conversion curves are shown as temperature function over H-Co,Al-silicates which Co content is varied from 0.32-3.83 wt.%. The conversion of NO to N_2 and CH_4 to CO_x monotonously increases with the increase in temperature. Likewise to Co/H-ZSM-5, the NO conversion of H-Co,Al-silicate displays a volcano-shape curve as temperature further increases while methane consumption profile continuously increases until reach 100 % conversion at temperature higher than 500 °C. The concentration of cobalt incorporated into MFI-aluminosilicate does contribute to the activity for NO conversion and cause the light off temperature lower when increase in cobalt content

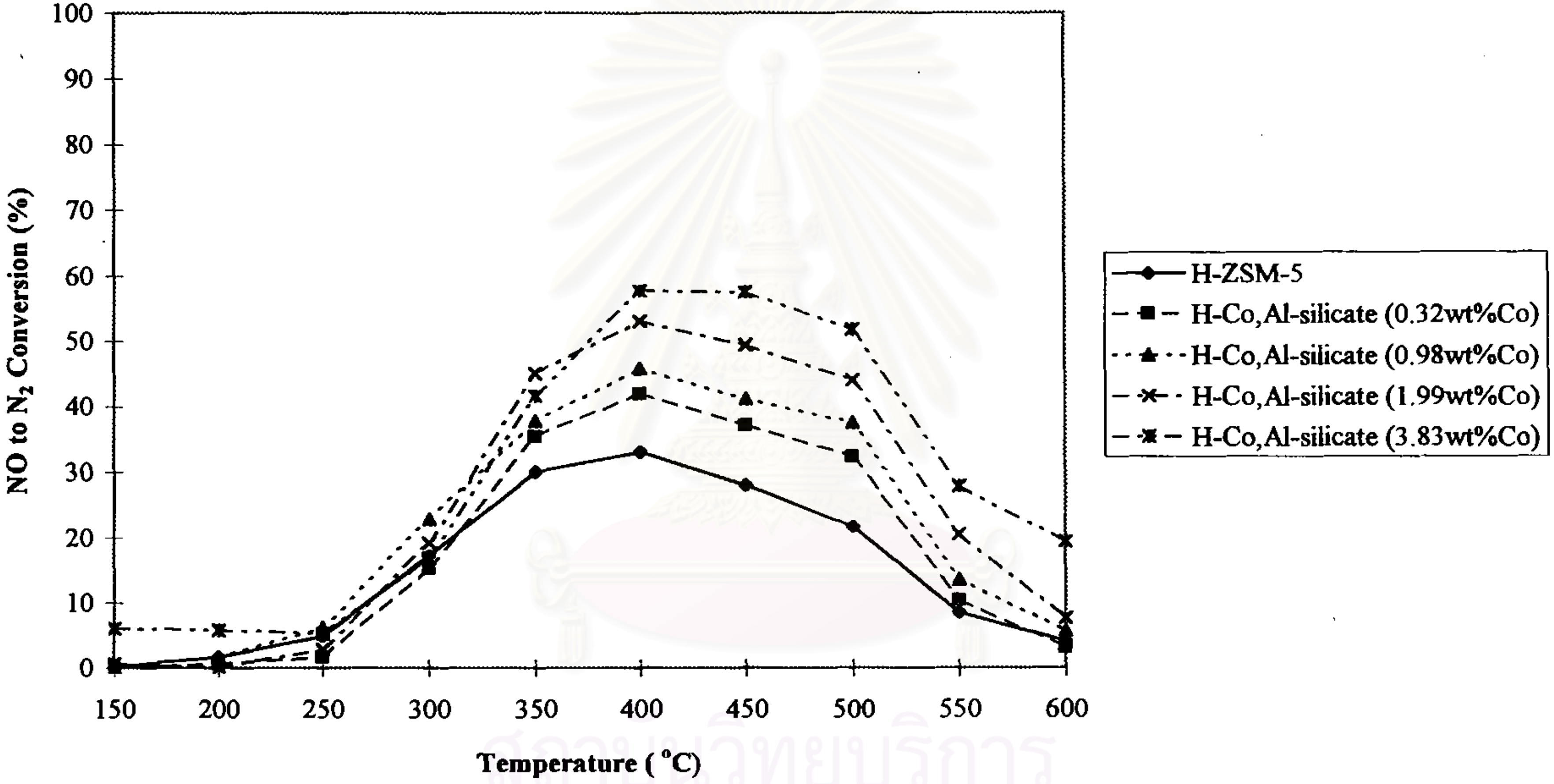

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Figure 5.18 Nitric oxide conversion as a function of temperature and cobalt content on H-ZSM-5 and H-Co,Al-silicate catalysts. [NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

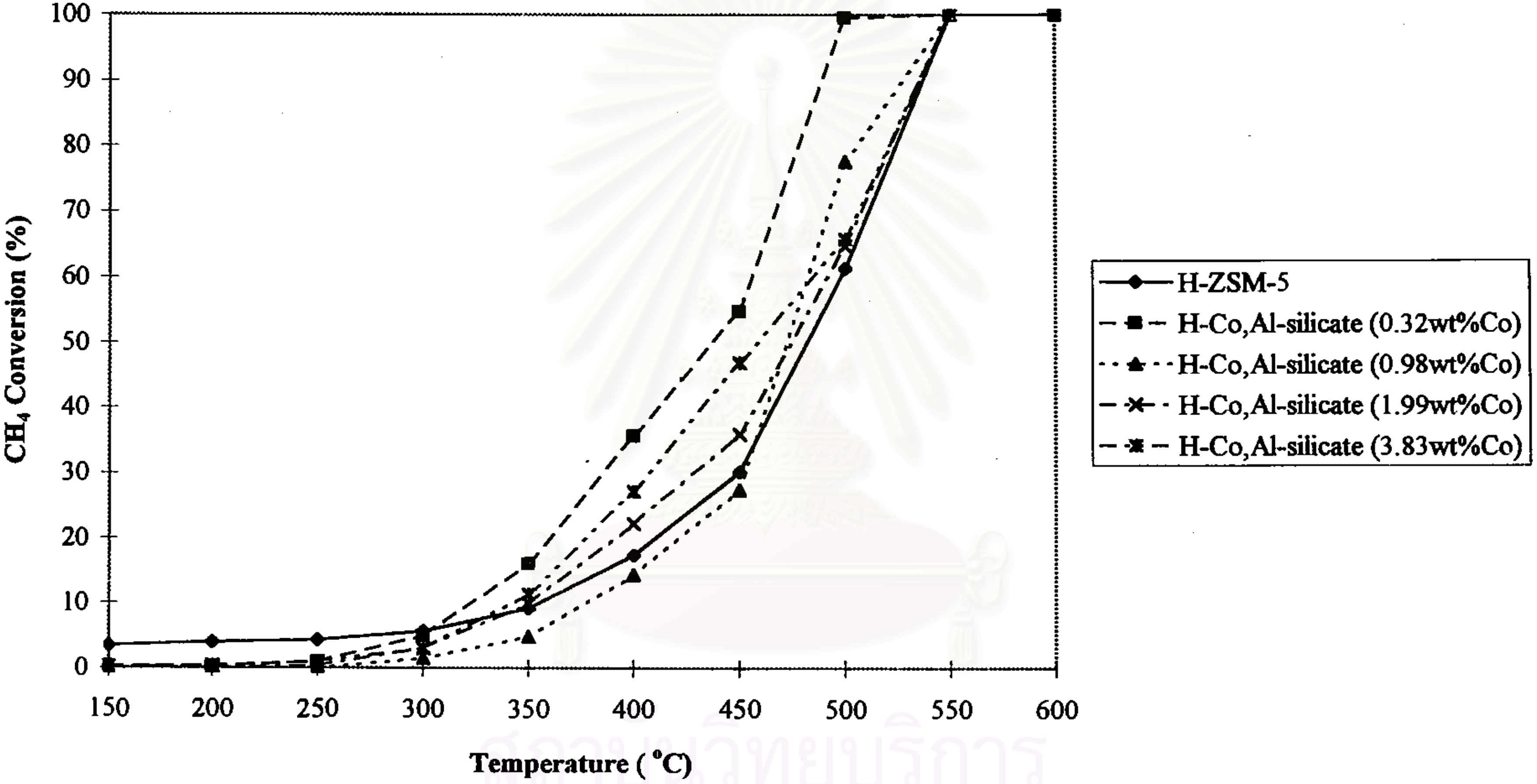

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Figure 5.19 Methane conversion as a function of temperature and cobalt content on H-ZSM-5 and H-Co,Al-silicate catalysts. [NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

into Co,Al-silicate except H-Co,Al-silicate with 3.83 wt.% Co which has higher light off temperature and more maximum conversion than other catalysts that have less amount of cobalt.

NO conversion of H-Co,Al-silicate inclines to increase with Co content, similarity and contrariety to Co/H-ZSM-5. Increasing in activity of Co/H-ZSM-5 for NO removal increases with limit range of cobalt content. According to Li and Armor [3] and Stakheev et al. [33], limit range for Co/H-ZSM-5 is the maximum exchange capacity while NO conversions of H-Co,Al-silicates increase with Co content which no limit is known in this study and widen its reaction temperature window together but only up to some limit of amount of cobalt. Higher than this limit, it shifts reaction temperature window to higher temperature, in the mean time, its NO conversion still increases. Unlike Co/H-ZSM-5, the activity of H-Co,Al-silicate can not be described by the ion-exchange capacity, probable, but may be its acidic property that pitches in NO conversion activity.

Comparison of methane conversion between H-Co,Al-silicate and H-ZSM-5 results that small amount of cobalt incorporated in MFI structure of H-Co,Al-silicate can improve methane conversion but it can not point out that methane conversion increases with Co content in framework, this effect is insignificant related to that of Co/H-ZSM-5. In experiments of Inui et al. [55], they found that the catalytic activity of NO elimination reaction was improved by enhancing *n*-octane combustion on cobalt-oxide clusters dispersed in framework of H-Co-silicate, but it is not clear in this study.

In previous reports [18,19,21], acidic property and redox capacity, in other word, activities for hydrocarbon conversion and hydrocarbon combustion are the characteristic of metallosilicate in catalytic reduction of NO under oxygen excess condition with the addition of hydrocarbon. Al-silicate shows high acidity but low redox property, while Co-silicate exhibits lower acidity but higher redox property [18,19,21], the combination of Al and Co in Co,Al-silicate may display the proper activity for SCR of NO, particularly, when using methane as reductant since methane is difficult to activate due to strong C–H bond [3]. This hypothesis almost coincides with the study of Inui et al. [21] that clarified that the acidic property of catalyst will come to be more significant when the combustion activity of that catalyst is not high enough.

5.4 Comparison of catalytic property between Co ion-exchanged ZSM-5 and Co incorporated MFI type aluminosilicate catalysts

Figure 5.20 shows the effect of Co position in MFI structure for NO conversion. Each catalyst in Figure 5.20 has almost the same amount of Co in bulk volume (about 1 wt.%) but two of those, Na-Co,Al-silicate and H-Co,Al-silicate, have cobalt incorporated in framework while the other, Co/Na-ZSM-5 and Co/H-ZSM-5, have cobalt in cation exchange site of framework. As mention before, Co,Al-silicate in Na-form has low activity for SCR of NO with methane under oxidizing condition, while H-Co,Al-silicate is much more active for the same reaction. Nevertheless, comparison between Co ion-exchanged MFI zeolites in Na-form and H-form, (according to many report (see Chapter II), both Co/H-ZSM-5 and Co/Na-ZSM-5 are active for NO removal by methane in excess oxygen) in this research results that Co ion-exchanged in H-form of ZSM-5 has more activity and broader effective reaction

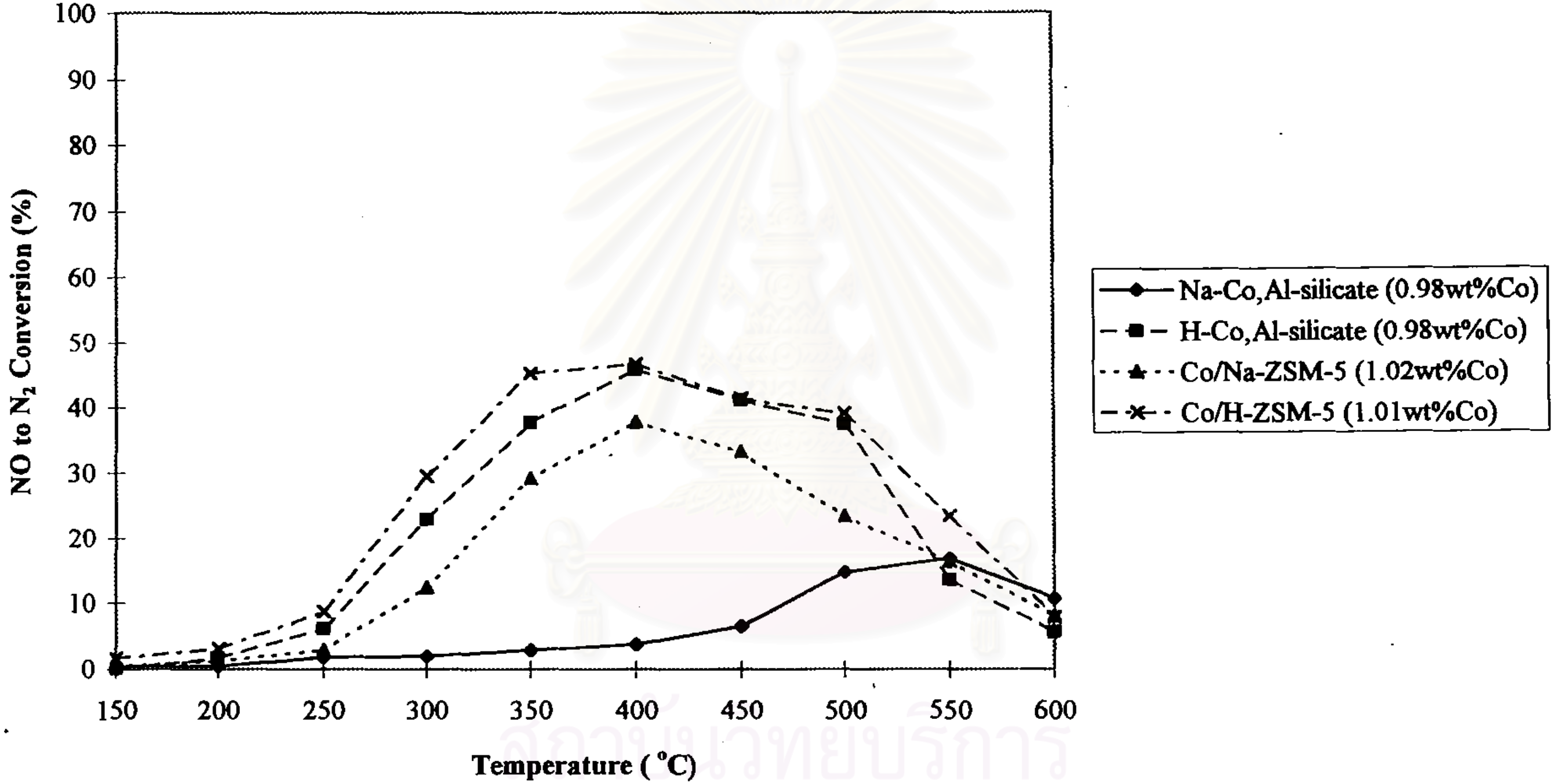

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Figure 5.20 Catalytic comparison of nitric oxide conversion between Co/ZSM-5 and Co,Al-silicate catatysts.
[NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

temperature window for SCR of NO with methane in excess oxygen than those of Co/Na-ZSM-5 when either forms of catalysts have the same quantity of cobalt located at the cation position in MFI structure. This indicates that Brønsted acidity plays the role in SCR process when methane is used as reducing agent. Although this suggestion is contrary to that reported by Campa et al. [32] which points out to both Co/Na-ZSM-5 and Co/H-ZSM-5, having a similar cobalt content have very similar activity, the study in 1997 conducted by Budi et al. [45] believed that the residual Brønsted acid sites may play a role in reducing catalyst performance. For H-Co,Al-silicate, its activity toward SCR is consistent with that of Co/H-ZSM-5 but with a little narrower reaction temperature range, while its Na-form shows, opposite result, very low SCR activity, suggested that Co incorporated in MFI framework may not the active center for SCR reaction, unlike Co ion-exchanged MFI both H-form and Na-form which Co ion sites are postulate to be the active site for NO-SCR [31,32,34,50]. NO reduction activity of H-Co,Al-silicate should come from Brønsted acid site (proton ion-exchanged site) [28,54] as H-ZSM-5 is active for this reaction and incorporation of cobalt may modify acidity or redox property of H-Co,Al-silicate to more suitable state for SCR reaction.

Consider methane conversion over these four catalysts in the same condition, Figure 5.21. Co/ZSM-5 catalysts both Na-form and H-form are more active for methane conversion compared with the other two form of Co,Al-silicate. Interestingly, the result in Figure 5.21 indicates that proton ion at exchanged position has no effect on methane conversion, as evaluated before, cobalt ion-exchanged site in ZSM-5 is responding to methane conversion. Satsuma et al. [44] indicated that acidity of H-form zeolite is the controlling factor in SCR of NO with methane while

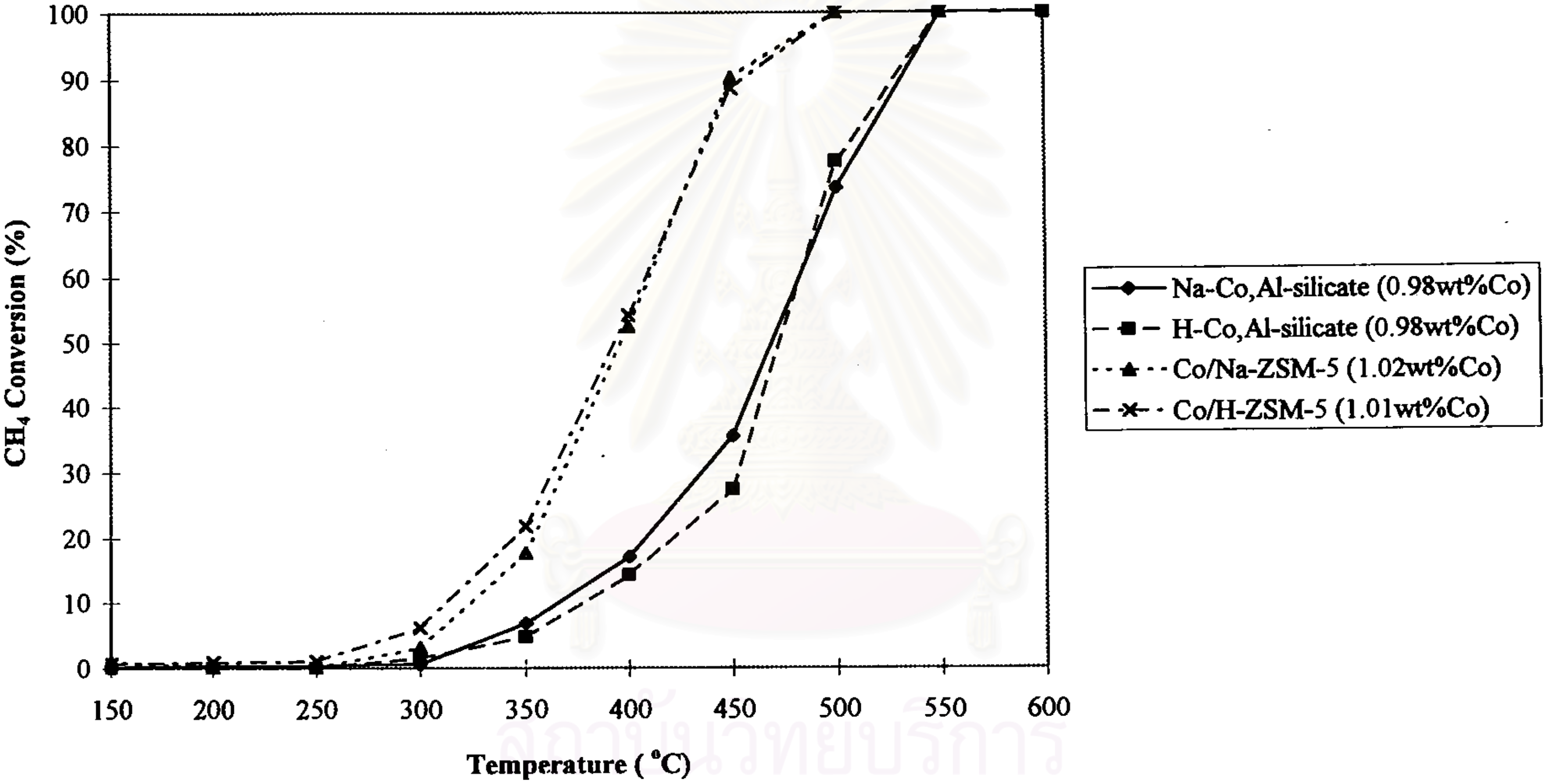

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Figure 5.21 Catalytic comparison of methane conversion between Co/ZSM-5 and Co,Al-silicate catalysts. [NO] = 1000 ppm,[CH_4] = 10000 ppm, [O_2] = 10 %, GHSV = 4000 h^{-1}

Halasz et al. [35] suggested that probably Brønsted acidic bridging hydroxyls of H-ZSM-5 appears to be the active site for all oxidation and reduction on the catalyst. In case of bimetallosilicate, both aluminium and cobalt has its own acidic characteristic. H-Al-silicate (H-ZSM-5) has Brønsted acidic property due to the substitution of aluminium in the framework of silicate resulting the negative unit cell. Another substitution of cobalt into H-Al-silicate by incorporation, forming H-Co,Al-silicate, changes the overall acidic property which leads to improve the activity for NO reduction by methane under excess oxygen condition of its parent, H-Al-silicate. However H-Co,Al-silicate exhibits no higher activity for SCR of NO than that of Co ion-exchanged ZSM-5 which has similar concentration of cobalt, this may be due to the difference in methane oxidation activity. The evidences shown in Figures 5.20 and 5.21 show that cobalt incorporated in MFI structure is not attributed to the conversion of methane. For H-Co,Al-silicate, Brønsted acid site is not more active for methane combustion as well as H-ZSM-5 [30].

5.5 Variable parameters effect in SCR process for the abatement of NO with methane in the presence of oxygen on Co/H-ZSM-5 and H-Co,Al-silicate and characteristics of the catalysts

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In order to compare the performance between cobalt ion-exchanged MFI type zeolite and cobalt incorporated alunimosilicate, having MFI structure due to the effect of variable parameters that can occur in the system, two type of catalysts that have the similar concentration of cobalt were chosen. Co/H-ZSM-5 with 1.92 wt.% Co exhibiting the highest activity of NO reduction in series of ZSM-5 in this study was selected to compare with that of H-Co,Al-silicate with 1.99 wt.% Co although the latter seems to show the lower performance in low temperature region than the former. Nevertheless some characteristics related to their activity of both catalysts were also determined.

5.5.1 Concentration of reducing agent

NO reduction on Co/ZSM-5 is strongly dependent on the concentration of methane. As reported in literatures [2,3], the removal of nitric oxide does not occur without methane in the stream. When methane is present, the conversion of NO is proportional to the partial pressure of methane but the percentage of methane consumption is inversely proportional to the methane concentration in the feed. For new synthetic catalyst, H-Co,Al-silicate, it was suggested to determine the dependency of catalyst on the inlet concentration of methane. Figures 5.22 and 5.23 display the data.

Figure 5.22 demonstrates the effect of methane concentration to NO conversion as a function of temperature. The NO conversion on H-Co,Al-silicate monotonically increases with methane concentration and higher concentration of methane also broadens the effective reaction temperature window both at high and low temperature region. In Figure 5.23, influence of methane concentration on methane conversion is shown as increase in reaction temperature. Like to Co/ZSM-5, high concentration of methane inhibits the methane consumption. The lowest concentration of methane at the reactor inlet displays the highest methane consumption, probably as the strong competition among methane to react with the

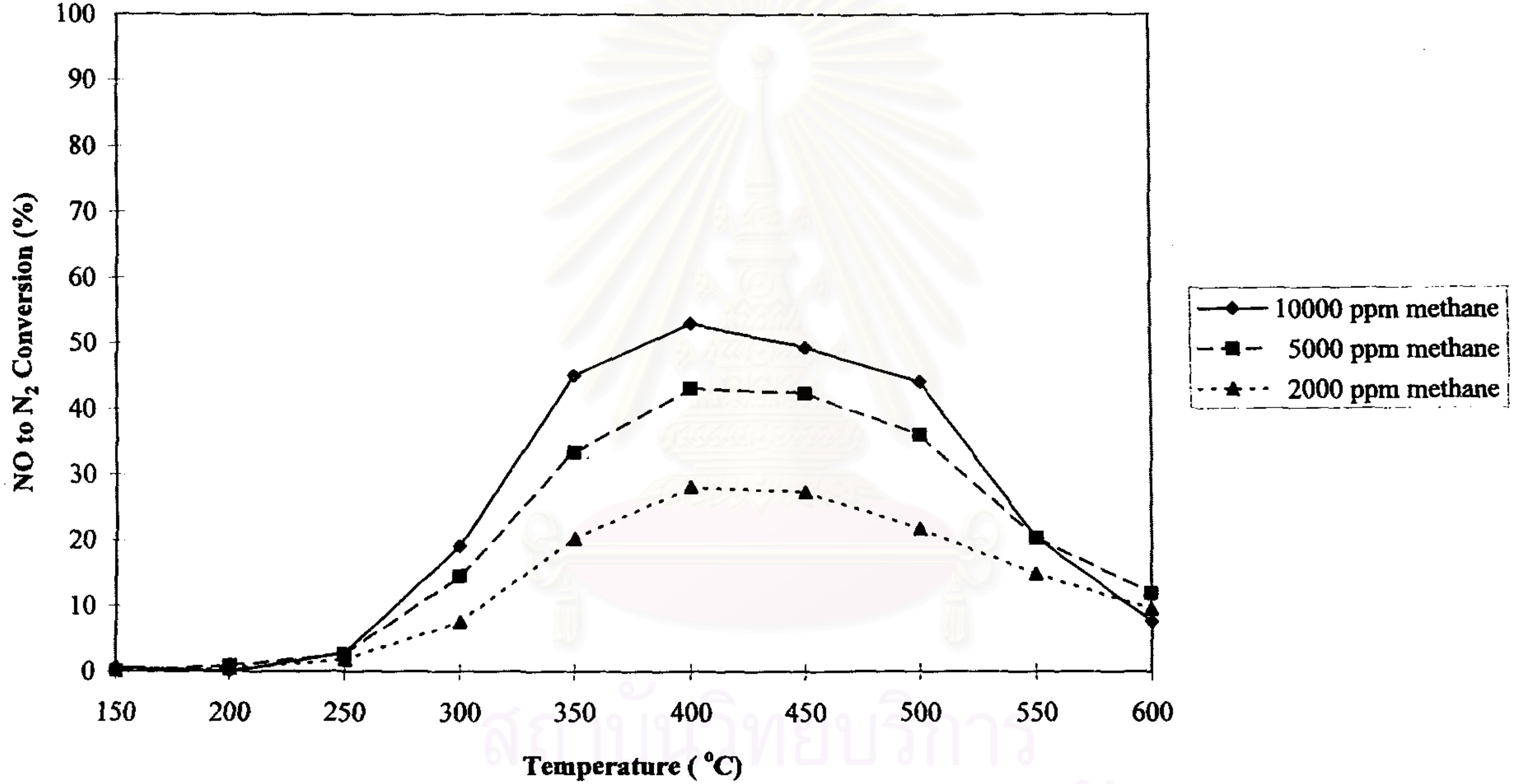

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Figure 5.22 Comparison of NO conversion as a function of temperature and methane inlet concentration on H-Co,Al-silicate. [NO] = 1000 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

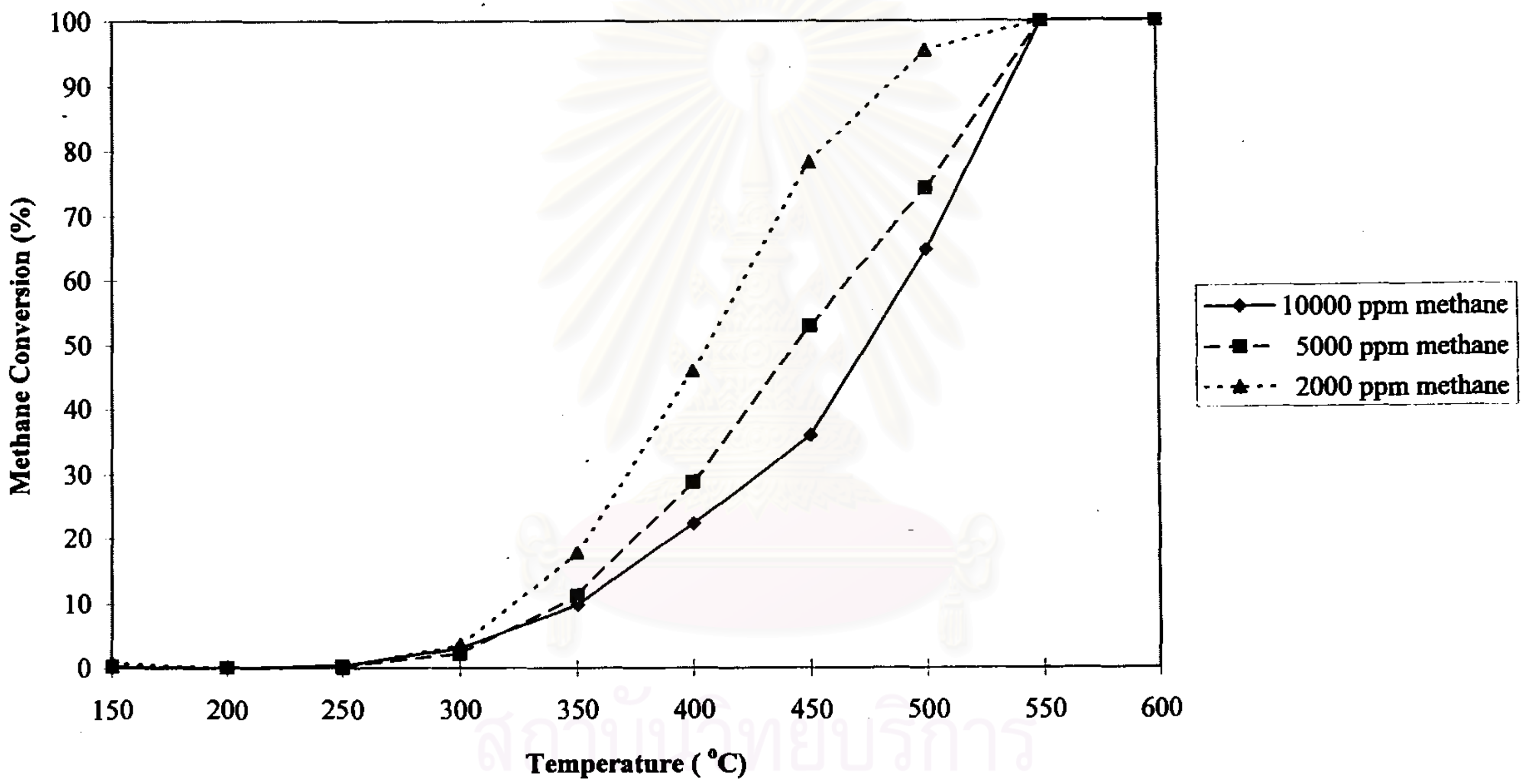

Figure 5.23 Comparison of methane conversion as a function of temperature and methane inlet concentration on H-Co,Al-silicate.
[NO] = 1000 ppm, [O_2] = 10 %, GHSV = 4000 h^{-1}

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tiny substance or to adsorb on a few remained active sites. The data obtained are in a good agreement with the general viewpoint of Co/ZSM-5 [2,3].

5.5.2 Kinds of reducing agent

In order to investigate the effect of the kinds of hydrocarbon in NO removal, propane was added instead of methane. Here, the carbon mol % in each hydrocarbon was set as a constant level. Figure 5.24 compares the NO conversions with methane and propane over Co/H-ZSM-5 and H-Co,Al-silicate as a function of reaction temperature. When methane was used as reducing agent in the SCR reaction, Co/H-ZSM-5 showed higher activity with lower light off temperature for NO conversion than H-Co,Al-silicate, but the latter exhibited larger reaction temperature window than the former. Similarly, when the reducing agent was changed from methane (10000 ppm) to propane (3300ppm), both catalysts showed higher NO removal activity and the light off temperature was shifted to the lower region. Again, Co/H-ZSM-5 exhibited higher activity of NO reduction and lower light off reaction temperature with propane than that H-Co,Al-silicate. Although NO reduction by propane on H-Co,Al-silicate is pronounced at higher light off temperature with lower conversion but it provides broader effective reaction temperature range, particularly to high temperature region. Compared with methane as reductant, propane promotes NO conversion over H-Co,Al-silicate with higher activity to lower light off temperature and widens effective reaction temperature window. These phenomena can be explained by focus on the hydrocarbon conversion in Figure 5.25.

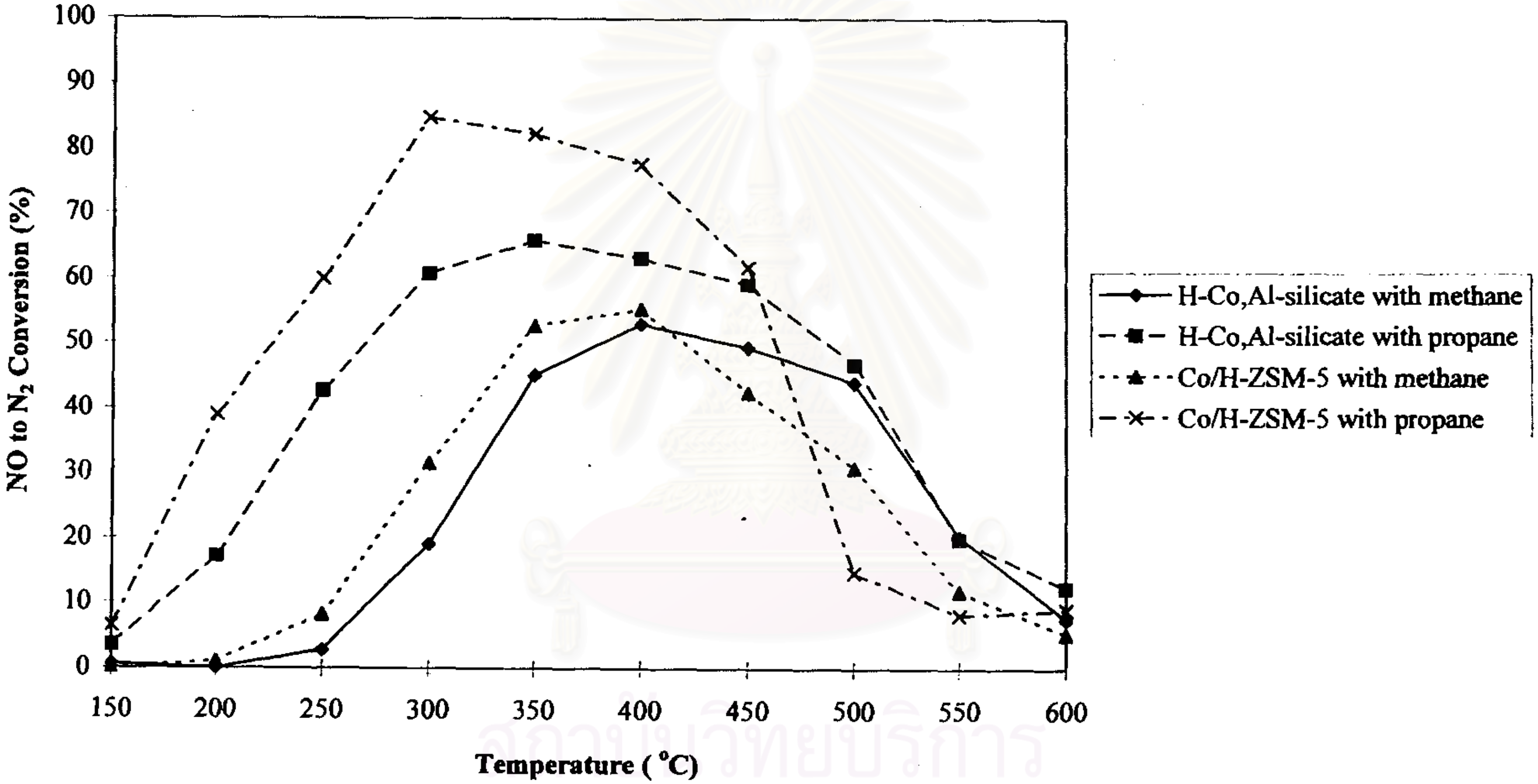

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Figure 5.24 Comparison of NO conversion as a function of temperature and kinds of hydrocarbon on zeolite catalysts. [NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, or $[C_3H_8]$ = 3300 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

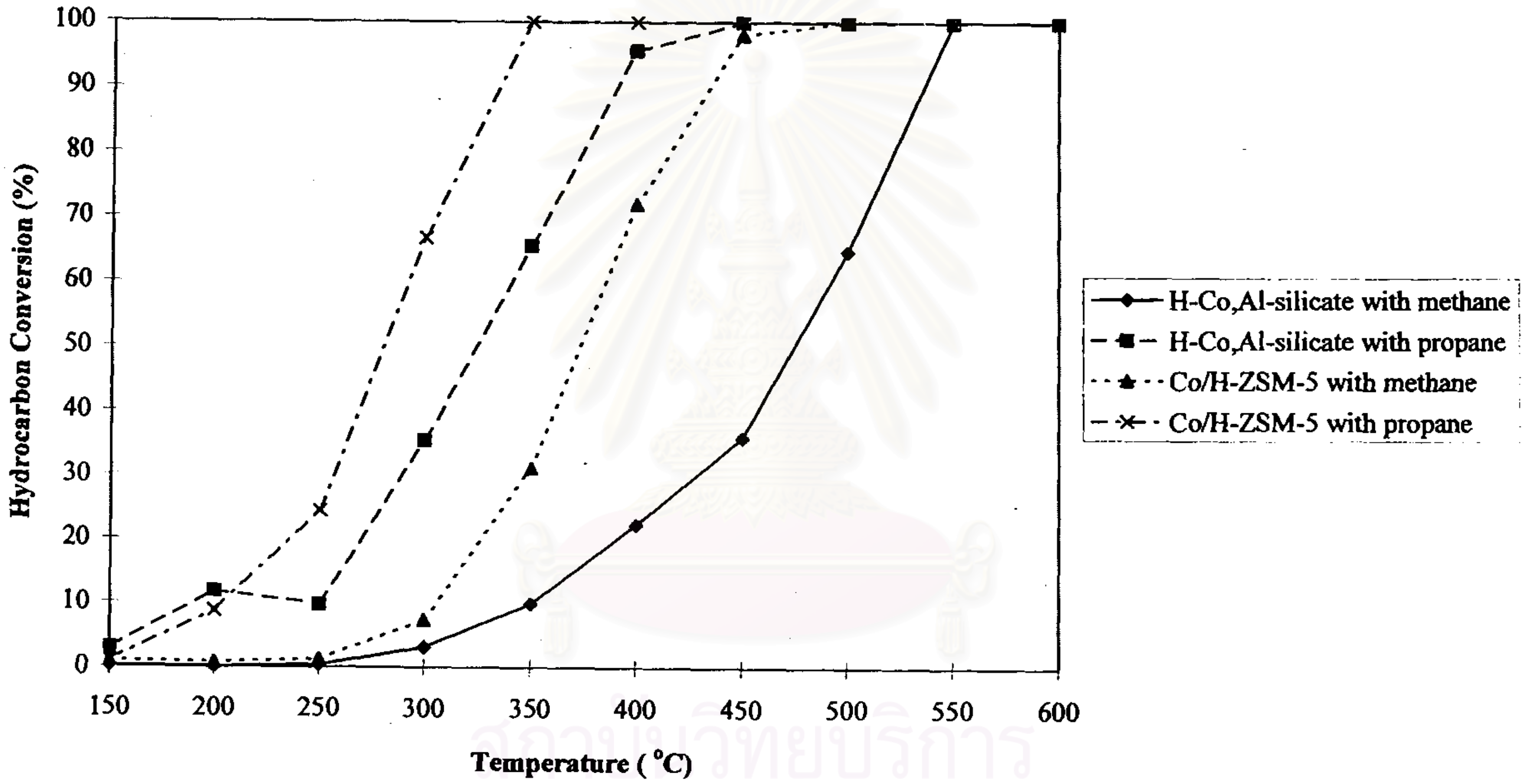

Figure 5.25 Comparison of methane conversion as a function of temperature and kinds of hydrocarbon on zeolite catalysts. [NO] = 1000 ppm, [CH_4] = 10000 ppm, or [C_3H_8] = 3300 ppm, [O_2] = 10 %, GHSV = 4000 h^{-1}

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Figure 5.25 shows the methane and propane consumption over Co/H-ZSM-5 and H-Co,Al-silicate as reaction temperature increases. Consider hydrocarbon conversion on either catalysts, expectably, both exhibit higher activity on consumption of propane than that of methane. This result obtained for SCR follows the similar trend as that report by Sachtler et al. [34]. Because methane is known to react more slowly than propane but propane is a less selective reductant, then Co/ZSM-5 and H-Co,Al-silicate require a higher temperature with methane than with propane to obtain similar conversion. In early report [60], it was evaluated that the activity increases with molecular weight for straight-chain saturated hydrocarbon. The reason is related to the order of combustibility of the hydrocarbon added. The combustibility of straight-chain saturated hydrocarbon increases with an increase in carbon number up to C_7 [21]. In this study, conclusively, propane is more efficient than methane as the reducing agent

Not surprising, hydrocarbon conversion that occur on H-Co,Al-silicate showed lower activity, on the other word, higher selectivity, particularly, at high reaction temperature, than that occur over Co/H-ZSM-5 even all range of reaction temperature either use methane or propane as reducing agent. As prior discussion, H-Co,Al-silicate utilizes smaller amount of methane and causes lower activity in NO reduction than Co/H-ZSM-5 and it is true in this case for propane. H-Co,Al-silicate activates propane oxidation with lower activity compared to Co/H-ZSM-5 and consequently, produces in lower NO reduction.

5.5.3 Acidity property

Since acidic properties of zeolites of the ZSM-5 family have been reported and discussed in the literature [21,41,43,54]. Although some ammonia temperature-programmed-desorption (TPD) data are also available [21,41,42,44], the main contribution to the understanding of the acidic properties of H-ZSM-5 (the protonated form of zeolite ZSM-5) has been through the use of infrared (IR) spectroscopy [65].

The nature of the acid sites and their relative strengths for Co/H-ZSM-5 with 1.92 wt.% Co and H-Co,Al-silicate with 1.99 wt.% Co were studied by mean of infrared spectra with pyridine adsorption. Pyridine was adsorbed at room temperature in vacuum and then evacuated at 100 °C such that only chemisorbed pyridine remained on the zeolite. This eliminates the difficulty caused by overlapping bands of physically adsorbed and hydrogen-bond pyridine which may obscure the bands due to coordinated pyridine [65]. The bands due to the chemisorbed pyridine of Co/H-ZSM-5 and H-Co,Al-silicate are shown in Figures 5.26 and 5.27 respectively. These occur at ~ 1650-1600, 1540, 1485, and 1450 cm^{-1} in the bending region. The 1540 cm^{-1} band attributed to the C–C stretching vibration of the pyridinum ion and is most commonly used for detecting the presence of Brønsted acidity. On the other hand, Lewis aluminium acidity, being an electron pair acceptor, is indicated by the band at 1450 cm^{-1} which arises from the C–C stretching of a coordinate covalent bond of pyridine complex. The 1485 cm^{-1} band is not as useful for identification since it is common to both species [43,65,66].

Figure 5.26 shows the relevant region of the IR spectrum of Co/H-ZSM-5 after exposure to pyridine as a function of temperature of evacuation. Admission of

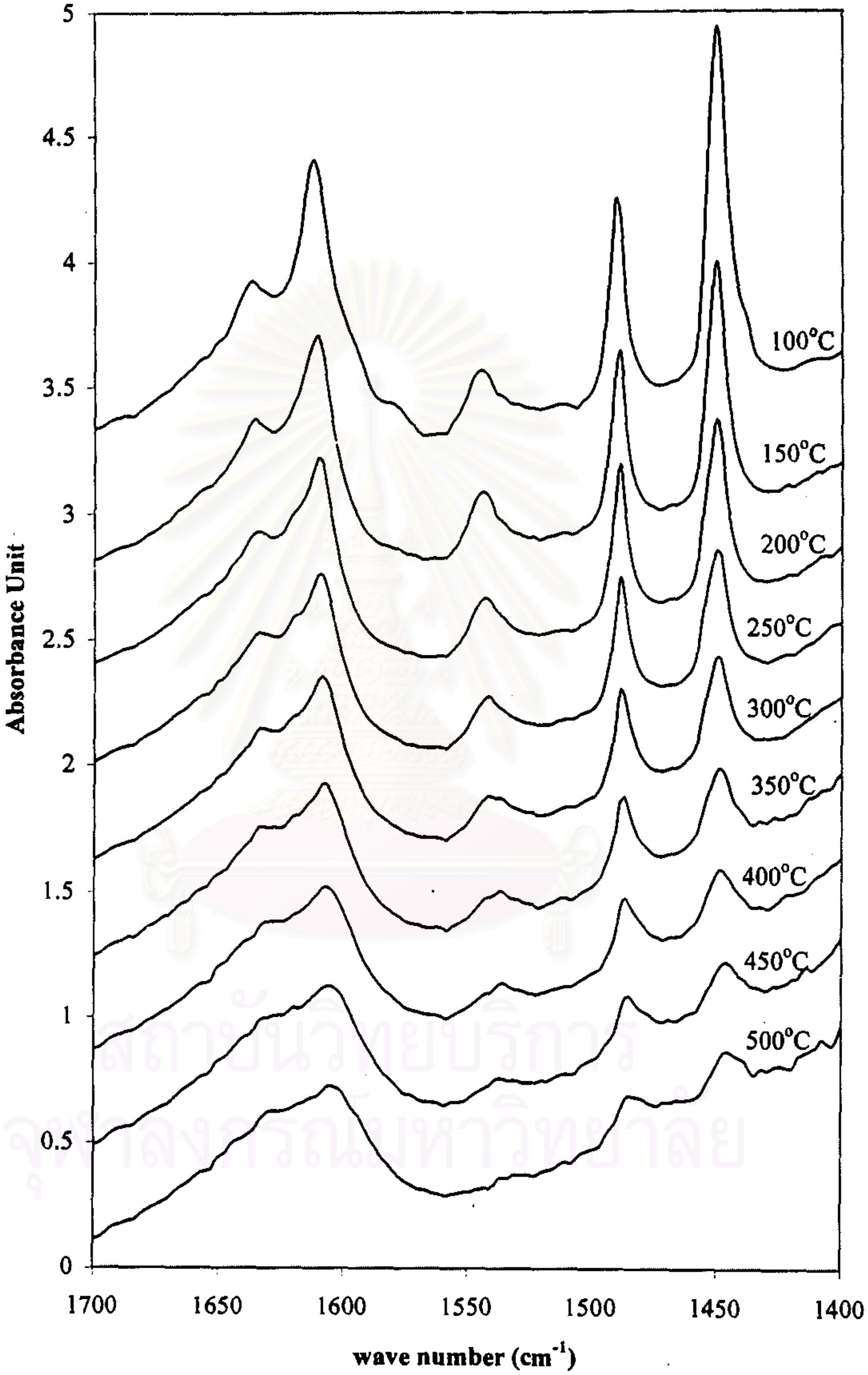

Figure 5.26 IR spectra taken during pyridine-TPD in vacuum of fresh-Co/H-ZSM-5

pyridine resulted in the appearance of a number of bands in the region of interest, between 1400-1700 cm^{-1}. The appearance of bands at 1540 and 1450 cm^{-1} demonstrates the presence of both Brønsted and Lewis sites in this catalyst. A number of changes are observed on evacuation at increasing temperature. After evacuation between 100-500 °C, a gradual reduction in the intensity of the band due to pyridine bound both at Lewis and Brønsted sites appeared. Comparing the intensity of each band after evacuation at each temperature gives an indication of each acid site strength, showing that the Lewis acid sites are stronger than Brønsted acid centers, the same result with Derouane et al. [65] since the pyridinium ions were removed more rapidly than coordinatively bound pyridine with increasing temperature of desorption and the band at 1540 cm^{-1} disappeared at 500 °C while the band of Lewis acidity (1450 cm^{-1}) still remained.

The IR spectra of H-Co,Al-silicate with the admission and desorption of pyridine as a function of temperature in vacuum shown in Figure 5.27 contain features at 1540 and 1450 cm^{-1}, characteristics of Brønsted and Lewis acid sites, respectively. In this catalyst, the strength of acid site can not be determined because, at temperature above 450 °C, some changes had occurred in H-Co,Al-silicate and these caused the phenomenon that the infrared radiation could not transmit through the catalyst causing the bad scan, however, comparing with Co/H-ZSM-5 indicates that the amount of Lewis acid sites of H-Co,Al-silicate is smaller than that of Co/H-ZSM-5. As investigated by Inui et al. [18,21,41], the amount and strength of acid sites of H-Co-silicate is much smaller and weaker than that of H-Al-silicate (H-ZSM-5), thus, it can be suspected that the incorporation of cobalt into H-Al-silicate may reduce or generate weaker Lewis acidity.

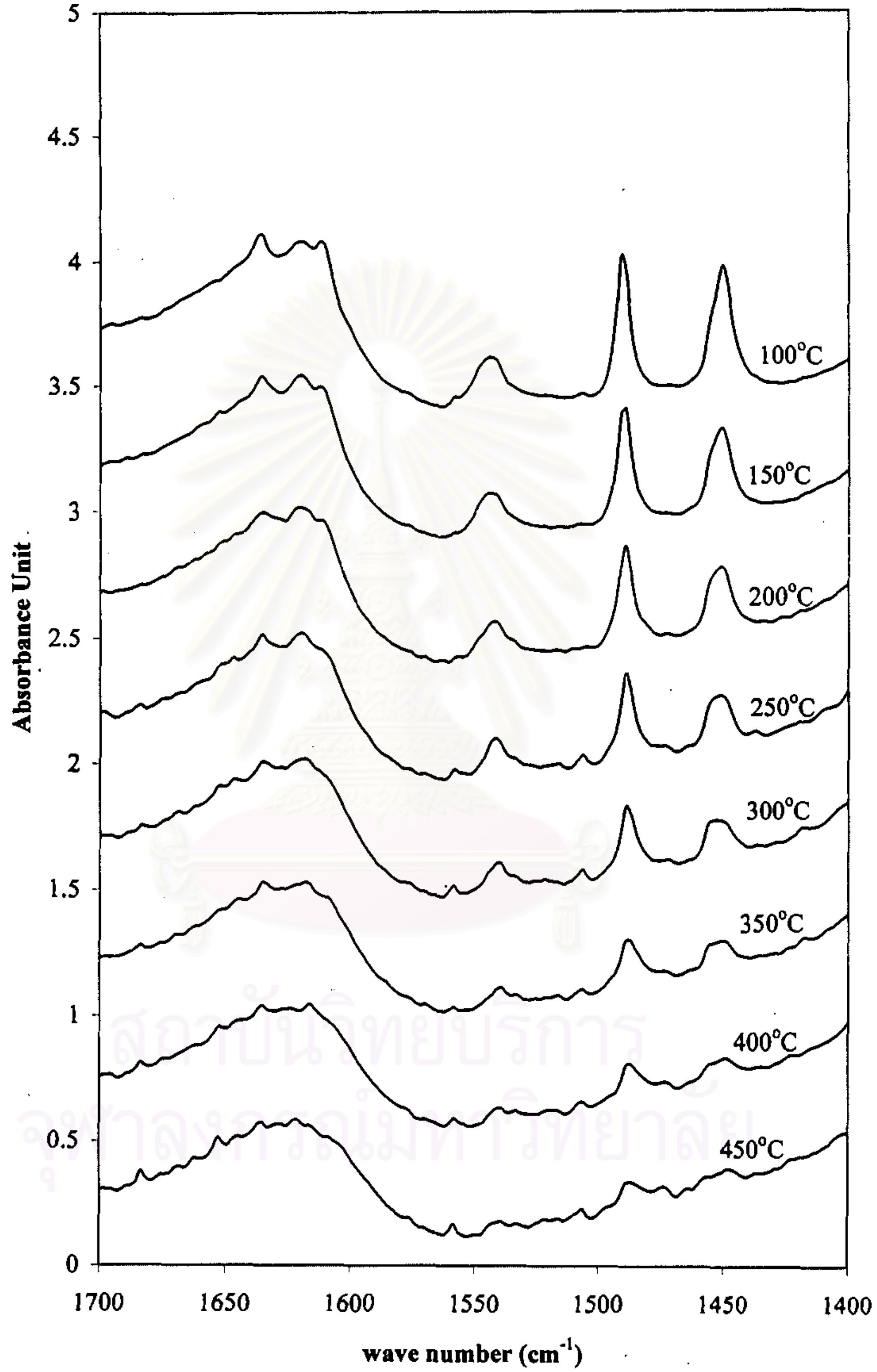

Figure 5.27 IR spectra taken during pyridine-TPD in vacuum of fresh-H-Co,Al-silicate

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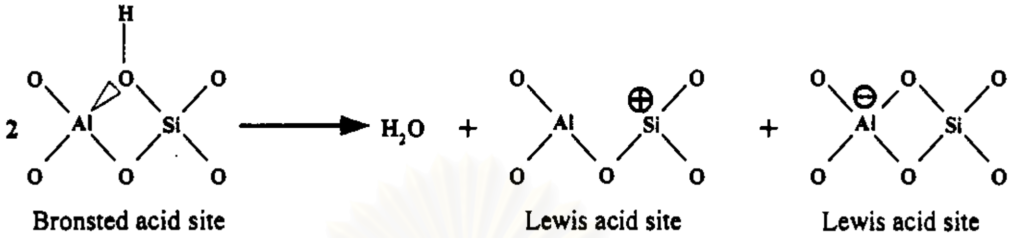
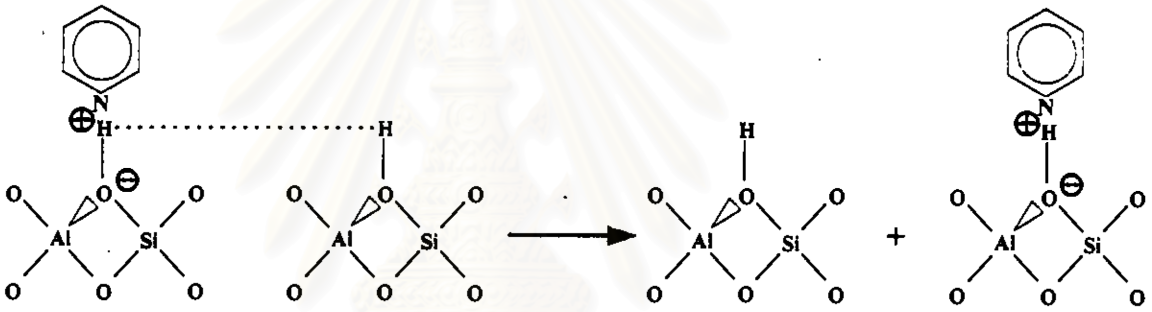
The faster decrease upon progressive desorption of the pyridinium ion band intensity as compared to coordinated pyridine may be explained in two way [65]. One could conclude that Lewis acidic sites are stronger than Brønsted acidic sites. Another possibility would be that the zeolite functions as an ionizing solvent such that pyridinium ions have apparently a higher mobility than coordinated pyridine molecules. It should also be recalled that the binding modes of pyridine are drastically different in both cases: electrostatic interactions prevail for the pyridinium ions while coordinated pyridine interacts by its electron lone pair, i.e., in a configuration where it will tend to be perpendicular to the (adsorption site) surface. This would imply larger diffusion restrictions in the case of coordinated pyridine, mainly at high concentration in Lewis sites, due to the restricted pore size of ZSM-5 type zeolites. A scheme such as Figure 5.28 may account for these observations. The desorption of pyridinium ions, Figure 5.28b-2, includes diffusion steps in which pyridine jumps from one Brønsted site to another (Figure 5.28b-1) and occurs in a way nearly identical to thermal dehydroxylation (Figure 5.28a), which releases water. In the presence of pyridine, however, dehydroxylation seems to occur faster (probably due to the highly basic character of pyridine) and coordinated pyridine species may be formed to some extent. The latter will of course also desorb and the slower decrease in intensity of the coordinated pyridine IR band could then be explained by a near compensation in the formation and decomposition of pyridine Lewis acid site adducts.

A) Dehydraxylation



B) Pyridinium ions desorption

1) Intracrystalline diffusion



2) Dehydroxylation and pyridine desorption

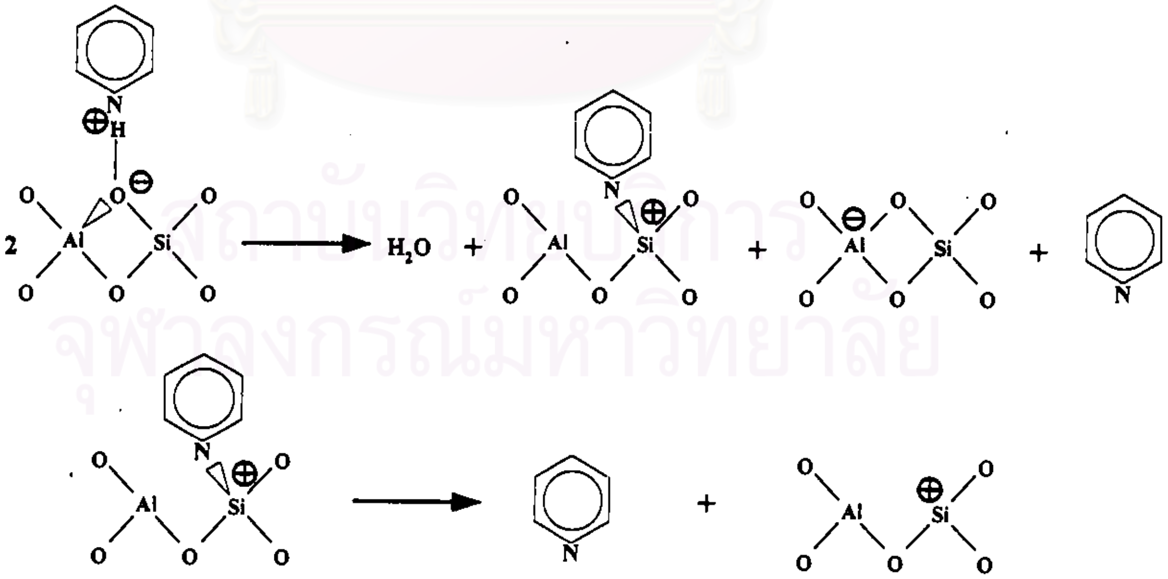


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Figure 5.28 Interaction of pyridine with Brønsted and Lewis acidic sites [65]

5.5.4 The presence of sulfur dioxide

Low level of sulfur compounds existing in most of the fuel sources we use today are known to poison many catalysts. From early report [20,25], the presence of sulfur dioxide in gas feed can display either positive effect or negative effect toward NO conversion and methane consumption over Co/H-ZSM-5 and H-Co-silicate upon reaction temperature.

Figure 5.29 and 5.30 show the effect of sulfur dioxide addition in feed of SCR reaction over Co/H-ZSM-5 with 1.99 wt% Co content at 400 °C and 550 °C respectively. Consider the reaction at 400 °C (Figure 5.29), As once sulfur dioxide 500 ppm was exposed to the catalysts with a dry feed, NO conversion, at the first time, quickly increased to ca. 90 % but after that it was slowly gone down with the time until reached a stable level. The dramatic change of NO conversion in the initial period upon SO_2 addition reflects the accumulation process of sulfur dioxide on the catalyst, similar phenomenon was denoted by Li and Armor [25]. Obviously, the first portion of sulfur dioxide deposited on the catalyst has the highest impact on the NO conversion, and the steady state NO conversion obtained after 90 minute in the SO_2 containing stream indicates an achievement of an equilibrium condition for adsorption and desorption of sulfur dioxide. Although sulfur dioxide adsorption is thought to be an irreversible process [20], this experiment clarified that it is partially reversible. The same feature was occurred on methane conversion. Addition of sulfur dioxide decreases the methane conversion in a way consistent with the change in NO conversion. When sulfur dioxide was added to the feed at 400 °C, a continuous decrease in methane conversion was observed. For steady state

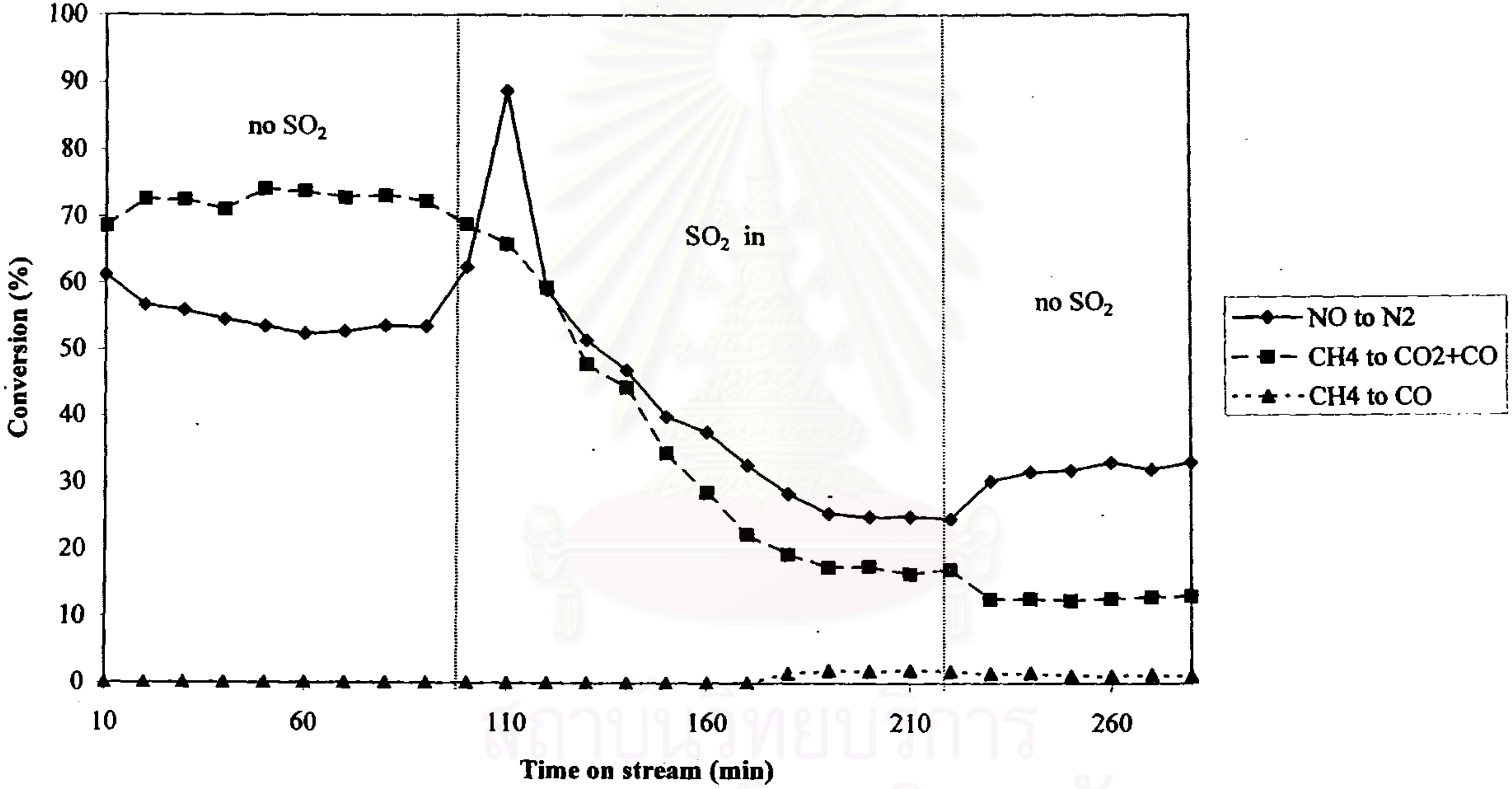

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Figure 5.29 Effect of SO_2 addition on SCR reaction at 400 °C over Co/H-ZSM-5
[NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, $[SO_2]$ = 500 ppm, GHSV = 4000 h^{-1}

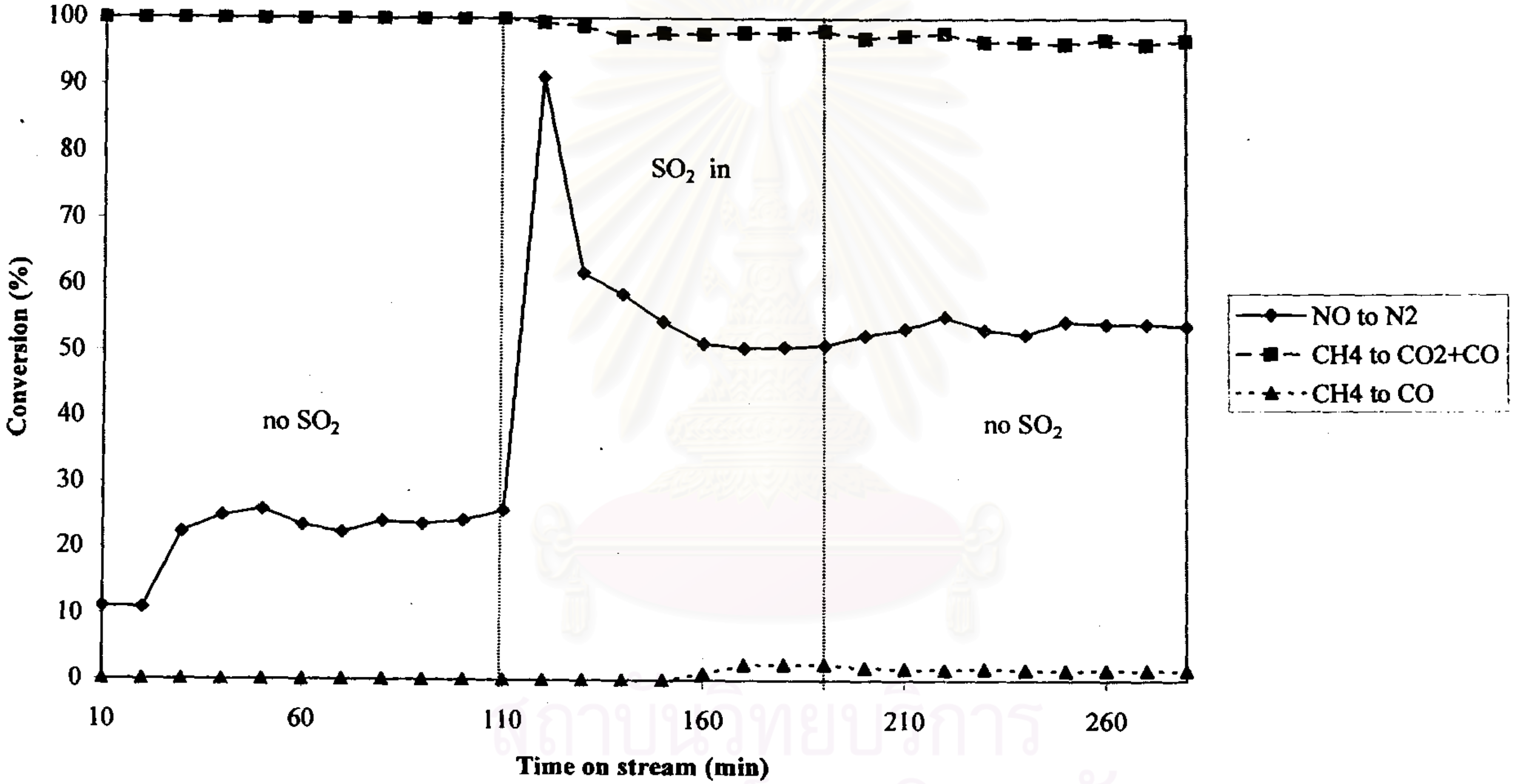

Figure 5.30 Effect of SO$_2$ addition on SCR reaction at 550 °C over Co/H-ZSM-5
[NO] = 1000 ppm, [CH$_4$] = 10000 ppm, [O$_2$] = 10 %, [SO$_2$] = 500 ppm, GHSV = 4000 h^{-1}

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conversion, substantially lower methane conversion resulted from sulfur dioxide addition. These obtained results are in the good agreement with that reported by Li and Armor [25] and they also claimed that the selectivity of methane toward NO reduction is greatly enhanced as the result of sulfur dioxide addition. Another interesting view, after eliminating the sulfur dioxide from the gas feed while the reaction is in steady state condition, NO conversion reversibly increased while methane conversion continuously declined. It implied the interaction of gas phase molecules. Another effect of the presence of sulfur dioxide in feed is the incomplete combustion of carbon monoxide to carbon dioxide. However, it is not clear that carbon monoxide occurring in the system came from the SCR of NO or steam reforming of methane [51].

Li and Armor also demonstrated in reference [25] that, at low temperature, sulfur dioxide poisons catalytic activity of NO conversion causing it decreasing but at higher temperature, sulfur dioxide enhances that activity. The same phenomena can be observed in this report. Figure 5.30 shows the effect of sulfur dioxide through conversion of feed components in SCR reaction of NO by methane in oxygen atmosphere at 550 °C. As so on as sulfur dioxide was exposed to Co/H-ZSM-5, NO conversion strongly increased and then gradually dropped until reached a steady state level. In contrast to the phenomenon at 400 °C is that the conversion of NO at new steady state at 550 °C is higher than that at the initial condition when sulfur dioxide is not presence in the feed. However, the similarity at both temperatures are that after sulfur dioxide removal, NO conversion increase but only a little. A change in methane conversion at 550 °C, similar to that at 400 °C: the decrease of methane consumption was found due to sulfur dioxide addition, is also showed in Figure 5.30. As the presence of sulfur dioxide in gas feed, the conversion declined and slightly reduced after elimination of poison gas. However, the change in methane conversion at 550 °C is hardly observed because at this high temperature region, methane combustion reaction is promoted by thermal effect [2]. The decrease is well pronounced at lower temperature. Furthermore, sulfur dioxide additionally plays the role of anti-oxidant of carbon monoxide to carbon dioxide at either temperatures.

Two parallel reaction, i.e., NO reduction by methane and methane combustion by oxygen, occur simultaneously during a reaction run [2]. NO conversion is proportional to the methane concentration in the catalyst bed [3], thus the enhancement of NO conversion by sulfur dioxide in a dry feed at 550 °C may be the result of decreasing methane combustion rate [25]. Therefore, more methane is available for NO reduction. The enhanced methane selectivity suggests that sulfur dioxide inhibits the methane combustion rate to a larger extent than the reduction of NO. This suggestion implied that the catalyst sites are not uniform, and sulfur dioxide poisons preferentially the sites that are more active for methane combustion [25]. It is also suspected that sulfur dioxide preferentially adsorbs on the sites on the outer surface of the zeolite or at the entrance of the 10-menber rings and these sites are less selective for the NO reduction but more active for the combustion of methane [25]. Exposure of sulfur dioxide at high temperature may selectively poison these sites. In addition, the strongly adsorbed sulfur dioxide molecules may slightly reduce the channel openings of ZSM-5: channel restriction [25].

H-Co,Al-silicate with 1.99 wt.% Co displays such behavior not like to Co/H-ZSM-5 with the presence of sulfur dioxide in the system. Consider Figure 5.31 which shows SCR reaction conversions of H-Co,Al-silicate at 400 °C. Exposed to sulfur dioxide caused the slight decrease in NO conversion activity of H-Co,silicate but enhanced methane conversion. Through eliminating of sulfur dioxide from the system, amazingly, SO_2-adsorbed catalyst futuristically showed even higher NO removal activity but at the same time, suppressed methane conversion, slightly lower the initial value. The rhythm of the presence and absence of sulfur dioxide in gas feed originates the contrary cycle between NO and methane conversion, that is, with sulfur dioxide, NO conversion decreases while methane increases but without SO_2, NO conversion is enlarged despite to lessening of methane. The effect of sulfur dioxide toward the oxidation of carbon monoxide to carbon dioxide in oxidizing atmosphere is that, in sulfur dioxide containing feed, SO_2 exposed catalyst promoted methane conversion but put down the oxidation of carbon monoxide, for the absence of sulfur dioxide, carbon monoxide formation was abates along with the decrease in methane conversion. Finally, NO and CH_4 conversion tend to continuously decreases with time on stream.

Such behavior like to Co/H-ZSM-5 of H-Co,Al-silicate with 1.99 wt-% Co is the SCR reaction of NO by methane in excess oxygen at 550 °C with and without sulfur dioxide which is displayed in Figure 5.32. As shown, instantly the catalyst was impacted with sulfur dioxide, NO conversion increased and then unflagging declined until attained a new steady state. NO conversion at this new steady level is higher than that of SO_2-free steady condition. Astonishingly, removal of sulfur dioxide did not drop NO conversion back to its initial value but slightly increased to new higher value. SO_2 exposed H-Co,Al-silicate catalyst shows little lower activity for methane conversion and no impact on carbon monoxide formation.

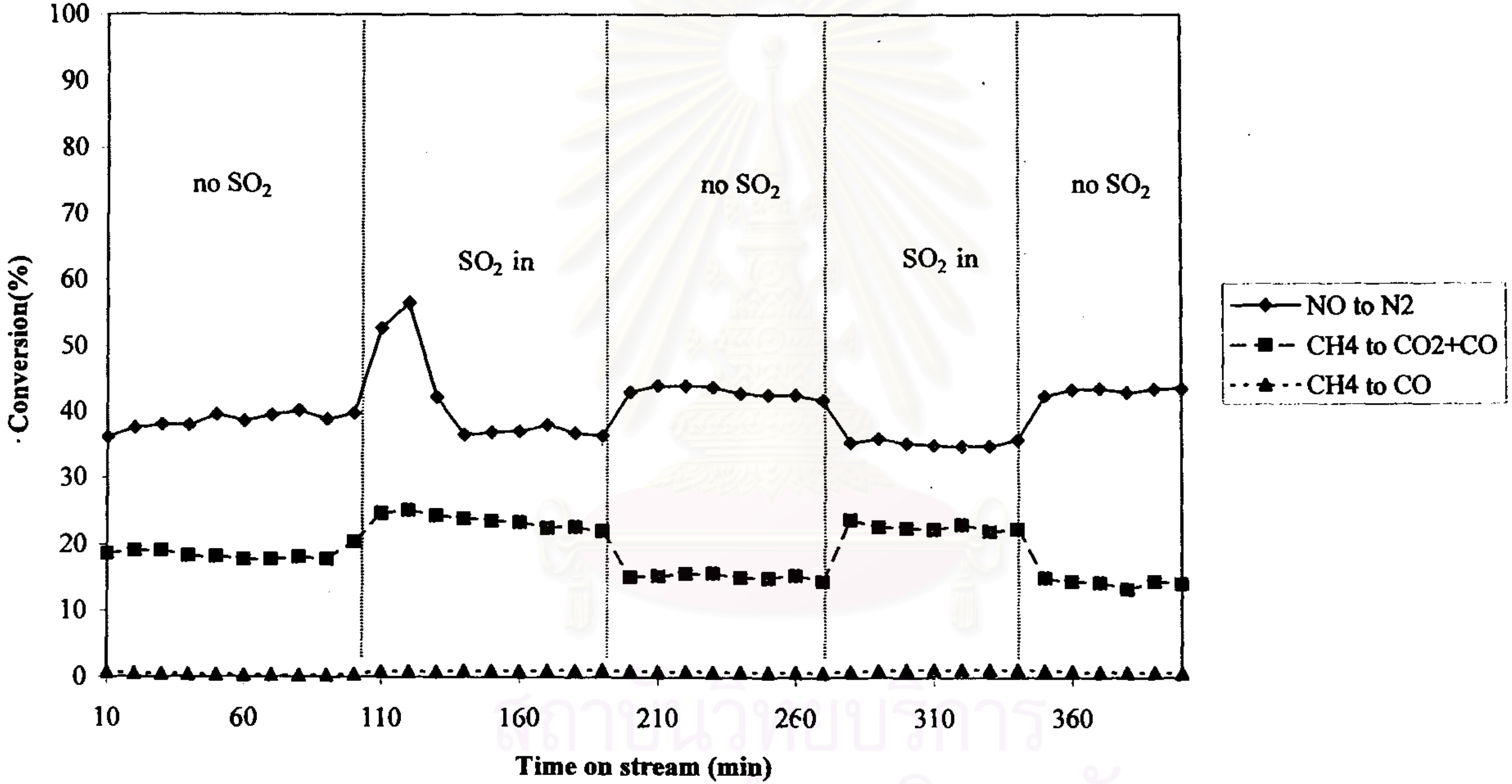

Figure 5.31 Effect of SO_2 addition on SCR reaction at 400 °C over H-Co,Al-silicate
[NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, $[SO_2]$ = 500 ppm, GHSV = 4000 h^{-1}

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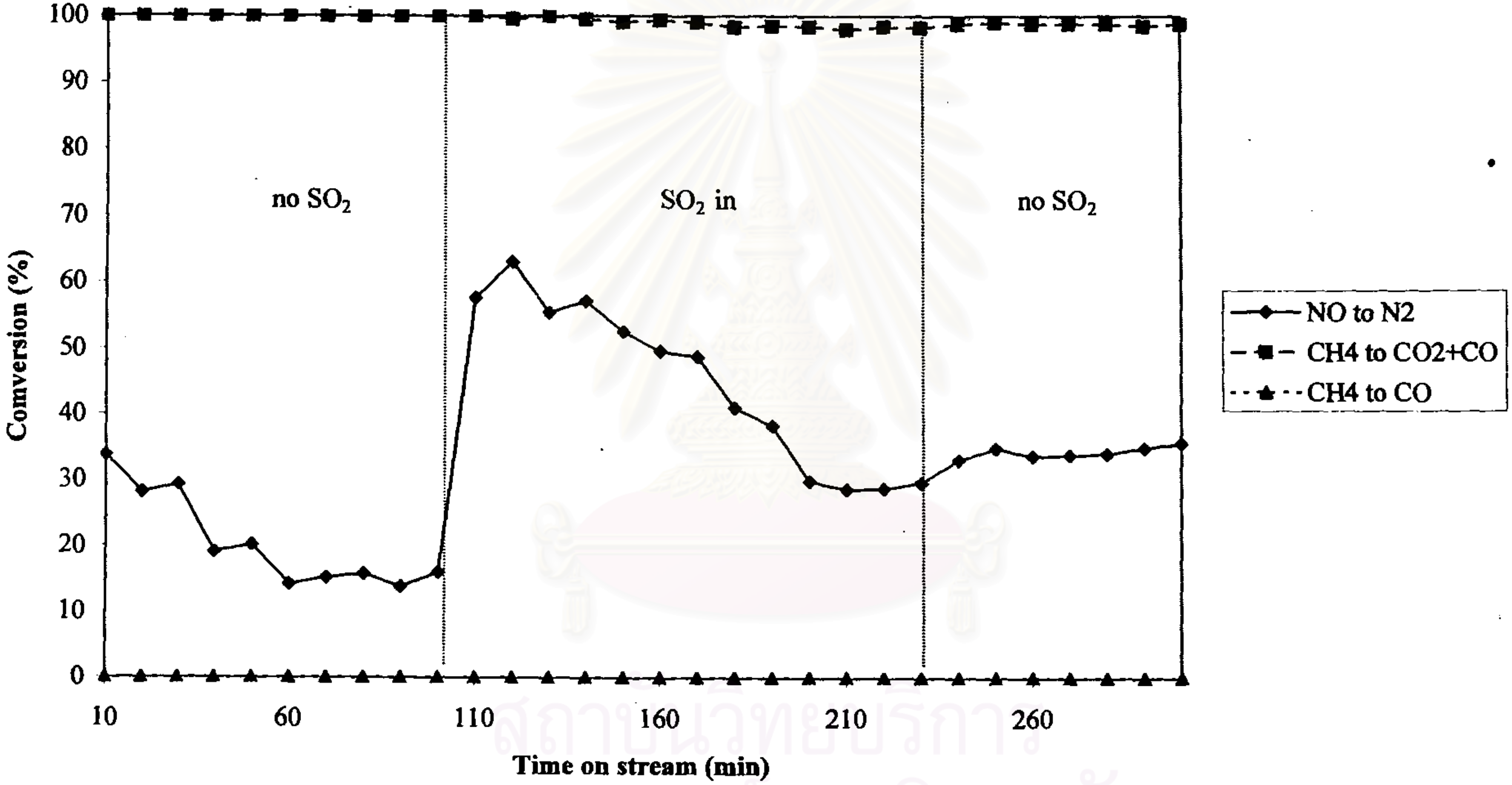

Figure 5.32 Effect of SO_2 addition on SCR reaction at 550 °C over H-Co,Al-silicate
$[NO] = 1000$ ppm, $[CH_4] = 10000$ ppm, $[O_2] = 10$ %, $[SO_2] = 500$ ppm, GHSV = 4000 h^{-1}

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In order to investigate the role of acid sites of catalysts in the presence of sulfur dioxide, admission of pyridine resulted in the IR spectra of SO_2-exposed Co/H-ZSM-5 and H-Co,Al-silicate as a function of evacuated temperature was performed and shown in Figures 5.33-5.34, respectively. Comparing with those of SO_2-free catalysts evaluates the important view of acid sites adsorbed by sulfur dioxide. In case of Co/H-ZSM-5 (Figure 5.26,5.33), it is clear that the acid sites on which sulfur dioxide adsorbed is Lewis acid sites according to the decrease in intensity of Lewis-coordinative pyridine band at 1450 cm^{-1}. With the suggestion of Li and Armor [25], i.e., sulfur dioxide poisons preferentially the sites of Co/H-ZSM-5 that are more active for methane combustion, the data obtained indicates that Lewis acid sites may be support the methane oxidation. In case of H-Co,Al-silicate (Figure 5.27,5.34), the significant display is that the decrease in intensity of Lewis-coordinative pyridine acid sites (1450 cm^{-1}) and of Brønsted-pyridinium ions acid sites at 1540 cm^{-1}. In addition, sulfur dioxide exhibited the impact on the strength of Brønsted-pyridinium ions acid sites which disappeared at lower temperature (400 °C). In contrast to Co/H-ZSM-5, the presence of sulfur dioxide at 400 °C enhanced methane conversion of H-Co,Al-silicate. If methane oxidation occurred on Lewis acid sites, the phenomenon that methane conversion increased even the restriction of Lewis active sites due to sulfur dioxide adsorption may be unraveled by this: because Al-silicate has low redox property but Co-silicate shows higher redox activity [18,19,21], sulfur dioxide adsorption on Lewis-aluminium acid sites should suppress the role of these sites in oxidation reaction, at the same time, sulfur dioxide could adsorb on incorporated Co sites but with weak interaction [20] and should dominate its role in methane combustion, resulting in increasing the methane conversion. After elimination of

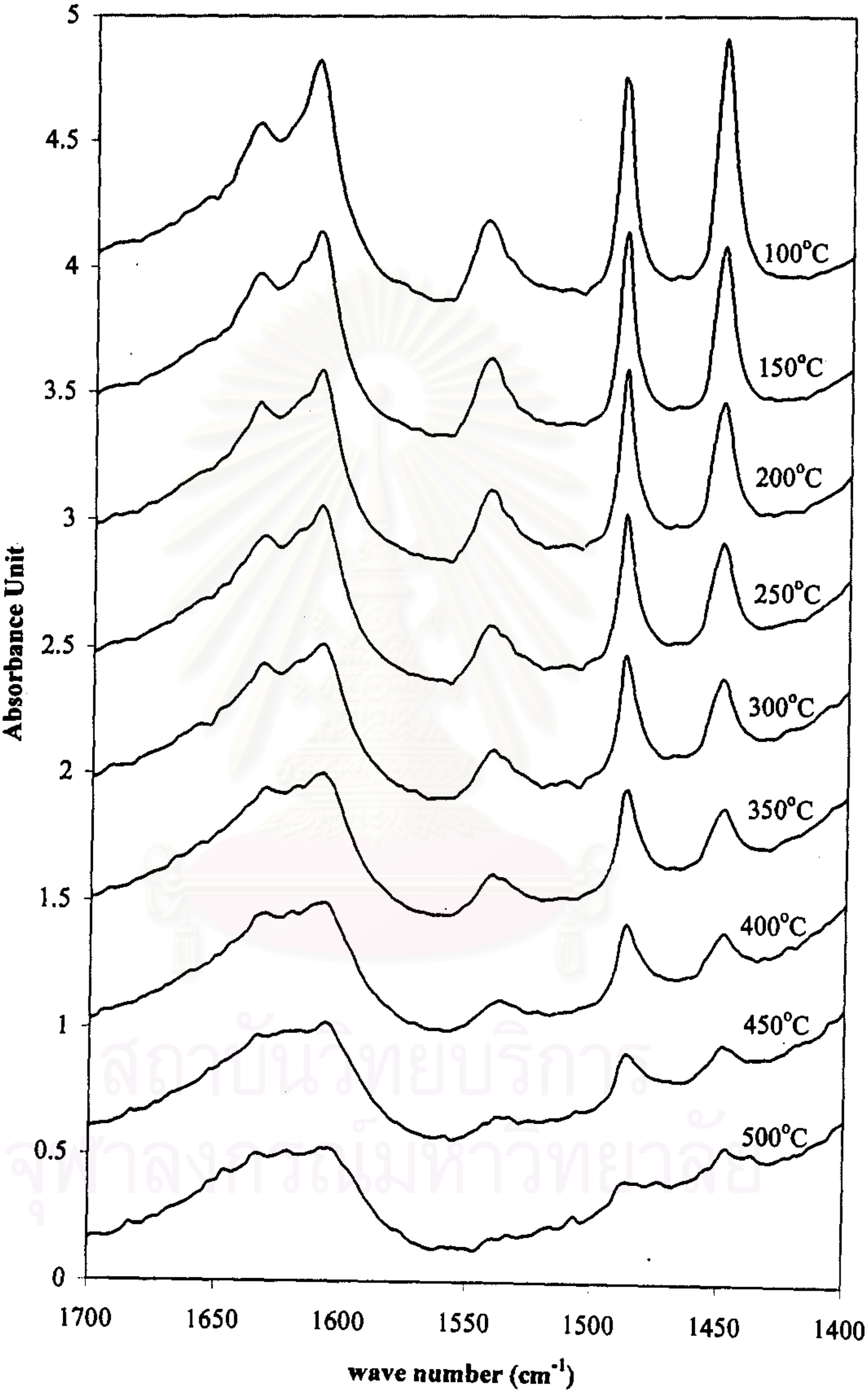

Figure 5.33 IR spectra taken during pyridine-TPD in vacuum of SO_2-exposed-Co/H-ZSM-5

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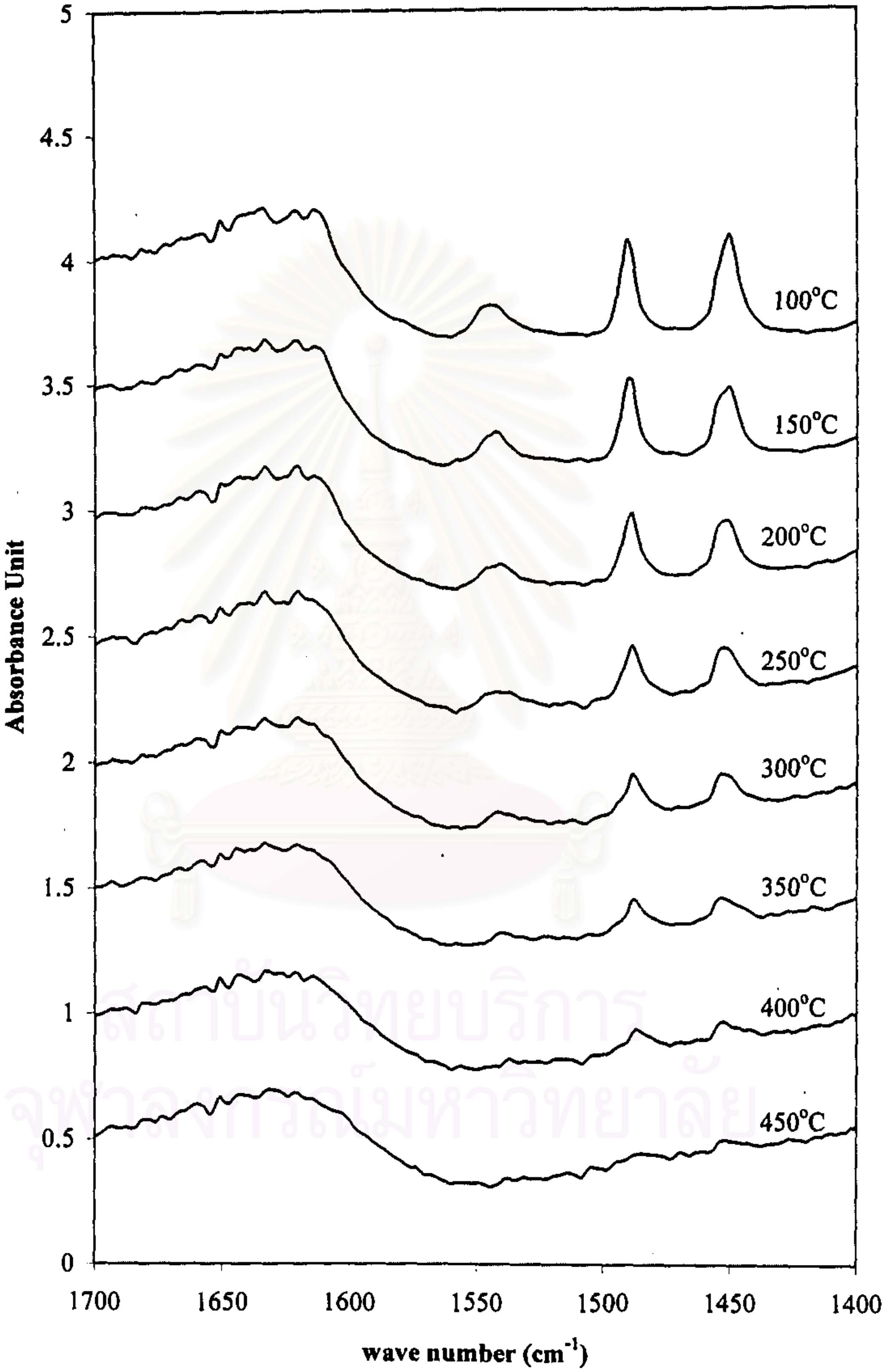

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Figure 5.34 IR spectra taken during pyridine-TPD in vacuum of SO_2-exposed-H-Co,Al-silicate sulfur dioxide from the feed, some Lewis-aluminium acid sites was still deposited by sulfur dioxide but might be a few ratio, the initial role of Lewis-aluminium acid sites resumed

Stakheev et al. [18] proposed that Brønsted acid sites of H-ZSM-5 are active for NO oxidation, the initial step requirement for SCR reaction [30,36}. Figures 5.27 and 5.34 indicates that a part of Brønsted acid sites of H-Co,Al-silicate was adsorbed by sulfur dioxide with slightly decreasing in NO conversion. In SO_2-containing feed, although methane conversion increased, NO conversion or N_2 formation did not increase but, conversely, increased with the decreased of methane oxidation when SO_2 was removed from the system. This leads to the speculation that Brønsted acid sites may contribute to the formation of N_2. Brønsted acid sites that some part occupied by sulfur dioxide exhibited little lower NO conversion in SO_2-containing stream but showed higher N_2 formation when oxidation of methane declined. This may be due to no change of the number of SO_2-occupied Brønsted acid sites with the in/out cycle of sulfur dioxide addition but some changes of role of Lewis acid sites in the same condition conversely enhance NO to N_2 conversion that was suspected to occur on Brønsted acid sites. This speculation almost coincides with that finding by Miller et al. [54] who pronounced that the formation of N_2 occur at proton sites by protonation of the reducing agent followed by attack of the carbocation by gas phase NO_2. They also reported that the formation rate of nitrogen increases with the number of protons and the specific rate increases as the acid strength increases, which is in a good agreement with this study.

5.5.5 Temperature Programmed-Reduction, TPR

TPR profiles of fresh catalysts, Co/H-ZSM-5 and H-Co,Al-silicate which have the similarity of cobalt content, are depicted in Figure 5.35. Note that, the same amount of catalysts was used but the H_2 consumption of H-Co,Al-silicate was higher. Both catalysts have the significant peaks at the same temperature, 630 °C, nearby the result of Sachtler et al. [34] who have indicated that the peak at ca. 625 °C of Co/ZSM-5 is due to the reduction of Co^{2+} while Burch and Scire [23] and Stakheev et al. [38] pronounced that the reduction of Co^{2+} in Co/ZSM-5 occurs at higher temperature ca. 720 °C. In addition, Co/H-ZSM-5 in this study shows shoulders at about 570 and 460 °C. The lower temperature shoulder may occur from reduction of cobalt oxide [69] which is suspect to originate at the stage of ion-exchanging and oxidizing in TPR process [38,55] while the higher temperature one may be the characteristic peak of H-form MFI type zeolite [38]. The reducibility of Co^{2+} cations to metallic Co particles has been reported by Rosynek and Polansky [69] to be strongly dependent on the cobalt loading, the selective of precursor molecules, and the nature and structural characteristic of the support material. It has been known that the reduction potential of metal cations can be altered when they reside in zeolite cavities and channels [59]. The framework of zeolites can function as a huge ligand to coordinate and stabilize its cations, preventing the latter from oxidation or reduction. The stable nature of Co^{2+} cations can thus be attributed to the matrix effect imposed by the zeolite framework [59] and distinguish Co/ZSM-5 from Co supported on Al_2O_3. The latter experienced hydrogen reduction at 400 °C leading to the formation of Co metal species [69].

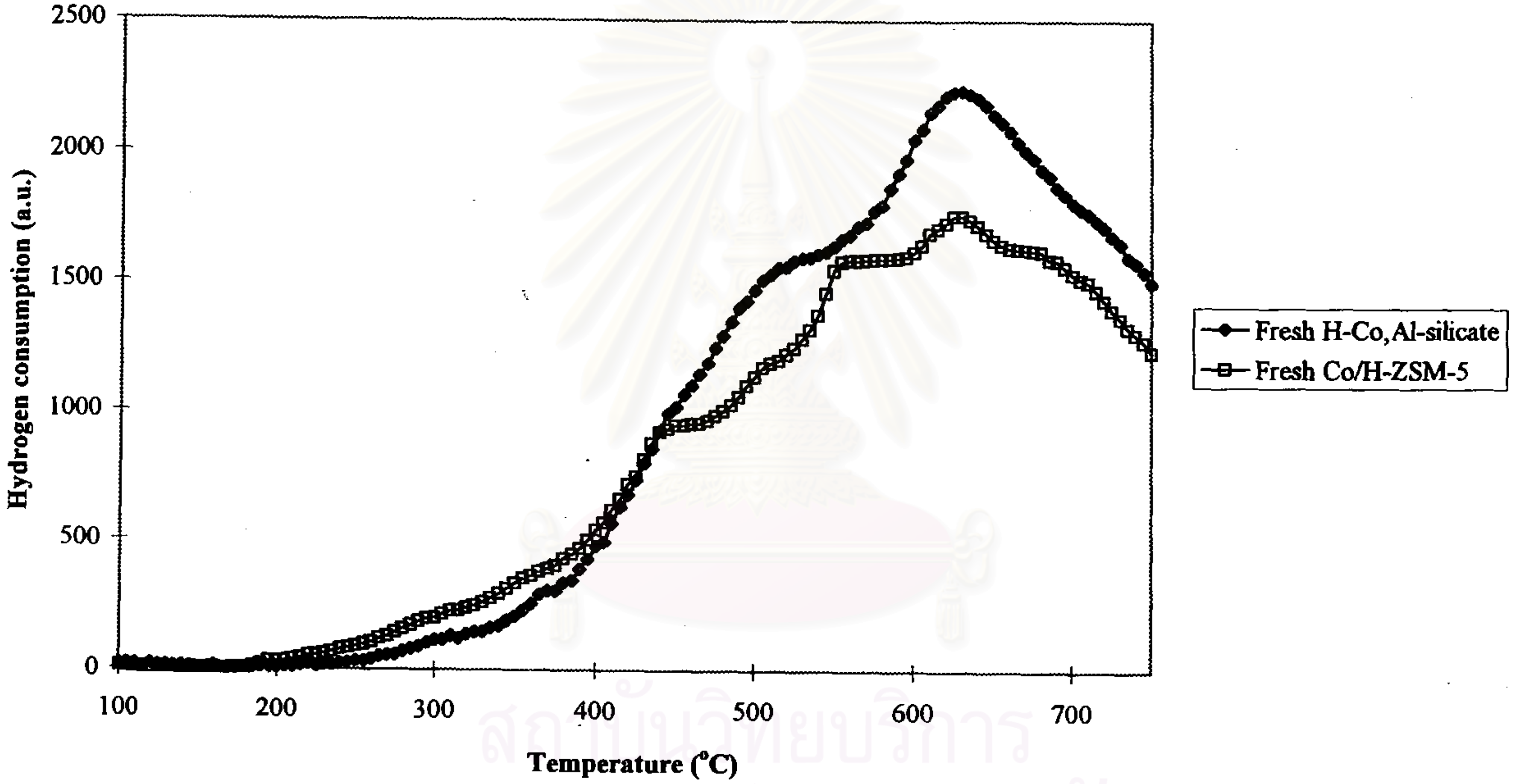

Figure 5.35 H_2-TPR profiles of fresh catalysts

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In report of Inui et al. [55], they found the distribution of Co(II) species in a tetrahedral crystal and a very small concentration of Co(III) in a tetrahedral environment occurring in the MFI structure H-Co-silicate. Co(III) was formed by mean the partial oxidation of Co(II) during the calcination to remove the organic template and/or decompose NH_4-Co-silicate to the protonated form. These phenomena were expected to form in the synthesis of H-Co,Al-silicates, which have similar MFI framework. In TPR profile of H-Co,Al-silicate, the signal peak at ca. 630 °C and shoulder at 530 °C could be suspected to the reduction of cobalt with, however, the unclear explanation of the reduction capacity of metal incorporated in framework.

Figure 5.36 shows the activity of spent catalysts, also Co/H-ZSM-5 and H-Co,Al-silicate in the same reaction condition, in TPR method. Surprisingly, either catalyst displays the H_2 consumption profiles with triplet peaks close to each other. One can expect, the middle peak of Co/H-ZSM-5 at 630 °C is related to the reduction of Co^{2+} ion. As Co^{2+} in ZSM-5 cannot undergo Co^{2+}/Co^{+} cycling [48] and the treatment in an oxygen-containing gas stream at elevated temperature showed no significant generation of diamagnetic Co^{3+} in the Co/ZSM-5 [17,59], thus, the other TPR peaks of this catalyst cannot be considered to the oxidation state change of cobalt. In the study of Chang and McCarty [48], the adsorption nature of Co/ZSM-5 was found. Co/ZSM-5 does not adsorb significant oxygen when treated in O_2 alone, also supported by the O_2-TPD experiments conducted by Bell [4] and Tabata et al. [40] but when treated in a mixture of NO + O_2, large amount of adsorbed NO_2, NO and O_2 are observed. It suggests that the spent catalyst which was exposed to the mixture of NO and O_2 in the reaction run can adsorb oxidizing species which cannot

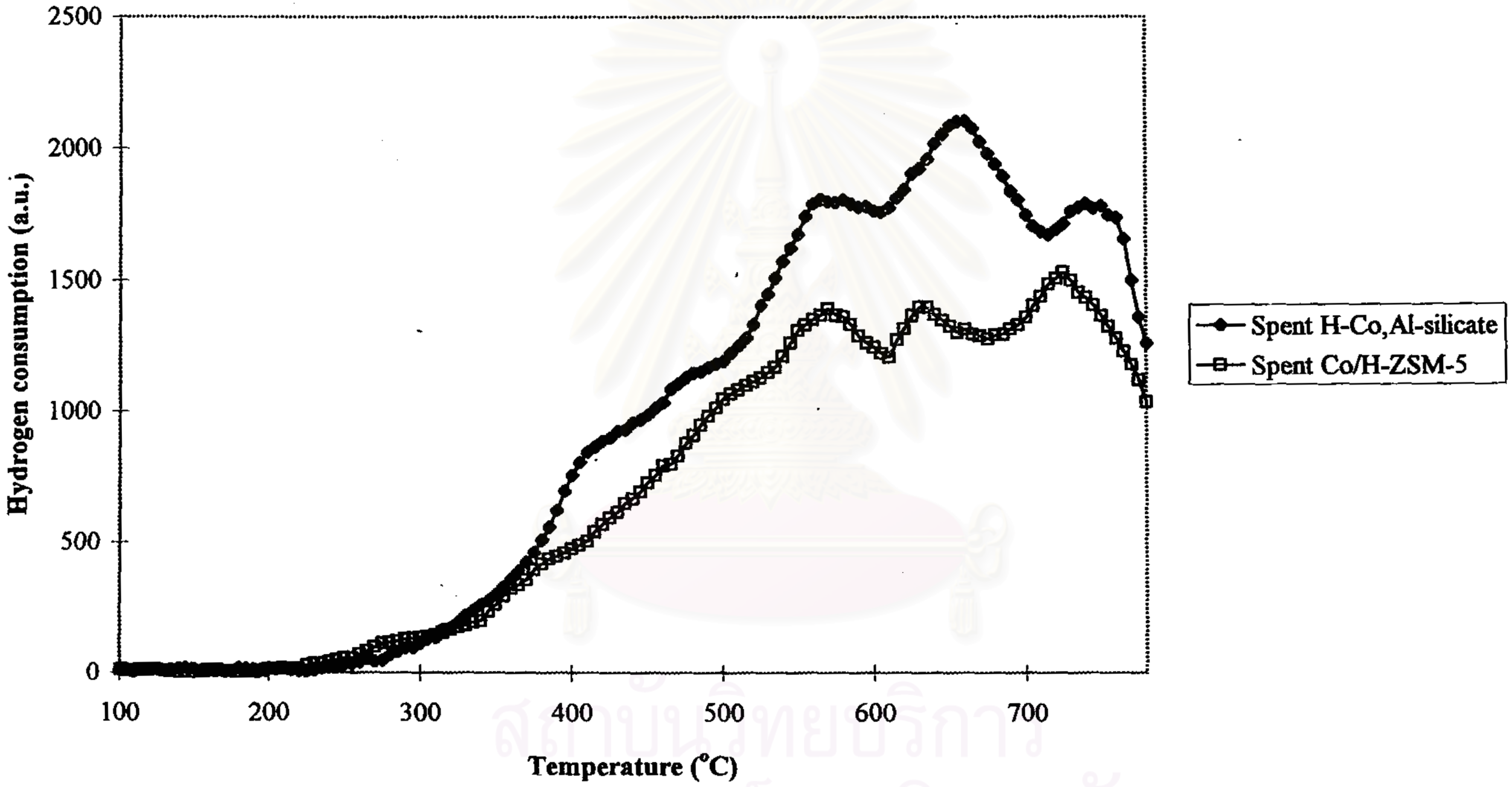

Figure 5.36 H_2-TPR profiles of spent catalysts
SCR Reaction: [NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

be removed by pretreatment in O_2 at 500 °C due to the strong adsorption [50] and, thus, can tolerate reduction run, giving the H_2-consumption peaks. The other two TPR-peaks of Co/H-ZSM-5, around the peak of Co^{2+} reduction at 630 °C, could be reflected on the characteristic peaks of strongly adsorbed-oxidizing species presence in SCR process.

The TPR profile of spent H-Co,Al-silicate should be discussed in the same way of Co/H-ZSM-5. The alteration of reduction temperature may be due to the interaction of H-Co,Al-silicate matrix, dissimilar to that of Co/H-ZSM-5, with the molecules in gas phase. Nevertheless, the more H_2 consumption of H-Co,Al-silicate compared to Co/H-ZSM-5 with using about the same weight both in fresh and spent catalysts was doubted to the more active site for adsorption or more amount of adsorbed species.

5.5.6 CO adsorption

In Table 5.1, the amount of the adsorbed carbon monoxide is shown for both fresh and spent catalysts, Co/H-ZSM-5 and H-Co,Al-silicate. The carbon monoxide uptakes were found to increase with spent Co/H-ZSM-5 but decrease with spent H-Co,Al-silicate.

For Co support catalysts in study of Lipidus et al. [70], the dried sample adsorbed a substantially lower amount of carbon monoxide than did the calcined one. The increase in the amount of adsorbed carbon monoxide may be connected with the formation of some new carbon monoxide adsorption centres in the course of thermal pretreatment in air [70]. As spent Co/H-ZSM-5 was exposed to high temperature during the reaction run, some sites may be converted to be active for carbon monoxide adsorption. ESR and XPS study of Co/ZSM-5 by Ying et al. [59] suggested that Co cation occupied two possible sites with low coordination symmetry in ZSM-5 and FTIR study of CO adsorption on Co/ZSM-5 by Campa et al. [32] showed the formation of carbonyls band with one type stretching mode. These may imply that upon high temperature experience such sites that active for carbon monoxide adsorption from two possible sites occupied by Co cation were regenerated with higher ratio. However, the report of Campa et al. [32] also revealed that carbon monoxide can adsorb on sites of the zeolite matrix, therefore, alternation of zeolite matrix by thermal treatment in reaction run should effect to the amount of adsorbed carbon monoxide.

In case of H-Co,Al-silicate, the decrease in quantity of carbon monoxide adsorption of spent catalyst may be illustrated by the decline in active centre due to strongly adsorbed species presence in the SCR process (see TPR result) or due to educing of Co active sites by experiment in steam-high temperature reaction which usually occurs in H-Co-silicate [52,55]

Table 5.1 CO Adsorption (molecules/g cat.) on active sites of catalysts

Catalyst	**Fresh**	**Spent**
Co/H-ZSM-5	4.41×10^{18}	25.96×10^{18}
H-Co,Al-silicate	10.75×10^{18}	2.08×10^{18}

5.5.7 Electron spin resonance, ESR

All the catalysts were exposed to air prior to ESR study due to the lack of *in situ* experimental setup. However, the oxidation state was not expected to be changed in air at room temperature. Water molecules from the atmospheric moisture might cause a coordination change, but this factor was not expected to play a significant role for the ESR study [59]. Since there were always water molecules in the reaction gas stream for NO reduction with methane, the ESR spectrum collection in air should well simulate the actual reaction conditions. Figures 5.37-5.44 show the ESR spectra of Co/H-ZSM-5 and H-Co,Al-silicate in various conditions. In each spectrum, the Y-axis represents the amount of absorption of microwave radiation while the parallel axis represents the intensity of magnetic field used and the useful curve for interpretation is the first derivative one.

The catalysts in conditions of fresh (as prepared), spent (exposed to reaction run), SO_2 effect (exposed to reaction run with SO_2 co-existence) and H_2O effect (exposed to reaction run with steam co-existence) were performed and resulted in different shapes of ESR spectra which shows that all Co/ZSM-5 and H-Co,Al-silicate are ESR active due to un pair electron in *d*-orbital in metal ion and all the Co species in Co/ZSM-5 are paramagnetic[59]. A significant change in the shape of line of the signal obtained from all spent catalysts suggests either a change in the coordination environment of the Co^{2+} or that some aggregation of Co has occurred, casing broadening of the signal [53].

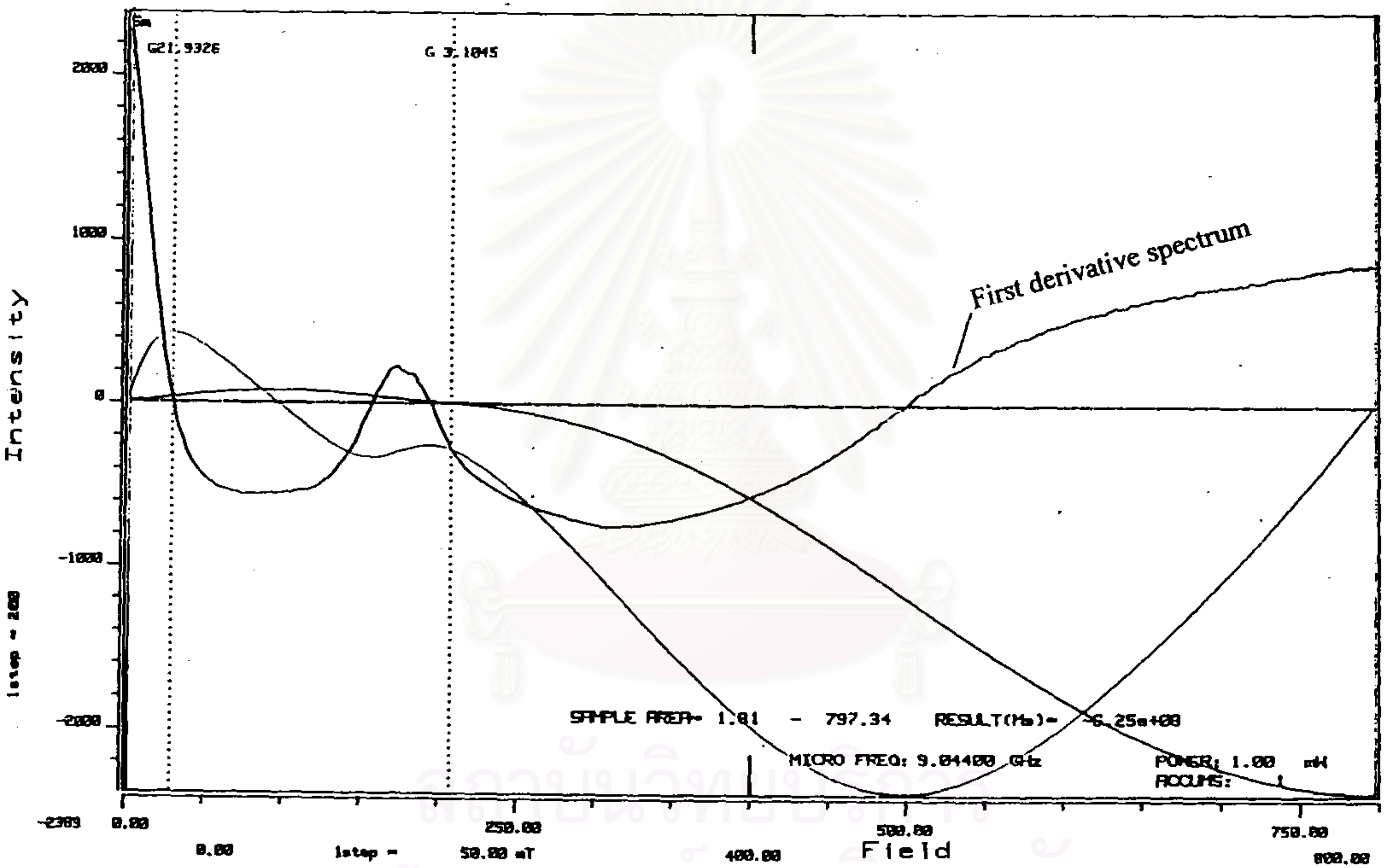

Figure 5.37 ESR spectrum of fresh Co/H-ZSM-5

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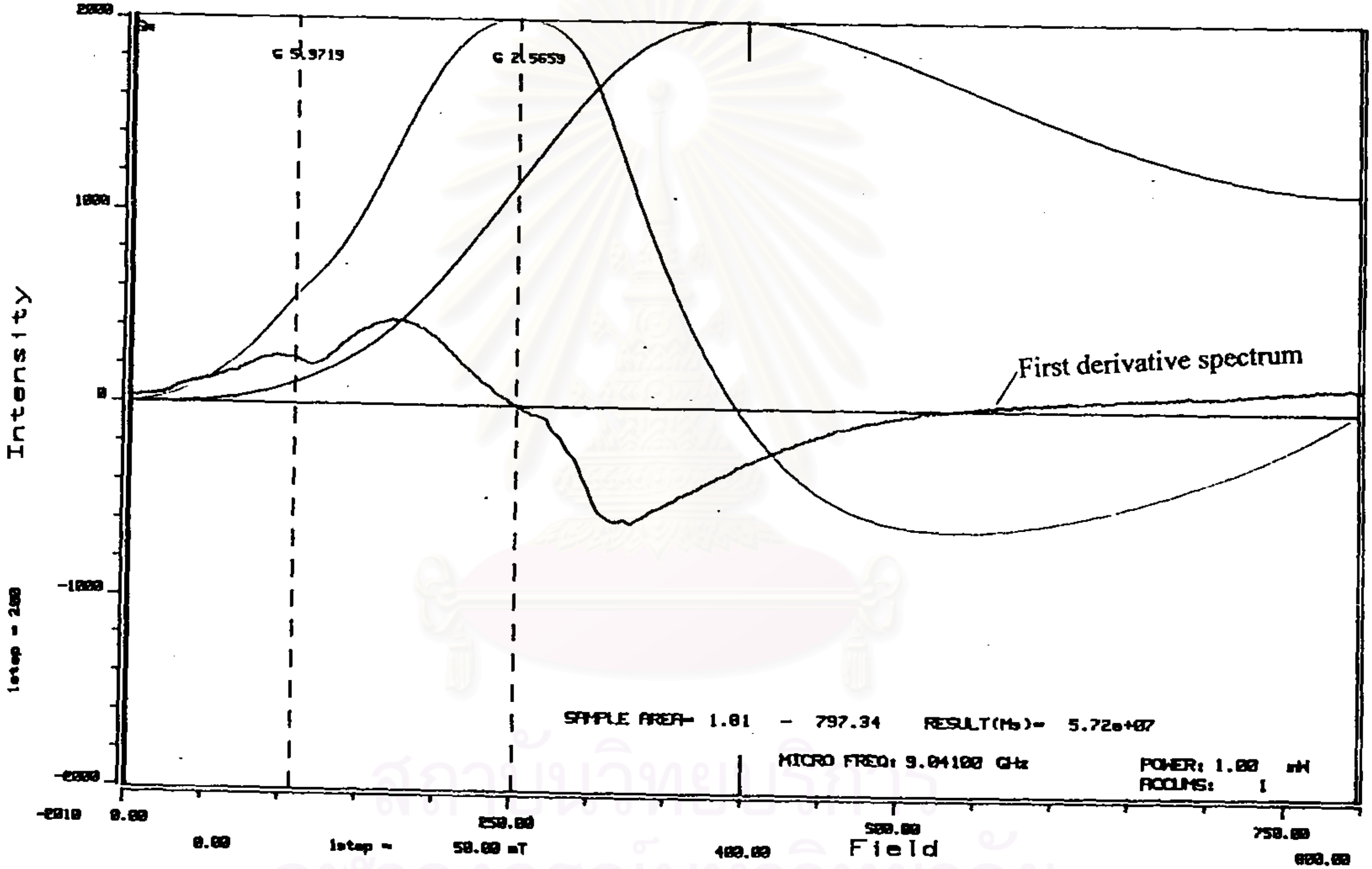

Figure 5.38 ESR spectrum of spent Co/H-ZSM-5

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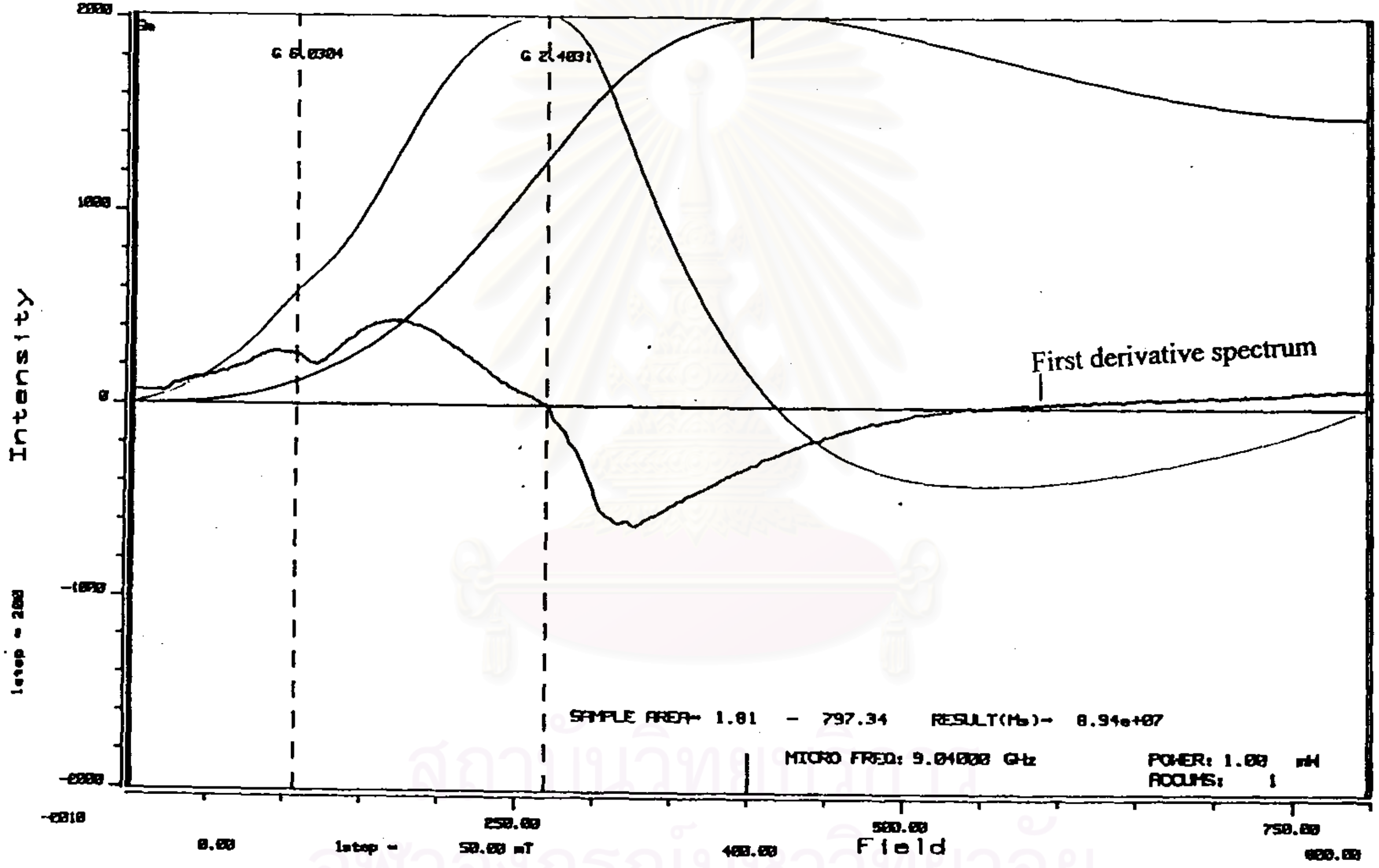

Figure 5.39 ESR spectrum of spent Co/H-ZSM-5 with the presence of SO_2

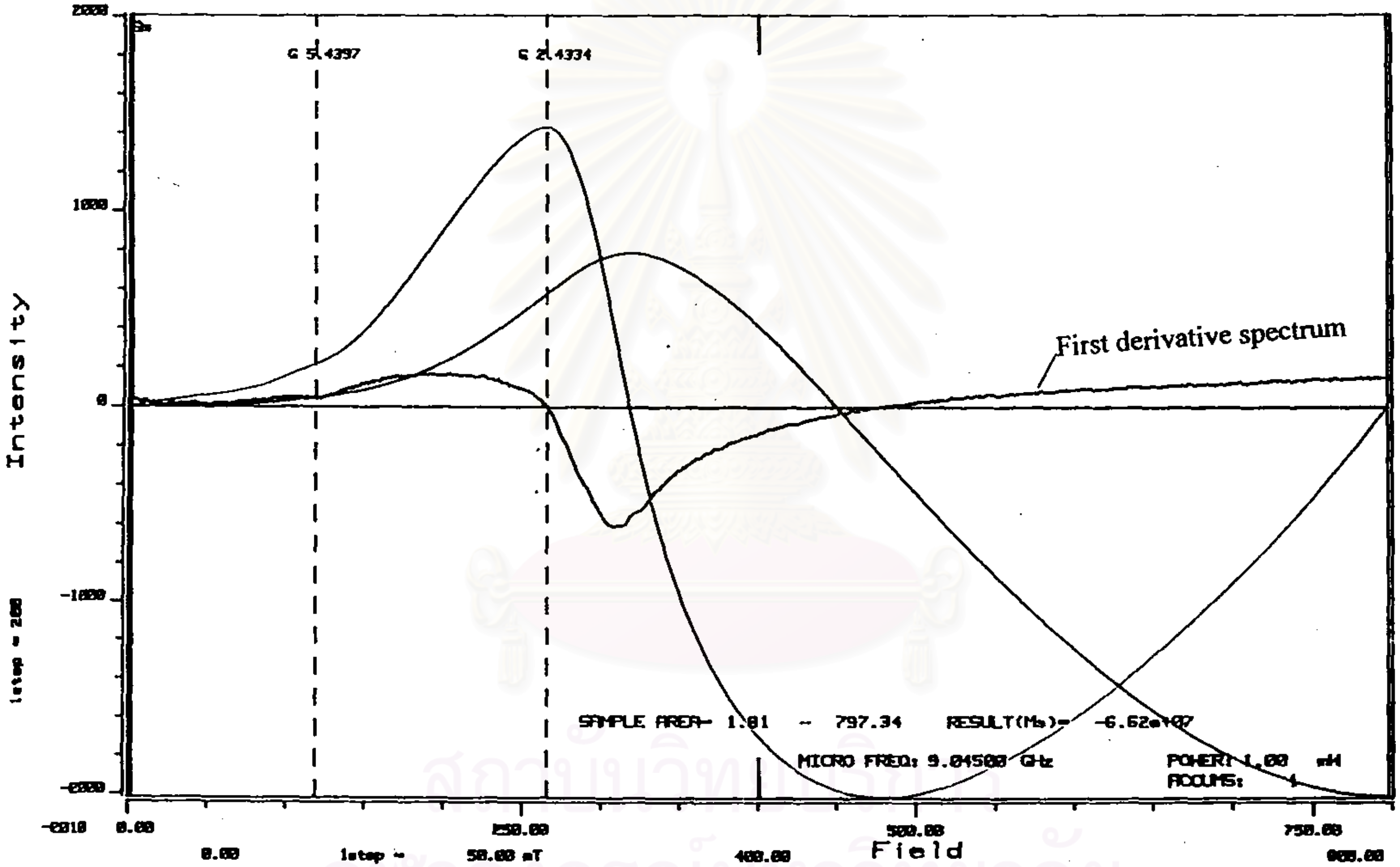

Figure 5.40 ESR spectrum of spent Co/H-ZSM-5 with the presence of H_2O

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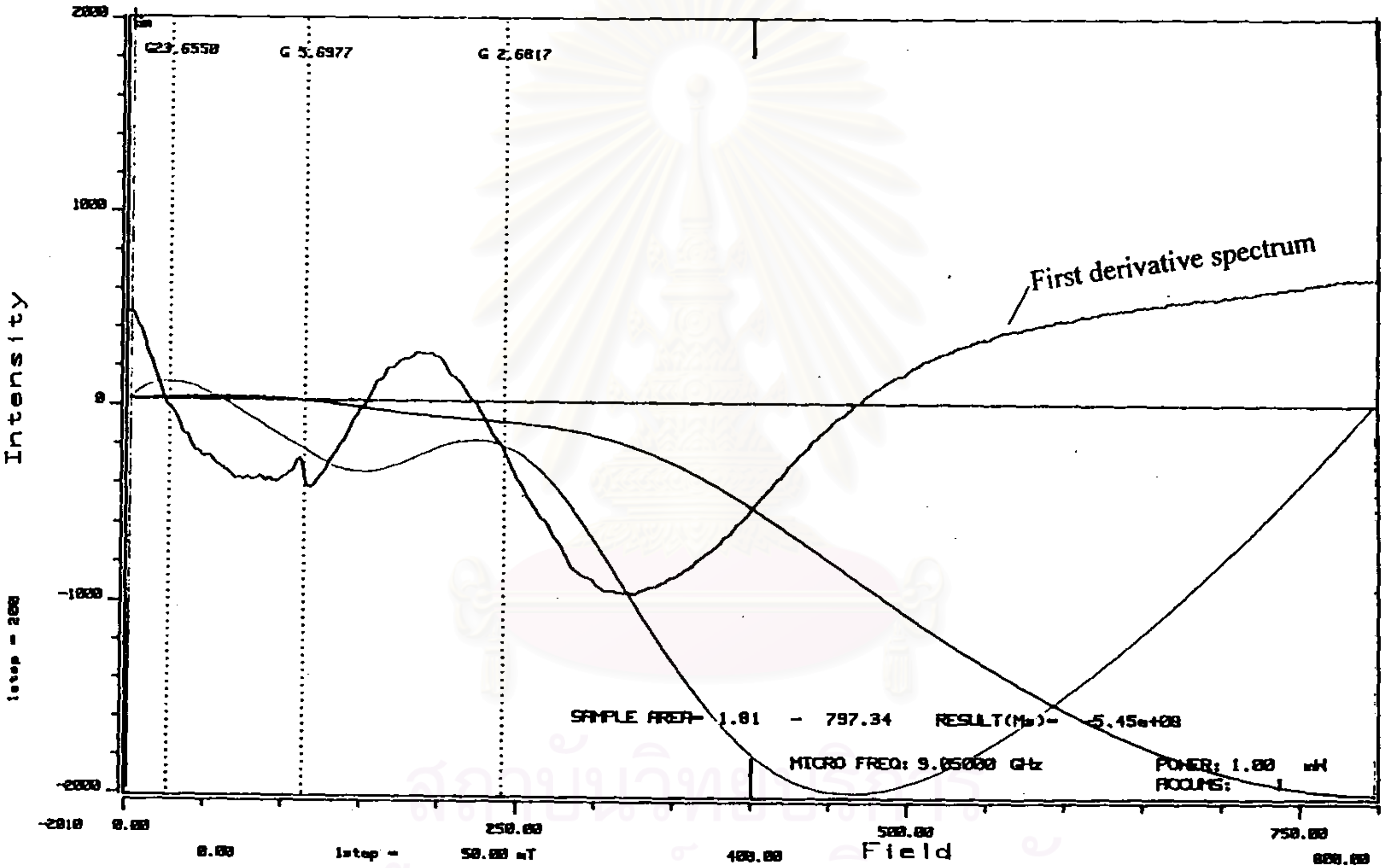

Figure 5.41 ESR spectrum of fresh H-Co,Al-silicate

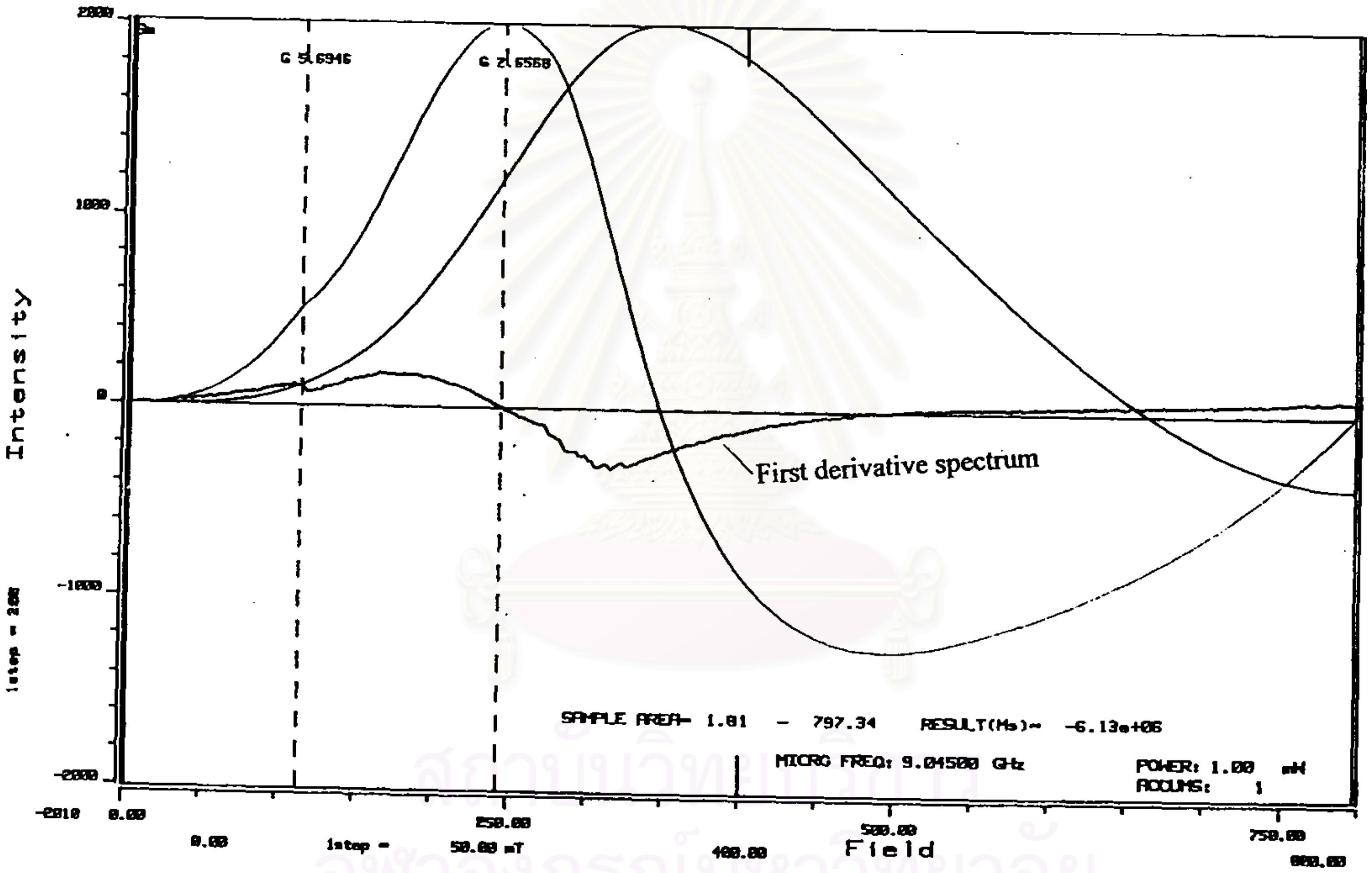

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Figure 5.42 ESR spectrum of spent H-Co,Al-silicate

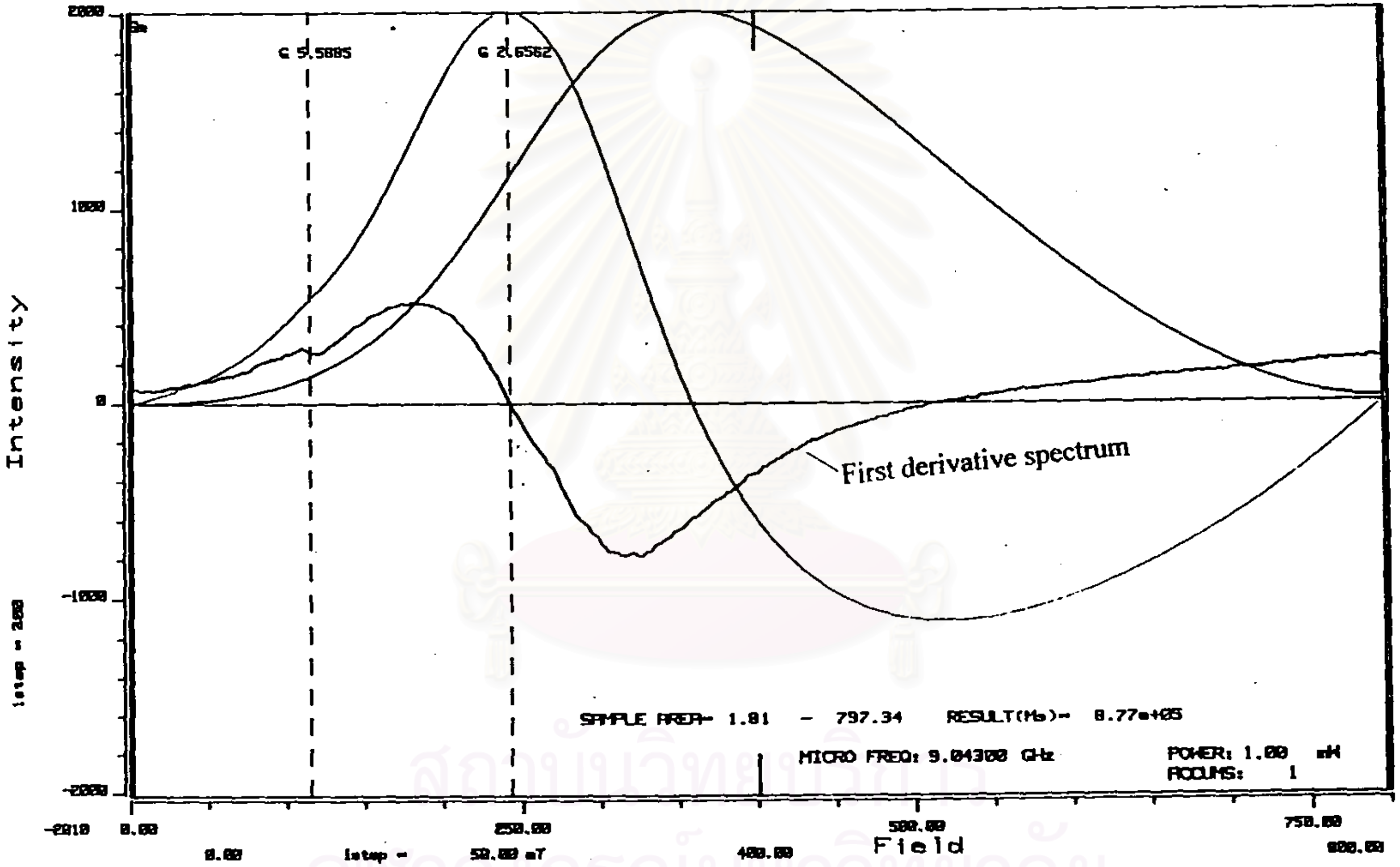

Figure 5.43 ESR spectrum of spent H-Co,Al-silicate with the presence of SO_2

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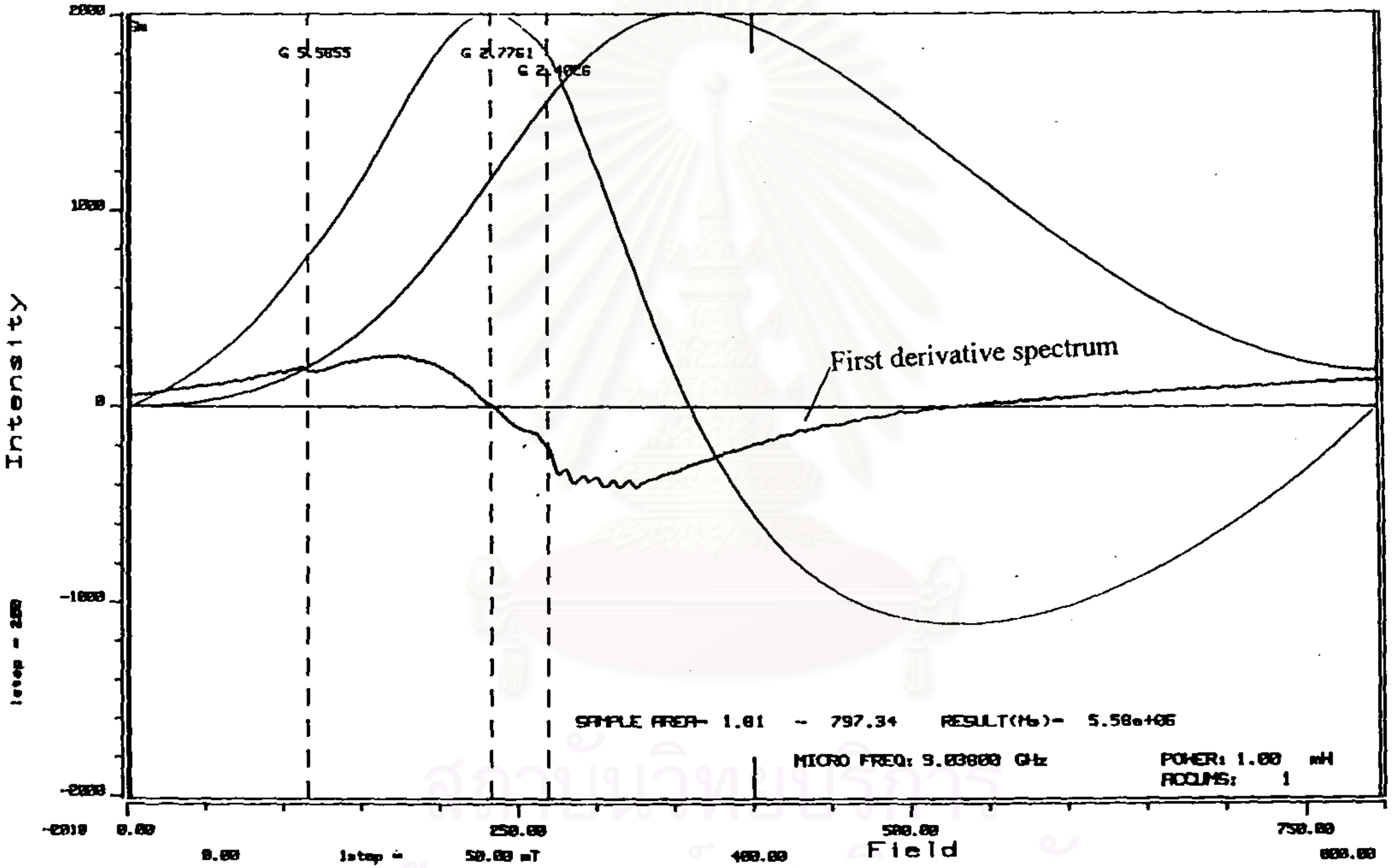

Figure 5.44 ESR spectrum of spent H-Co,Al-silicate with the presence of H_2O

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In study of Co/H-ZSM-5 by Ying et al. [59] indicated the presence of two types of cobalt species with different coordinations. Their ESR studies of Co/ZSM-5 suggest that there are more than one position (most likely two) for cobalt cations in ZSM-5 even when the loading of Co^{2+} is only slightly higher than 100%. However, unlike the axial symmetry imposed on copper cations, low symmetry is exhibited for cobalt cations in ZSM-5. The possibility that the cobalt cations are located in different sites from copper cations in ZSM-5 can be rule out since the distribution of aluminium in ZSM-5 is not altered by cation exchange. The low symmetry of cobalt in ZSM-5 may be attributed to the different strength of interaction between cobalt and some framework oxygen. Such preferential attraction may have caused the cobalt to reside closer to certain framework oxygen sites, away from the axially symmetric positions. The exact position and coordination symmetry for cobalt in ZSM-5 are unknown and difficult to be determined by X-ray crystal lography. DRIFT studies of Co/ZSM-5 by Ying et al. [59] also indicated the stronger chemical coordination between Co^{2+} cations and zeolite framework oxygen. Nevertheless, Armor and Farris [24] found that Co/ZSM-5 had a remarkably high hydrothermal stability due to the stabilization of Co^{2+} cations to the zeolite structure. The strong interaction of Co^{2+} with framework oxygen could have accounted for such characteristics. However, the presence of O_2, NO_2 and also steam can change their binding nature. In the presence of O_2 or $NO + O_2$ (which simulates the actual exhaust gas stream), the interaction of cobalt with zeolite framework was weakened due to the formation of Co^{2+} complex with molecular oxygen, nitrogen dioxide or water species [59] and changing the coordination number of cobalt ion. These results of ESR experiment are in agree with the TPR result. The Co(II) species in a tetrahedral environment of H-Co,Al-silicate may be educed from the framework during the reaction run, like the behavior of H-Co-silicate [52,55]. However, the alteration in ESR shapes should be caused by both guesses, the change in coordination number of cobalt in MFI framework H-Co,Al-silicate indicating by the irreversible adsorption of SO_2 and the educing of framework cobalt.

5.6 The effect of cobalt content loading by ion-exchange method on Co,Al-silicate catalysts in selective NO reduction with the presence of methane in lean-burn condition

5.6.1 Co/Na-Co,Al-silicate

For indication the dependencies of metal content loading by ion-exchanged method on Na-Co,Al-silicate catalysts on the NO removal in selective catalytic reduction by CH_4 in oxidizing atmosphere, Co ion-exchanges were carried on Na-Co,Al-silicate by several times for different requirement of amount of cobalt. Figure 5.45 and 5.46 show the conversions of NO and CH_4 as a function of temperature and cobalt content on Na-Co,Al-silicate and Co/Na-Co,Al-silicate catalysts respectively.

According to Co/Na-ZSM-5 which has much more NO reduction activity than that of its parent, Na-ZSM-5, by which ion-exchange Co cation into, Co/Na-Co,Al-silicate was expected to have NO conversion activity much more than that of Na-Co,Al-silicate in the same manner. Cobalt was ion-exchanged into Na-Co,Al-silicate by common method. The amount of Co that was dispersed either on cation exchanged position and in MFI framework of Na-from of Co,Al-silicate varies from

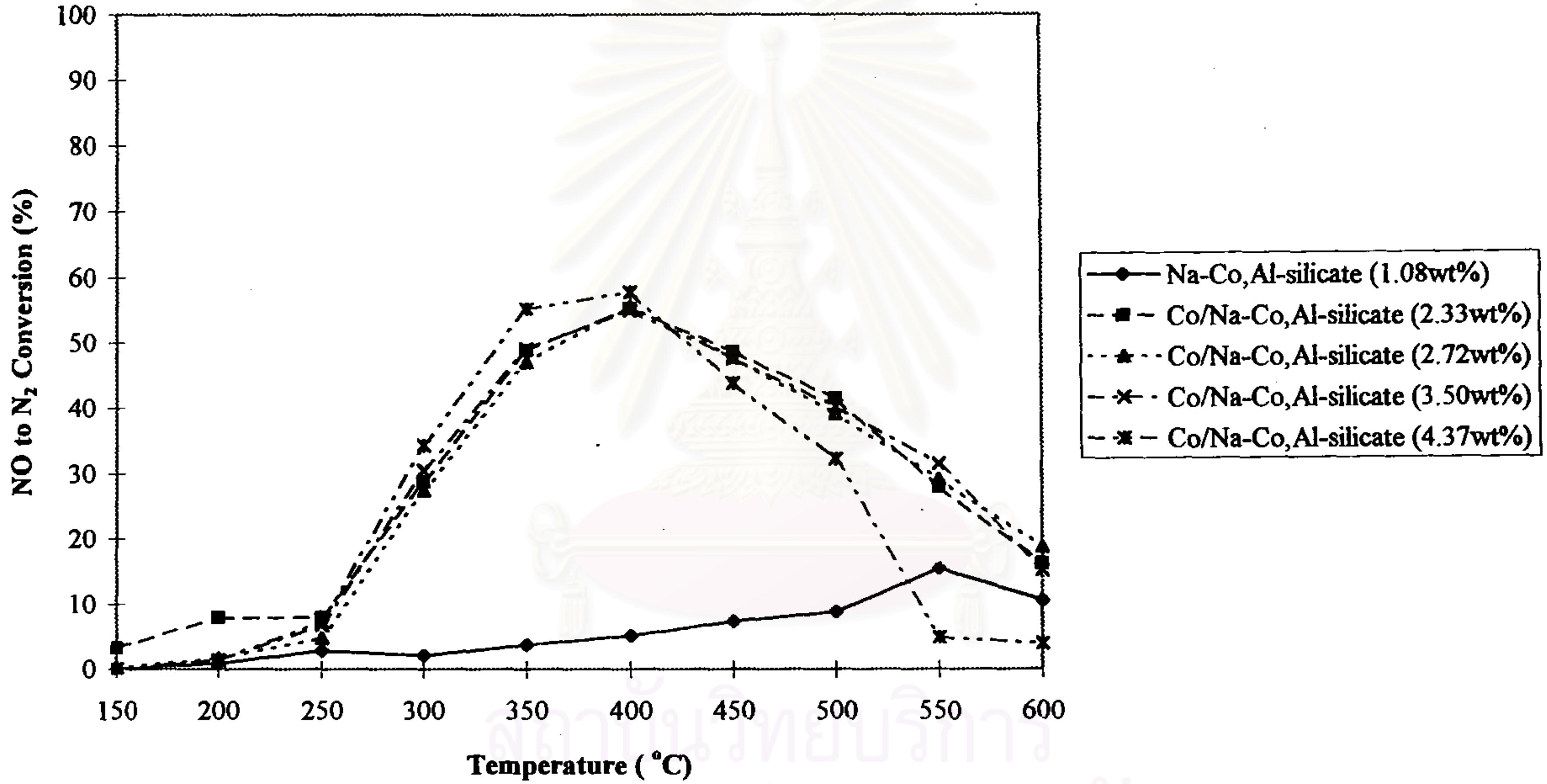

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Figure 5.45 Nitric oxide conversion as a function of temperature and cobalt content on Na-Co,Al-silicate and Co/Na-Co,Al-silicate [NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

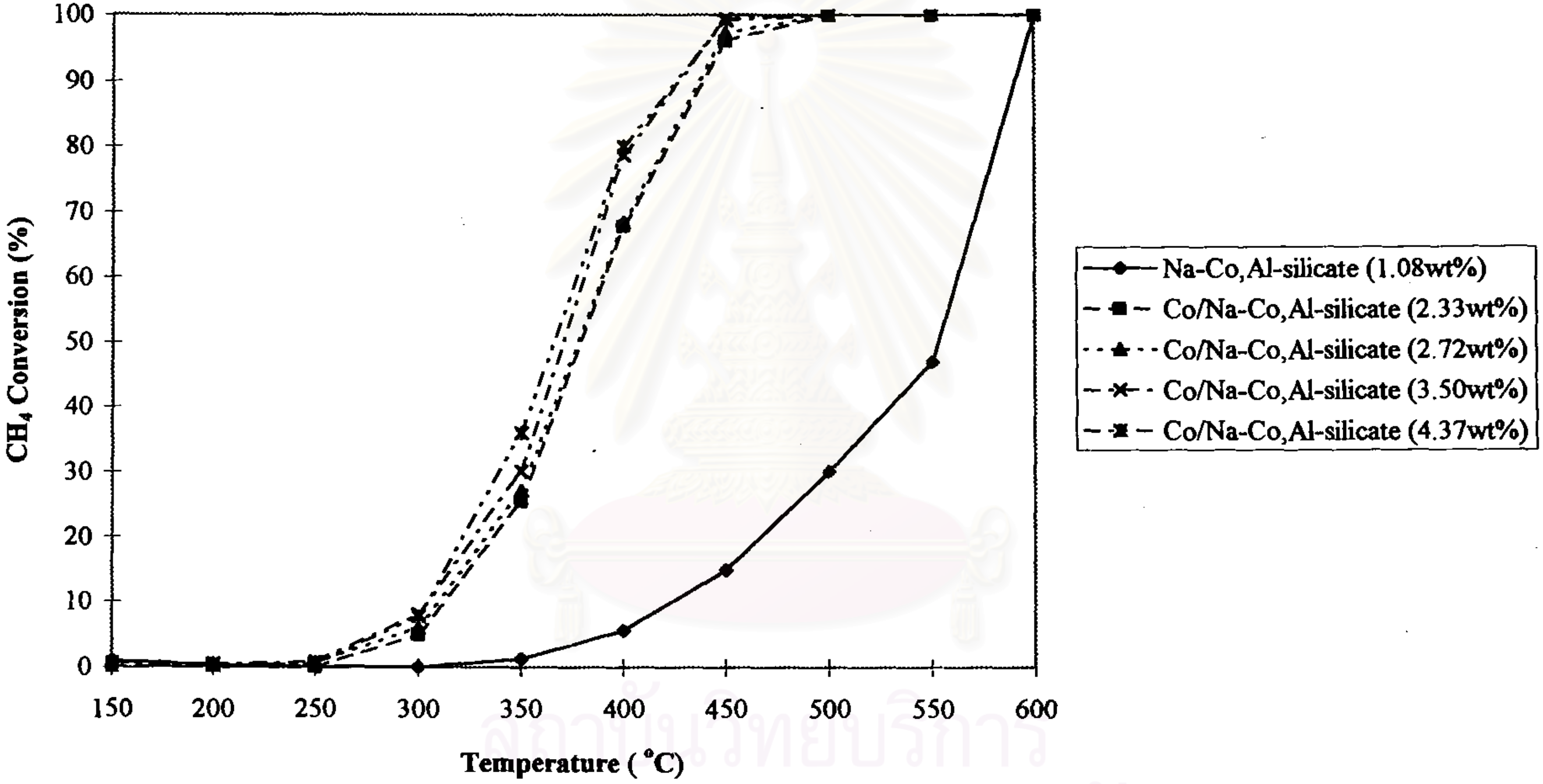

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Figure 5.46 Methane conversion as a function of temperature and cobalt content on Na-Co,Al-silicate and Co/Na-Co,Al-silicate
[NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

2.33 to 4.37 % by wt., but their NO conversion can be implyed to almost the same. Certainly, in Figure 5.45, Co ion-exchanged Na-Co,Al-silicate can monotonically increase NO conversion activity for all reaction temperature range and decrease maximum conversion temperature from 550 °C to 400 °C (the same as Co/Na-ZSM-5), however, the level of cobalt concentration seems to has little function on NO conversion. For Co/Na-ZSM-5 which has 4.37 % Co content, the highest cobalt concentration in this study, it has more NO conversion activity than the other and its light-off temperature is shifted to the lower temperature, this may be due to the formation of cobalt oxide which is known to active for NO oxidation, the initial step of SCR reaction, during the ion-exchanged stage [38].

Expectantly, Co ion-exchanged into Na-Co,Al-silicate enhanced CH_4 conversion (Figure 5.46) and also improved NO conversion too. This demonstrated that mechanism of selective catalytic reduction of NO by CH_4 in oxygen atmosphere may be the same on both Co/Na-ZSM-5 and Co/Na-Co,Al-silicate catalysts. On the other hand, the much more activity of NO and CH_4 conversions on Co/Na-Co,Al-silicate caused by the addition of metal ion sites in Na-Co,Al-silicate are reasoned by that cobalt cation can activate methane oxidation and this reaction is important for SCR reaction [21,76].

5.6.2 Co/H-Co,Al-silicate

Figures 5.47 and 5.48 demonstrate NO and CH_4 conversion as a function of temperature and cobalt content on Co/H-Co,Al-silicate catalysts comparing to that of H-Co,Al-silicate respectively.

In Figure 5.47, NO conversion curves with temperature function over Co/H-Co,Al-silicates which total Co content varies from 1.08-3.99 wt. % sharply increases with the increase in temperature. Unlike Co/H-ZSM-5 and H-Co,Al-silicate, the NO conversion of Co/H-Co,Al-silicate displays two-volcano-shaped curve as temperature further increases when lower amount of cobalt was ion-exchanged into while much more increase in cobalt content reduces conversion of NO all reaction temperature range. As prospect , increasing amount of Co into H-Co,Al-silicate by ion-exchange method as the same way of Co catalysts mention before enhances NO conversion activity up to a limit value. Like the activity of Co/H-ZSM-5, NO conversion of Co/H-Co,Al-silicate increases as a function of Co content and also significantly shifts the light off temperature to lower temperature region. However, ion-exchange capacity of protonated Co,Al-silicate for substituting proton with Co ion hardly occurs but substitution of Co ion to Na ion of Co,Al-silicate easily practice.

Once, more increasing in activity of Co/H-Co,Al-silicate even less Co content compared to Co/Na-Co,Al-silicate was found and indicated some role of Brønsted acidity playing in conversion activity. Another support is that the NO conversion activity rapidly decline when Brønsted acidity is less than some limit due to over amount of Co ion-exchanged. The presence of two volcanic shape of Co/H-Co,Al-silicate represents the two different active site, one is the cobalt cation site responding for the maximum conversion at lower reaction temperature and the other is the active site of H-Co,Al-silicate, may be Brønsted acid site, responding to the higher reaction temperature maximum conversion peak. Increasing in cobalt ion-exchanged content leads to the decrease in Brønsted acid sites and clearly exhibits in the decreasing in activity of NO conversion particularly at the maximum conversion peak at higher

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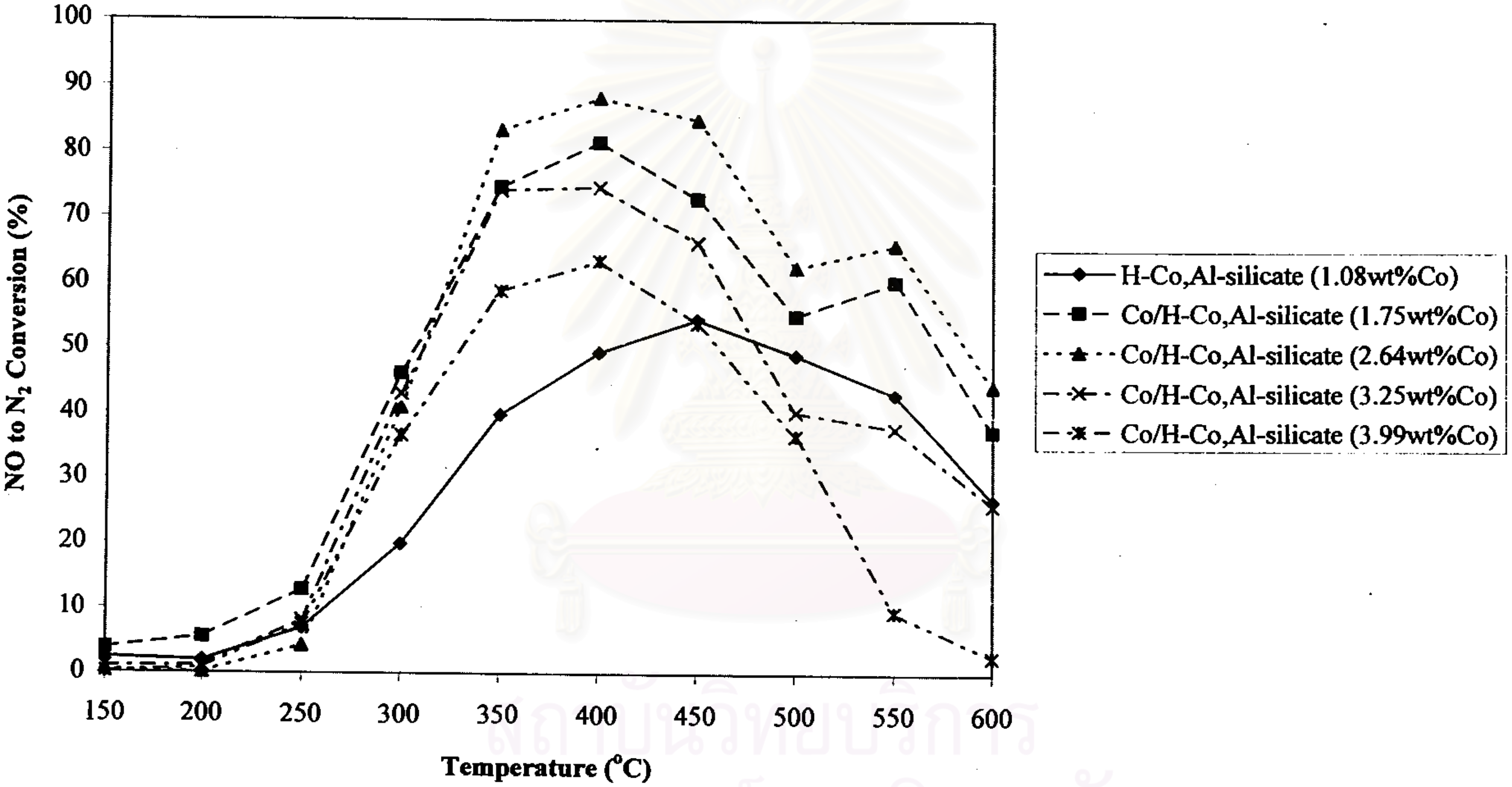

Figure 5.47 Nitric oxide conversion as a function of temperature and cobalt content on H-Co,Al-silicate and Co/H-Co,Al-silicate [NO] = 1000 ppm, [CH_4] = 10000 ppm, [O_2] = 10 %, GHSV = 4000 h^{-1}

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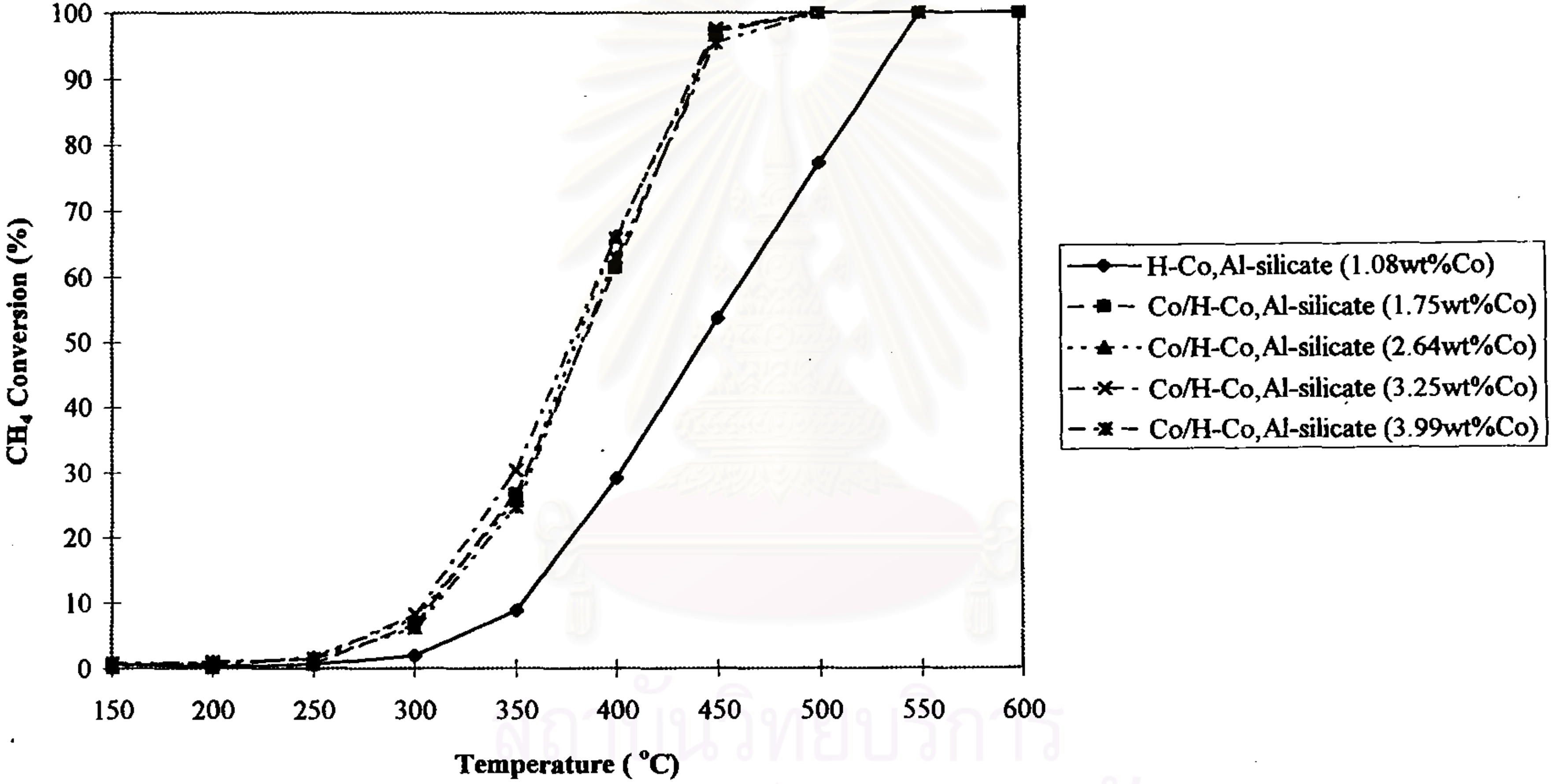

Figure 5.48 Methane conversion as a function of temperature and cobalt content on H-Co,Al-silicate and Co/H-Co,Al-silicate
$[NO] = 1000$ ppm, $[CH_4] = 10000$ ppm, $[O_2] = 10$ %, GHSV = 4000 h^{-1}

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reaction temperature which disappears over catalysts containing 3.99 wt. % Co, the highest cobalt content.

Consider methane conversion of Co/H-Co,Al-silicate in Figure 5.48. It is clear that Co ion-exchanged into H-Co,Al-silicate enhance methane conversion, but amount of Co is not a function to convert methane. Note that the decrease in NO conversion with higher cobalt content by ion-exchange may be due to more active site for methane combustion, Co cation site.

5.6.3 Catalytic Comparison among H-form of Co/ZSM-5, Co,Al-silicate and Co/Co,Al-silicate with controlling the quantity of cobalt in selective reduction of NO by methane in oxygen excess condition

To compare the selective catalytic reduction of NO by methane in excess oxygen condition of H-form MFI structure zeolites, i.e., Co/H-ZSM-5, H-Co,Al-silicate and Co/H-Co,Al-silicate, the catalyst of each group which has similar concentration of cobalt, about 2 wt.%, was chosen. Because Na-Co,Al-silicate is poorly active for SCR reaction, the activity comparison by controlling the amount of metal dispersed over that catalyst is more useful to conduct on H-form of MFI type zeolites.

H-Co,Al-silicate with 0.98 wt.% Co was ion exchanged with a desired amount of cobalt acetate solution to obtain the total concentration of cobalt equal to 2.01 wt.%

Figure 5.49 shows the NO conversion as a function of temperature of Co/H-Co,Al-silicate compared to those of Co/H-ZSM-5 and H-Co,Al-silicate catalysts which all have equal content of cobalt. It is clear that for three kinds of MFI structure zeolites with the same quantity of cobalt, Co/H-Co,Al-silicate which has two types of metal positions with almost the same number, exhibits the highest activity for NO removal among the other two. As this catalyst has two types of position that occupied by cobalt ion, is that, some disperse in zeolite framework and the other disperse over cationic positions. It was expected that these two types of cobalt will promote with each other, leading to the superior NO conversion activity over those catalysts which have only Co ion at cationic exchanged site or incorporatred Co in the MFI structure.

Methane conversion of Co/H-Co,Al-silicate as compared in Figure 5.50 to those of Co/H-ZSM-5 and H-Co,Al-silicate, the same catalysts in Figure 5.49 indicates that Co ion exchanged sites enhance methane oxidation of H-Co,Al-silicate, similar behavior to Co ion exchanged H-ZSM-5.

The results conclusively demonstrate the high potential of Co ion exchanged H-Co,Al-silicate for the removal of NO in exhaust gases from lean burn facilities and also diesel engines.

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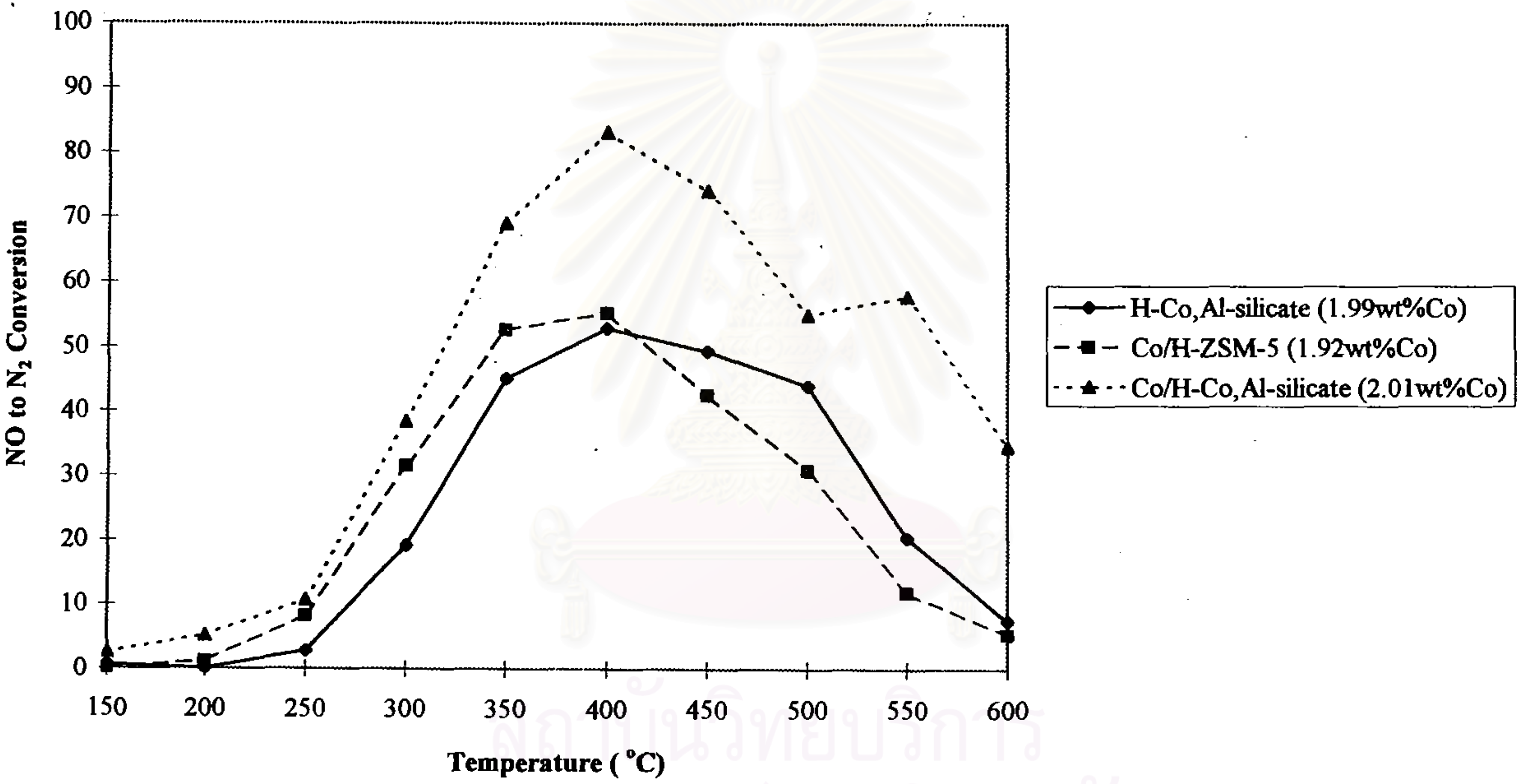

Figure 5.49 Catalytic comparison of nitric oxide conversion between Co/H-ZSM-5, H-Co,Al-silicate and Co/H-Co,Al-silicate [NO] = 1000 ppm, $[CH_4]$ = 10000 ppm, $[O_2]$ = 10 %, GHSV = 4000 h^{-1}

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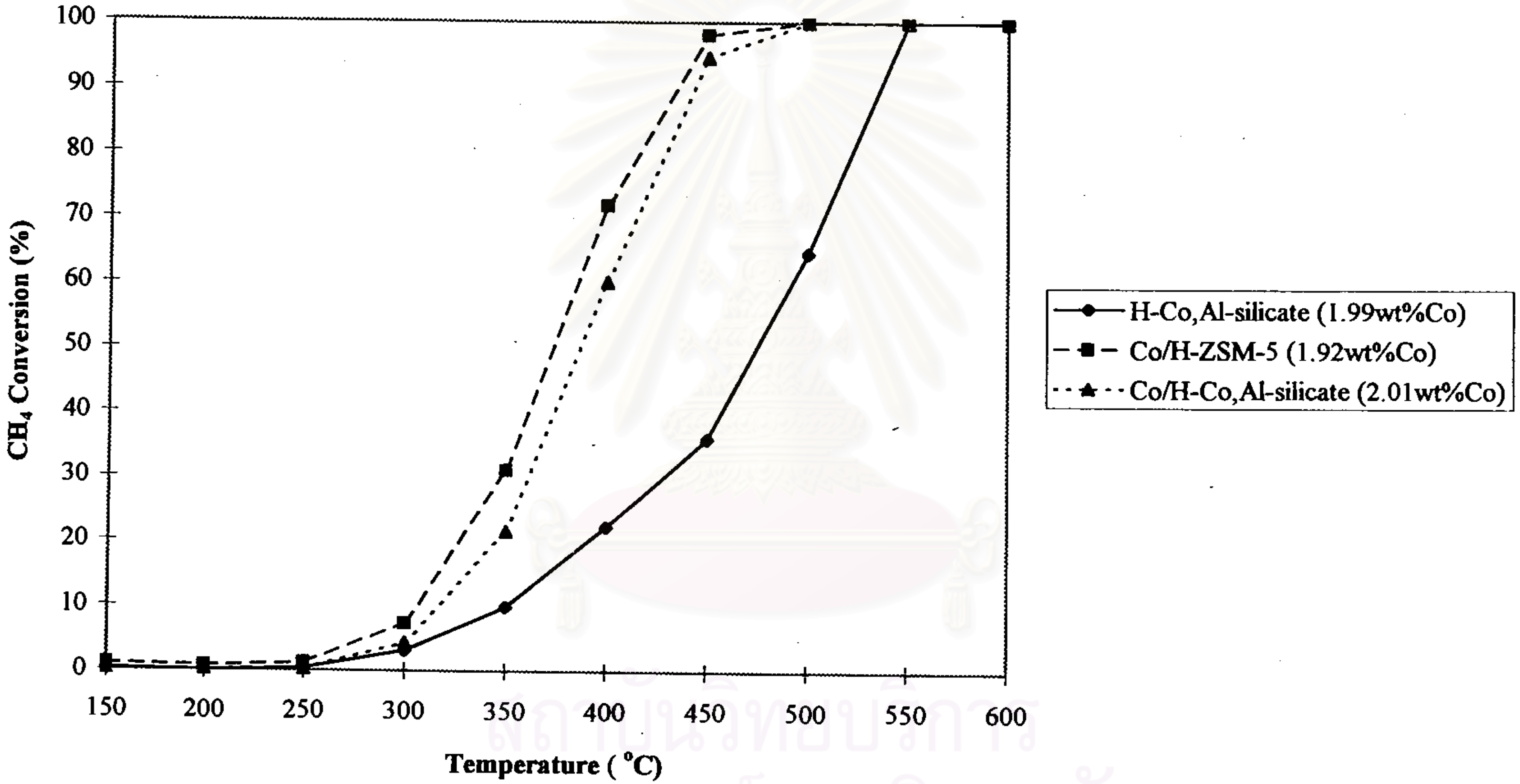

Figure 5.50 Catalytic comparison of methane conversion between Co/H-ZSM-5, H-Co,Al-silicate and Co/H-Co,Al-silicate $[NO] = 1000$ ppm, $[CH_4] = 10000$ ppm, $[O_2] = 10$ %, GHSV = 4000 h^{-1}

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