

CHAPTER VII

ENHANCEMENT OF THE ACTIVITY OF H-Co-silicate FOR NITRIC OXIDE REMOVAL BY HIGH THERMAL-TREATMENT

7.1 Introduction

Removal of nitric oxide using hydrocarbons as the reductant has been studied in the presence of excess oxygen in the past decade. Among the catalysts, zeolites and their related materials were extensively used for this purpose. Copper ion-exchanged MFI (Cu/MFI) catalyst is well known to be an effective catalyst for removal of nitric oxide in the presence of excess oxygen [8,9,59-62]. Unfortunately, since Cu/MFI is easily deactivated at high temperatures ($>800^{\circ}\text{C}$) and the co-existence of steam which possibly occurred in practical use [44-47]. As mentioned above, many researchers have tried to find a new catalyst that can suffer in severe condition especially under co-existence of steam in nitric oxide removal. Budi et al. [79] and Armor et al. [82] found that cobalt ion-exchanged MFI catalyst (Co/MFI) can suffer in the condition of steam and temperature less than 800°C . Nevertheless, in owing to the ease of sintering of exchanged metal component and dislocation of alumina in the framework under high severe condition, the decrement of activity on nitric oxide conversion occurred. On the other hand, protonated cobalt-incorporated silicate having MFI structure (H-Co-silicate) is proposed to be a powerful catalyst which can protect against the deterioration under severe condition at high temperature even with water [48,49]. It was found that the loss of activity of metallosilicates in nitric oxide removal was much smaller than those of ion-exchanged zeolites after high temperature calcination. Moreover, in previous studies it was found that the pretreatment affected the activity of H-Co-silicate for nitric oxide elimination [117]. As referred above, the thermal-treatment of H-Co-silicate is worth for improvement of nitric oxide removal. Accordingly, the objective of this study is to find out the optimum condition of thermal-treatment enhancing the activity of H-Co-silicate in nitric oxide removal. We also describe the activity on nitric oxide removal observed here compared with similar studies on Cu/MFI.

7.2 Experimental

7.2.1 Catalyst preparation

Co-silicate MFI type zeolite was prepared by the rapid crystallization method [97]. The charged Si/Co atomic ratio of Co silicate was set at 20. As-synthesized crystals were washed, dried and heated at the temperature of 540°C for 3.5 h in an air stream. Subsequently, they were ion-exchanged twice with an NH_4NO_3 aqueous solution and followed by the calcination at 540°C for 3.5 h in air. They are designated as H-Co-silicate. As for copper ion-exchanged zeolite, MFI zeolite was synthesized by the same method as mentioned above. The charged Si/Al atomic ratio was set at 50. After transformation into H-type, it was ion-exchanged using copper acetate solution as source and followed by the same approach to gain 200% ion-exchanged Cu on MFI (200%Cu/MFI). Then, the catalysts were pretreated by thermal-treatment and carried out for reaction tests.

7.2.2 Characterization

In order to measure the crystallinity of samples, X-ray diffraction patterns recorded by an X-ray refractometer, Shimadzu XD-D1, with Ni-filtered $\text{CuK}\alpha$ radiation were analyzed. Additionally, BET surface area and the bulk metal composition of catalyst were measured using a Shimadzu Flow Sorb II 2300 and Inductively Coupled Plasma analysis (ICP Shimadzu ICPS-1000 III), respectively. UV-visible spectra were analyzed by Shimadzu MPS-2000 spectrometer installed with a multi-purpose reflectometry attachment, RTA-2000 using BaSO_4 as a reflectance standard. Furthermore, a Jeol model JEOL JES-RE2X spectrometer equipped with a JEOL microwave power 1 mW was used to recorded X-band spectra for electron spin resonance method of the catalyst at liquid nitrogen temperature. In situ-FTIR spectra analyzed by Nicolet model Impact 400 was applied to acidity measurement of sample using pyridine as probe. Additionally ^{29}Si MAS NMR analysis was performed using a JEOL 270 SGX. For TPR measurement, 0.2 g portions of catalyst was reduced in a 5% H_2/Ar stream. The concentration of hydrogen in the effluent gas was recorded by a TCD gas chromatograph after water vapor was removed using a cold trap at methanol-dry ice temperature.

7.2.3 Pretreatment by thermal-treatment condition

For studying the effect of pretreatment on nitric oxide removal, H-Co-silicate

and Cu/MFI were calcined in the temperature range from 600°C to 1,100°C in a He atmosphere. The catalysts were heated at a constant heating rate of 10°C/min from room temperature to 600°C and 1.67°C/min from 600°C to 1,100°C using an electric oven. The catalyst was then kept at the desired temperature for 30 min and then cool down to room temperature.

7.2.4 Reaction test

The catalytic reaction was carried out using an ordinary flow microreactor under atmospheric pressure. To avoid pressure drop during the reaction test, the catalyst as powder form was tabletted, crushed, and sieved into 12 - 22 mesh. In order to investigate the activity for NO removal, catalyst was heated in He to 600°C and maintained at that temperature 30 min. After that, a feed gas composed of 1,000 ppm NO, 1,000 ppm n-C₈H₁₈, 2mol% O₂, 10mol% H₂O balance with He was allowed to flow with a GHSV of 30,000 h⁻¹. Every 10 min after feed gas introducing to ensure the steady state of catalytic activity, the reactants and products were analyzed by gas chromatographs (Chrompack, Micro GC CP 2002 with MS-5A and porapak Q column) equipped with integrators. The reaction test was undertaken every 50°C diminishing from 600°C to 200°C followed the same procedure as mentioned above. The catalytic activities of nitric oxide reduction and n-octane combustion were investigated as the amount of N₂ and carbon oxides (CO_x; CO₂+CO) produced, respectively.

7.3. Results and discussion

7.3.1 Influence of thermal-treatment on conversion of NO to N₂ of 200%Cu/MFI and H-Co-silicate catalysts

The resistance to high temperature is one factor that should be paid attention as well. In this study the condition of thermal-treatment was considered in the range of 600°C-1,100°C. Conversions of NO to N₂ of 200%Cu/MFI and H-Co-silicate are demonstrated in Figures 7.1 and 7.3 consecutively. The conversions of n-octane of both catalysts are respectively depicted in Figures 7.2 and 7.4. As illustrated in Figures 7.1 and 7.2, 200%Cu/MFI loses the activities for both NO and n-octane conversions obviously with the thermal-treatment condition. Especially with the pretreatment temperature of 1,000°C, conversions of NO and n-octane of 200%Cu/MFI are diminished remarkably. As compared with conversion of NO to N₂ for 200%Cu/MFI without

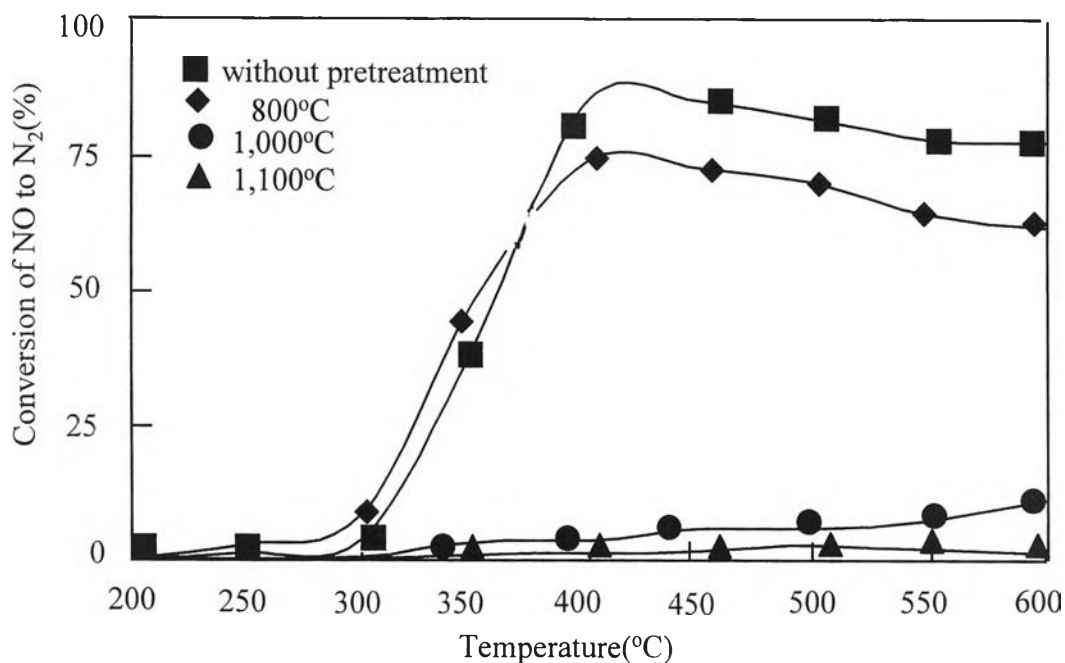


Figure 7.1 The effect of thermal-treatment on conversion of NO of 200%Cu/MFI
 Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O₂ 2mol%, H₂O 10mol%, He balance,
 GHSV 30,000 h⁻¹

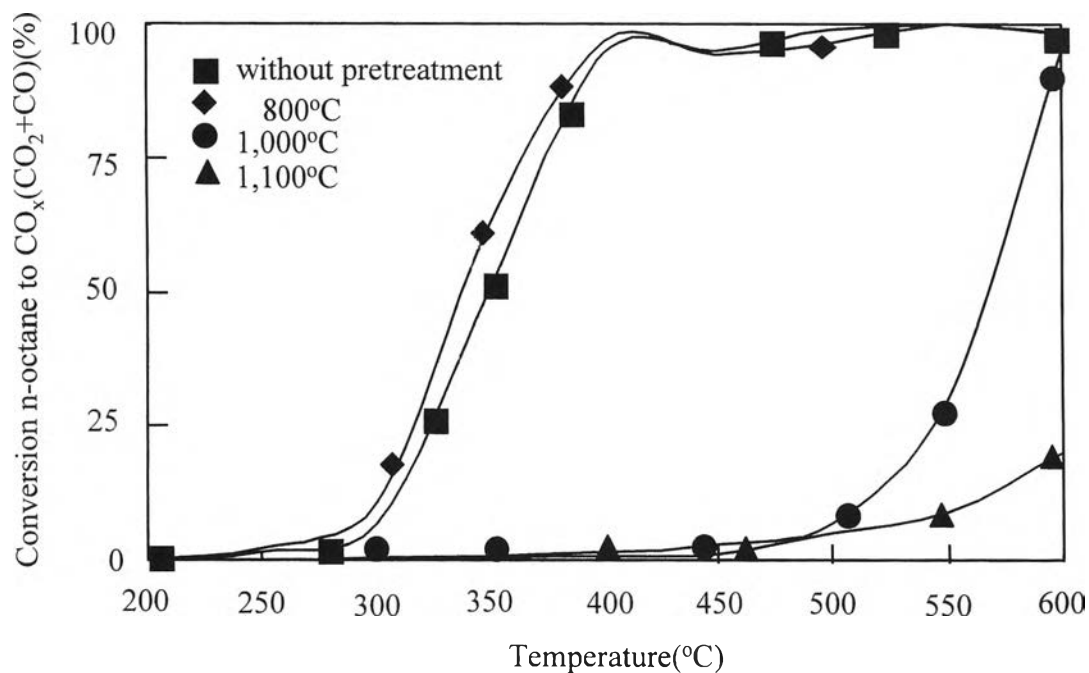


Figure 7.2 The effect of thermal-treatment on conversion of n-octane of 200%Cu/MFI
 Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O₂ 2mol%, H₂O 10mol%, He balance,
 GHSV 30,000 h⁻¹

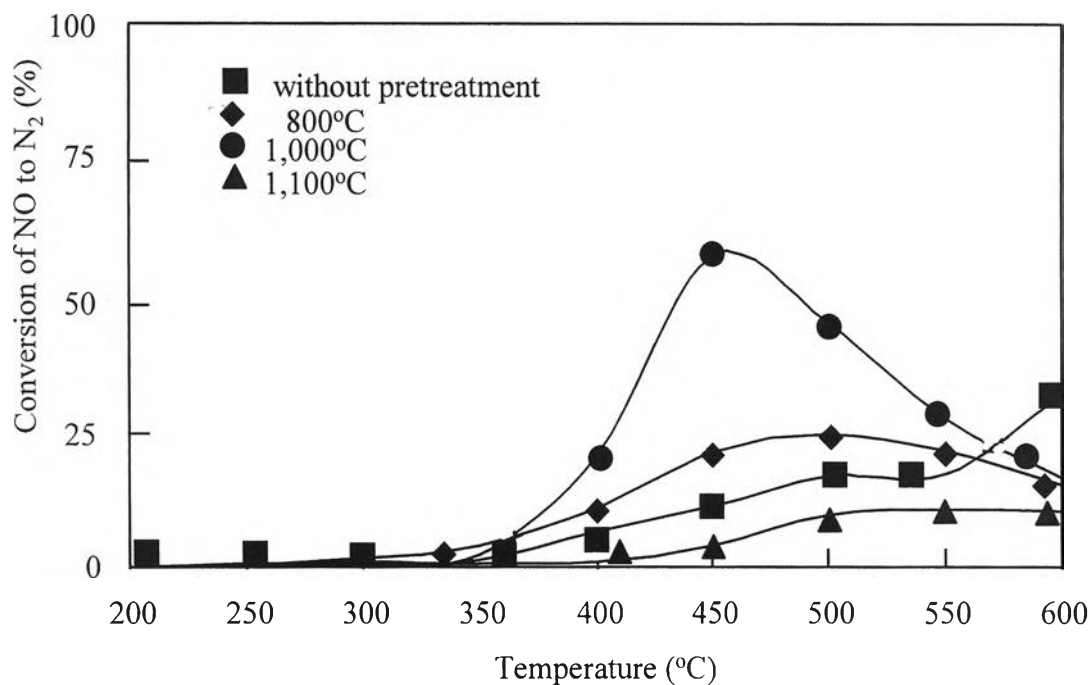


Figure 7.3 The effect of thermal-treatment on the activity for conversion of NO of H-Co-silicate. Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O₂ 2mol%, H₂O 10mol%, He balance, GHSV 30,000 h⁻¹

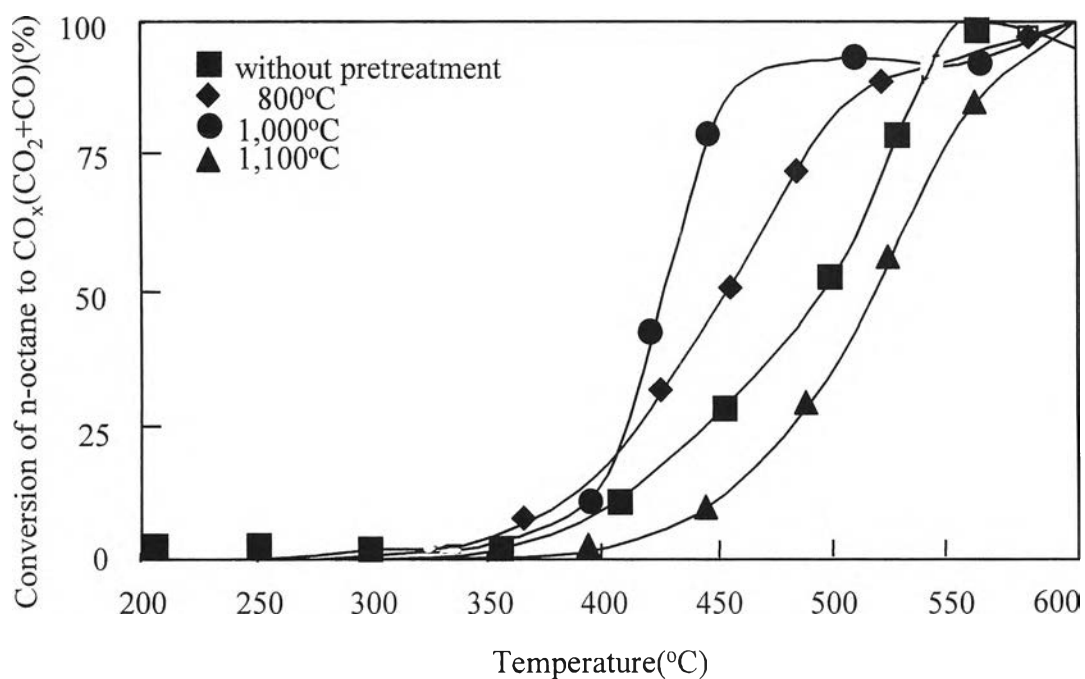


Figure 7.4 The effect of thermal-treatment on the activity for conversion of n-octane of H-Co-silicate. Feed gas: NO 1,000 ppm, n-octane 1,000 ppm, O₂ 2mol%, H₂O 10mol%, He balance, GHSV 30,000 h⁻¹

pretreatment, it was observed that conversion of NO to N₂ for 200%Cu/MFI after thermal-treatment at 1,000°C decreases remarkably more than 3 times at 450°C.

Interestingly, the activity for conversion of NO of H-Co-silicate increases with thermal-treatment condition except at the pretreatment temperature of 1,100°C as shown in Figure 7.3. From these results, the reaction temperature of 450°C is chosen to be the optimum reaction temperature condition to investigate the performance of H-Co-silicate for nitric oxide removal. By observing conversion of NO to N₂ at 450°C, it indicates that the order of the activity for conversion of NO to N₂ conversion was 100°C < without pretreatment < 800°C < < 1,000°C.

Without pretreatment, the conversion of NO to N₂ on H-Co-silicate was only 15% at 450°C. Fortunately, the conversion of NO to N₂ after thermal-treatment at 1,000°C increased up to 60%. This conversion is approximately 4 times larger than that without pretreatment. Therefore, it is elucidated that for H-Co-silicate the pretreatment at high temperature is valuable for enhancement of conversion of NO to N₂.

7.3.2 Characterization of 200%Cu/MFI and H-Co-silicate catalysts with and without thermal-treatment

7.3.2.1 BET surface area and bulk composition data

Table 7.1 shows BET surface area and bulk composition of 200%Cu/MFI and H-Co-silicate with pretreatment temperature. From the results of ICP data shown as Si/Me ratio of 200%Cu/MFIs and H-Co-silicates, it was found that the amount of metal loaded in both catalyst are still existed even after high thermal-treatment. The BET surface area of 200%Cu/MFI after thermal-treatment decreased with thermal-treatment condition especially at 1,000°C. On the other hand, BET surface area of H-Co-silicate with thermal-treatment did not change differently comparing with that of H-Co-silicate without pretreatment. To clarify the crystallinity of zeolite structure, catalysts were analyzed using XRD method and the results are depicted in figures 7.5 and 7.6 for 200%Cu/MFIs and H-Co-silicates, respectively.

7.3.2.2 Crystallinity of catalyst by XRD characterization

For XRD method, we investigate the intensity of the diffraction line at 23.1 2 θ as the main index of crystallinity of zeolite. Considering XRD patterns of 200%Cu/MFIs in Figure 7.5, 200%Cu/MFI pretreated at 800°C has still high crystallinity compared with

XRD pattern of 200%Cu/MFI without pretreatment. But there is a change in crystallinity of 200%Cu/MFI after thermal-treatment at 1,000°C. The intensity of X-ray diffraction lines of 200%Cu/MFI pretreated at 1,000°C decreases remarkably.

Table 7.1 BET surface area and bulk composition of 200%Cu/MFI and H-Co-silicate with pretreatment temperature.

Sample	Pretreatment temperature (°C)	BET surface area (m ² /g.cat)	Si/Me atomic ratio
200%Cu/MFI	without pretreatment	360	51
	800	300	54
	1,000	120	56
	1,100	2*	57
H-Co-silicate	without pretreatment	350	257
	800	345	257
	1,000	400	258
	1,100	355	258

* drawn from the data in the ref. 110

There is a change of crystallinity pattern from MFI structure to crystobalite form that can be observed the diffraction lines at around 23.1°, 8.03° and 23.94° representative of silicon oxides as crystobalite. The computer program for X-ray refractometer recorded this appearance of diffraction line. Accordingly, it means that MFI structure of 200%Cu/MFI is destroyed by the high thermal-treatment supported by previous paper [117] and it is a reason for the sharp decrease in NO conversion of 200%Cu/MFI pretreated at 1,000°C. As for H-Co-silicates in Figure 7.6, H-Co-silicate maintains MFI structure even at 1,100°C. However, the intensity of X-ray diffraction lines of H-Co-silicate pretreated at 1,100°C is lower than that without pretreatment. It can be indicated that after thermal-treatment at 1,100°C, H-Co-silicate has lower crystallinity causing the loss of performance for nitric oxide removal as demonstrated above. From reaction data

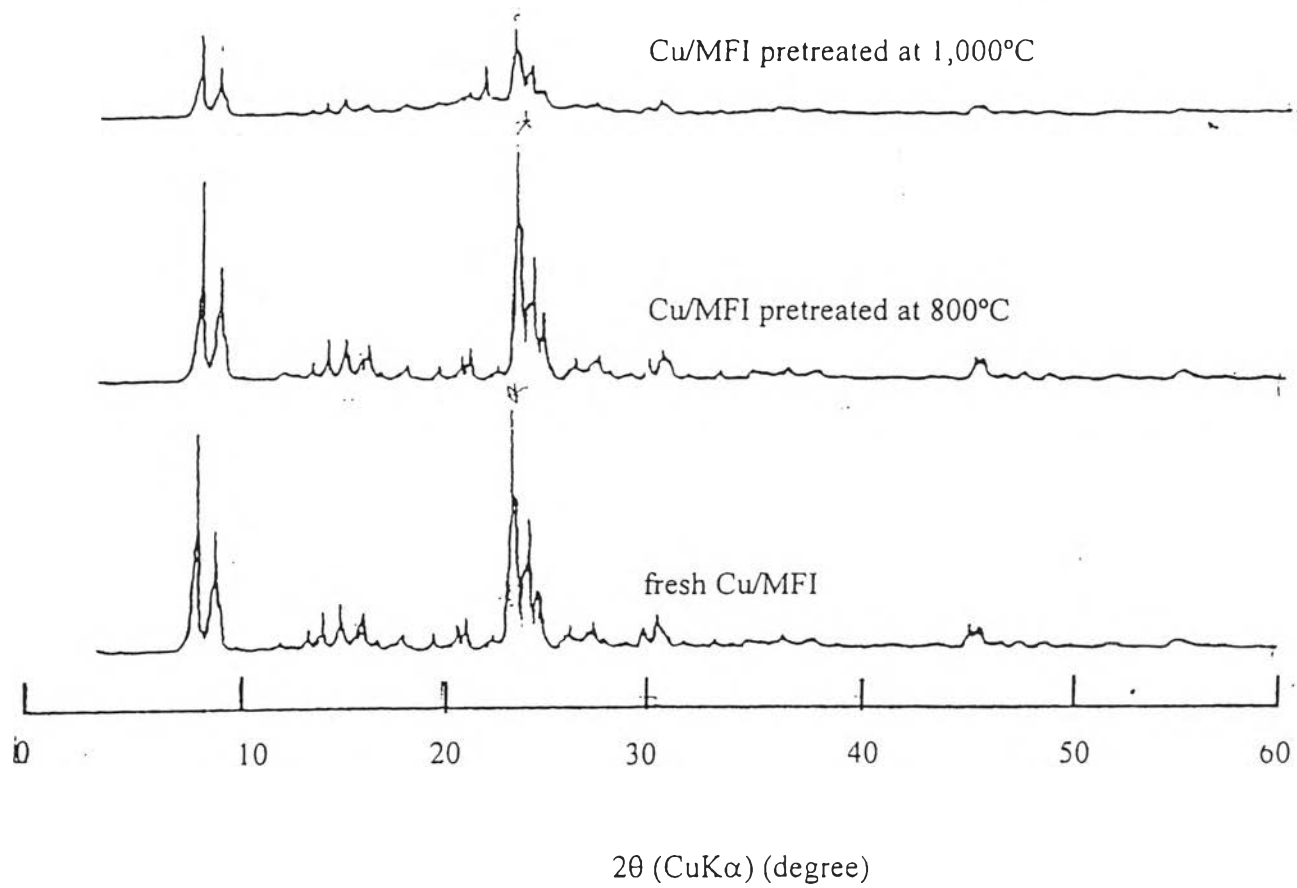


Figure 7.5 XRD patterns of Cu/MFIs with thermal-treatment

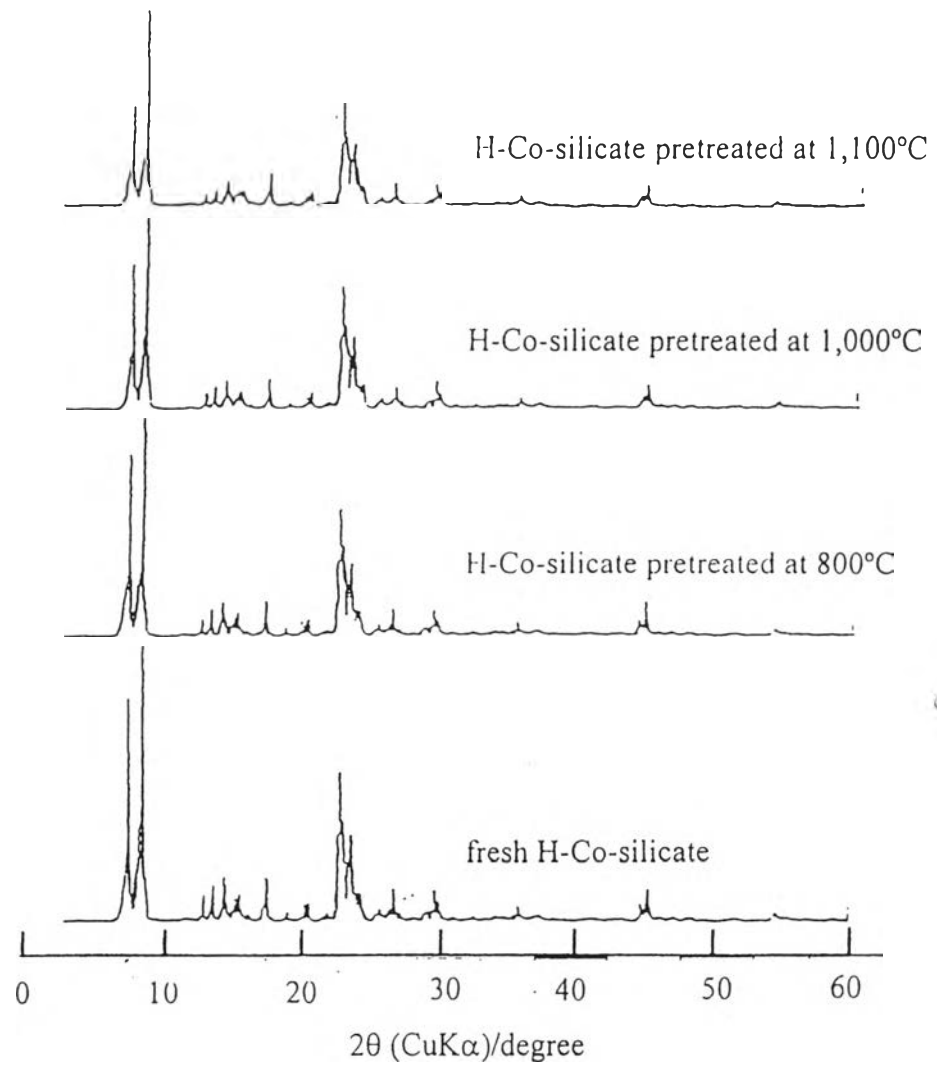


Figure 7.6 XRD patterns of H-Co-silicates with thermal-treatment

demonstrating the effect of thermal-treatment on 200%Cu/MFI and some physical characterizations, these show the low stability of metal ion exchanged MFI type zeolite catalyst against high thermal-treatment that is well known so far. In this study the interesting items are the high stability of H-Co-silicate and the optimum condition for conversion of NO of H-Co-silicate with thermal-treatment. It is advantage for trying to find out the reason promoting the activity for conversion of NO of H-Co-silicate with thermal-treatment.

7.3.2.3 ^{29}Si MAS NMR technique for H-Co-silicates

^{29}Si MAS NMR spectra of H-Co-silicates with and without pretreatment at 1,000°C were illustrated in Figure 7.7. The major signal at around -111 ppm indicative of Si(0Al) and lower signal at -105 ppm representative of Si(1Al) that is similar to the study of Budi et al.[79] and Woolery et al.[118] appeared. As for H-Co-silicate pretreated at 1,000°C, the shape of the line signal was changed from the shape of the line signal of H-Co-silicate without pretreatment and roughly similar to that of standard silicalite indirectly indicating the change of Si-O-Co bonding of H-Co-silicate pretreated at 1,000°C. Nevertheless, H-Co-silicate still maintained MFI structure even after thermal-treatment.

7.3.2.4 Techniques for characterization of H-Co-silicates

In order to investigate the framework and non-framework Co in H-Co-silicate, UV-Vis spectra of H-Co-silicate with and without thermal-treatment at 1,000°C were recorded in Figure 5.14. As illustrated in Figure 7.8, UV-Vis spectra of H-Co-silicates show the absorption band between 500 and 650 nm typical of high-spin (d7) Co(II) species in a tetrahedral crystal field and around 350 nm representative of high-spin Co (III) species [119, 120]. After thermal-treatment at 1,000°C, the absorption band at 350 nm is broaden, and charge-transfer is observed while the intensity of a remnant at 500-650 nm becomes flat even still remains. It can be suggested that after thermal-treatment at 1,000°C, some part of tetrahedral Co(II) can be changed to Co(III). Furthermore, cobalt oxides clusters are also observed on H-Co-silicate pretreated at 1,000°C similar to the study of Kagawa et al. [117]. ESR method is a further characterization to investigate high spin Co(II) in H-Co-silicates. Figure 7.9 depicts ESR spectra of H-Co-silicate with and without pretreatment. The g factor detected by the ESR method is useful to identify

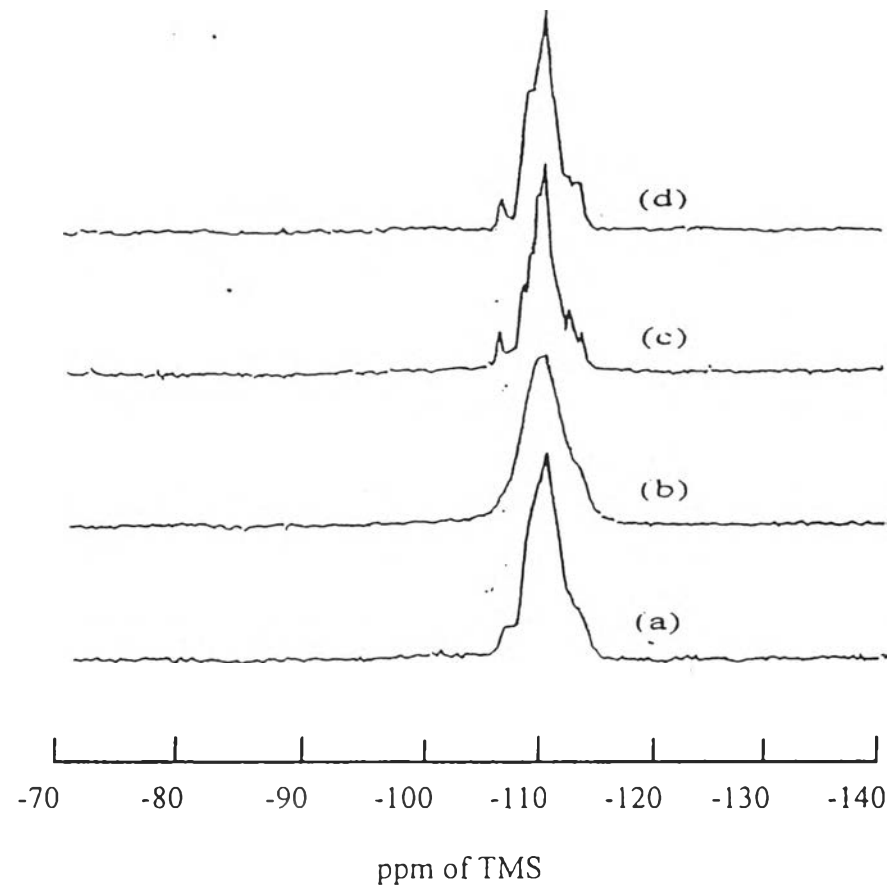


Figure 7.7 The change of ^{29}Si MAS NMR of (a) fresh H-Co-silicate, (b) H-Co-silicate pretreated at 800°C, (c) H-Co-silicate pretreated at 1,000°C and (d) fresh silicalite

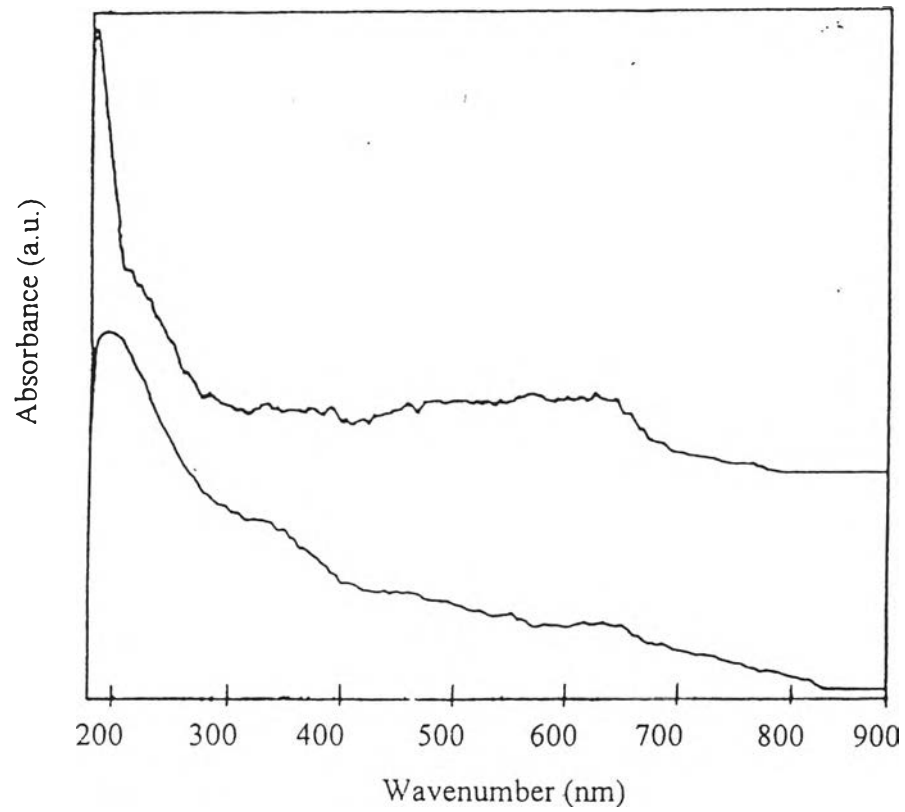


Figure 7.8 Electron absorption spectra of samples. Top: fresh H-Co-silicate; bottom: H-Co-silicate pretreated at 1,000°C

the sample occupied unpaired electron or free radical. By using the fingerprints exhibiting the signals of high spin Co(II) as referred from reference no. 93, 120, and 121, the g factor at around 5.8 can be distinguished as high spin Co(II) existing on both H-Co-silicates with and without pretreatment at 1,000°C in this study. Due to the short relaxation time high spin Co(II) expresses, the intensity of high spin Co(II) was not high even it was recorded at liquid nitrogen temperature (-196°C). The signal can be observed more clearly if it was operated at lower temperature such as at liquid helium temperature (-269°C). From Figure 7.9, the shape and intensity of ESR signals of H-Co-silicate pretreated at 1,000°C infinitesimally changed from that of H-Co-silicate without pretreatment. It can be indicated that there is a change of coordination state of high spin Co(II) implying the formation of a part of Co aggregates by thermal-treatment at 1,000°C. In situ FTIR spectra of H-Co-silicates using pyridine as a probe molecule were recorded and depicted in Figure 7.10 to study the acidity of the sample. The acidity of various solids is studied by investigating the changes in the 'ring' vibrations of pyridine and other bands in the region of 1,700 cm⁻¹ to 1,400 cm⁻¹. Silicalite materials that have same structure as H-Co-silicate except without the incorporation of Co species in the material were also analyzed and shown in Figure 7.11. Normally, this characterization can show separate IR bands of Brønsted acidity and Lewis acidity at the wavenumber of around 1,540 and 1,440-1,465 cm⁻¹, respectively. The number of acid sites and strength of acidity can be implied from the intensity and the presence of IR band with increasing temperature. It was found from Figures 7.10 and 7.11 that both H-Co-silicates and silicates have a little amount of Brønsted acid site. However, the intensity of IR band indicating Lewis acidity of H-Co-silicates without pretreatment is higher than that of silicalite without pretreatment. The appearance is caused by the addition of Co species in the framework. By using the study of Parry [122], the amount of pyridine pumped off at 150°C can be indicated as the pyridine weakly held to the surface sites. From the consideration of IR spectra above 150°C, it was found that silicalite has no Lewis acidity even without thermal-treatment at 1,000°C. As for H-Co-silicate pretreated at 1,000°C, the intensity of Lewis acidity is lower than that of H-Co-silicate without pretreatment. This also indicates that a part of tetrahedral Co moved out from the framework structure.

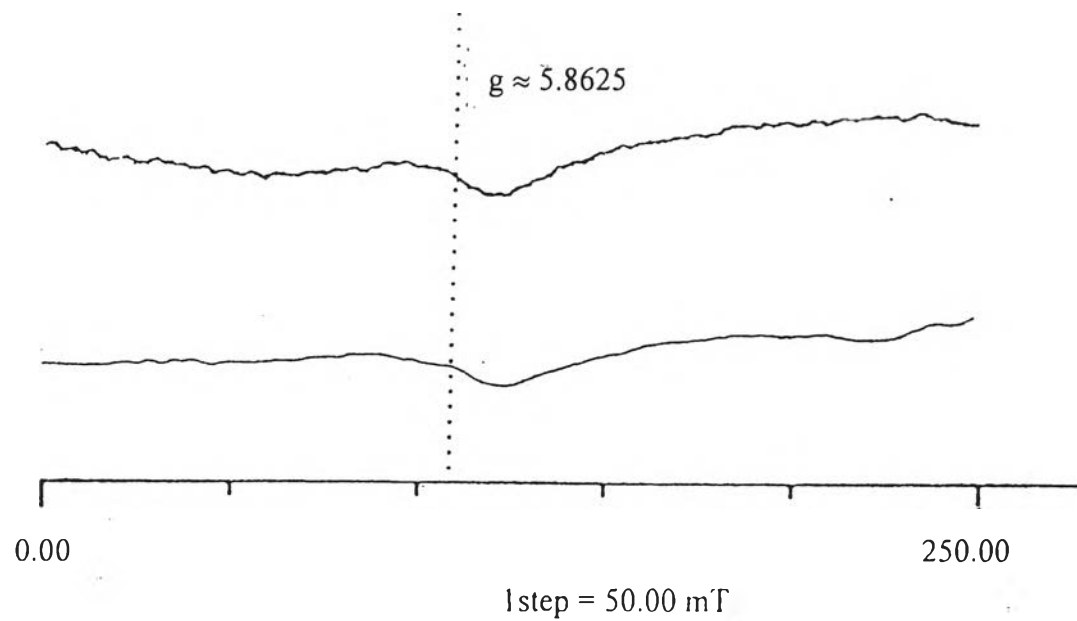


Figure 7.9 ESR spectra of samples. Top: fresh H-Co-silicate; bottom: H-Co-silicate pretreated at 1,000°C

Temperature programmed reduction of H_2 was also carried out to analyze cobalt species in H-Co-silicates and shown in Figure 7.12. In addition to the coexistence with a hydrogen uptake peak of H-Co-silicate without pretreatment at around $700^\circ C$, a new hydrogen uptake peak is observed at approximately $500^\circ C$ for H-Co-silicate pretreated at $1,000^\circ C$. It can be indicated the presence of a part of cobalt oxides [123, 124] highly dispersed on H-Co-silicate pretreated at $1,000^\circ C$. From the results mentioned above, it can be concluded that after thermal-treatment at $1,000^\circ C$, some part of tetrahedral Co(II) in the framework changed to Co(III) and formed cobalt oxide species that enhance the activity for nitric oxide removal. The possible appearance is the migration of a part of cobalt in the framework to the extraframework that is supported by the study of Kagawa et al. [117].

7.3.2.5 Conversion of n-octane to carbon oxides (CO_x) of catalysts

As illustrated in figure 7.2, 200%Cu/MFI loses the activity for conversion of n-octane obviously with the pretreatment temperature. Especially with the thermal-treatment at $1,000^\circ C$, conversion of n-octane of 200%Cu/MFI is diminished remarkably. In contrast, from Figure 7.4 it is observed that after thermal-treatment at $1,000^\circ C$ the activity for conversion of n-octane of H-Co-silicate increased significantly. As compared with H-Co-silicate without pretreatment, H-Co-silicate pretreated at $1,000^\circ C$ exhibits conversion of n-octane that its light off temperature is shifted to lower temperature. From these results and previous studies [103, 117, 125, 126], it can be proposed that after thermal-treatment at $1,000^\circ C$ some part of cobalt educed from the framework and became dispersed cobalt oxide species. In addition to cobalt incorporated in the framework, dispersively educed cobalt species enhance n-octane combustion activity and encourage the conversion of NO to N_2 . These results above reveal that H-Co-silicate can survive in severe temperature condition better than 200%Cu/MFI. In contrast with 200%Cu/MFI, H-Co-silicate with thermal-treatment enhances the activity for nitric oxide removal. Although the activity for conversion of NO of H-Co-silicate pretreated at $1,100^\circ C$ became decreasing due to the loss of framework crystallinity, the optimum thermal-treatment condition at $1,000^\circ C$ can promote high conversion of NO of H-Co-silicate. This phenomenon is useful for the application in severe temperature condition.

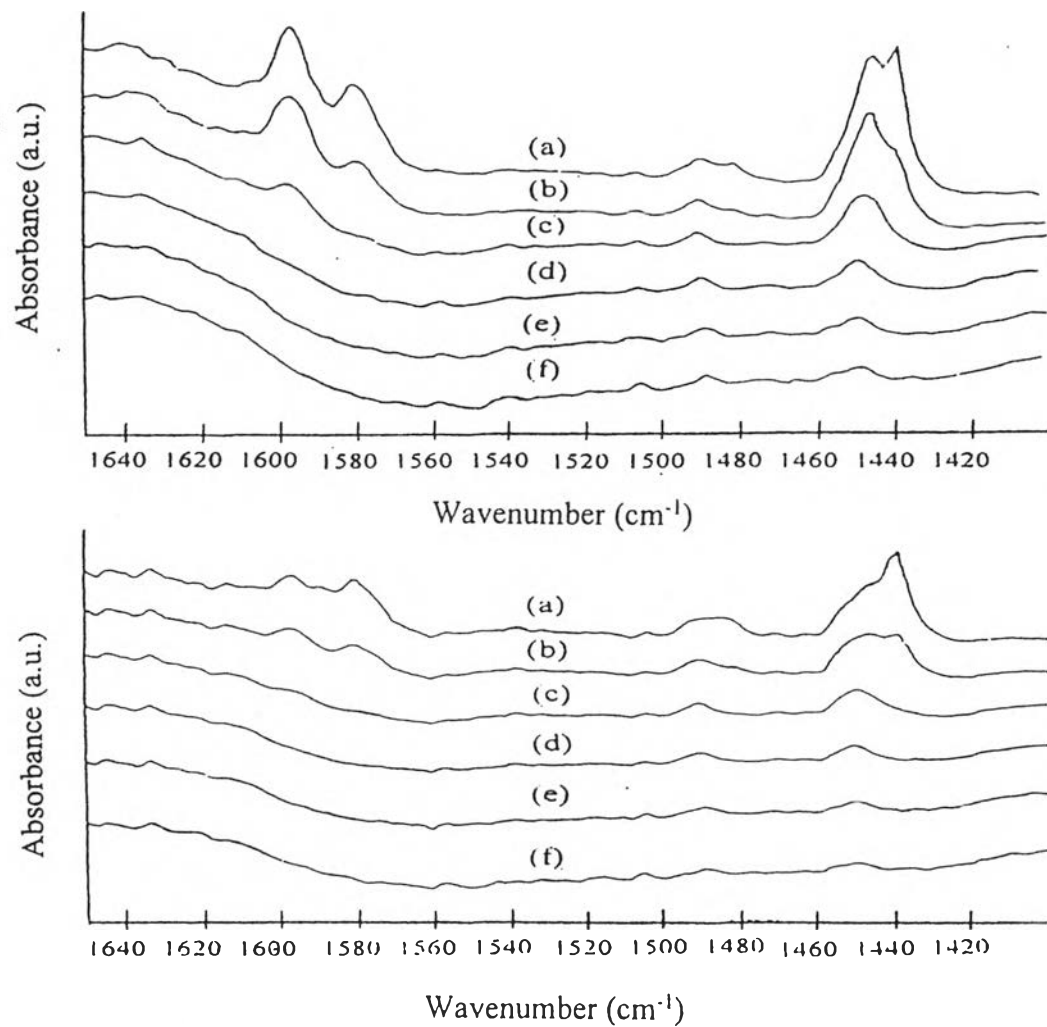


Figure 7.10 In situ FT-IR spectra of pyridine adsorbed on H-Co-silicates. Top: H-Co-silicate without pretreatment; bottom: H-Co-silicate pretreated at 1,000°C: (a) at room temperature; (b) at 50°C; (c) at 100°C; (d) at 150°C; (e) at 200°C; (f) at 250°C.

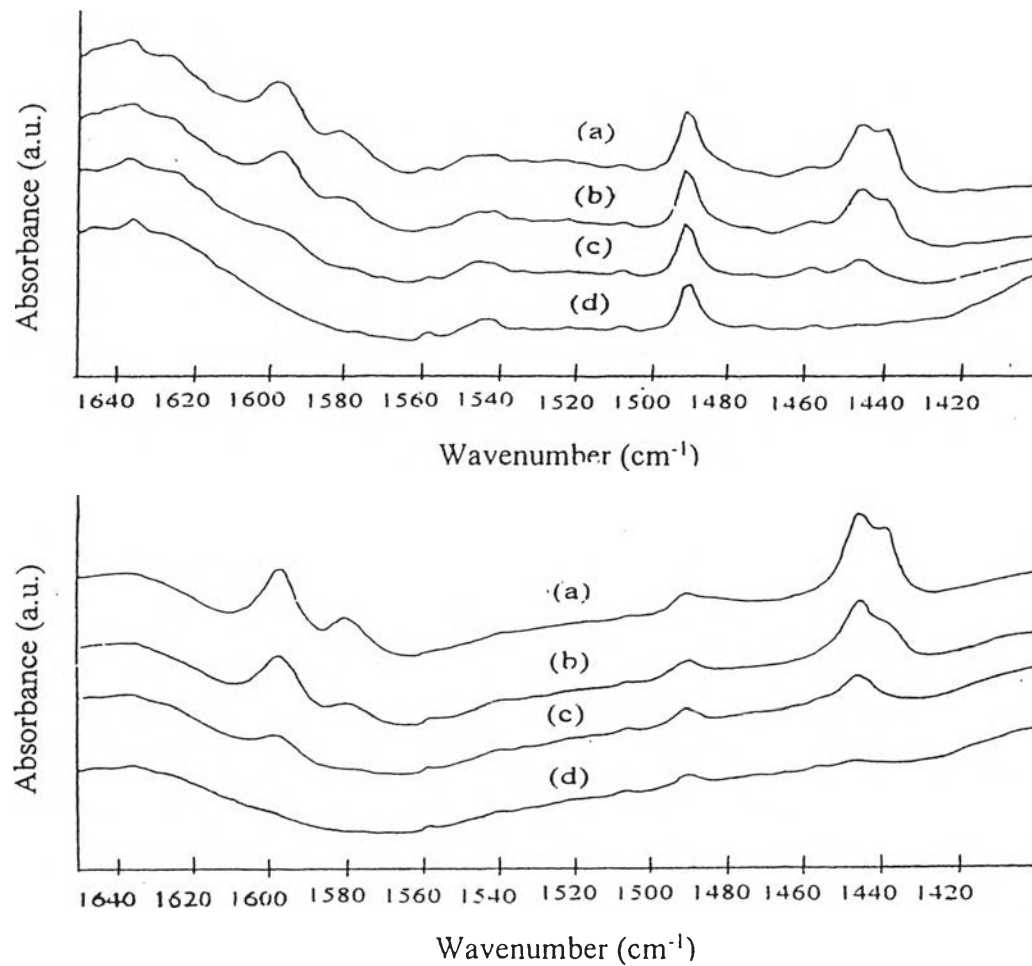


Figure 7.11 In situ FT-IR spectra of pyridine adsorbed on silicalites. Top: fresh silicalite; bottom: silicalite pretreated at 1,000°C: (a) at room temperature; (b) at 50°C; (c) at 100°C; (d) at 150°C.

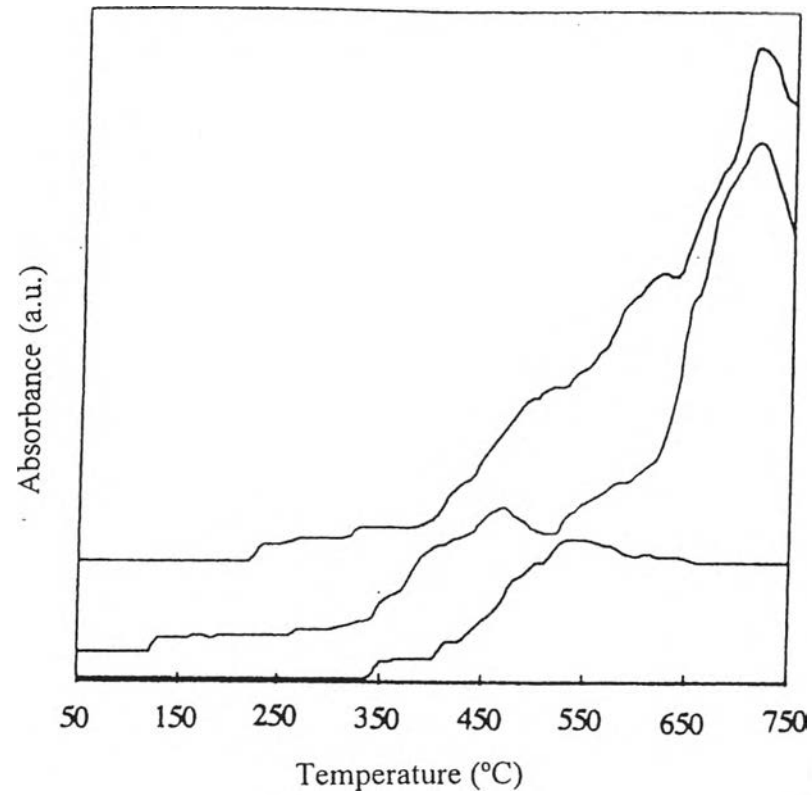


Figure 7.12 Temperature programmed reduction profiles of catalysts.
From top to bottom: H-Co-silicate without pretreatment; H-Co-silicate pretreated at 1,000°C,
silicalite without pretreatment

7.4. Conclusion

The pretreatment at high thermal-treatment condition can enhance the activity of H-Co-silicate for nitric oxide removal. For H-Co-silicate, the thermal-treatment at 1,000° C is the optimum condition to improve the performance for nitric oxide removal effectively. The activity for conversion of NO of H-Co-silicate after thermal-treatment at 1,000°C was around 4 times higher than that without pretreatment. H-Co-silicate exhibits high structural stability of the framework during pretreatment even at the severe condition of 1,000°C. The effect of thermal-treatment at 1,000°C is to change the state of cobalt species that enhance the activity for nitric oxide removal.