



PB90141219

**NTIS**

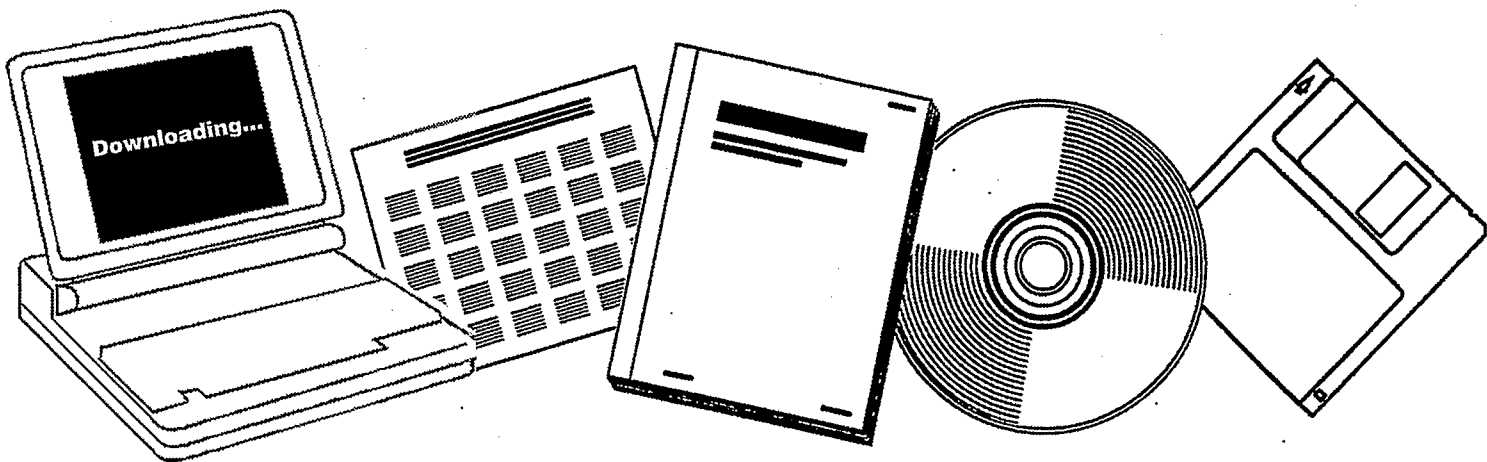
**One Source. One Search. One Solution.**

---

## **ZEOLITE SUPPORTED CATALYSTS**

**ACADEMIA SINICA, TAIPEI (TAIWAN)**

**1988**



U.S. Department of Commerce  
**National Technical Information Service**

---

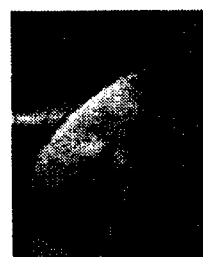
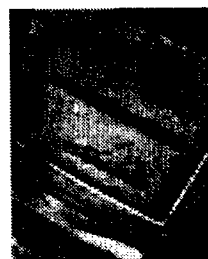
**One Source. One Search. One Solution.**

# NTIS



## **Providing Permanent, Easy Access to U.S. Government Information**

National Technical Information Service is the nation's largest repository and disseminator of government-initiated scientific, technical, engineering, and related business information. The NTIS collection includes almost 3,000,000 information products in a variety of formats: electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.



### **Search the NTIS Database from 1990 forward**

NTIS has upgraded its bibliographic database system and has made all entries since 1990 searchable on [www.ntis.gov](http://www.ntis.gov). You now have access to information on more than 600,000 government research information products from this web site.

### **Link to Full Text Documents at Government Web Sites**

Because many Government agencies have their most recent reports available on their own web site, we have added links directly to these reports. When available, you will see a link on the right side of the bibliographic screen.

### **Download Publications (1997 - Present)**

NTIS can now provides the full text of reports as downloadable PDF files. This means that when an agency stops maintaining a report on the web, NTIS will offer a downloadable version. There is a nominal fee for each download for most publications.

For more information visit our website:

**[www.ntis.gov](http://www.ntis.gov)**



U.S. DEPARTMENT OF COMMERCE  
Technology Administration  
National Technical Information Service  
Springfield, VA 22161

PB90141219



# Zeolite Supported Catalysts

Author: Chien, Shu-Hua

National Science Council  
Taiwan, Republic of China

## GENERAL DISCLAIMER

This document may have problems that one or more of the following disclaimer statements refer to:

- This document has been reproduced from the best copy furnished by the sponsoring agency. It is being released in the interest of making available as much information as possible.
- This document may contain data which exceeds the sheet parameters. It was furnished in this condition by the sponsoring agency and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures which have been reproduced in black and white.
- The document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

<b>REPORT DOCUMENTATION PAGE</b>		1. REPORT NO.	2.	3. Recipient's Accession No. <b>90 1412197AS</b>
4. Title and Subtitle Zeolite Supported Catalysts			5. Report Date 1988	
7. Author(s) Chien, Shu-Hua			6.	
9. Performing Organization Name and Address Institute of Chemistry, Academia Sinica Taiwan, Republic of China			8. Performing Organization Rept. No.	
12. Sponsoring Organization Name and Address National Science Council Taiwan, Republic of China			10. Project/Task/Work Unit No.	
15. Supplementary Notes			11. Contract(C) or Grant(G) No. (C) NSC76-0402-E001-01 (G)	
16. Abstract (Limit: 200 words)			13. Type of Report & Period Covered Aug.'86-Nov.'87	
17. Document Analysis a. Descriptors			14.	
b. Identifiers/Open-Ended Terms Foreign Technology			15.	
c. COSATI Field/Group			16.	
18. Availability Statement No restriction on distribution Available from National Technical Information Service, Springfield, VA 22161		19. Security Class (This Report) UNCLASSIFIED	21. No. of Pages 38	
		20. Security Class (This Page) UNCLASSIFIED	22. Price E04	

## ABSTRACT

A comparative study of nickel catalysts supported on X- and y- zeolites had been reported in the previous annual report. The influence of the catalyst preparation on the structure and the properties of the nickel zeolite catalysts had also been emphasized. Several experimental results have shown that addition of cerium cations to zeolite supported nickel catalysts was found to cause a synergetic effect and a dramatic influence on the surface nickel dispersion and the catalytic properties. The possibility of cerium cations as chemical anchoring sites, the doping induced metal-support interaction, or the SMSI" (strong metal-support interaction) needed to be verified. The present paper is a comparative study of the cerium-containing nickel catalysts supported on x- and y- zeolites. In general, the addition of cerium ions caused an increase in the catalytic activity for CO hydrogenation and shifted the product selectivity to high molecular weight hydrocarbons. The degree of the effect of cerium additive depends on the ratio of cerium to nickel contents, the reduction temperature, and the nature of the supporting materials. Catalyst characterization, including volumetric hydrogen chemisorption, temperature programmed reduction/desorption, x-ray diffraction, surface area measurements, in-situ infrared spectroscopy and x-ray photoelectron spectroscopy, was performed in order to interpret the phenomena due to the effects of cerium additives and the support effect on Ni/zeolite catalysts.

Keywords: Ce-Ni/(x-, y-)zeolite, CO/H<sub>2</sub> reactions, Ni dispersion, TPR, TPD, IR, XRD, XPS.

## ABSTRACT

A comparative study of nickel catalysts supported on X- and y- zeolites had been reported in the previous annual report. The influence of the catalyst preparation on the structure and the properties of the nickel zeolite catalysts had also been emphasized. Several experimental results have shown that addition of cerium cations to zeolite supported nickel catalysts was found to cause a synergetic effect and a dramatic influence on the surface nickel dispersion and the catalytic properties. The possibility of cerium cations as chemical anchoring sites, the doping induced metal-support interaction, or the SMSI" (strong metal-support interaction) needed to be verified. The present paper is a comparative study of the cerium-containing nickel catalysts supported on x- and y- zeolites. In general, the addition of cerium ions caused an increase in the catalytic activity for CO hydrogenation and shifted the product selectivity to high molecular weight hydrocarbons. The degree of the effect of cerium additive depends on the ratio of cerium to nickel contents, the reduction temperature, and the nature of the supporting materials. Catalyst characterization, including volumetric hydrogen chemisorption, temperature programmed reduction/desorption, x-ray diffraction, surface area measurements, in-situ infrared spectroscopy and x-ray photoelectron spectroscopy, was performed in order to interpret the phenomena due to the effects of cerium additives and the support effect on Ni/zeolite catalysts.

Keywords: Ce-Ni/(x-, y-)zeolite, CO/H<sub>2</sub> reactions, Ni dispersion, TPR, TPD, IR, XRD, XPS.

# ZEOLITE SUPPORTED CATALYSTS

NSC 76-0402-E001-01

SHU-HUA CHIEN

INSTITUTE OF CHEMISTRY, ACADEMIA SINICA

## ABSTRACT

A comparative study of nickel catalysts supported on X- and Y- zeolites had been reported in the previous annual report. The influence of the catalyst preparation on the structure and the properties of the nickel zeolite catalysts had also been emphasized. Several experimental results have shown that addition of cerium cations to zeolite supported nickel catalysts was found to cause a synergistic effect and a dramatic influence on the surface nickel dispersion and the catalytic properties. The possibility of cerium cations as chemical anchoring sites, the doping induced metal-support interaction, or the SMSI" (strong metal-support interaction) needed to be verified. The present paper is a comparative study of the cerium-containing nickel catalysts supported on X- and Y- zeolites. In general, the addition of cerium ions caused an increase in the catalytic activity for CO hydrogenation and shifted the product selectivity to high molecular weight hydrocarbons. The degree of the effect of cerium additive depends on the ratio of cerium to nickel contents, the reduction temperature, and the nature of the supporting materials. Catalyst



characterization, including volumetric hydrogen chemisorption, temperature programmed reduction/desorption, x-ray diffraction, surface area measurements, in-situ infrared spectroscopy and x-ray photoelectron spectroscopy, was performed in order to interpret the phenomena due to the effects of cerium additives and the support effect on Ni/zeolite catalysts.

## INTRODUCTION

Addition of cerium ions to the highly dispersed nickel/x-zeolite catalysts was reported to show a significant influence on the catalytic properties [1-2]. The suppression in hydrogen chemisorption and the enhanced reactivity of CO hydrogenation was proposed to be due to the strong metal-support interaction (SMSI) [3] as described for the unique characteristics of the high-temperature reduced Ni/TiO<sub>2</sub> catalysts [4]. Several experimental results have shown that addition of the second metal ions to a supported metal catalyst can cause a synergetic effect as well as a dramatic influence on the surface metal dispersion and the catalytic properties. Besides the SMSI, other phenomena have been proposed, such as the presence of chemical anchors [5], the formation of bimetallic alloys [6], or the Dopant-Induced Metal-Support Interactions [7].

The nickel-catalyzed reactions between carbon monoxide and hydrogen have been of considerable interest to catalysis researchers for many years. Recent reports have provided evidence that the supporting materials can significantly influence the adsorp-

tion and hydrogenation of carbon monoxide on the activity and/or selectivity properties of nickel [4, 8-10]. The observed difference in the activity/selectivity properties for different supports was ascribed to the metal-support interaction. Vannice and Garten [4] suggested that the enhanced activity and selectivity towards higher molecular weight hydrocarbons for CO/H<sub>2</sub> reactions over Ni/TiO<sub>2</sub> as compared to silica or alumina supported nickels were due to the SMSI effect [3]. Bartholomev *et al.* drew the same conclusion [8-9]. However, this interpretation was criticized and the role of the nature of SMSI state was still ambiguous [10].

The purpose of this study on the cerium-containing nickel catalysts supported on zeolites is to elucidate the function of cerium additives in the different zeolite sites acting as chemical anchoring points for the effective nickel dispersion, or playing a role in the metal-support interaction, and the coincident effects on the properties of nickel catalysts.

## EXPERIMENTAL

### *Material*

The employed x- and y- zeolites supported nickel catalysts were prepared by the incipient-wetness impregnating technique as described in ref. [11, 12]. The cerium-containing nickel catalysts were prepared by co-impregnation of cerium ions and nickel ions to the supporting materials to incipient wetness. NaX zeolite (350 m<sup>2</sup>/g) and NaY zeolite (700 m<sup>2</sup>/g), were obtained from Applied Science and Strem Chemicals respectively. Nickel nitrate,

$\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , was obtained from Ferak, Berlin and cerium nitrate hexahydrate,  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , was from Strem Chemicals. The impregnated samples were subsequently dried at room temperature for two days and sat in oven at  $110^\circ\text{C}$  for several hours before stored in a desiccator. The contents of metal or metal ions in each sample were shown as the notation of each catalyst, for example, 2-10 Ni-Ce/X represents the x-zeolite supported catalyst with 2 wt% of nickel and 10 wt% of cerium.

The Matheson Purity grade CO (99.99%) was used by passing through a molecular sieve (5A) trap for removing the carbonyls. Hydrogen gas was generated by a hydrogen generator (Mark V. L/Milton Roy, USA). High purity argon gas was further purified through a multipurge purifier supplied by Milton Roy Co.

#### *Apparatus and Procedure*

The measurement of the activity/selectivity of each catalyst for CO hydrogenation was carried out in a steady state flow-mode microreactor system operating at atmospheric pressure with a gas flow rate ratio of  $\text{H}_2/\text{CO} = 3$ . The exit gases were analyzed by a on-line Varian 3760 gas chromatograph with a 6 ft. x 1/8" poropak QS (80-100 mesh) column at  $110^\circ\text{C}$ . A FID detector was used. The peak areas were determined by a Hewlett Packard 3392A integrator. Detailed procedures were as described in Ref [12]. The temperature programmed reduction (TPR) profiles were monitored by a thermal conductivity detector, with a mixed gas stream of argon and hydrogen ( $\text{Ar}/\text{H}_2 = 4$ , total flow rate = 22.5 ccm) as a carrier.

The temperature programmed desorption (TPD) of hydrogen was carried out in an argon stream (flow rate = 30ccm), the catalyst was previously activated in-situ as the same procedures for the activity measurements and cooled to room temperature under a hydrogen flow.

Surface area of each sample was determined following the BET method for N<sub>2</sub> adsorption at 77°K, the data were collected with a Micromeritics AccuSorb 2100E surface area analyzer. The x-ray diffraction measurement was performed on a Rigaku D/Max-III diffractometer with nickel-filtered Cu-K<sub>α</sub> radiation. Particle sizes of metal catalysts were estimated from x-ray line broadening measurements using the Scherrer formula [13].

For the infrared spectroscopic studies, the dried catalyst powder was pressed into a thin self-supporting wafer which was placed in a quartz high-vacuum IR cell. The cell, in which NaCl windows were attached to the Cajon Ultra-Torr adapter with Varian high vacuum Torr Seal, is capable of achieving a vacuum of 10<sup>-5</sup> torr and designed so that be easily attached to a vacuum line for sample treatments either under a flow mode or the vacuum conditions. A thin self-supporting catalyst wafer (20-30 mg/cm<sup>2</sup>) was achieved by pressing the dried catalyst powder with a 20 mm die under a pressure of 6 tons. Infrared spectra were taken on a Bruker IFS-85 Fourier transform spectrometer.

X-ray photoelectron spectroscopic (XPS) measurements were performed on Vacuum General VG200 ESCA spectrometer.

## RESULTS AND DISCUSSION

### *Catalytic activity/selectivity for CO hydrogenation*

The influence of cerium cations on zeolite supported nickel catalysts for CO hydrogenation was summarized in Table 1, in which each catalyst was reduced in hydrogen flow at 500°C for 3 hours, and the reaction temperature of CO hydrogenation (with flow rate ratio of  $H_2/CO = 3$ ) was held at 300°C. It is clear that the catalytic activity of zeolite supported nickel catalysts for CO hydrogenation was significantly enhanced by addition of cerium cations, except that of 5-2.5 Ni-Ce/X. The enhanced reaction rate over Ni-Ce/X catalysts due to the presence of cerium additives might be attributed to the chemical anchoring properties of the  $Ce^{3+}$  cations for nickel dispersed on zeolite, since the high value of  $Ce^{3+}/Ni$  ratio leads to the high activity. A drawback in the apparent activity of 5-2.5 Ni-Ce/X might be possibly because that all the  $Ce^{3+}$  cations got into the  $S_1$  sites in the hexagonal prism during the dehydration or reduction processes prior to acting as the anchoring sites for nickel as suggested by Delafosse [14]. The effect of cerium additives on  $\gamma$ -zeolite supported nickel catalysts was somewhat different: the 5-5 Ni-Ce/Y catalyst exhibited a better activity than the 5-10 Ni-Ce/Y sample and the product selectivities were more significantly shifted to the higher molecular weight hydrocarbons. Effects of  $Ce^{3+}$  cations on  $x$ - and  $\gamma$ -zeolite supported nickel were quite different.

The  $Ce^{3+}$  cations were believed to be able to stabilize the

nickel particles in the zeolite cavities [15]. The performance of Ni-Ce/x-zeolite, prepared by incipient-wetness impregnation in the present study, seemed to well demonstrate the role of  $Ce^{3+}$  ions as "chemical anchors" as well. The higher activity of catalysts with higher Ce/Ni ratio might be resulted from a well dispersed nickel particles on the zeolite surface as chemical anchoring properties of  $Ce^{3+}$  cations were concerned. But the Ni-Ce/y-zeolite samples did not tell the same story. The nature cations such as  $Na^+$  or  $Ca^{2+}$  in the zeolites or the acidity of the supporting materials might also heavily affected the catalytic properties.

Because a SMSI (Strong Metal-Support Interaction) state was suspected to be induced by  $Ce^{3+}$  additives as proposed by Sauvion *et al.* [1], we have examined the reactivities of CO hydrogenation over the high- and low- temperature ( $500^{\circ}C$  and  $300^{\circ}C$  respectively) reduced samples. It is interesting to find that the 5-5 Ni-Ce/x-zeolite sample displayed the reversible phenomenon that the high-temperature reduced (HTR) sample exhibited higher activity as compared to the low-temperature reduced (LTR) sample. Figure 1 illustrated the reversibility. This behavior is similar to the performance of Ni/TiO<sub>2</sub> catalysts [11]. This plausible "SMSI" catalyst seems only true for the Ni-Ce/X system. The reversibility of the reactivity for CO hydrogenation did not find over y-zeolite supported cerium-containing nickel catalysts.

It was also noticed that the catalytic activity of the x-zeolite supported Ni-Ce catalyst was very much dependent on the

reduction temperature of the catalyst, while the  $\gamma$ -zeolite supported catalysts only showed a subtle change. The product selectivity, in both cases, did not give significant changes due to various reduction temperatures. Examples of the effect of reduction temperature on the catalytic activity of the Ce-containing zeolite supported nickel catalysts were summarized in Table 2.

#### *Chemisorption of hydrogen and particle size of nickel*

Table 3 lists the comparative results obtained from hydrogen chemisorption and further analyses thereafter of the characteristic properties of x- and  $\gamma$ - supported nickel-cerium catalysts. The metallic Ni dispersion deduced from the  $H_2$  chemisorption was expressed by the ratio of H/M ( $M = Ni^0$ ), which was obtained by assuming one active surface Ni atom chemisorbed one hydrogen atom. The particle sizes of the nickel crystallites after the chemisorption measurements were estimated from the powder x-ray diffraction pattern of Ni(111) at  $2\theta = 44.5^\circ$  following the line-broadening Scherrer formula [13]. The total surface area of each sample listed at the last column was obtained by BET method for nitrogen adsorption at 77°K.

In most cases, the total surface area of the catalyst was not affected much by  $Ce^{3+}$  additives or the high reduction temperature, except the 5-10 Ni-Ce samples which showed the significant drops in surface area. Some of the zeolite pores might be blocked by the  $Ce^{3+}$  cations for the samples with the high concentration  $Ce^{3+}$  cations. Addition of  $Ce^{3+}$  cations to the zeolite supported nick-

els did not suppress the hydrogen chemisorption as in the case of Ni/SiO<sub>2</sub> [16]. The amount of hydrogen chemisorption does not linearly relate to the activity of the catalyst for CO hydrogenation. Besides, the amount of H<sub>2</sub> chemisorption did not show a significant change as the reduction temperature of the catalyst varied from 300 to 500°C. The performance is completely not the case for the SMSI catalysts.

It was found that the higher value of hydrogen chemisorption corresponded to the smaller Ni crystallite size, and the decrease in Ni particle size due to the presence of cerium additive is evident. Actually in most cases, especially when the reduction temperature was low, the nickel particle size was too small (less than ~4nm) to be detected by x-ray diffraction spectra. In the present paper, we present the results of the high temperature reduced samples of various Ce/Ni ratios in order to clearly show the function of cerium additives as "chemical anchors" for the nickel particle dispersed on zeolites and its resistance to sintering. It was noted that, for either Ni-Ce/X or Ni-Ce/Y samples, the reduced 5-5 Ni-Ce samples tended to show the larger H<sub>2</sub> chemisorption and the smaller Ni particle size as compared to the reduced 5-10 Ni-Ce samples. Excess Ce<sup>3+</sup> seems to show a negative effect on the nickel dispersion. The 5-5 Ni-Ce/Y samples exhibited higher ability for H<sub>2</sub> chemisorption, but formed larger particle sizes, as compared to the 5-5 Ni-Ce/X samples no matter what the reduction temperature was.

The H/M values deduced from H<sub>2</sub> chemisorptions may not cor-



rectly represent the metallic Ni dispersion due to the possible electronic effect of Ce<sup>3+</sup> cations. The metallic Ni surface area may be estimated from the Ni particle size by assuming that the Ni crystallites were spheres and that all surface atoms are accessible according to the following equation:

$$S \text{ (m}^2\text{/g-Ni)} = (6 \times 10^4) / [(8.91 \text{ g/cm}^3)(d(\text{\AA}))]$$

where d is the particle size in Å, 8.91 g/cm<sup>3</sup> is the density of metal. Because 1 m<sup>2</sup> Ni surface corresponds to 1.54 x 10<sup>19</sup> atoms of Ni [17], the metallic Ni dispersion is then derived:

$$\text{Ni dispersion} = 10.112/d(\text{\AA}).$$

By using the particle size of Ni obtained from XRD method, the calculated values are listed in Table 4 for comparison. The active metallic Ni sites, obtained either from the H<sub>2</sub> chemisorption or from the calculated metallic Ni dispersion from XRD results, was certainly affected by the cerium additives.

Efforts have been made to use the turnover frequency (TOF) to interpret the catalytic activity. The turnover frequency was defined as the number of CO molecules converted into the products per active-site per second. Reactivities for CO hydrogenation over various Ni-Ce/zeolite catalysts represented by TOF were shown in Table 4. Column [A] was calculated based on the H<sub>2</sub> chemisorption measurements, column [B] was taking the XRD results as the number of active sites. The deduced values of TOF were quite different. Neither of the results was not as straightforward as in the case of Ni-Ce/SiO<sub>2</sub> in which the TOF was increased by increasing the content of cerium additives. However the TOF of various

cerium containing supported nickel based on Ni particle size (column [B]) showed about the same trend as the "Activity" as listed in Table 1. It indicated that use of "Activity" as defined previously for describing the performance of the Ni-Ce/Zeolite catalysts was reasonable and practical.

Although the nickel dispersion was poor for the impregnated samples in this study as compared to the reported ion-exchanged samples, the anchoring ability of  $Ce^{3+}$  cations to the nickel dispersion on zeolites and its resistance to sintering were concluded.

#### *Temperature programmed reduction (TPR) profiles*

Figure 2 showed the temperature programmed reduction (TPR) profiles of hydrogen for x- and y- zeolite supported nickel and cerium-containing nickel samples. The relative reducibility of each catalyst is legible. The diminishing peaks on the high-temperature side in the TPR profiles of cerium-containing x- and y- zeolite supported nickels as compared to those of the bare zeolite supported nickels indicated that the reducibility of the catalyst was improved due to the presence of cerium additives. The TPR peaks on the high-temperature side might correspond to the reduction of the nickel of the  $S_1$  sites inside the hexagonal prisms. As declared by Jeanjean et al. [18], there is a competition between  $Ce^{3+}$  and  $Ni^{2+}$  cations to occupy  $S_1$  sites during the dehydration process. The presence of  $Ce^{3+}$  ions in  $S_1$  sites prevented the nickel ions getting into the hexagonal prism and

spreaded on the accessible sites of zeolite, which resulted in a better reducibility and a better dispersion.

#### *Temperature Programmed Desorption of Hydrogen*

Figure 3 exhibited the temperature programmed desorption (TPD) profiles of hydrogen for various amount of cerium content in Ni-Ce/x-zeolite system, all the samples were previously reduced at 500°C for 3 hours. Except for the 5-2.5 Ni-Ce/X sample, all the TPD profiles showed two peaks. It was evident that two kinds of active sites, from where H<sub>2</sub> molecules were desorbed, were created. If we took the area under the peaks into account, a very good correlation between the catalytic activity (see Table 1) and the peak area of the TPD profiles was established. It will be a good example for the 5-10 Ni-Ce/X that the high activity corresponds to the large peak area. The amount of the desorbed hydrogen might be considered to be proportional to the active sites of the catalyst, as well as the number of the effectively active surface nickel atoms. Therefore, the Ni dispersion may be also represented by the peak area on the TPD profile of hydrogen. The high dispersion of nickel on 5-10 Ni-Ce/X clearly led to the high catalytic activity. Figure 4 showed the temperature programmed desorption profiles of hydrogen for the 5-5 Ni-Ce/X samples reduced at different conditions. Reduction of the sample at 300°C, a large peak around 280°C with a small shoulder at 460°C appeared on the TPD profiles. Increase the reduction temperature to 425°C, the peak area obviously increased and the center of the shoulder peak

shifted to 660°C. As the reduction taken at 500°C, the first peak decreased and the second peak appeared clearly around 700°C. Both peaks might be all responsible for the catalytic activity.

Figure 5 shows the TPD profiles of hydrogen for various amount of cerium-containing  $\gamma$ -zeolite supported nickel samples. Again, the correlation between the peak area of the TPD profile and the values of the catalytic activity of each catalyst is nearly perfect. The highest intensity of the the peak for 5-5 Ni-Ce/Y gave the good explanation of it being the most active catalyst for CO hydrogenation.

We have estimated the upper limit for the heat of adsorption of hydrogen to be 6.5 and 26 Kcal/mole corresponding to the first and the second peak of the TPD profiles of 5-10 Ni-Ce/X, by taking two TPD profiles at two different heating rate,  $B=9^\circ\text{C}/\text{min}$  and  $18^\circ\text{C}/\text{min}$  (see figure 6) and following the method as described in Ref [19]. The two peaks of TPD spectra might be considered as the hydrogen desorbed from chemisorbed hydrogen on surface nickel particles and the hydrogen released from the reactions between the surface atomic Ni and the surface hydroxyl group of the zeolites. It is the reason that the peak area of TPD spectra are responsible for the catalytic activity of the nickel catalysts. Precisely quantitative analysis is somewhat difficult due to the shifting in background line of the spectra. However estimation of the relative active sites is very straightforward.

We also carried out the TPD profile of CO with helium as a carrier at  $B = 10^\circ\text{C}/\text{min}$ , a single peak appeared around 680°C. We

believe that the adsorption of CO, usually dissociative adsorbed on surface nickel or on the interface of nickel and the supporting oxide, was the primary factor for CO hydrogenation. Effect of hydrogen adsorption or desorption on CO hydrogenation was not as sensitive as that for alkane hydrogenolysis. However, the present studies indicated that using the TPD of hydrogen to account for the nickel dispersion seems to be quite satisfactory.

#### *Infrared spectra of CO adsorption*

Adsorption of CO was examined by in-situ infrared measurement. The IR spectra of CO adsorption were quite similar for the same supporting material, no matter whether the cerium ions were added. Figure 7 showed IR spectra of the adsorption of CO on 2-2 Ni-Ce/X. It is quite clear that desorption of surface CO is difficult at room temperature but possibly at 120°C, besides, the ability of re-adsorption of CO insured the stability of the active sites which led to the better performance in CO hydrogenation. The reversibility of the catalytic behavior as shown in figure 1 might be also ascribed to this character. Readsorption of CO onto Ni-Ce/Y-zeolite was not detected. Figure 8 showed the effects of Ce<sup>3+</sup> additives on IR spectra of CO adsorption of x-zeolite supported nickel catalysts under the low pressure of carbon monoxide. Figures 8a and 8b were the spectra taking at initial and equilibrium states of adsorption respectively. The peak intensities were well correlated to the catalytic reactivities for CO hydrogenation over various cerium containing Ni-Ce/X-zeolite

catalysts. The well dispersed Ni (with CO adsorption peak around  $2080\text{ cm}^{-1}$ ) along with the easy migration of the bridged CO adsorption form (around  $1950\text{ cm}^{-1}$ ) was definitely responsible to the high reactivity of CO hydrogenation over the cerium containing zeolite supported nickel catalyst.

#### *Surface composition and the bulk structure*

Figure 9 showed the x-ray photoelectron (XPS) spectra of 5-5 Ni-Ce/X and 5-5 Ni-Ce/Y before and after the high temperature reduction. Three peaks shown in the XPS spectra in figure 9 correspond to the presence of photoelectrons of Na (2s), Ni(3p) and Al (2p) (from left to right). It showed that the ratio of surface Ni/Al over the surface of x-zeolite was higher than the y-zeolite, either before or after the reduction. The nickel cations were more easily to impregnated or reduced over the surface of x-zeolite than over the y-zeolite. The surface composition was quite different that more  $\text{Na}^+$  ions appeared on surface of y-zeolite. Besides, the significant concentration of  $\text{Ca}^{2+}$  ions were detected in x-zeolite samples. No  $\text{Ca}^{2+}$  ions were found in y-zeolite samples. From the present studies, it was not surprised that effect of  $\text{Ce}^{3+}$  cations on 5-5 Ni-Ce/Y catalysts resulted in a larger  $\text{H}_2$  chemisorption, larger particle size, and lower catalytic activity for CO hydrogenation as compared to the x-zeolite supported 5-5 Ni-Ce samples. Effects of cerium additives on zeolite supported nickel catalysts were not only dependent on the kind of zeolite but also on the nature of cations in the zeolites.

The bulk structures of the reduced samples were examined by X-ray diffraction spectroscopy. In most cases, the x-ray diffraction analyses showed that the zeolite lattice was crystallographically intact, without significant structure breakdown neither after impregnation with or without  $Ce^{3+}$  cations additives, nor after reduction at high temperature. But after the very high temperature reduction ( $700^\circ$ ), as for the TPR or TPD samples, various degrees of structure breakdown were observed according to the presence of  $Ce^{3+}$  cations. Figures 10 and 11 were the examples, peaks corresponding to the 220 and 311 planes almost vanished for the 5-10 Ni-Ce samples. Fortunately the reduction and reaction conditions were not held at such high temperatures.

#### CONCLUSION

Based on the above experimental results and discussion, we understand that due to the strong electrostatic field of  $Ce^{3+}$  cations, it is conceivable to allow the cerium ions to modify the strength of the interaction between nickel and the support materials. We conclude that the cerium additive in the non-reducible oxide supported nickel catalysts are possibly either work as the chemical anchors to get better metallic nickel dispersion or as an inductor to induce some kind of metal-support interaction which prevented the catalyst from sintering. However, the degree of the effect of cerium additive depends on the nature of the supporting materials.

The different effects of cerium additives on x- and y- sup-

ported nickels were suggested to be due to the support acidity and the nature of cations in the zeolites.

#### ACKNOWLEDGEMENT

We gratefully acknowledge the financial support from the National Science Council, Republic of China [NSC76-0402-E001-01].

#### REFERENCES

1. G.N. Sauvion, J.F. Tempere, M.F. Guilleux, G.D. Mariadassou, and D. Delafosse, *J. Chem. Soc. Faraday Trans. I*, 81, 1357 (1985).
2. J. Jeanjean, S. Djemel, M.F. Guilleux, and D. Delafosse *J. Phys. Chem.*, 85, 4145(1981)
3. S.J. Tauster, S.C. Fung, and R.L. Garten, *J. Am. Chem.Soc.* 100, 170(1978).
4. M.A. Vannice and R.L. Garten, *J. Catal.* 56, 236(1979).
5. M.S. Tzou, H.J. Jiang, and W.M.H. Sachtler, *Applied Catalysis*, 20, 231 (1986).
6. B.J. Tatarchuk, and J.A. Dumesic, *J. Catal.* 70, 308(1981).
7. E. C. Akubuiro, and X.E. Verykios, *J. Catal.* 103, 320(1987).
8. C.H. Bartholomew, R.B. Pannell, and J.L. Butler, *J. Catal.* 65, 335(1980).
9. C.H. Bartholomew and C.K. Vance, *J. Catal.* 91, 78(1985).
10. R. Burch and A.R. Flambard, *J. Catal.* 85, 16(1984).



11. S.H. Chien, J.C. Chang, K.L. Lu and J.N. Wang, Bull. Inst. Chem. Academia Sinica, 31, 17(1984).
12. S.H. Chien, K.L. Lu, and H.W. Huang, J. Chin. Chem. Soc., 32, 309 (1985).
13. B.D. Cullity, "Elements of X-ray Diffraction", Addison-Wesley, 1965.
14. D. Delafosse, in "Catalysis by Zeolites", B. Imelik *et al.* (eds), (Elsevier, Amsterdam), 1980, p235.
15. S. Djemel, M.F. Guilleux, J. Jeanjean, J.F. Tempere and D. Delafosse, J. Chem. Soc., Faraday Trans. I, 78, 835(1982)
16. S.H. Chien, L.Y. Shao and Y.R. Chiou, Bull. Inst. Chem., Academia Sinica, 35, 53 (1988)
17. J.R. Anderson, "Structure of Metallic Catalysts" Academic Press, 1975. p296.
18. J. Jeanjean, S. Djemel, M.F. Galleux, and D. Delafosse. J. Phys. Chem. 85, 4145(1981)
19. J.M. Thomas and W.J. Thomas, "Introduction to the Principles of Heterogeneous Catalysis", Academic Press, 1975, p110.

Table 1. Activity and Selectivity of Zeolite Supported Ni Catalysts for CO/H<sub>2</sub> Reactions<sup>a</sup>.

CATALYST <sup>b</sup>	Activity		Mole % Product					
	( $\mu$ mole CO/g-Cat)	C <sub>1</sub>	C <sub>2</sub> <sup>=</sup>	C <sub>2</sub>	C <sub>3</sub> <sup>=</sup>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>
5 wt% Ni/X	9.05	92.14	0.04	5.62	0.13	1.60	0.42	0.05
5-2.5 Ni-Ce/X	1.73	86.58	0.18	8.05	0.80	3.27	1.12	--
5 - 5 Ni-Ce/X	17.59	90.94	0.01	6.67	--	1.97	0.40	0.01
5 -10 Ni-Ce/X	32.27	89.10	0.04	7.54	--	2.58	0.60	0.14
5 wt% Ni/Y	4.90	87.72	--	5.34	--	5.16	1.78	--
5 - 5 Ni-Ce/Y	12.02	67.72	1.45	18.27	4.62	5.45	3.01	3.75
5 -10 Ni-Ce/Y	6.69	74.59	1.01	12.29	3.74	4.47	3.09	0.81

a. Flow-rate ratio of H<sub>2</sub>/CO = 3 at atmospheric pressure; Reaction Temp. = 300 C.

b. Each catalyst was reduced in hydrogen at 500°C for 3 hours.

Table 2. Effect of the reduction temperature on the activity of Ni-Ce/zeolite catalysts for CO/H<sub>2</sub> reactions.

Catalyst	5-5 Ni-Ce/X	5-5 Ni-Ce/Y
Rdn Temp		
300°C	5.40	10.65
350°C	16.09	10.17
425°C	28.76	10.29
500°C	17.59	12.02

\* Activity was expressed in umole CO/g-catalyst.

Table 3. Sample characterization.

Sample	Rdn Temp (°C)	H <sub>2</sub> chemisorption (H/M)	Particle Size of Ni (nm)	Surface area (m <sup>2</sup> /g-Cat)
5 wt% Ni/X	500	0.026	14.2	330
5-2.5 Ni-Ce/X		0.029	9.7	340
5- 5 Ni-Ce/X		0.101	5.1	327
5- 10 Ni-Ce/X		0.078	9.0	265
5 wt% Ni/Y	500	0.029	13.1	468
5- 5 Ni-Ce/Y		0.187	9.6	495
5- 10 Ni-Ce/Y		0.030	12.4	320
5- 5 Ni-Ce/X	425	0.101	5.2	338
	350	0.100	< 4	355
	300	0.099	< 4	320
5- 5 Ni-Ce/Y	425	0.201	9.2	497
	350	0.187	9.5	499
	300	0.186	9.7	512

Table 4. Comparison of Ni dispersion and TOF for CO/H<sub>2</sub> reactions based on the results of CO chemisorption [A] and XRD particle size estimation [B].

Sample	Ni Dispersion		TOF (sec.site) <sup>-1</sup> x 10 <sup>3</sup>	
	[A]	[B]	[A]	[B]
5 wt% Ni/X	0.026	0.074	96.89	34.04
5-2.5 Ni-Ce/X	0.029	0.104	21.90	6.11
5- 5 Ni-Ce/X	0.101	0.198	65.44	33.38
5- 10 Ni-Ce/X	0.078	0.112	171.32	121.48
5 wt% Ni/Y	0.029	0.077	42.30	15.93
5- 5 Ni-Ce/Y	0.187	0.105	39.13	69.69
5- 10 Ni-Ce/Y	0.030	0.081	67.15	24.87

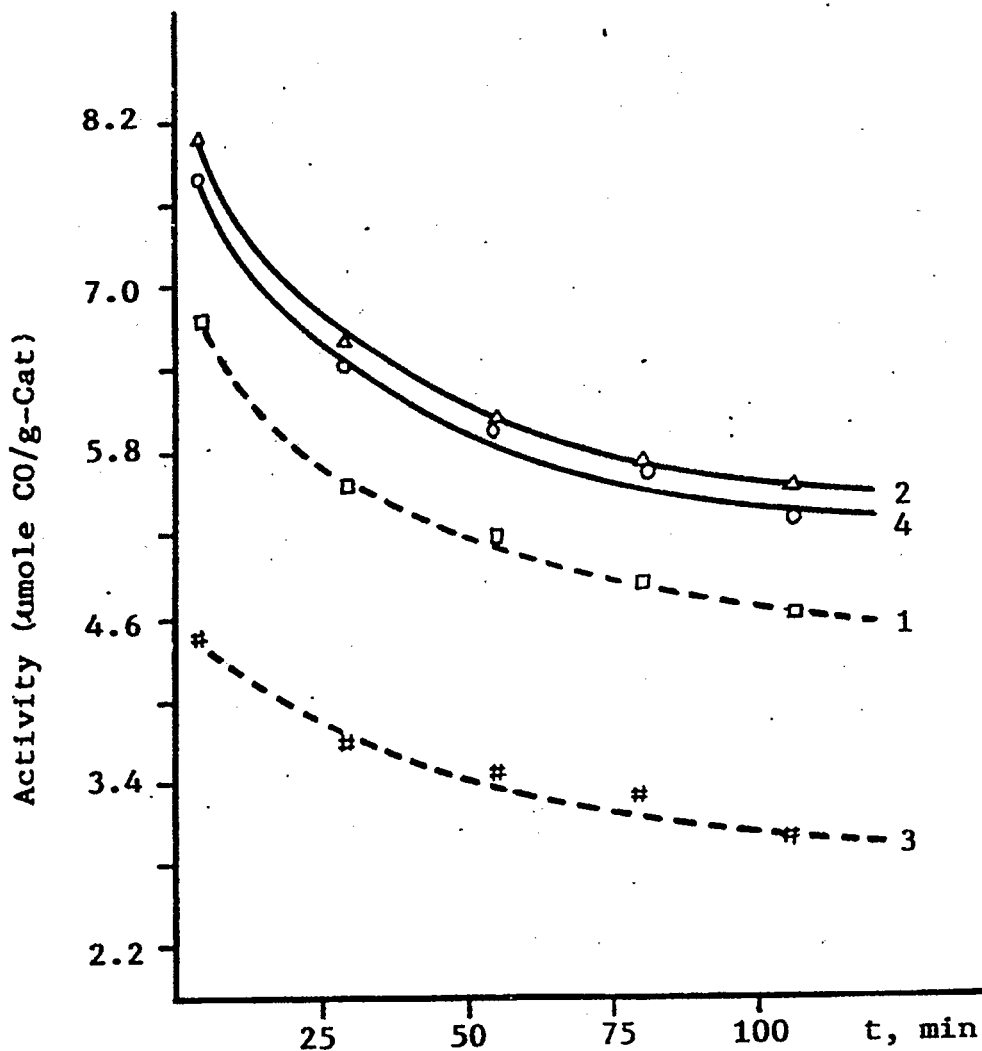


Figure 1. Catalytic Activity of 5-5 Ni-Ce/X for CO hydrogenations. Solid line: after HTR, dashed line: after LTR; 1,2,3....: sequential number for the measurements.

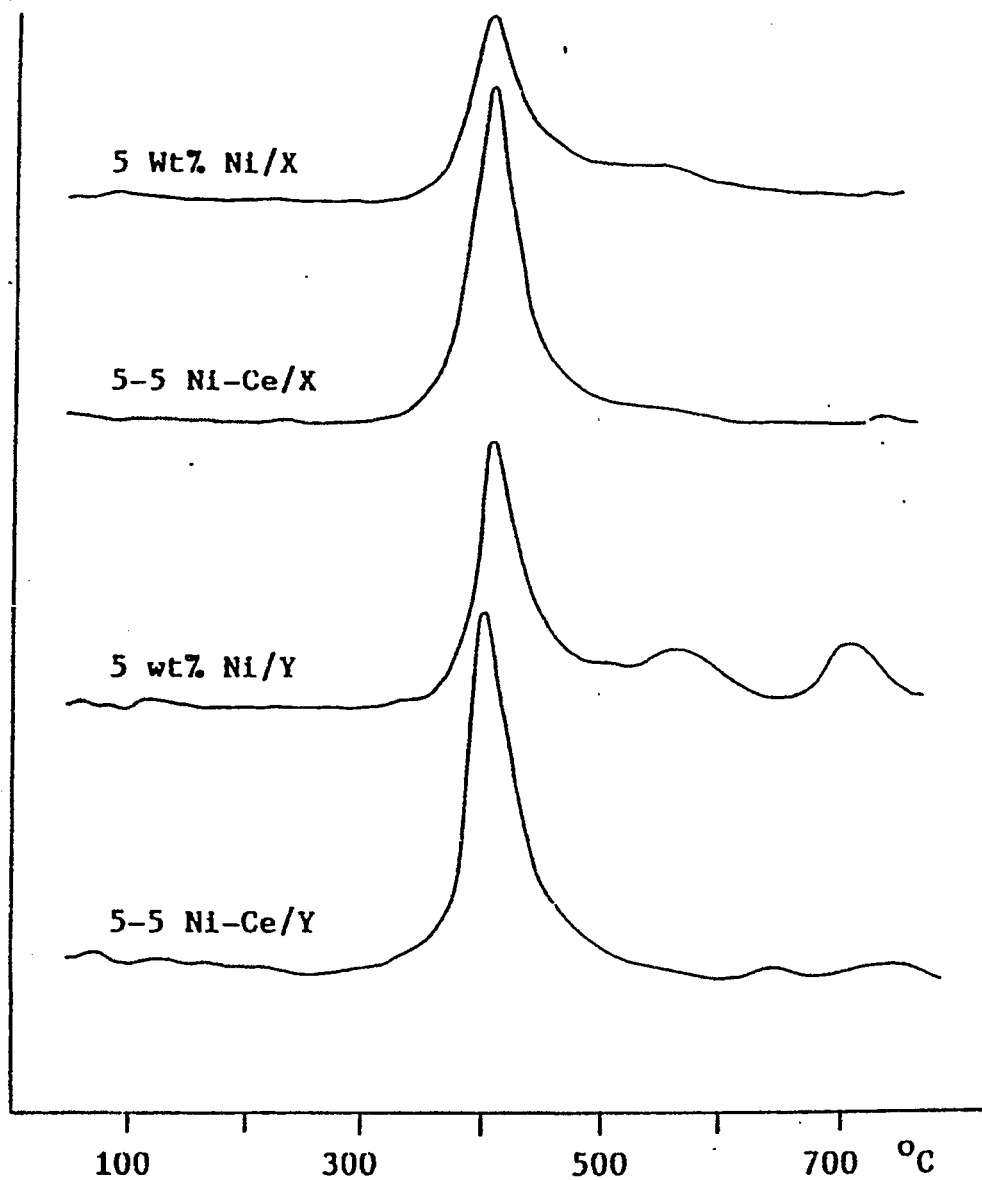
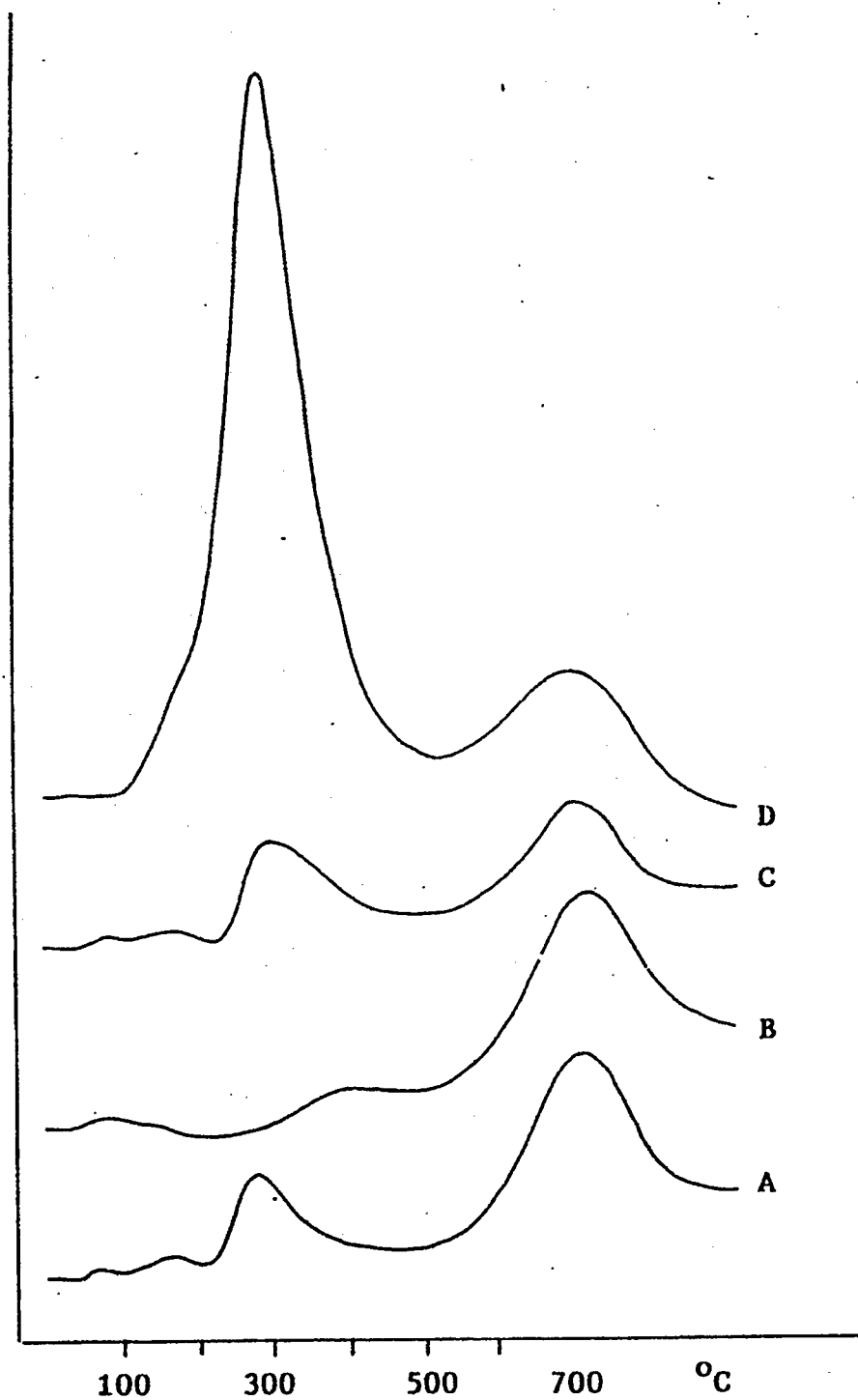


Figure 2. Temperature Programmed Reduction Profiles for various supported Ni-Ce Catalysts:  
Ar/H<sub>2</sub> = 4, Flow rate = 22.5 ccm, B = 10°C/m.



**Figure 3.** TPD Profiles of x-zeolite supported samples:  
A: 5 wt% Ni, B: 5-2.5 Ni-Ce, C: 5-5 Ni-Ce,  
D: 5-10 Ni-Ce.



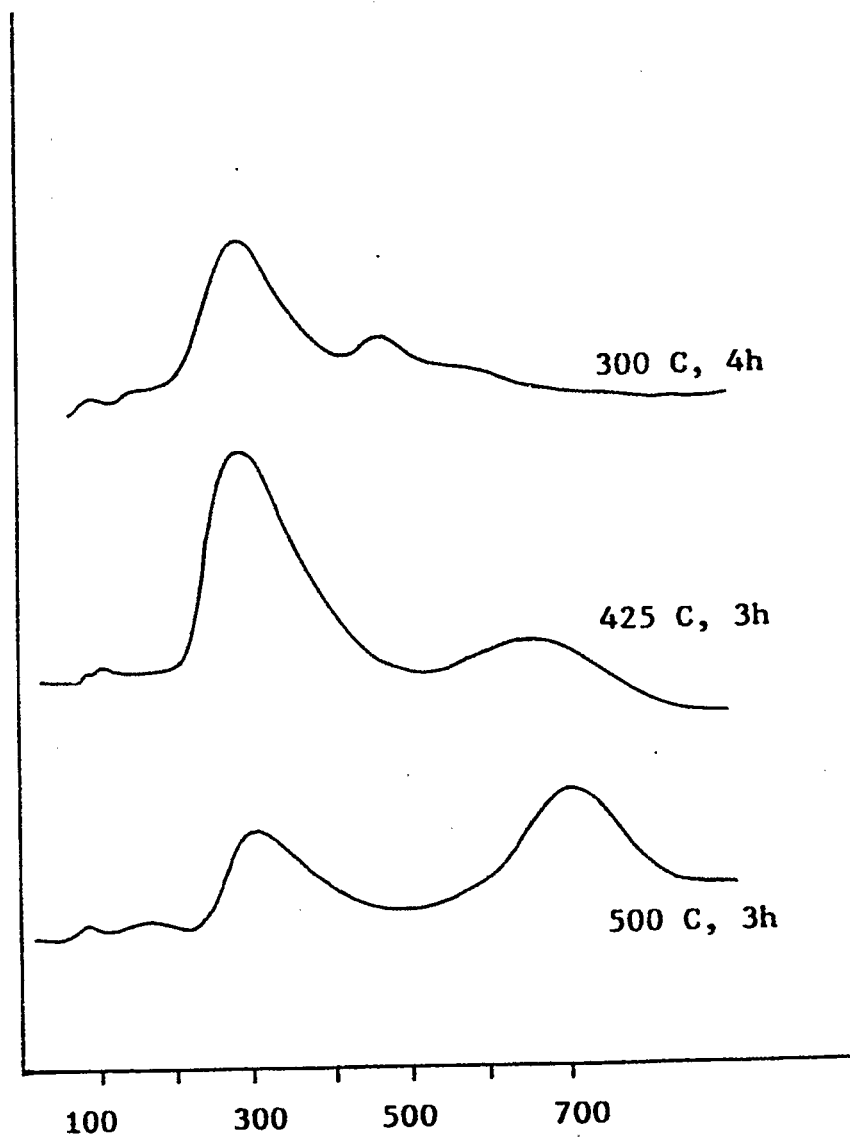


Figure 4. TPD profiles of 5-5 Ni-Ce/X reduced at various temperature. Ar: 30 ccm, B = 19°C/min.

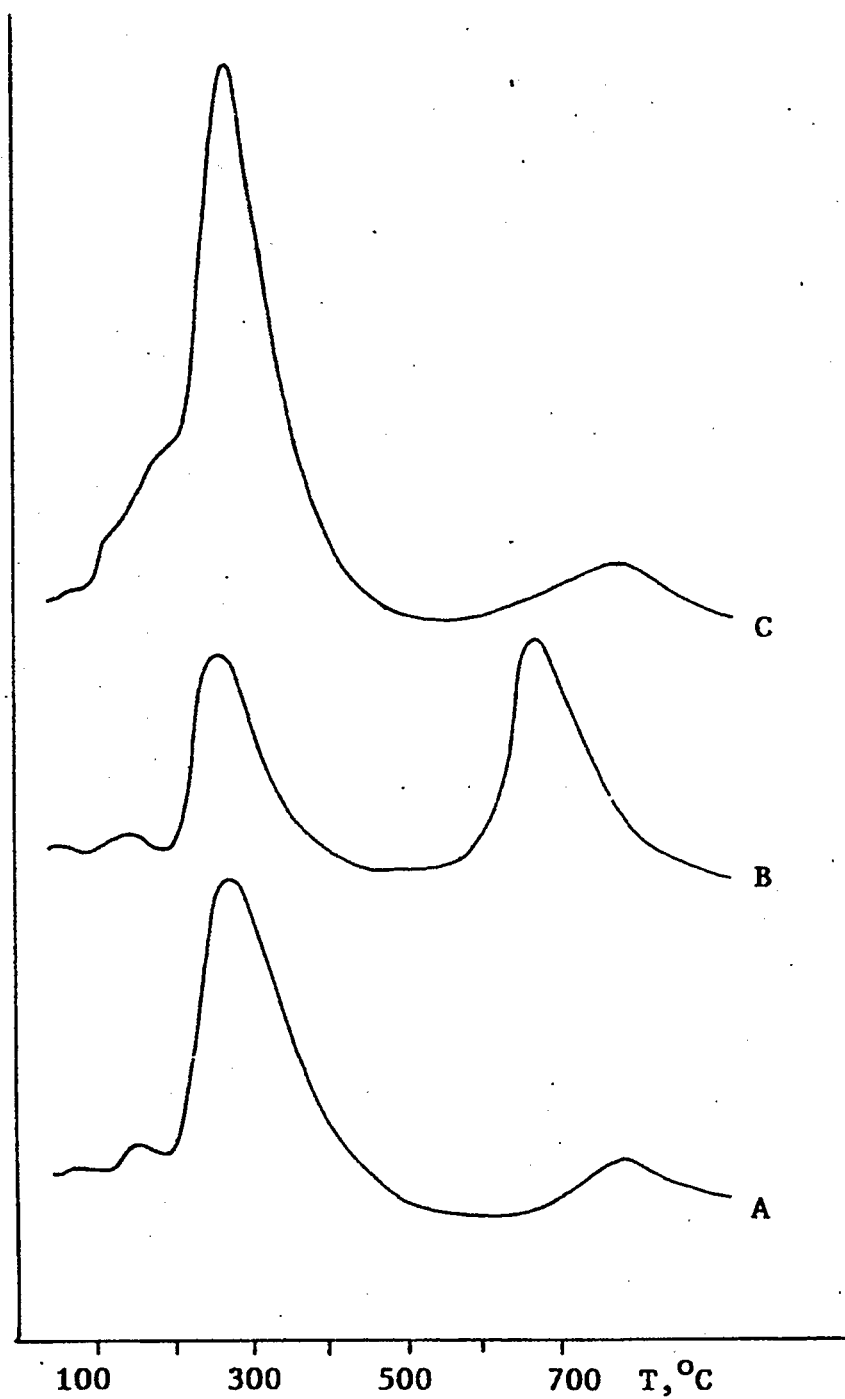


Figure 5. TPD profiles of Y-zeolite supported samples:  
A: 5 wt% Ni, B: 5-10 Ni-Ce, C: 5-5 Ni-Ce.

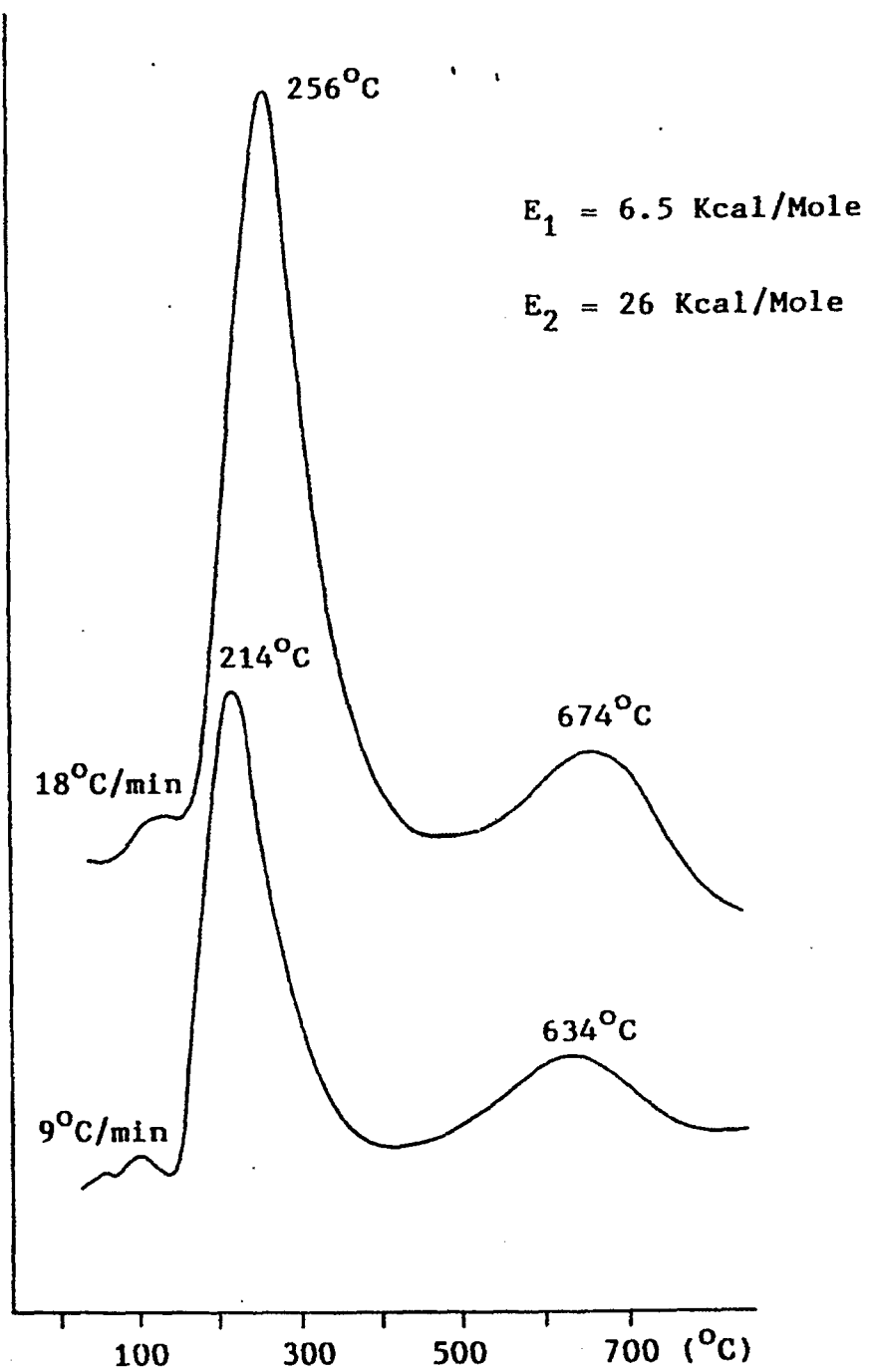


Figure 6. TPD PROFILES OF 5-10 Ni-Ce/X ( Rdn, H<sub>2</sub>, 500°C, 3 hrs)

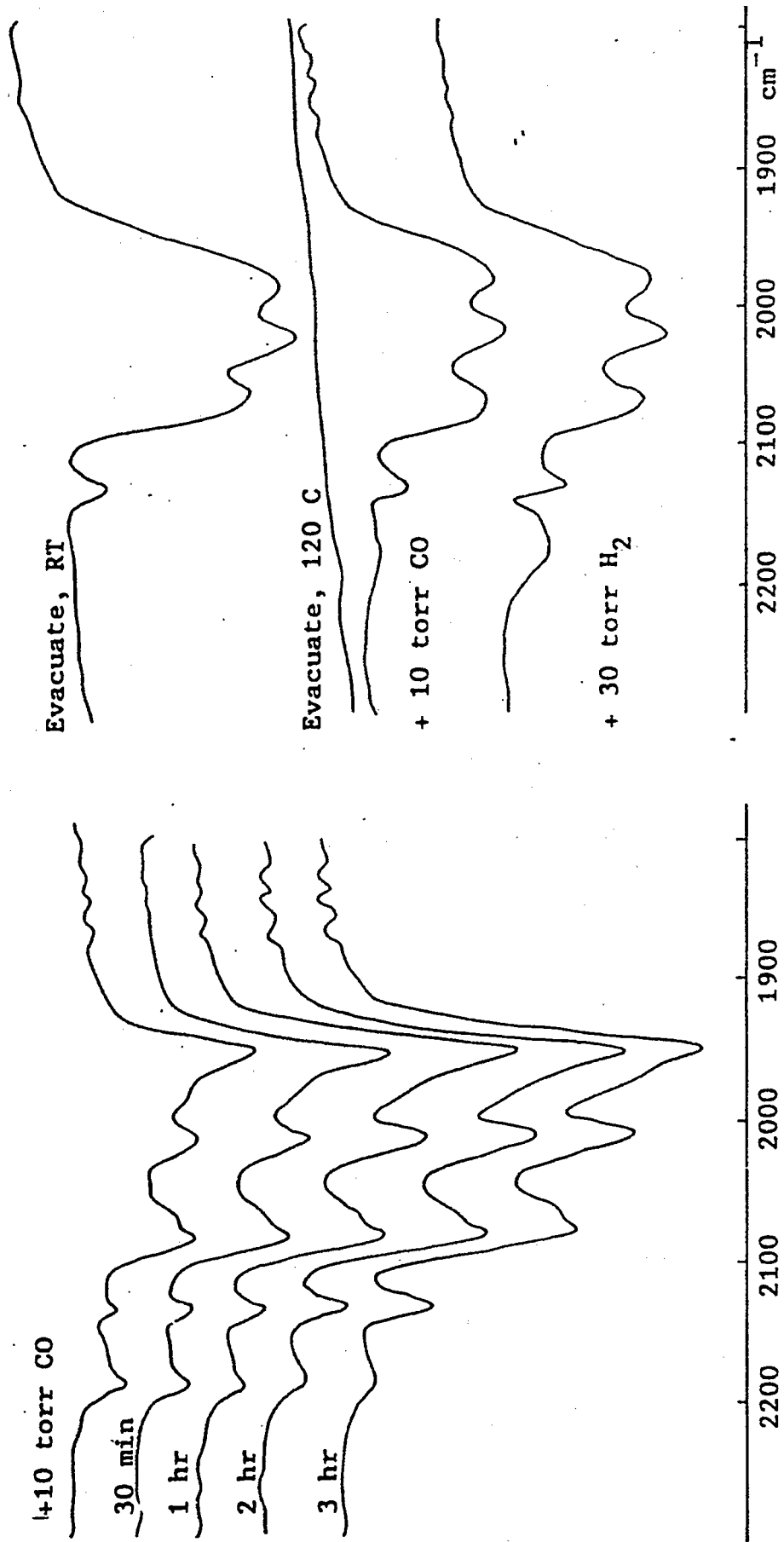


Figure 7. Infrared spectra of adsorption of CO on 2-2 Ni-Ce/X-Zeolite.

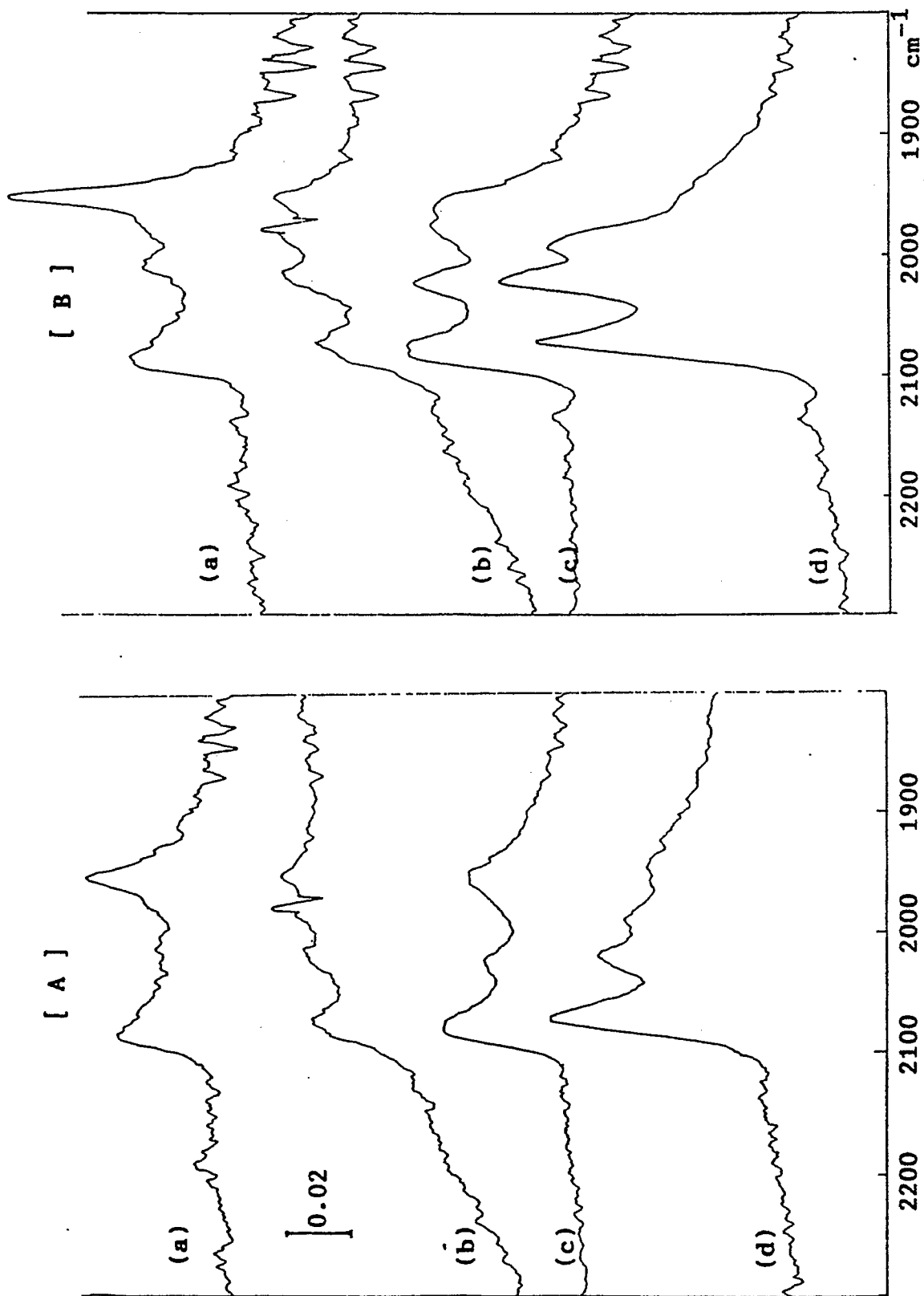


Figure 8. Infrared spectra of adsorption of CO on x-zeolite supported catalysts:

(a) 5 wt% Ni (b) 5-2.5 Ni-Ce (c) 5-5 Ni-Ce (d) 5-10 Ni-Ce.

[A] Spectra taken at 5 min. of adsorption; [B] at equilibrium state, ~2hr.

$P_{CO} = 1$  torr.

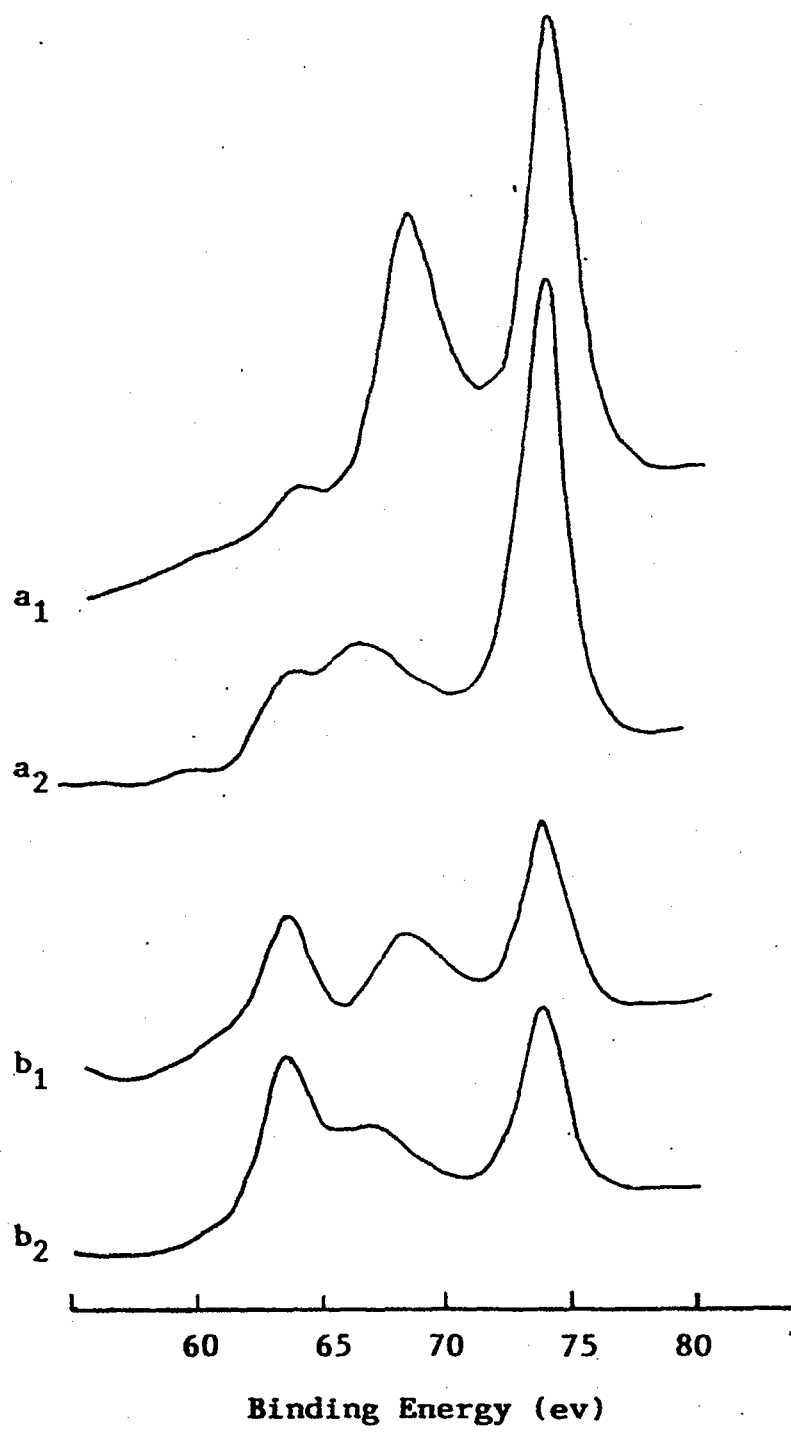


Figure 9. XPS spectra for 5-5 Ni-Ce catalysts supported on X- (a) and Y- (b) zeolites before (1) and after (2) high temperature (500°C) reduction.

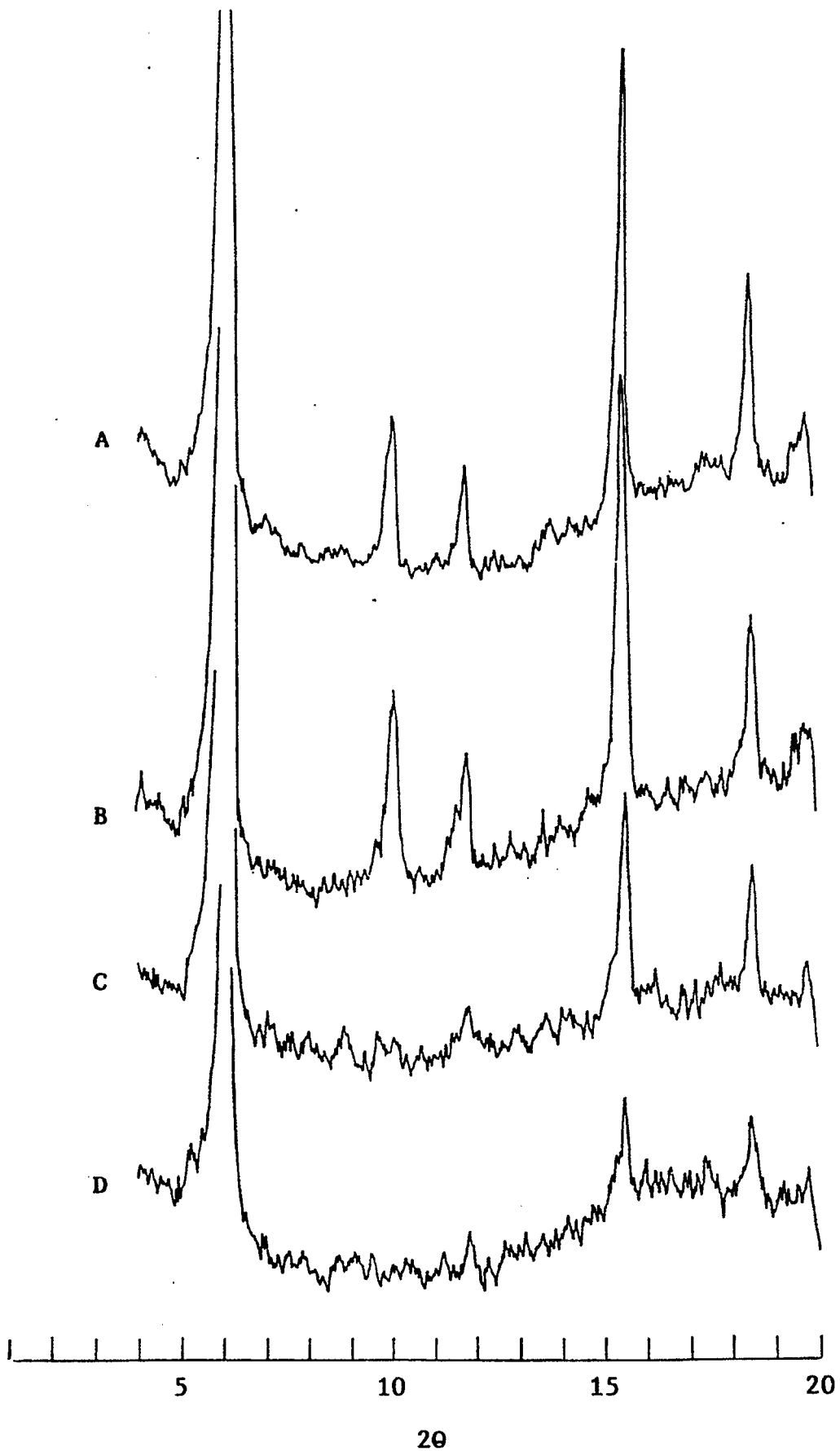


Figure 10. XRD spectra of x-zeolite and supported samples reduced at 700°C : A, x-zeolite; B, 5 wt% Ni/X; C, 5-5 Ni-Ce/X; D, 5-10 Ni-Ce/X.



Figure 11. XRD spectra of  $\gamma$ -zeolite and supported samples reduced at  $700^{\circ}\text{C}$  : A,  $\gamma$ -zeolite; B, 5 wt% Ni/Y; C, 5-5 Ni-Ce/Y; D, 5-10 Ni-Ce/Y.



## **SATISFACTION GUARANTEED**

**NTIS strives to provide quality products, reliable service, and fast delivery. Please contact us for a replacement within 30 days if the item you receive is defective or if we have made an error in filling your order.**

▲ **E-mail: [info@ntis.gov](mailto:info@ntis.gov)**

▲ **Phone: 1-888-584-8332 or (703)605-6050**

# **Reproduced by NTIS**

National Technical Information Service  
Springfield, VA 22161

***This report was printed specifically for your order from nearly 3 million titles available in our collection.***

For economy and efficiency, NTIS does not maintain stock of its vast collection of technical reports. Rather, most documents are custom reproduced for each order. Documents that are not in electronic format are reproduced from master archival copies and are the best possible reproductions available.

Occasionally, older master materials may reproduce portions of documents that are not fully legible. If you have questions concerning this document or any order you have placed with NTIS, please call our Customer Service Department at (703) 605-6050.

## **About NTIS**

NTIS collects scientific, technical, engineering, and related business information – then organizes, maintains, and disseminates that information in a variety of formats – including electronic download, online access, CD-ROM, magnetic tape, diskette, multimedia, microfiche and paper.

The NTIS collection of nearly 3 million titles includes reports describing research conducted or sponsored by federal agencies and their contractors; statistical and business information; U.S. military publications; multimedia training products; computer software and electronic databases developed by federal agencies; and technical reports prepared by research organizations worldwide.

For more information about NTIS, visit our Web site at <http://www.ntis.gov>.

# **NTIS**

**Ensuring Permanent, Easy Access to  
U.S. Government Information Assets**



U.S. DEPARTMENT OF COMMERCE  
Technology Administration  
National Technical Information Service  
Springfield, VA 22161 (703) 605-6000

---

---