Thermochimica Acta 345 (2000) 19–23

thermochimica
acta

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# Microcalorimetric and infrared spectroscopic studies of $C_2H_4$ adsorption on $Ni/SiO_2$ and $NiBi/SiO_2$ catalysts

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Received 21 April 1999; received in revised form 27 October 1999; accepted 1 November 1999

## Abstract

Microcalorimetric adsorption and FTIR were used to study the surface species and energy of surface bonding for ethylene adsorption on $Ni/SiO_2$ and $NiBi/SiO_2$ catalysts. Microcalorimetric adsorption of $H_2$ was employed to titrate the surface sites of Ni in the catalysts. It was found that addition of a small amount of Bi ($Ni/Bi = 64$ and 16) significantly decreased the number of Ni surface sites for $H_2$ adsorption. The adsorption of ethylene at room temperature on the $Ni/SiO_2$ and $Ni_{64}Bi/SiO_2$ produced mainly ethylidyne species on the surface plus adsorbed hydrogen atoms, generating the initial adsorption heats of 170 and 160 kJ/mol, respectively. In contrast, the adsorption of ethylene on the $Ni_{16}Bi/SiO_2$ at room temperature produced mainly molecularly adsorbed surface species (di-$\sigma$ or $\pi$-bonded species) with much lower adsorption heat. The enrichment of Bi on the surface may change the ensemble size of Ni for the adsorption of ethylene, thereby changing the adsorption state and energy of ethylene on the surface of Ni. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Microcalorimetric adsorption; Nickle–bismuth catalysts; Ethylene adsorption; FTIR; Surface adsorption states

## 1. Introduction

Metals and alloys are important catalysts for the conversion of hydrocarbons [1]. The formation of alloys or multimetallic clusters dramatically change the activity and selectivity of many reactions such as hydrogenolysis, hydrogenation, dehydrogenation, isomerization, cyclization and cracking [2]. The effects of alloying are mainly classified into a geometric effect (or ensemble effect) and an electronic effect (or ligand effect) [3]. Group VIII metals are widely used as active components and IB group metals often serve as inert or less active components to modify the catalytic behavior of group VIII metals [2].

The Ni–Cu system is probably the most extensively studied bimetallic catalyst. However, it is difficult to determine the role of Cu in the modification of Ni since Cu is also an active component in some catalytic processes. Recently, Besenbacher et al. [4] found that addition of a very small amount of Au to Ni could improve the selectivity and stability for the methane steam reforming reaction. The effect of Au was attributed to the ensemble effect since Au itself is inert for the reaction [5]. We choose Bi since it is cheaper than Au but may be as inert as Au for many reactions [6].

The purpose of the present work is to describe the effect of Bi on the formation of surface species and the strength of the bonds to Ni on adsorption of ethylene. The reactions, such as isomerization, aromatization and hydrogenolysis may first involve the formation of surface species with a carbon–carbon double bond that

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PII: S0040-6031(99)00396-2

is similar to those formed on the ethylene adsorption. In addition, Sheppard and De La Cruz [7] showed that the surface species on metals formed from adsorption of other olefins with longer carbon chains might be similar to those formed from adsorption of ethylene. Therefore, measurements of heats of formation of the species on various metals and alloys on ethylene adsorption are important as a fundamental data base. These data may be essential in constructing reaction mechanisms for the conversion of hydrocarbons on metallic catalysts. In this work, the techniques of infrared spectroscopy and microcalorimetric adsorption [8] were employed to identify the surface species and to measure the strength of the bond to the surfaces of NiBi/$SiO_2$ catalysts. Microcalorimetric adsorption of $H_2$ was used to titrate the surface sites of the catalysts before ethylene adsorption.

## 2. Experiments

### 2.1. Catalyst preparation and treatment

The catalysts were prepared by the incipient wetness impregnation method. The support used was a Cab-o-sil fumed silica (EH-5) provided by Cabot (IL, USA). The precursor used for preparing the Ni/$SiO_2$ and NiBi/$SiO_2$ were $Ni(NO_3)_2{\cdot}6H_2O$ (AR) and $Bi(NO_3)_3{\cdot}5H_2O$ (AR). The loading of nickle in all the Ni/$SiO_2$ and NiBi/$SiO_2$ catalysts was fixed at 10 wt.%, while the atomic ratio of Ni to Bi in the NiBi/$SiO_2$ catalysts were 64:1 and 16:1. The required amount of precursors were dissolved in deionized water, then mixed with the silica powder to form a gel. The gel was dried at room temperature for 24 h and then further dried at 393 K overnight.

Temperature-programmed-reduction (TPR) showed that the temperature of all the TPR peaks of Ni/$SiO_2$ and NiBi/$SiO_2$ catalysts appeared below 723 K. Accordingly, the catalysts were pre-reduced in flowing $H_2$ at 473 K for 1 h, 573 K for 1 h and then 723 K for 4 h.

### 2.2. Microcalorimetric adsorption

The measurements were performed at 313 K using a Tian-Calvet type heat-flux microcalorimeter [8,9]. The calorimeter was connected to a gas handling system and a volumetric system employing Baratron capacitance manometers for precision pressure measurement (0.001 Torr). The maximum apparent leak rate of the volumetric system (including calorimetric cells) was $10^{-4}$ Torr/min in a system volume of approximately 35 $cm^3$ (i.e. about $2 \times 10^{-4}$ μmol/min). The ultimate dynamic vacuum of the system was ca. $10^{-5}$ Torr.

The microcalorimetric procedures used in this study have been described in detail elsewhere [8,9]. Briefly, the pre-reduced sample was reduced again in situ in the microcalorimetric cell under highly pure $H_2$ in the static mode at 473 K for 1 h, 573 K for 1 h and 723 K for 2 h, during which the $H_2$ gas in the cell was flushed with fresh $H_2$ every 0.5 h. Then, the sample was outgassed at 723 K for 1 h. After cooling the cell to room temperature, about 600 Torr highly pure helium was admitted into the cells to minimize possible surface contamination by leakage during thermal equilibrium (ca. 10 h). After thermal equilibrium was reached, the helium in the cell was evacuated. The microcalorimetric data were then collected by sequentially introducing small doses (1–10 μmol) of probe molecules ($H_2$ or $C_2H_4$) onto the sample until it became saturated (equilibrium pressure reached $5 \sim 6$ Torr). The heat response for each dose was recorded as a function of time and integrated to determine the energy released (mJ). The amount of a gas adsorbed (μmol) was determined volumetrically. The differential heat (kJ/mol), defined as the negative enthalpy change, was then calculated for each dose by dividing the heat released by the amount of gas adsorbed.

### 2.3. Infrared spectroscopic (FTIR) measurements

The IR cell used was homemade and similar to one described elsewhere [10]. The cell can be heated to 773 K in a flowing gas and a sample pellet can be reduced in situ in the cell. In addition, the IR cell was directly connected to a vacuum system equipped with a dosing section with known volume and a Baratron capacitance manometer (accuracy: 0.001 Torr) thus allowing quantitative dosing of probe molecules onto the pellet.

A catalyst sample of about 30 mg was pressed to form a self-supporting pellet 13 mm in diameter. The pellet was reduced in flowing $H_2$ for 3 h and evacuated for 1 h at 723 K. After the cell was cooled down to room temperature, a spectrum for the pellet was collected. Then a known amount of ethylene was dosed onto the pellet, corresponding to about 100% coverage of metal sites in the pellet. Since the number of sites were known from microcalorimetric adsorption before the IR measurement, the advantage of this procedure is that the dose size can be monitored to ensure all dosed molecules were adsorbed by the pellet. Thus, there are no gas phase molecules detectable in the cell and it is not necessary to evacuate the cell before the spectrum collection. This approach also has the advantage that weakly adsorbed species, which may otherwise be removed during evacuation, can also be detected. About 30 min after the dosing, the spectrum was collected again. The difference in the two spectra is the spectrum of adsorbed species. All the spectra were collected in the transmittance mode with 4 $cm^{-1}$ resolution and 1000 scans by using a Brucker IFS66V FTIR spectrophotometer.

Ethylene (99.9%), used for both microcalorimetric adsorption and IR studies, was purified by successive freeze/pump/thaw cycles with liquid nitrogen.

## 3. Results and discussion

Fig. 1 shows plots of the differential heat vs adsorbate coverage for the adsorption of $H_2$ on the Ni/$SiO_2$ and NiBi/$SiO_2$ catalysts. The initial heat and coverage for the 10% Ni/$SiO_2$ catalyst are 83 kJ/mol and 119 µmol/g, respectively. This initial heat is in agreement with the value of 90 kJ/mol reported for a Ni powder sample [11]. The initial heat of 79 kJ/mol for the $Ni_{64}Bi/SiO_2$ (Ni/Bi atomic ratio = 64) is close to that of Ni/$SiO_2$, while the $Ni_{16}Bi/SiO_2$ (Ni/Bi atomic ratio = 16) catalyst exhibits a lower initial heat, 72 kJ/mol. The initial heat and the saturation coverage of $H_2$ adsorption decrease with increasing Bi/Ni ratio. A small amount of Bi causes a substantial decrease of $H_2$ uptake on Ni, which may be due to a decrease of Ni dispersion (increase of particle size upon the addition of Bi), or part of the Ni surface is covered by Bi owing to the surface segregation of Bi. Fig. 1b shows the differential heat curves normalized to the coverage of $H_2$. It is seen that the $Ni_{64}Bi/SiO_2$ and Ni/$SiO_2$ exhibit similar differential heat curves, while the $Ni_{16}Bi/SiO_2$ exhibits much weaker sites. This indicates that the addition of a very small amount of Bi in the $Ni_{64}Bi/SiO_2$ blocks some surface Ni sites, but does not alter significantly the size of surface Ni ensembles so that the nature of $H_2$ adsorption is not affected. In contrast, the nature of $H_2$ adsorption on the $Ni_{16}Bi/SiO_2$ seems to be changed. Suppose that Bi only affects the ensemble effect [6], then this change in $H_2$ adsorption implies that the ensemble size of the Ni clusters on the surface of the $Ni_{16}Bi/SiO_2$ catalyst are substantially decreased so that part of hydrogen atoms occupy sites other than the threefold hollow sites which are the most stable sites for hydrogen adsorption.

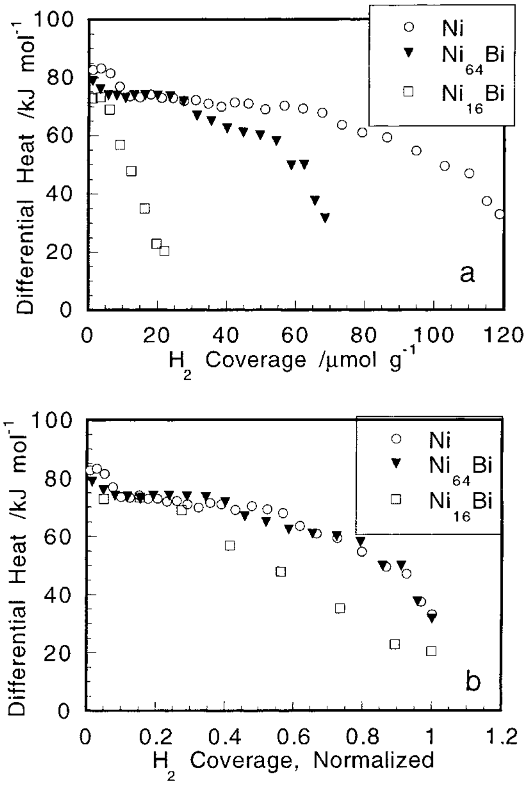

Fig. 1. Differential heat vs adsorbate coverage in µmol/g (a) and normalized to coverage (b) for $H_2$ adsorption at room temperature on the 10% Ni/$SiO_2$ (○), $Ni_{64}Bi/SiO_2$ (▼) and $Ni_{16}Bi/SiO_2$ (□) catalysts.

Fig. 2 shows the microcalorimetric results for adsorption of ethylene on the Ni/$SiO_2$ and NiBi/$SiO_2$ catalysts at room temperature. The initial heat of ethylene adsorption on the Ni/$SiO_2$ was 170 kJ/mol, which is similar to that on Pt/$SiO_2$ (160 kJ/mol) [10]. The initial heats on the $Ni_{64}Bi/SiO_2$ and $Ni_{16}Bi/SiO_2$

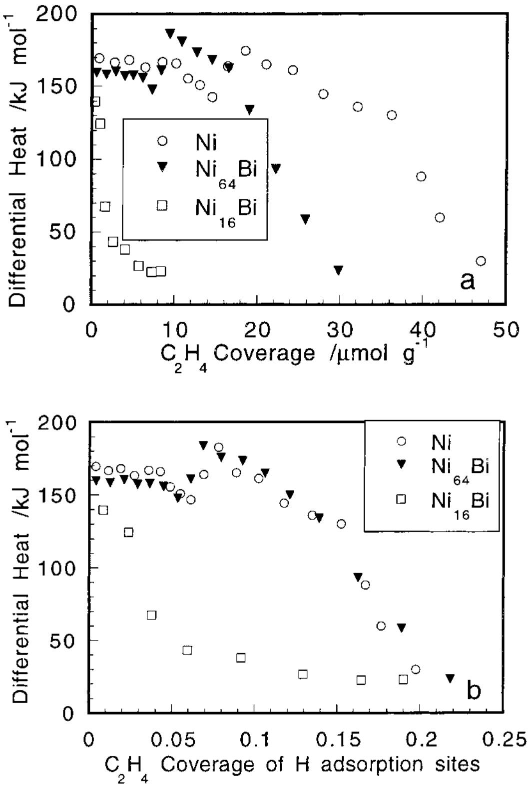

Fig. 2. Differential heat vs adsorbate coverage in μmol/g (a) and normalized by H adsorption sites (b) for ethylene adsorption at room temperature on the 10% $Ni/SiO_2$ (○), $Ni_{64}Bi/SiO_2$ (Ni/Bi = 64) (▼) and $Ni_{16}Bi/SiO_2$ (Ni/Bi = 16) (□) catalysts.

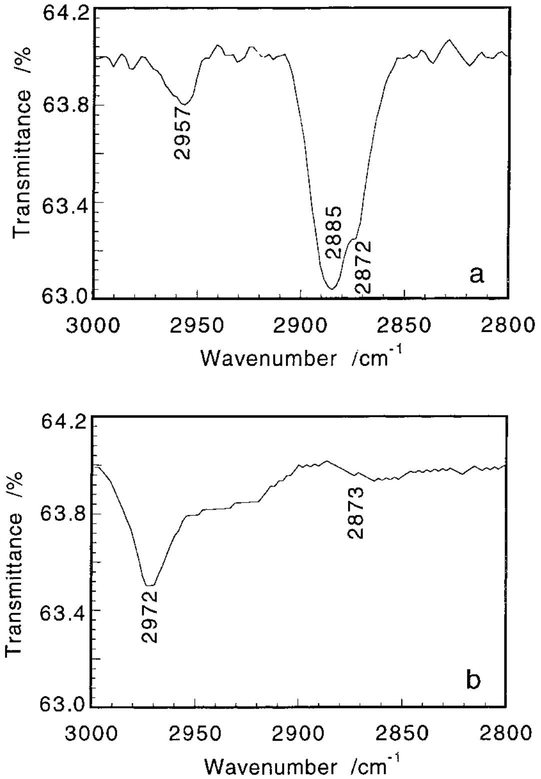

Fig. 3. Infrared spectra for ethylene adsorption at room temperature on the 10% $Ni/SiO_2$ (a) and $Ni_{16}Bi/SiO_2$ (Ni/Bi = 16) (b).

are 160 and 140 kJ/mol, respectively. When the curves of differential heat vs ethylene coverage were normalized by the number of sites determined by $H_2$ adsorption (Fig. 2b), the $Ni/SiO_2$ and $Ni_{64}Bi/SiO_2$ exhibited similar behavior for ethylene adsorption, while the $Ni_{16}Bi/SiO_2$ displayed a curve with much lower adsorption heat. It should be mentioned that there were peaks on the heat vs coverage curves for the $Ni/SiO_2$ and $Ni_{64}Bi/SiO_2$ catalysts, which will be explained according to the FTIR results.

Sheppard and De La Cruz [7] have recently reviewed the infrared spectra of ethylene adsorbed on various metal surfaces. In this study, the FTIR spectra were collected for ethylene adsorption on the $Ni/SiO_2$ and $Ni_{16}Bi/SiO_2$ catalysts at room temperature (Fig. 3). Only bands with frequencies higher than 2800 $cm^{-1}$ were seen. No bands between 1300 and 1600 $cm^{-1}$ were observed for ethylene adsorbed on these two samples. In Fig. 3a, three bands can be seen around 2872, 2885, and 2957 $cm^{-1}$, which are in agreement with the results reported for $Ni/SiO_2$ catalysts in the literature [12]. The band around 2872 $cm^{-1}$ can be assigned to ethylidyne on Ni whereas the bands around 2887 and 2953 $cm^{-1}$ can be assigned to the dimer of ethylidyne on Ni at high coverage according to Sheppard and De La Cruz [7]. In Fig. 3b, a band around 2972 $cm^{-1}$ is clearly observed, and there is only a trace of the band around 2873 $cm^{-1}$. Lehwald and Ibach observed a band at 2950 ~ 2995 $cm^{-1}$ for ethylene adsorbed on single crystal Ni at 80 ~ 150 K and assigned the band to di-$\sigma$ species [13]. The molecularly adsorbed ethylene (di-$\sigma$ species and $\pi$-species) usually seen on single metal surfaces at low temperatures were also observed on $Pt–Sn/SiO_2$ and $Pt–Au/SiO_2$ samples at room temperature [10,14]. Therefore, we assign the band around 2972 $cm^{-1}$ to molecularly adsorbed species of ethylene (either di-$\sigma$ or $\pi$) and the weak band around 2873 $cm^{-1}$ to ethylidyne on the Ni modified by Bi. These results indicate that the main surface species for ethylene adsorption on the $Ni/SiO_2$ sample and probably also on the $Ni_{64}Bi/SiO_2$ sample was ethylidyne, as formulated below

$$C_2H_4 + 4Ni \rightarrow Ni_3{\equiv}CCH_3 + Ni{-}H \qquad (1)$$

when more ethylene is introduced, the adsorbed ethylene may react with surface hydrogen to produce ethane

$$\text{Adsorbed-}C_2H_4 + 2Ni{-}H \rightarrow C_2H_6 \uparrow + 2Ni \qquad (2)$$

This hydrogenation reaction produces extra heat besides the heat of ethylene adsorption and the evolution of ethane over-estimate the equilibrium pressure of ethylene in the gas phase, both of which cause an incorrect calculation of the differential heat for the ethylene adsorption. This may explain the peaks in Fig. 2. The initial heats of 170 kJ/mol for the $Ni/SiO_2$ and 160 kJ/mol for the $Ni_{64}Bi/SiO_2$ can be attributed to the formation of ethylidyne and H on the Ni surfaces. The initial heat of 140 kJ/mol for the $Ni_{16}Bi/SiO_2$ sample may be produced by formation of associative adsorbed species (di-$\sigma$ or $\pi$-species) plus a little dissociative adsorbed species (ethylidyne) on the Ni surface modified by Bi. With the increase of ethylene coverage, the associative adsorbed species may dominate the surface species on the $Ni_{16}Bi/SiO_2$, which is evidenced by the low differential heat observed for ethylene adsorption on this sample. This indicates that the presence of Bi substantially inhibits the decomposition of ethylene on a Ni surface. Hence, the selectivity and stability of Ni catalysts for the steam reforming of methane might be improved by the addition of Bi as well as by Au [4].

## 4. Conclusions

The addition of a small amount of Bi significantly decreases the surface sites of Ni for hydrogen adsorption. For example, the addition of 1.5 at.% (Ni/Bi = 64) and 6 at.% Bi (Ni/Bi = 16) in Ni decreases the $H_2$ coverage from 120 to 68 and 22 μmol/g, respectively. This may indicate that Bi is greatly enriched on the surface in the Ni–Bi alloys. However, the adsorption of ethylene seems to be similar for the $Ni_{64}Bi/SiO_2$ and $Ni/SiO_2$ samples, as revealed by their differential heat vs coverage curves for the ethylene adsorption. This implies that the ensemble sizes of Ni clusters on the surface of the $Ni_{64}Bi/SiO_2$ sample are not small enough to change the surface species for the adsorption of ethylene. The FTIR results show that the surface species on the $Ni/SiO_2$ at room temperature are ethylidyne-type. On the other hand, the heat and coverage for the adsorption of ethylene on the $Ni_{16}Bi/SiO_2$ sample are significantly lower, indicating a change in the ensemble size of surface Ni in this sample, leading to the change of surface species for the adsorption of ethylene as evidenced by the FTIR spectrum which reveals the formation of mainly associatively adsorbed ethylene species.

## Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 29673021).

## References

[1] V. Ponec, G.C. Bond, Catalysis by Metals and Alloys, Studies in Surface Science and Catalysis, vol. 95, Elsevier, Amsterdam, 1995.
[2] J.H. Sinfelt, Bimetallic Catalysts: Discoveries, Concepts, and Applications, Wiley, New York, 1983.
[3] V. Ponec, Adv. Catal. 32 (1983) 149.
[4] F. Besenbacher, I. Chorkendorff, B.S. Clausen, B. Hammer, A.M. Molenbroek, J.K. Norskov, I. Stensgaard, Science 279 (1998) 1913.
[5] B. Hammer, J.K. Norskov, Nature 376 (1995) 238.
[6] M.T. Paffett, R.G. Windham, B.E. Koel, Surf. Sci. 207 (1989) 274.
[7] N. Sheppard, C.De La Cruz, Adv. Catal. 41 (1996) 1.
[8] B.H. Handy, S.B. Sharma, B.E. Spiewak, J.A. Dumesic, Measurement Sci. Technol. 4 (1993) 1350.
[9] S.A. Goddard, M.D. Amiridis, J.E. Rekoske, N. Cardona-Martines, J.A. Dumesic, J. Catal. 117 (1998) 155.
[10] J. Shen, J.M. Hill, R.M. Watwe, B.E. Spiewak, J.A. Dumesic, J. Phys. Chem. B 103 (1999) 3931.
[11] B.E. Spiewak, J. Shen, J.A. Dumesic, J. Phys. Chem. 99 (1994) 17640.
[12] B.A. Morrow, N. Sheppard, J. Phys. Chem. 70 (1966) 2406.
[13] S. Lewald, H. Ibach, Surf. Sci. 89 (1979) 425.
[14] J. Shen, J.M. Hill, R.M. Watwe, S.G. Podkolzin, J.A. Dumesic, Catal. Lett., submitted for publication.