Infrared spectra of dinitrogen adsorbed on bimetallic lanthanide (Eu or Yb)–Ni/SiO_2 catalysts

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Received 8 December 1998; accepted 1 March 1999

Bimetallic lanthanide (Ln: Eu or Yb)–Ni/SiO_2 catalysts prepared by the use of dissolution of lanthanide metals in liquid ammonia have been studied by infrared spectroscopy for dinitrogen adsorption. The infrared spectra were measured at 133–300 K using Ln–Ni/SiO_2 obtained when the Eu or Yb metal dissolved in liquid ammonia reacted with 20 mass% Ni/SiO_2 in different ratios. Infrared spectra for Eu–Ni/SiO_2 showed absorption bands at 2336, 2265, 2254 and 2227 cm^{-1} at 133 K, which disappeared upon evacuation. The adsorbed state was found to be all molecular from the isotope shift using $^{28}N_2$ and $^{30}N_2$. The bands at 2254 and 2227 cm^{-1} of them were assigned to new adsorbed dinitrogen species resulting from synergetic interactions between the europium and nickel metal. The concentration of adsorbed dinitrogen on Eu–Ni/SiO_2 varied markedly with the Eu/Ni ratios, and particularly, it increased in the region of high Eu content. Upon introduction of ytterbium onto nickel, new bands at 2254 and 2226 cm^{-1} similarly appeared. However, the dependence of dinitrogen adsorption as a function of Yb content in Yb–Ni/SiO_2 was somewhat different from that for Eu–Ni/SiO_2. The effects of lanthanide on the surface of Ln–Ni/SiO_2 were discussed in connection with the variation in catalytic properties.

Keywords: infrared spectroscopy, nitrogen adsorption, lanthanide, bimetallic catalyst, europium, ytterbium

1. Introduction

Recently, the surface properties of the lanthanide (Ln)–transition metal intermetallics and lanthanide metal overlayers have attracted a growing interest from the standpoint of catalysis and hydrogen-absorbing characteristics [1]. However, despite the intrinsic interest and considerable potential of these novel materials, very little detailed work has been carried out with a view to unveiling the specific properties upon interactions of lanthanides with transition metals.

It has been shown that Eu and Yb metals dissolve in liquid ammonia to yield homogeneous solutions containing the ammoniated electrons [2]. When the transition metal powders are added to this solution, the metal powders react with the dissolved lanthanide metals in liquid ammonia to form novel lanthanide metal overlayers or bimetallic catalysts [3–6]. Such systems can be used as a catalyst probe for studying the catalytic actions induced by interaction between the lanthanide and transition metals.

Infrared spectra of CO adsorbed on the bimetallic catalysts have been previously studied to characterize the nature of the surface [7]. Infrared spectroscopy is one of powerful techniques for characterizing the surfaces of alloys and bimetallic catalysts, in which adsorbed CO or N_2 is often used as a molecular probe directly reflecting variations in the surface [8]. The present study was extended to include SiO_2-supported bimetallic systems obtained when Eu or Yb dissolved in liquid ammonia reacts with Ni/SiO_2. To provide information as to the factors responsible for the changes in catalytic properties of Ln–Ni/SiO_2 (Ln: Eu or Yb) with the Ln content, infrared studies for dinitrogen adsorption were carried out.

2. Experimental

A SiO_2-supported Ni (20 mass%) sample was prepared by impregnation of SiO_2 (Degussa Aerosil 380) with aqueous solutions of $Ni(NO_3)_2\cdot 6H_2O$ (Wako Pure Chemical; research grade), followed by calcination in air at 573 K. The sample (30 mg) thus obtained was pressed into a self-supporting pellet, which was reduced at 673 K under H_2 flow in an atmospheric pressure. In the preparation of Ln–Ni/SiO_2 for infrared spectroscopy, the pellet of Ni/SiO_2 was placed in a Schlenk tube containing a solution of liquid ammonia, to which Eu or Yb (99.9%; Shin-Etsu Chemical Co., Ltd.) was added in varied Ln/Ni ratios. The pellet of Ln–Ni/SiO_2 thus prepared was transferred to an infrared cell without exposure to air. The infrared cell was connected with a closed gas-circulation reactor equipped with a high vacuum system. The temperature of the cell can be controlled from 133 to 723 K by vapor of liquid nitrogen and an electric heater. The samples of Ni/SiO_2 and Ln–Ni/SiO_2 were evacuated at 673 K for 2 h in the cell as a pretreatment.

Infrared spectra were recorded on a JASCO 7300 Fourier transform infrared spectrometer equipped with a MCT detector. The method for infrared spectra was similar to that previously described [7]. Infrared spectra were obtained from the ratio of the background spectrum of catalysts to that of adsorbed dinitrogen on the catalysts.

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3. Results and discussion

First, infrared spectra of dinitrogen adsorbed on 20% Ni/SiO_2 were examined (figure 1). A strong absorption was observed at 2206 cm^{-1} when the Ni/SiO_2 sample, previously evacuated at 673 K for 2 h, was cooled to 133 K, exposed to N_2 of 180 Torr. For 20% Ni/SiO_2 treated with ammonia (dipping the pellet of Ni/SiO_2 in liquid ammonia), infrared spectra were also measured in a similar manner as above. As shown in figure 1(b), a new absorption appeared at 2266 cm^{-1}. Infrared studies on the adsorption of dinitrogen over SiO_2-supported Ni [9–11] have shown that the N≡N stretching mode is observed at 2202 cm^{-1}, which is assigned to the structure of $Ni–N≡N^+$ by Eischens et al. [9]. The band of 2266 cm^{-1} was also assigned to adsorbed dinitrogen, additionally evidenced as molecular state from the isotope shift (2266 and 2189 cm^{-1} for $^{28}N_2$ and $^{30}N_2$, respectively). It has been shown that the absorption band of dinitrogen is strongly affected by co-adsorbed species to shift to lower or higher wavenumbers [9,10,12,13]. In particular, the presence of co-adsorbed hydrogen causes the wavenumbers of the N≡N stretching band to higher wavenumbers by 50–60 cm^{-1}. During the evacuation of NH_3-pretreated Ni/SiO_2 at 673 K, the decomposition of adsorbed ammonia on the Ni surface with subsequent forming of co-adsorbed hydrogen is expected, and consequently, the absorption band of dinitrogen adsorbed on nickel appeared at 2266 cm^{-1}, as shown in figure 1(b).

Figure 2 shows infrared spectra of adsorbed dinitrogen on Eu–Ni/SiO_2 with varied levels of Eu. When Eu–Ni/SiO_2 (Eu/Ni = 0.031) was exposed to N_2 at 133 K, broad bands at 2265 cm^{-1} with shoulders at 2254 and 2227 cm^{-1} were observed. The adsorbed state of these bands was confirmed to be molecular from the isotope shift using $^{28}N_2$ and $^{30}N_2$. Upon introduction of europium onto nickel, new N≡N stretching bands appeared at 2254 and 2227 cm^{-1} besides 2265 cm^{-1}. Thus this strongly reflects the occurrence of synergetic actions between the europium and nickel metal.

In figure 2, another absorption band was observed at 2334–2336 cm^{-1}. For $^{30}N_2$ adsorption, this band was shifted to 2262 cm^{-1}, in fair agreement with the estimate from the isotope shift. According to previous studies [14–20], adsorbed dinitrogen species with N≡N stretching vibrations above 2330 cm^{-1} are often observed on oxide or cationic sites. The vibration band of 2337 cm^{-1} was similarly observed when dinitrogen adsorption was carried out for comparison using Eu/SiO_2 prepared by impregnating SiO_2 with Eu metal solutions in liquid ammonia. Therefore, this band seems to be assigned to dinitrogen weakly bound to an Eu cation (≡Si–O–Eu–NH_2) formed by the reaction of europium with a surface hydroxyl group [21].

The variation of spectra of adsorbed dinitrogen on Eu–Ni/SiO_2 were examined with measured temperatures (figure 3). The intensities of these bands (2265, 2254 and 2227 cm^{-1}) decreased with increasing the temperature and completely disappeared above 300 K. In addition, these bands also disappeared upon evacuating N_2 in the gas phase at 133 K.

Figure 4 shows the relationship between the infrared intensities of the bands and the Eu content in Eu–Ni/SiO_2. For Eu–Ni/SiO_2, the total absorbance assigned to adsorbed dini-

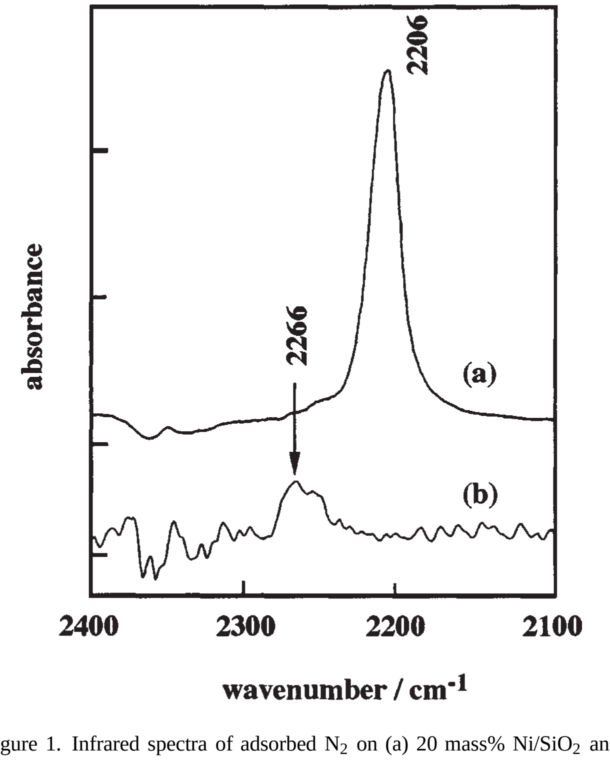

Figure 1. Infrared spectra of adsorbed N_2 on (a) 20 mass% Ni/SiO_2 and (b) 20 mass% Ni/SiO_2 treated with ammonia.

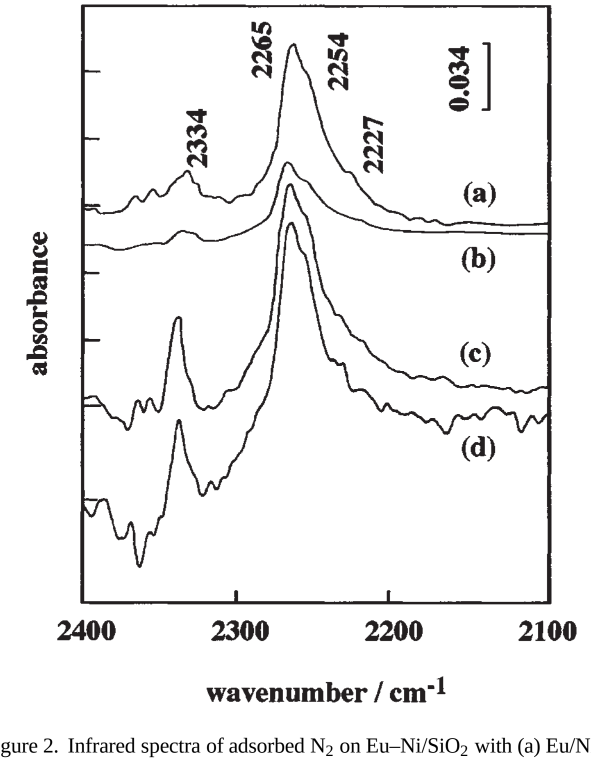

Figure 2. Infrared spectra of adsorbed N_2 on Eu–Ni/SiO_2 with (a) Eu/Ni = 0.031, (b) Eu/Ni = 0.19, (c) Eu/Ni = 0.45 and (d) Eu/Ni = 1.0 at 133 K.

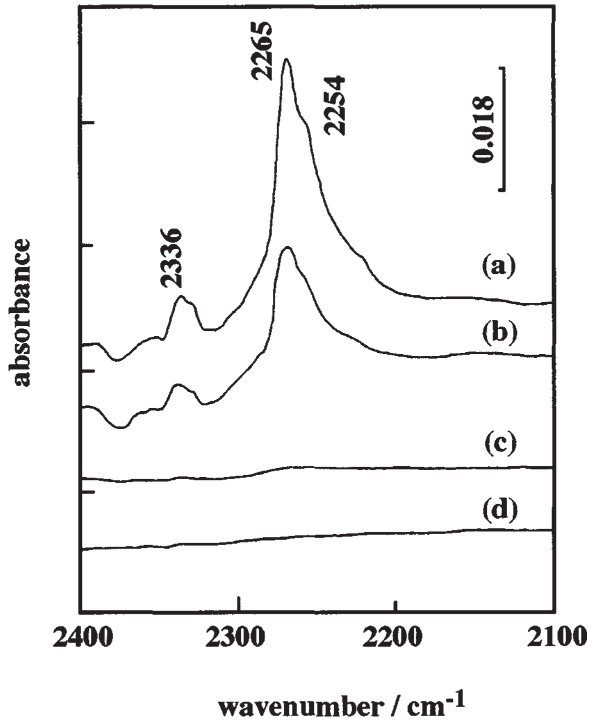

Figure 3. Infrared spectra of adsorbed N_2 on Eu–Ni/SiO_2 (Eu/Ni = 0.19) at (a) 133 K, (b) 173 K, (c) 223 K and (d) 300 K.

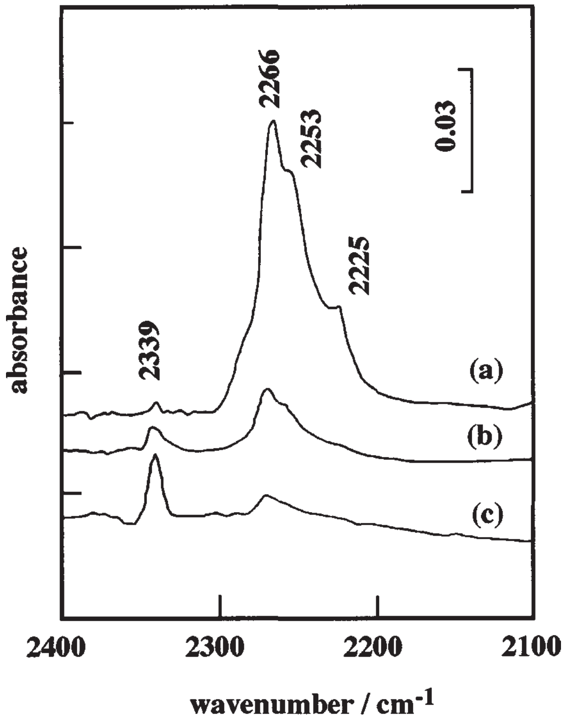

Figure 5. Infrared spectra of adsorbed N_2 on Yb–Ni/SiO_2 with (a) Yb/Ni = 0.020, (b) Yb/Ni = 0.11 and (c) Yb/Ni = 0.25 at 133 K.

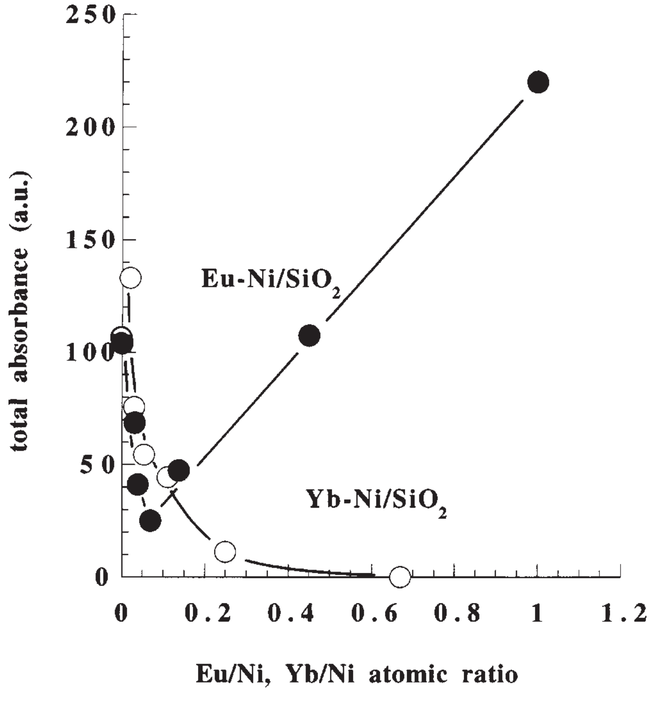

Figure 4. Total concentration of adsorbed N_2 on Ln–Ni/SiO_2 at 133 K vs. Ln/Ni ratios.

trogen species (2265, 2254 and 2227 cm^{-1}) decreased upon introduction of small amounts of Eu onto Ni/SiO_2, subsequently passed through a minimum around Eu/Ni = 0.064 and increased with increasing the Eu content. Such a mode of the variation in adsorption behavior as a function of lanthanide content is very similar to that observed for catalytic properties of lanthanide metal overlayers (Ln–Ni) obtained when lanthanide metals dissolved in liquid ammonia react with Ni metal powders [3,4,22]. From H_2 chemisorption [3], IR studies of CO [7] and XPS measurements [3], the dependence on the lanthanide content has been usually interpreted as follows: the active surfaces of parent nickel are gradually covered with the lanthanide metals and simultaneously synergetic interactions between the lanthanide and nickel metals occur to promote the catalysis, particularly in the region of higher lanthanide content. Therefore, the decrease in N_2 adsorption on Eu–Ni/SiO_2 in the low-content region is deemed to be a consequence of lanthanide coverage on the active nickel surface and in the high-content region, the synergy enhances the adsorption with the formation of new active sites. It has been shown that upon addition of lanthanide, Ln–Co [22,23], Ln–Cu [24] and Ln–Ag [24,25] besides Ln–Ni markedly accelerate the hydrogenation of ethene or the dehydrogenation of cyclohexane. Aika et al. [26] have reported that lanthanide (La, Ce or Sm)-added Ru/Al_2O_3 exhibits an enhanced activity for ammonia synthesis.

When Yb–Ni/SiO_2 (Yb/Ni = 0.020) was examined, infrared spectra of dinitrogen adsorption were similar to that for Eu–Ni/SiO_2 (Eu/Ni = 0.031); thus, adsorbed dinitrogen on Yb-promoted Ni was observed at 2266, 2253 and 2225 cm^{-1} besides physisorbed dinitrogen on ytterbium of 2336 cm^{-1} (figure 5). In contrast to Eu–Ni/SiO_2, Yb–Ni/SiO_2 showed somewhat different dependence of dinitrogen adsorption on the Yb/Ni ratios. The total concentration of adsorbed species corresponding to 2266, 2253 and 2225 cm^{-1} was reduced with increasing the Yb content, reaching almost zero at Yb/Ni = 0.67, as shown in figure 4. It seems quite certain that the introduction of ytterbium onto Ni/SiO_2 results in occurrence of the synergetic action with the formation of new adsorbed species at 2253 and 2225 cm^{-1}. However, in the high-content region, the coverage effect of active nickel surfaces with ytterbium is likely more predominant than the synergetic effect, compared to that for Eu–Ni/SiO_2. In the hydrogenolysis of ethane, both Eu–Ni and Yb–Ni show a decrease in the hydrogenolysis rates owing to a decrease in concentration of surface nickel available for structure-sensitive reactions by lanthanide coverage [3]. However, the degree of the decrease with increasing lanthanide content is more pronounced in Yb–Ni. In infrared spectra of adsorbed carbon monoxide, Eu–Ni/SiO_2 and Yb–Ni/SiO_2 have shown rather similar behavior in the amounts of adsorbed CO and the ratios of bridged CO to linear CO [7]. It has been shown that the Eu- and Yb-containing systems, in most cases, exhibit a similar tendency for their catalysis, but quantitatively, there are differences in effectiveness of the two actions (coverage and synergetic action) depending on types of catalytic reactions examined.

Acknowledgement

This work was partly supported by a Grant-in-Aid for Scientific Research on Priority Areas (No. 283, "Innovative Synthetic Reactions") from Monbusho.

References

[1] H. Imamura and S. Tsuchiya, Hyomen 26 (1988) 857;
F.P. Netzer and E. Berter, in: *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 5, eds. K.A. Gschneidner, Jr. and L. Eyring (North-Holland, Amsterdam, 1983) ch. 3;
S.T. Oyama and G.T. Haller, *Catalysis*, Specialist Periodical Report, Vol. 5 (Chemical Society, London, 1982) p. 333;
W.E. Wallace, CHEMTECH (1982) 752.

[2] J.C. Thompson, *Electrons in Liquid Ammonia* (Clarendon Press, Oxford, 1976).

[3] H. Imamura, K. Yoshimura, S. Hiranaka, Y. Sakata and S. Tsuchiya, J. Chem. Soc. Faraday Trans. 87 (1991) 2805.

[4] H. Imamura, S. Hiranaka, Y. Sakata and S. Tsuchiya, J. Chem. Soc. Faraday Trans. 88 (1992) 1577.

[5] H. Imamura, K. Igawa, Y. Kasuga, Y. Sakata and S. Tsuchiya, J. Chem. Soc. Faraday Trans. 90 (1994) 2119.

[6] H. Imamura, Y. Miura, K. Fujita, S. Sakata and S. Tsuchiya, J. Mol. Catal., in press.

[7] H. Imamura, H. Sugimoto, Y. Sakata and S. Tsuchiya, J. Catal. 136 (1992) 271.

[8] V. Ponec and G.C. Bond, *Catalysis by Metals and Alloys*, Stud. Surf. Sci. Catal., Vol. 95 (Elsevier, Amsterdam, 1995) p. 401, and references therein.

[9] R.P. Eischens and J. Jacknow, in: *Proc. 3rd Int. Congr. Catal.*, eds. W.M.H. Sachtler et al. (North-Holland, Amsterdam, 1965) p. 627.

[10] R. van Hardeveld and A. van Montfoort, Surf. Sci. 4 (1966) 396.

[11] R. van Hardeveld and A. van Montfoort, Surf. Sci. 17 (1969) 90.

[12] N. Kinoshita, K. Domen, K. Aika and T. Onishi, Appl. Surf. Sci. 18 (1984) 342.

[13] N. Kinoshita, K. Kido, K. Domen, K. Aika and T. Onishi, J. Chem. Soc. Faraday Trans. I 82 (1986) 2269.

[14] C.C. Chang and R.J. Kokes, J. Phys. Chem. 77 (1973) 2640.

[15] E. Cohen de Lara and Y. Delaval, J. Chem. Soc. Faraday Trans. II 74 (1978) 790.

[16] H.P. Wang and J.T. Yates, Jr., J. Phys. Chem. 88 (1984) 852.

[17] Y. Sakata, N. Kinoshita, K. Domen and T. Onishi, J. Chem. Soc. Faraday Trans. I 83 (1987) 2765.

[18] Y. Sakata, H. Abe, J.N. Kondo, K. Maruya, K. Domen and T. Onishi, Chem. Lett. (1989) 711.

[19] F. Wakabayashi, J.N. Kondo, A. Wada, K. Domen and C. Hirose, J. Phys. Chem. 97 (1993) 10761.

[20] T. Nakata and S. Matsushita, J. Catal. 4 (1965) 631.

[21] H. Imamura, T. Konishi, Y. Tokunaga, Y. Sakata and S. Tsuchiya, Bull. Chem. Soc. Jpn. 65 (1992) 244.

[22] H. Imamura, Y. Kasuga, K. Abe, Y. Sakata and S. Tsuchiya, Catal. Lett. 32 (1995) 115.

[23] H. Imamura, S. Hiranaka, M. Takamoto, Y. Sakata and S. Tsuchiya, J. Mol. Catal. 77 (1992) 333.

[24] H. Imamura, M. Yoshinobu, T. Mihara, Y. Sakata and S. Tsuchiya, J. Mol. Catal. 69 (1991) 271.

[25] H. Imamura, K. Fujita, Y. Sakata and S. Tsuchiya, Catal. Today 28 (1996) 231.

[26] S. Murata and K. Aika, J. Catal. 136 (1992) 118.