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Infrared Spectra of Carbon Monoxide Adsorbed on SiO_2-Supported Lanthanide–Ni Bimetallic Catalysts and Their Catalytic Properties

Recently the surface properties of the lanthanide (rare earth)–transition metal intermetallics and lanthanide metal overlayers have attracted a growing interest from the point of view of technical applications in catalyst and hydrogen storage (*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 bimetallic catalysts (*3, 4*). Such a system can be used as a catalyst probe for studying the catalytic actions induced by interactions between the lanthanide and transition metals. The present investigation was extended to include to SiO_2-supported bimetallic systems obtained when Eu or Yb dissolved in liquid ammonia reacts with silica-supported Ni. Using Fourier transform (FT)-IR studies of adsorbed carbon monoxide we provided information about the way the surface components were disposed in this bimetallic system. Adsorbed carbon monoxide was used as a molecular probe for the nature of a bimetallic surface since the IR spectra of adsorbed probe molecules directly reflected variations in the surface.

Silica-supported Ni catalysts (9.1% Ni/SiO_2) were prepared by impregnation of SiO_2 (Degussa Aerosil) with aqueous solutions of $Ni(NO_3)_2 \cdot 6H_2O$. The samples were subsequently dried and reduced at 573 K for 8 h with flowing hydrogen as a standard pressure. For the addition of lanthanide, Ni/SiO_2 was placed in a Schlenk tube containing a solution of liquid ammonia. Eu or Yb (99.9%; Shin-Etsu Chemical Co., Ltd.) was added to Ni/SiO_2 suspended in the ammonia with vigorous stirring at 198 K. Upon dissolution of the lanthanide metals in liquid ammonia, a blue homogeneous solution was formed, characteristic of solvated electrons (*2*). The blue colour gradually disappeared as a result of the reaction of the dissolved lanthanide with Ni/SiO_2. On disappearance of the blue colour, the vessel was allowed to warm to room temperature and the excess of ammonia was pumped off leaving SiO_2-supported Eu–Ni and Yb–Ni bimetallic catalysts with varied levels of lanthanide content. Unless otherwise stated, the content of lanthanides in the catalysts was represented by the fraction of the atomic %. All sample preparation steps were carried out in an atmosphere of dry argon, otherwise the catalysts became unreactive.

The catalytic reactions were tested using a Pyrex gas-circulation system. Prior to the reaction the catalysts were subjected to evacuation treatment at 673 K for 2 h. IR spectra were recorded on a JASCO FT-IR 7000 spectrometer. Samples for IR studies were similarly prepared according to the method described above. The lanthanide metals were added to liquid ammonia containing an IR disc of 9.1% Ni/SiO_2 which had been reduced at 673 K for 5 h. The disc thus treated was transferred to the IR cell without exposure to air. IR spectra were obtained from the ratio of the background spectrum of catalysts to that of adsorbed CO on the catalysts.

When the lanthanide dissolved in liquid

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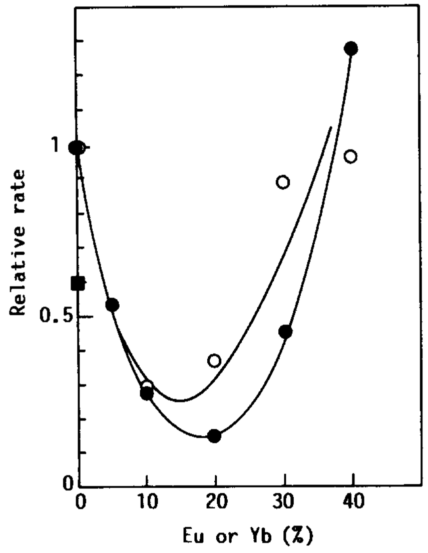

FIG. 1. Relative rates of ethene hydrogenation (203 K) vs lanthanide content (%) in Eu–Ni/SiO_2 (●) and Yb–Ni/SiO_2 (○). ■: the result on Ni/SiO_2 treated with liquid ammonia without lanthanide. The catalysts were evacuated at 673 K for 2 h prior to the reaction. Reaction conditions: C_2H_4 = 20 Torr; H_2 = 40 Torr.

ammonia was brought into contact with Ni/SiO_2, the lanthanide reacted readily with nickel to form active bimetallic catalysts, changing the colour of solution from blue to colourless. For the hydrogenation of ethene the relative rates of the lanthanide–Ni/SiO_2 catalysts varied markedly with changes in Eu or Yb content (%) (Fig. 1). The reaction was largely studied by admitting ethene (20 Torr) and hydrogen (40 Torr) at 203 K. Ni/SiO_2 was normally very active, whereas lanthanide metal catalysts (*5*) showed negligible activity at a low temperature of 203 K. Upon the addition of small amounts of lanthanide to Ni/SiO_2 the hydrogenation activity decreased slightly and then increased with further increasing the addition of lanthanide. For comparison, Fig. 1 contains the results (■) on Ni/SiO_2 treated with liquid ammonia without lanthanide. For Eu–Ni/SiO_2 and Yb–Ni/SiO_2 the dependence of activity on lanthanide content revealed a distinct minimum in the region of 15–20 atomic%. On the whole, the mode of the variation of activity as a function of lanthanide content was analogous to that observed for the support-free bimetallic systems (*4*), although, seemingly, relatively large quantities of lanthanide were required for the present system, due to extra lanthanide deposited on the SiO_2 support.

Figure 2 shows infrared spectra of adsorbed carbon monoxide on Eu-Ni/SiO_2 obtained when the catalysts were previously evacuated at 673 K for 1 h, exposed to CO of about 10 Torr and evacuated briefly to remove CO in the gas-phase at room temperature. For Ni/SiO_2, in agreement with previous IR data (*6*), two adsorption states, a linear form and a bridged form, could be discerned, which occurred at 2048 and 1972 cm^{-1}, respectively (Fig. 2b). The supported Ni showed no distinct differences in IR spectra between treatment with and without liquid ammonia. Europium-treated SiO_2 (Eu/SiO_2) which was prepared by impregnation of SiO_2 with a solution of Eu dissolved in liquid ammonia showed negligible ad-

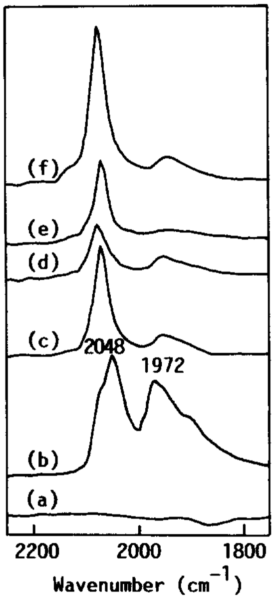

FIG. 2. IR spectra of (a) Eu/SiO_2, (b) Ni/SiO_2, (c) Eu(5%)-Ni/SiO_2, (d) Eu(10%)-Ni/SiO_2, (e) Eu(20%)-Ni/SiO_2, and (f) Eu(40%)-Ni/SiO_2 at room temperature.

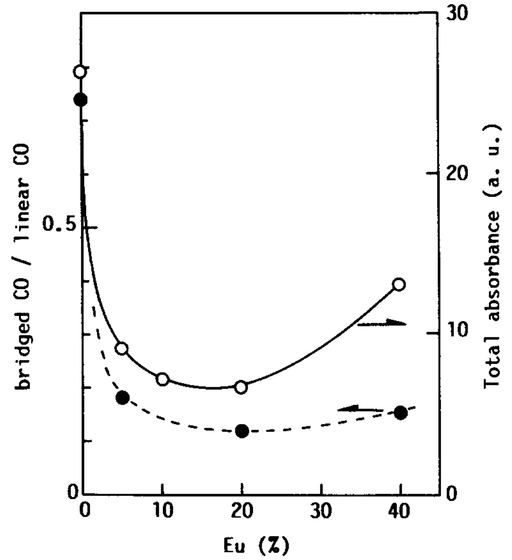

FIG. 3. Ratios of bridged CO to linear CO (●), and total absorbance of adsorbed CO (○), vs lanthanide content (%) in Eu–Ni/SiO$_2$.

sorbing ability of carbon monoxide (Fig. 2a); a band of CO adsorbed on lanthanides appeared at about 2190 cm^{-1} at a CO pressure exceeding 1 Torr, but upon pumping at room temperature it disappeared. Upon the introduction of lanthanides onto Ni/SiO$_2$ the relative concentration of the bridged CO species decreased much more rapidly than that of the linear ones. The ratio of the absorbance between the bridged and linear form assigned to CO adsorbed on the Eu–Ni surface as a function of lanthanide content is shown in Fig. 3. It decreased strongly in the lanthanide region (0–10%). In addition, it is evident in Fig. 2 that the CO linear bands shifted somewhat to higher frequencies with increasing lanthanide content.

TABLE 1

Hydrogen Chemisorption on Eu–Ni/SiO$_2$[a]

Eu content (%) in Eu–Ni/SiO$_2$	H_2 chemisorption (μmol · g^{-1})
0	18.8
10	16.6
20	15.2
40	23.7

[a] The catalysts were evacuated at 673 K for 2 h prior to the measurement.

Figure 3 also contains the dependence of total absorbance assigned to adsorbed CO on lanthanide content, which exhibited a distinct minimum at ~20% lanthanide.

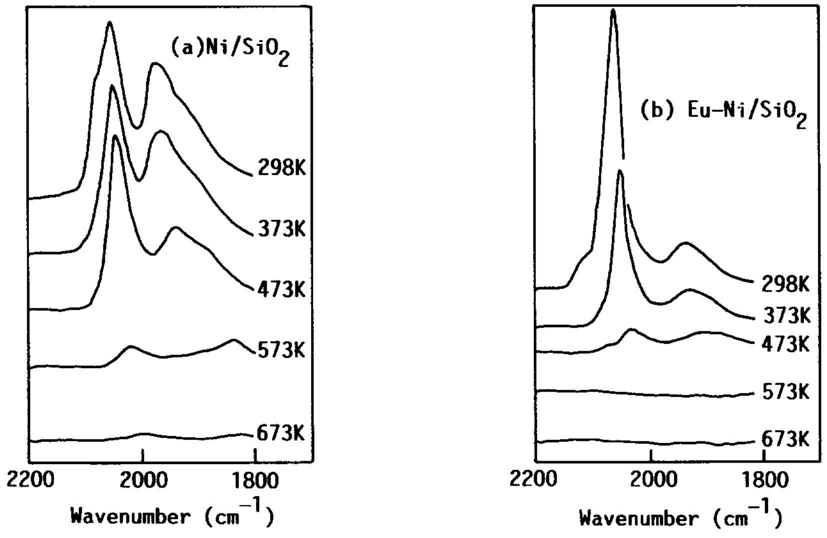

FIG. 4. Effect of evacuation temperatures on CO adsorbed on (a) Ni/SiO$_2$ and (b) Eu(40%)–Ni/SiO$_2$.

These results were evidently analogous to those observed for the hydrogenation of ethene (Fig. 1). The presence of lanthanide on Ni, in particular in the high content region, strongly influenced the state of adsorption of carbon monoxide with enhanced activity. Eu–Ni/SiO_2 and Yb–Ni/SiO_2 exhibited rather similar behaviour. A remarkable feature of these active sites induced by the presence of lanthanide on Ni is that the adsorption of CO on lanthanide–Ni was not as strong as that for pure Ni, as shown in the case of Ni/SiO_2 and Eu(40%)-treated Ni/SiO_2 in Fig. 4.

The relative proportions of the linear and bridged forms and the total extent of adsorption and their variations directly reflect changes in the surface composition or structure with changes in the content of lanthanide metals incorporated. Thus, the interpretation for the first decrease in the bridged form gives an indication that the lanthanide dissolved in liquid ammonia deposits on the active Ni surface, resulting in a relative decrease in the chance of finding an adjacent pair of Ni atoms compared with the chance of finding an isolated Ni atom. A similar behaviour has been found in the case of SiO_2-supported Ni–Cu (*7*). However, the introduction of more than a certain amount of lanthanide onto the Ni surface led to the formation of active surfaces. The arguments of IR studies of CO are the same as those for the hydrogenation and hydrogenolysis over the SiO_2-free Eu–Ni and Yb–Ni bimetallic catalysts (*4*); the initial deposition of lanthanide onto the active Ni surface with subsequent blocking of CO adsorption is expected due to coating with the lanthanide, while for lanthanide-rich catalysts (>20%) considerable interactions between the lanthanide and nickel metals occur to produce newly active centres. Volumetric measurements of hydrogen chemisorption (Table 1) to elucidate the number of active sites also strongly supported this interpretation.

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HAYAO IMAMURA[1]
HIROMI SUGIMOTO
YOSHIHISA SAKATA
SUSUMU TSUCHIYA

Department of Advanced Materials Science and Engineering
Faculty of Engineering
Yamaguchi University
2557 Tokiwadai
Ube 755, Japan

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[1] To whom correspondence should be addressed.