# Dehydrogenation of Cyclohexane on Lanthanide–Nickel Bimetallic Catalysts (Eu–Ni and Yb–Ni)

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The Eu–Ni and Yb–Ni (Ln–Ni) bimetallic catalysts, prepared by the reaction of nickel powders with lanthanides dissolved in liquid ammonia, have been characterised by the dehydrogenation of cyclohexane combined with isotopic exchange between cyclohexane and deuterium. Their catalytic behaviour varied markedly with different levels of lanthanide content. First, the relative rates of cyclohexane dehydrogenation decreased when the loading of lanthanide metals on the Ni surface was low and subsequently increased with increasing loading. Isotopic exchange reactions exhibited a similar dependence of activity on lanthanide content. An analysis of the initial decrease in the rates of reaction suggested a decrease in catalytically active nickel sites due to coating with lanthanide metals. The surface is gradually covered with the lanthanide metals and simultaneously certain interactions occur to produce newly active centres in the region of high loading, resulting in acceleration of the dehydrogenation and isotope-exchange reaction. The presence of lanthanide metals on Ni enhanced the capacity of this surface to dissociate the C—H bond. Multiple exchange for the reactions between cyclohexane and deuterium tended to decrease with increasing loading of lanthanides. Furthermore, the effects of a lanthanide metal overlayer on the reaction kinetics over an Ni metal surface were discussed.

Lanthanides (rare earths) combine with 3d transition metals Fe, Co or Ni to give various alloys or intermetallic compounds.<sup>1</sup> Recently there has been a growing interest in the surface properties, in particular as catalysts, of lanthanide–3d intermetallic componds and lanthanide metal overlayers. Our interest in the study of interactions of the lanthanide metals with the transition metals is aimed at unveiling the correlation of the electronic and geometric structure of these materials with their catalytic properties.

It is known that europium and ytterbium dissolve in liquid ammonia to yield a homogeneous solution of lanthanide cations and solvated electrons.<sup>2</sup> The lanthanides dissolved in liquid ammonia react readily with various transition-metal powders to form active bimetallic catalysts with varied levels of lanthanide loading.<sup>3</sup> By the use of dissolution of lanthanide metals in liquid ammonia, we have developed methods for the preparation of novel lanthanide-containing bimetallic catalysts and have demonstrated that they can effectively catalyse various reactions.<sup>4</sup> This work is a continuation of a series of studies performed in our laboratory, in which the chemical and catalytic properties of different lanthanidecontaining bimetallic systems have been examined. In previous papers<sup>4</sup>c catalytic studies of the Eu-Ni and Yb-Ni (Ln-Ni) bimetallic compounds have been made for alkane rearrangement reactions as a catalytic probe, elucidating structural characterisations to include phases present. In marked contrast to the hydrogenation of alkenes, the activity of rearrangement reactions shows a tendency to decrease with increasing loading of lanthanide metals on the Ni surface. Ln-Ni has been found to possess the specific capacity to activate the H-H bonds catalytically. This is analogous to the surface properties of lanthanide-transition-metal intermetallics, many of which can absorb hydrogen rapidly and in copious amounts.<sup>5</sup> Since hydrogen is absorbed dissociatively in these compounds,<sup>6</sup> the gas must exist at least fleetingly as monatomic hydrogen on the surface,<sup>7</sup> indicating that the surfaces of the alloys are active for the catalytic activation of hydrogen.

In this work, we investigated the bimetallic catalysts between lanthanide and nickel metals and presented the study of the effect of a lanthanide metal overlayer on the catalytic reactions and related properties over an Ni metal surface. The catalysts were characterised by the dehydrogenation of cyclohexane combined with isotope exchange between cyclohexane and deuterium. In particular, the present investigation provided information on the effects of a lanthanide overlayer on the C—H bond cleavage of alkanes, which is a very important process for the activation of hydrocarbons.

#### Experimental

#### Materials

Cyclohexane and deuterium were of research purity. The cyclohexane was further purified by distillation in the presence of sodium wire immediately before use. Deuterium (>99.5%) was stored in a reservoir for use as a reactant after having been passed through a liquid-nitrogen trap. Eu and Yb (99.9%) were obtained from the Shin-Etsu Chemical Co. Ltd. Ammonia (Iwatani Ind. Ltd.) was dried by passing it through calcium oxide and subsequently through a sodium hydroxide column. Reduced Ni powders were prepared conventionally by the incipient wetness technique; a solution of ammonium hydroxide was added dropwise to aqueous solutions of Ni(NO<sub>3</sub>)<sub>2</sub>  $\cdot$  6H<sub>2</sub>O with stirring. The resulting hydroxide precipitates were filtered off, washed thoroughly with distilled water, dried and finally reduced at 573 K with flowing hydrogen. The surface area of the Ni powders thus prepared was  $19 \text{ m}^2 \text{ g}^{-1}$  as measured by the BET method.

#### Procedures

Details regarding basic procedures of the catalyst preparation and catalytic reactions were described in earlier papers.<sup>4</sup> Eu or Yb was added to liquid ammonia containing the reduced Ni powder with stirring at 198 K. The lanthanide metals were immediately dissolved in liquid ammonia to yield a blue solution containing solvated electrons.<sup>2</sup> The blue colour gradually disappeared as a result of the deposition of the dissolved lanthanides on Ni. On completion of the deposition, the vessel was allowed to warm to room temperature and the excess ammonia was vaporized, leaving active Eu-Ni and Yb-Ni bimetallic catalysts. All operations were conducted in an atmosphere of dry argon to avoid contamination by air. Unless otherwise stated, the content of lanthanides in the bimetallic system was represented in at.%.

The reactions were carried out using a Pyrex gascirculation system. The dehydrogenation was largely studied by admitting cyclohexane (16 Torr†) at 473 K and the isotopic exchange was conducted with a mixture of cyclohexane (15 Torr) and deuterium (60 Torr). Prior to the reaction the catalyst (*ca.* 100 mg) was evacuated at 373-673 K, and was then exposed to the reactant gases. The reacting gas in the system was collected by a gas sampler and analysed by a Shimazu TCD gas chromatograph to determine the gas composition. Deuterated hydrocarbons were analysed by quadrupole mass spectrometry.

#### **Results and Discussion**

#### General Features of Cyclohexane Dehydrogenation

The dehydrogenation of cyclohexane was studied over Eu-Ni and Yb-Ni at lanthanide content of 0-14 at.% and a temperature of 473 K (Table 1). The relative rates of cyclohexane dehydrogenation as a function of Eu or Yb content in the catalysts are shown in Fig. 1. At first the rate of dehydrogenation decreased upon addition of small amounts (0-3%) of lanthanide to the sample. It passed through a minimum at ca. 3 at.% lanthanide with a decrease by a factor of ca. 10 and then was gradually increased for further addition of lanthanide (4-14%). The catalytic activity of an Ni surface with the 10% Yb is ca. two times higher than that seen for the Ni itself. Cyclohexane was highly selectively converted into benzene (ca. 100%) regardless of alteration in proportion of lanthanide metals incorporated. On the whole, Eu-Ni and Yb-Ni exhibited similar behaviour in the composition range investigated, but comparing both systems on the basis of the same atomic fractions of lanthanide metals incorporated, the activity of Yb-Ni was higher than that of Eu-Ni.

Pure nickel was very active for the dehydrogenation of cyclohexane to benzene and the specific activity obtained in this work was close to that observed for silica-supported Ni<sup>8</sup> under similar experimental conditions. In marked contrast to nickel, the lanthanide metal catalysts prepared by the metal vapour technique<sup>9</sup> exhibited negligible activity for the dehydrogenation under the same conditions. Therefore, it is suggested for the composition dependence of the activity of Ln–Ni that the existence of some synergetic effects between lanthanide and nickel metals rather than individual com-

Table 1 Results on the dehydrogenation of cyclohexane over  $Ln-Ni^{\alpha}$ 

| catalyst    | rate<br>/mmol min <sup>-1</sup> g <sup>-1</sup> | conversion <sup>b</sup><br>(%) |
|-------------|---|--------------------------------|
| Ni          | $6.3 \times 10^{-3}$                            | 14.5                           |
| 2.1% Eu-Ni  | $9.0 \times 10^{-4}$                            | 2.1                            |
| 4.9% Eu-Ni  | $5.7 \times 10^{-4}$                            | 1.3                            |
| 8.2% Eu-Ni  | $6.6 \times 10^{-4}$                            | 1.5                            |
| 13.9% Eu-Ni | $2.5 \times 10^{-3}$                            | 5.7                            |
| 2.5% Yb-Ni  | $7.7 \times 10^{-4}$                            | 1.8                            |
| 5.0% Yb-Ni  | $7.9 \times 10^{-4}$                            | 1.8                            |
| 7.5% Yb-Ni  | $2.3 \times 10^{-3}$                            | 5.3                            |
| 10.0% Yb-Ni | $1.1 \times 10^{-2}$                            | 25.2                           |

<sup>*a*</sup> The catalysts were evacuated at 673 K for 2 h prior to the reaction. Reaction conditions: 473 K,  $C_6H_{12} = 16$  Torr. <sup>*b*</sup> After 0.5 h.

† 1 Torr = (101 325/760) Pa.

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**Fig. 1** Relative rates of cyclohexane dehydrogenation (473 K) vs. lanthanide content in Eu-Ni ( $\bigcirc$ ) and Yb-Ni ( $\bigcirc$ ). The catalysts were evacuated at 673 K for 2 h prior to the reaction.  $P(C_6H_{12}) = 16$  Torr

ponent elements constitutes active sites for the present reaction.

When the lanthanide was originally introduced onto the Ni surface the activity decreased. This is explained by results from the following techniques: (i) hydrogen chemisorption, (ii) XPS studies and (iii) hydrogenolysis of hydrocarbons. The H<sub>2</sub> chemisorption measurements, which were carried out to evaluate the number of active sites present on the catalyst surfaces, exhibited similar variations (Fig. 2). Thus, the H<sub>2</sub> chemisorption at first decreased as the lanthanide loading was increased on the Ni surface, until a minimum was reached around 2-3% lanthanide. The chemisorption was reduced to roughly one-quarter or one-fifth compared to that observed for pure Ni, and in the region of high loading of lanthanide it increased. In the light of the results just described, the initial reduction in the rates of dehydrogenation can be qualitatively explained on the basis of a decrease in the number of active sites on Ni by surface



Fig. 2 Hydrogen chemisorption (298 K) vs. lanthanide content in Eu-Ni ( $\bigcirc$ ) and Yb-Ni ( $\bigcirc$ ). The catalysts were evacuated at 673 K for 2 h prior to the measurement

coating with inactive lanthanide metals. This was consistent with the results on the surface composition evaluated by the XPS measurements;<sup>4c</sup> for the Eu–Ni system the Ni 2p:Eu 3d peak intensity ratios decreased proportionally with increasing Eu loading on Ni. Moreover, the hydrogenolysis of cyclohexane or ethane over Eu–Ni and Yb–Ni was informative;<sup>4c</sup> the composition dependence of relative rates of the hydrogenolysis exhibited a monotonic decrease, due to a decrease in the concentration of surface nickel available for structuresensitive reactions caused by lanthanide coverage.

The addition of more than a certain amount of lanthanide metal led to acceleration of the dehydrogenation over Eu-Ni and Yb-Ni. Actually the H<sub>2</sub> chemisorption also increased in the region of high lanthanide loading, but the specific rates, expressed as turnover frequencies, increased simultaneously. Thus the nickel surface is gradually covered with the lanthanide metals and simultaneously certain interactions occur to produce new active centres for the dehydrogenation of cyclohexane. For such a variation of activity as a function of lanthanide content, at least two effects are competitively operative: reduced activity resulting from the coating of catalytically active nickel with lanthanide metals and enhanced activity arising from combined actions of lanthanide and nickel metals. The former effect is pronounced in the lowloading region and the latter becomes more pronounced than the former in the high-loading region. A similar dependence of activity on the level of lanthanide loading has been observed for the hydrogenation of alkenes<sup>3,4</sup> and  $H_2-D_2$ equilibration.10

Details on structure of the incorporated lanthanide metal were not obtained. The lanthanide-containing bimetallic catalysts may be those in which the lanthanide spreads over the surface, dissolves in the host lattice or aggregates to form microcrystals. For Eu-Ag we have previously reported that when the lanthanides were added to Ag, the lattice parameters of the parent Ag, as detected by XRD, change, indicating the formation of solid solutions in the surface region.<sup>4b</sup> However, for Ln-Ni XRD spectra showed only the existence of metallic nickel in the cubic structure and no XRD peaks could be assigned to lanthanides. The BET surface area for the nickel samples used here was estimated as 19 m<sup>2</sup> g<sup>-1</sup>. If the lanthanide exists uniformly in the metallic form on the nickel surface, the introduction of ca. 3 at.% lanthanide onto the Ni surface which led to the minimum activity (Fig. 1) roughly corresponds to, at most, one monolayer coverage of the nickel particles with Eu or Yb.

The explanation for the remarkable synergy in the region of high lanthanide loading is unknown. It is a complex effect which depends upon many factors including the electronic effect of the constituent on the bimetallic catalyst and a geometrical effect. Studies on lanthanide-3d transition metal intermetallics have made it abundantly clear that there is electron transfer from the lanthanide to the transition metal.<sup>1</sup> The interaction of lanthanide with single-crystal 3d substrates has been studied, and thin alloy films generated by controlled deposition of Nd, Sm or Yb onto Ni(100),<sup>11</sup> Cu(100)<sup>12,13</sup> or Cu(111)<sup>14</sup> under UHV conditions have been characterised. For Yb/Ni(100),<sup>11</sup> at low coverages the deposition can be described as adsorption of Yb on the surface, while at higher coverages a considerable reaction with the Ni substrate is observed. A  $c(10 \times 2)$  LEED pattern develops, owing to the formation of a specific surface intermetallic compound. Such behaviour has also been observed for Nd/Cu(100) with charge transfer from Nd to Cu.15 The lanthanide-3d intermetallic compounds are active as hydrogenation<sup>16</sup> and dehydrogenation catalysts;<sup>17</sup> Eu-Ni and Yb-Ni show enhanced activity for hydrogenation and dehydrogenation at high loadings.





**Fig. 3** Effect of evacuation temperatures of 13.9% Eu-Ni ( $\bigcirc$ ) and 10.0% Yb-Ni ( $\bigcirc$ ) on dehydrogenation rates. The catalysts were evacuated at various temperatures for 2 h prior to the reaction.  $P(C_6H_{12}) = 16$  Torr

Eu-Ni and Yb-Ni were characterised by their catalytic properties, which were affected significantly by the thermal pretreatment under evacuation. As reported previously for various lanthanide-containing bimetallic systems,<sup>4</sup> the catalytic activity increased noticeably with increasing evacuation temperature of the catalysts from 373 to 673 K (Fig. 3). For 10.0% Yb-Ni there was a ca. 500-fold increase in dehydrogenation activity in this temperature range. One of the reasons for this activation of Ln-Ni seems to be a consequence of removing residual adsorbed ammonia on the catalyst surface during the evacuation at elevated temperatures. In addition, it has been confirmed from XPS that the thermal treatment results in simultaneous rearrangement of surface morphology or structure.<sup>4c</sup> For structural studies of the Yb-Ni(100)<sup>11</sup> and Nd-Cu(100)<sup>12</sup> systems, lanthanide metal deposition at room temperature predominantly leads to the formation of disordered overlayers, whereas ordered intermetallic Yb-Ni and Nd-Cu surface compounds are formed at elevated temperatures. The overlayer-to-intermetallic transition has been observed for various systems, such as Nd-Cu(111),<sup>14</sup> Sm-Cu(100)<sup>13</sup> and Sm-Cu(111).<sup>18</sup> Considering the specific properties of the lanthanide-3d intermetallics for the catalytic reactions,<sup>16,17</sup> surface reconstruction seems to be the dominant effect rather than the removal of ammonia induced by the thermal pretreatment in improving the activity of the present systems.

#### **Reaction Kinetics**

In a study of the kinetics of dehydrogenation of cyclohexane over Ni and Ln-Ni, the rate data were represented by a rate law of the following form irrespective of the extent of lanthanide loading (Fig. 4):

rate = 
$$r = \frac{aP}{1 + bP}$$
  
 $1/r = 1/(aP) + b/a$ 

where P is the pressure of the cyclohexane, and a and b are constants. This rate expression was also found to be applicable for chromia-alumina and molybdena-alumina catalysts,<sup>19</sup> in which a stands for the rate constant of the first





Fig. 4 Plots of 1/rate vs. 1/P. The dehydrogenation of cyclohexane (16 Torr) was carried out at 473 K over Ni ( $\triangle$ ), 10.4% Eu-Ni ( $\bigcirc$ ) and 10.0% Yb-Ni ( $\bigcirc$ ) which had been evacuated at 673 K for 2 h

hydrogen abstraction and a/b for that of the second one. A general mechanism of dehydrogenation on heterogeneous catalysts is suggested, involving consecutive reaction steps in the reaction sequence.<sup>20</sup>

$$C_6H_{12} \rightarrow C_6H_{11}(ad) + H(ad) \rightarrow C_6H_{10}(ad) + H_2$$
  
 $C_6H_{10}(ad) \rightarrow C_6H_6 + 2H_2$ 

The active catalysts are those in which the first hydrogen atom can be abstracted easily.<sup>19,21</sup> The rate constant a increased with increasing loading of lanthanide (4–14%) in Ln–Ni.

For Eu-Ni and Yb-Ni with varied levels of loading the apparent activation energies for the dehydrogenation of cyclohexane varied between 70 and 83 kJ mol<sup>-1</sup>. For the variation in lanthanide loading Arrhenius behaviour was observed over the entire temperature range studied (453-493 K). An activation energy of  $83 \text{ kJ mol}^{-1}$  was determined for the dehydrogenation on pure Ni. This value was close to that observed for nickel-alumina.<sup>22</sup> For lanthanide-covered Ni surfaces, the apparent activation energies decreased to 70-71 kJ mol<sup>-1</sup>, particularly for catalysts with high loadings of lanthanide. The decrease in activation energy was more pronounced for Yb-Ni than for Eu-Ni and was compatible with the results of dehydrogenation rates (Fig. 1). The presence of lanthanide metals on the Ni surface enhanced the capacity of this surface to dissociate the C-H bond. For the hydrogenation of alkenes<sup>4c</sup> and H<sub>2</sub>-D<sub>2</sub> equilibration<sup>10</sup> we showed that the deposition of lanthanides onto Ni markedly promoted the adsorption of hydrogen with subsequent activation. Undoubtedly the introduction of lanthanide onto the Ni surface strongly influences efficiency of the catalytic activation of the C-H and H-H bonds, which controls the dehydrogenation and hydrogenation reactions, respectively.

### Isotopic Exchange between Cyclohexane and Deuterium

To investigate the property and reactivity of the adsorbed surface hydrocarbons on Eu-Ni and Yb-Ni, cyclohexanedeuterium exchange has been followed on Ln-Ni in the temperature range 473 K and at deuterium : cyclohexane ratios of *ca.* 4. For the exchange reaction between cyclohexane (15 Torr) and deuterium (60 Torr), measurements were made on the increase in the deuterium content of the hydrocarbon. The relative rates of exchange reaction as a function of lanthanide content in Eu-Ni or Yb-Ni are shown in Fig. 5. The



**Fig. 5** Relative rates of isotope exchange between cyclohexane and D<sub>2</sub> (473 K) vs. lanthanide content (%) in Eu-Ni ( $\bigcirc$ ) and Yb-Ni ( $\bigcirc$ ). The catalysts were evacuated at 673 K for 2 h prior to the reaction.  $P(C_6H_{12}) = 15$  Torr;  $P(D_2) = 60$  Torr

variations in activity were analogous those observed for the dehydrogenation of cyclohexane (shown in Fig. 1), although there were some differences in degree. In the dependence of activity on the evacuation temperature of Ln–Ni the isotopic exchange reaction also resembled the dehydrogenation. These facts support the conclusion that both reactions occur on the same catalyst surface through analogous intermediates. Usually the rates of adsorption and desorption of the deuterium and hydrogen deuteride are certainly rapid compared with the corresponding rates for the hydrocarbon; thus, the rate of exchange is limited by the rate of adsorption or subsequent dissociation of cyclohexane. This indicates that the presence of lanthanide on the Ni surface leads to acceleration of these processes, as described above.

Fig. 6 shows the initial distributions of deuteriocyclohexanes found for Eu-Ni with varied levels of lanthanide. All data are compared at conversion of ca. 10%. The effect of lanthanide loading on the isotopic distribution patterns of cyclohexane was evident and, moreover, was more pronounced at high loadings than low loadings of lanthanide. The isotopic exchange patterns on Ni exhibited a minimum between  ${}^{2}H_{3}$  and  ${}^{2}H_{7}$  species and a maximum at  ${}^{2}H_{1}-{}^{2}H_{2}$ and  ${}^{2}H_{8} - {}^{2}H_{12}$  species. The results on Ni used here closely resembled those reported earlier for nickel-silica,<sup>23</sup> reduced nickel oxide<sup>24</sup> and evaporated nickel films.<sup>24</sup> The discontinuity between  $C_6H_6D_6$  and  $C_6H_5D_7$  that is usually observed for the composition of exchanged species of cyclohexane was absent, presumably due to the high reaction temperatures. Ln-Ni with low loadings of lanthanide (0 and 2.1%) showed similar distribution patterns to those for pure Ni, whereas the catalysts with high loadings (8.2 and 10.2%) exhibited different behaviour. For 10.2% Eu-Ni cyclohexane yielded deuteriocyclohexanes characterised by a continuous decrease in concentration from  ${}^{2}H_{1}$  to  ${}^{2}H_{12}$  species; thus, increasing loading of lanthanide metals on Ni led to less multiple exchange.

In this case, the introduction of small amounts of lanthanide onto the Ni surface also resulted in a continuous decrease in active sites rather than changes in surface properties, probably due to increased coverage by lanthanide metals. The description given in the previous section was found to hold for the reactions between cyclohexane and deuterium. Upon further progressive introduction of lanthanide the combined actions of lanthanide and nickel metals appear



**Fig. 6** Initial distributions of deuteriocyclohexanes for (a) Ni, (b) 2.1% Eu-Ni, (c) 8.2% Eu-Ni and (d) 10.2% Eu-Ni. The catalysts were evacuated at 673 K for 2 h prior to the reaction. T = 473 K;  $P(C_6H_{12}) = 15$  Torr;  $P(D_2) = 60$  Torr

with qualitative improvement of active centres, resulting in marked changes in isotopic exchange patterns and simultaneous acceleration of the isotope-exchange reaction. The deuteriocyclohexane composition obtained also depends upon the temperature, the ratio of deuterium to hydrocarbon or the particle size distribution of the crystallites in active nickel. It is accepted that the multiple exchange requires a free site adjacent to the site or sites by which a hydrocarbon molecule is bound to the surface.<sup>25</sup> For such catalysts as Ln-Ni bearing enhanced capacity of this surface to activate hydrogen, the increased surface coverage by hydrogen which is induced by increasing lanthanide content would relatively depress multiple exchange by reducing the number of free sites. Such geometric discussion may provide a simple explanation for the variation of isotopic distribution patterns with the extent of lanthanide content in Ln-Ni.

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