Astrophys. **285**, 640 (1994)] show that at least 90% of the C_2 along this line of sight has v_{LSR} between ~6 and 15 km s^{-1}, whereas there is only a small component at v_{LSR} ~ 30 km s^{-1}. In addition, the K I spectroscopy of F. H. Chaffee Jr. and R. E. White [*Astrophys. J. Suppl. Ser.* **50**, 169 (1982)] shows evidence of K I absorption only near the observed velocity of H_3^+.

26. D. Uy, M. Cordonnier, T. Oka, *Phys. Rev. Lett.* **78**, 3844 (1997).
27. T. Oka, *Philos. Trans. R. Soc. London Ser. A* **303**, 543 (1981).
28. We thank G. Sandell and R. P. Tilanus for obtaining the JCMT CO spectra; E. Herbst, L. M. Hobbs, T. P. Snow, P. Thaddeus, and E. F. van Dishoeck for helpful conversations and correspondences; and J. H. Black for assistance in interpreting the C_2 data and for many other helpful comments. B.J.M. is supported by the Fannie and John Hertz Foundation. The University of Chicago portion of this work was supported by NSF grant PHYS-9722691 and NASA grant NAG5-4234.

15 December 1997; accepted 5 February 1998

Design of a Surface Alloy Catalyst for Steam Reforming

F. Besenbacher, I. Chorkendorff, B. S. Clausen, B. Hammer,
A. M. Molenbroek, J. K. Nørskov,* I. Stensgaard

Detailed studies of elementary chemical processes on well-characterized single crystal surfaces have contributed substantially to the understanding of heterogeneous catalysis. Insight into the structure of surface alloys combined with an understanding of the relation between the surface composition and reactivity is shown to lead directly to new ideas for catalyst design. The feasibility of such an approach is illustrated by the synthesis, characterization, and tests of a high–surface area gold-nickel catalyst for steam reforming.

Single crystal surfaces have long served as models of the active part of catalysts (*1*). Examples of catalyst design on the basis of fundamental, surface science–based insight are, however, extremely few. Recently, King and co-workers used a surface science approach to suggest new process conditions in which the effectiveness and stability of the usual Pt-based catalyst for the ammonia oxidation process can be markedly improved (*2*). Here we discuss an example in which the full step has been taken from atomistic surface science studies of model systems to the design of a high surface area alloy catalyst for the steam-reforming process. We present experimental results confirming the suggestion from a combination of scanning tunneling microscopy (STM), molecular beam scattering experiments, and density functional theory (DFT) calculations that Au alloyed into the surface layer of a Ni catalyst should increase the effectiveness of the catalyst in steam reforming.

In the steam-reforming process, hydrocarbon molecules (mainly CH_4) and water are converted into H_2 and CO. The usual catalyst for the reaction is based on Ni as the active element (*3*). The main problem with the reaction is that Ni also catalyzes the formation of graphite. Graphite formation impedes the activity and may eventually lead to a breakdown of the catalyst. One solution to this problem is to selectively poison the catalyst surface by adding H_2S to the reactants (*4*). Adsorbed S poisons the reforming process, but poisons the graphite formation to an even greater extent, so the net effect is an improved catalyst.

In a number of instances alloys have been shown to have superior catalytic properties (*5*) compared with elementary metals. In the past, research has focused on the class of binary metal systems that form ordered or random bulk alloys. Members of another class of two-component metal systems do not mix in the bulk. Even such metals may form stable alloys in the outermost surface layer (*6, 7*). The Au/Ni system belongs to this category. The heat of solution of Au in Ni is large and positive (27 kJ/mol). Yet it has been found in STM studies by Nielsen *et al.* (*7*) that when Au is added to any of the low index Ni surfaces, an alloy is formed in the first atomic layer (Fig. 1). The Ni atoms in the surface layer are undercoordinated compared with the Ni atoms in the bulk. The Au atoms have an electron density that is more extended than that of the Ni atoms. When the Au atoms are alloyed into the surface layer, the neighboring Ni atoms experience a higher electron density or, equivalently, a higher effective coordination number. One can say that the Au atoms that are alloyed into the surface layer help in lowering the Ni surface energy (*7*).

The existence of this class of two-component bulk-immiscible metals that form surface alloys allows synthesis of materials in which the properties are changed selectively at the surface.

It is possible to use Au to modify the reactivity of Ni with respect to the steam-reforming process. As discussed above, two factors determine the suitability of a surface as a catalyst for this process: (i) the ability of the surface to activate hydrocarbon molecules and (ii) the tendency of the surface to bind C and form graphite.

As a measure of the ability of the surface to activate hydrocarbon molecules, we consider the energy barrier for abstraction of the first H atom from CH_4. For pure Ni catalysts, this is the rate-limiting step in the steam-reforming process (*8*). The effect of Au on the activation barrier was studied both theoretically and experimentally.

DFT calculations of the dissociation of CH_4 were performed by Kratzer *et al.* (*9*), who used a Ni slab with varying amounts of Au substituted into the surface layer to

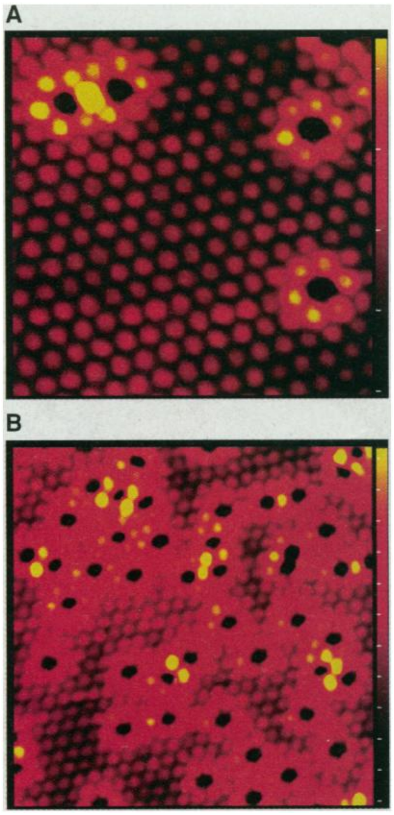

Fig. 1. Two STM images of a Ni(111) surface with 2% (**A**) and 7% (**B**) of a monolayer of Au. The Au atoms appear black in the images. The Ni atoms next to the Au atoms appear brighter because of a change in geometry and electronic structure, indicating that the chemical activity of the Ni atoms may be modified by nearest-neighbor Au atoms.

F. Besenbacher and I. Stensgaard, Center for Atomic-scale Materials Physics, Institute of Physics and Astronomy, University of Aarhus, DK-8000 Aarhus C, Denmark.
I. Chorkendorff and J. K. Nørskov, Center for Atomic-scale Materials Physics, Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark.
B. S. Clausen and A. M. Molenbroek, Haldor Topsøe Research Laboratories, Nymøllevej 55 DK-2800 Lyngby, Denmark.
B. Hammer, Institute of Physics, Aalborg University, DK-9220 Aalborg Øst, Denmark.

*To whom correspondence should be addressed. E-mail: norskov@fysik.dtu.dk

describe the surface. The transition state for CH_4 dissociation on Ni(111) is located with the C atom essentially being on top with respect to a Ni atom, and the process is highly activated (Fig. 2). The reaction path and the finding of a high barrier are both consistent with other calculations of this process based on a cluster model of the surface (*10*) and with experiment (*11*). In the DFT calculations, one or two of the nearest neighbors to the Ni atom under the transition state were exchanged for Au (Fig. 2). One Au neighbor increases the barrier for the CH_4 dissociation over a Ni atom by 16 kJ/mol, and two Au neighbors increase it by more than twice as much. Dissociation over the Au atom is expected to have a much higher barrier (*12*).

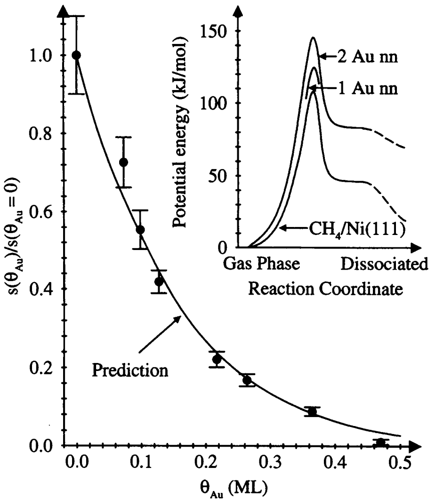

Fig. 2. The measured dissociation probability $s(\theta_{Au})$ for CH_4 on Ni(111) as a function of the Au coverage θ_{Au}. The dissociation probability has been normalized to the value for $\theta_{Au} = 0$. The full curve is the prediction of the model described in the text. (**Inset**) The calculated energy along the minimum-energy path for CH_4 dissociation over a clean Ni(111) surface and over a Ni atom in a Ni(111) surface with one or two nearest-neighbor (nn) Au atoms.

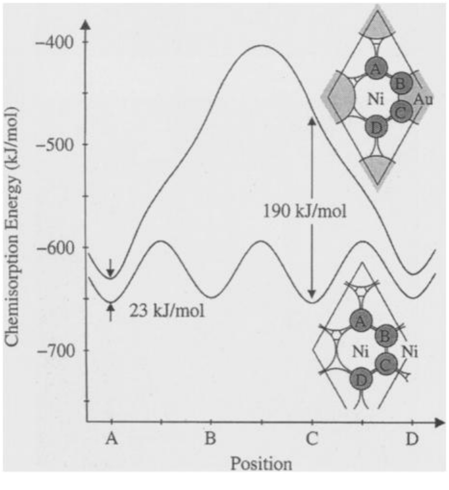

Fig. 3. (Bottom curve) The calculated adsorption energy of a C atom on a Ni(111) surface as a function of position along the surface. (Top curve) The same energy function is shown when one of the surface Ni atoms has been exchanged for a Au atom (*15*). The insets show the geometry in each of the two cases.

The predictions of the DFT calculations were tested experimentally for the same well-defined Ni(111) surface by Holmblad *et al.* (*13*). We measured the dissociation probability for CH_4 on Ni(111) using molecular beam scattering experiments (Fig. 2). As expected, Au impedes CH_4 dissociation. The DFT calculations suggest that the dissociation probability decreases mainly because Ni atoms next to the Au atoms have a higher barrier for dissociation and thus a lower dissociation rate. This can be quantified in the following way (*14*). From the STM experiments the surface composition is known at any Au coverage, and the number of Ni atoms with zero, one, two, or more Au neighbors can be counted directly. The DFT calculations show how the barrier depends on the number of Au neighbors. From independent beam experiments on clean Ni(111), it can be deduced how the dissociation probability depends on the translational energy and thus on the barrier height. Combining these three pieces of information gives a prediction of the variation of the dissociation probability with Au coverage that compares very well with the experimental one (Fig. 2).

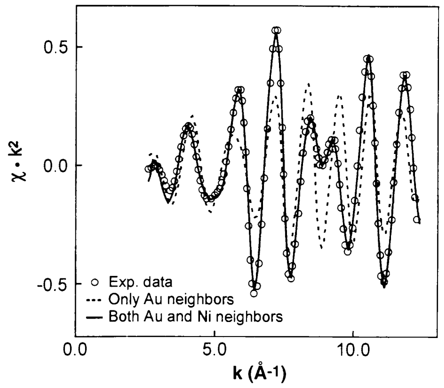

Fig. 4. k^2-weighted EXAFS spectrum, $\chi(k)$, after extraction of the nearest-neighbor shell contribution at the Au L_3-edge of the Au/Ni catalyst. The circles represent experimental data. The dashed curve shows the best fit to the experimental spectrum with only Au amplitude and phase functions. The solid curve shows the best fit to the data with Au and Ni reference functions.

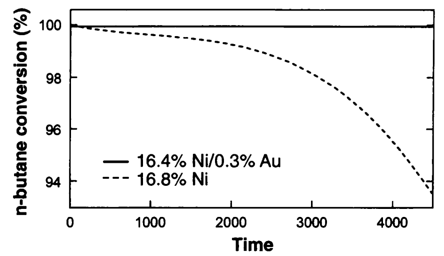

Fig. 5. Conversion of *n*-butane as a function of time during steam reforming in a 3% *n*-butane–7% hydrogen–3% water in helium mixture at a space velocity of 1.2 hour^{-1}. The dashed curve shows the *n*-butane conversion for the Ni and the solid curve is for the Au/Ni-supported catalyst.

It is not unexpected that Au added to a Ni surface reduces the ability to dissociate CH_4. We have treated the problem in some detail here for two reasons. First, it is important for the discussion below that the effect on the CH_4 activation of adding Au is reasonably small. Second, we emphasize that it is possible to predict changes in reactivity based on a knowledge of the surface composition. This strongly vindicates the general approach taken here.

As a measure of the tendency to form graphite, we consider the stability of adsorbed C on the Ni(111) surface. The probability of nucleation of graphite is determined by the coverage of C that is given by the stability of the adsorbed C atoms. The less stable the adsorbed C, the larger the tendency to react with adsorbed O to form CO and the lower the coverage. DFT calculations of the energy of an adsorbed C atom in the vicinity of a Au atom in a Ni(111) surface were compared with the same energy function on a pure Ni(111) surface (Fig. 3) (*15*). On the pure Ni surface, the most stable adsorption site is the threefold hexagonal close-packed site. The threefold sites next to a Au atom are seen to be completely unstable, and even the threefold sites that are next nearest neighbors to the Au atoms are substantially destabilized.

The effect of Au on atomic C adsorption is thus considerably stronger than the effect on CH_4 activation. In addition, from detailed studies of the effect of S adsorption on CH_4 activation and graphite formation on pure Ni surfaces and catalysts, we know that the ensemble size needed for CH_4 dissociation is smaller than for nucleation of graphite (*4*). The combined surface science work on the Au-Ni surface alloy therefore suggests the Au-Ni surface alloy to be a less reactive, but more robust, steam-reforming catalyst than pure Ni. It also shows that only a small fraction of Au is required to modify the surface chemical properties of Ni.

To convert these ideas into a practical industrial catalyst, we must synthesize a Au/Ni catalyst in a high surface area form. The catalyst to be discussed here is a $MgAl_2O_4$-supported Ni catalyst (with 16.5 weight % Ni) that has been modified with 0.3 weight % Au.

To verify that the Au is actually alloyed into the first layer of the Ni catalyst, we examined the structure and composition of the active catalyst by extended x-ray absorption fine structure spectroscopy (EXAFS). The EXAFS spectrum of the bimetallic catalyst was recorded in situ under synthesis conditions to make sure it is the active catalyst that is studied (Fig. 4). Only if we allow for the possibility that Au atoms have Ni neighbors at Ni interatomic distances can we account for the spectrum. Because Au is immiscible in bulk Ni, this demonstrates that Au is alloyed into the Ni surface layer as on the single crystal model systems.

The steam-reforming activity was measured for the Ni catalyst and for the Au/Ni catalyst for which the EXAFS data are recorded (Fig. 5). The only difference between the two samples is in the Au modification. Both samples were first reduced in pure H and subsequently exposed to a diluted *n*-butane gas at 550°C. We used *n*-butane to test the activity because it gives rise to the most severe graphite formation problems. The *n*-butane conversion as a function of time on stream starts out at about 99.99%. It is seen that the pure Ni catalyst deactivates rapidly, whereas the conversion for the Au/Ni sample is almost constant. The deactivation is typical of a Ni catalyst under these extreme conditions, and it can be associated with the formation of graphite as seen in, for example, electron microscopy. The Au-containing sample, in contrast, does not produce graphite. This has been checked by independent thermogravimetric measurements.

In conclusion, we are approaching a point where fundamental insight into surface structure and reactivity can be applied directly to the design of new catalysts. By combining several experimental surface science techniques with theory and insight into synthesis and in situ characterization of high surface area catalysts, it has been possible to go beyond our fundamental understanding of the atomic processes involved in catalysis to the design of an improved catalyst for the steam-reforming reaction.

REFERENCES AND NOTES

1. G. Ertl, in *Catalytic Ammonia Synthesis*, J. R. Jennings, Ed. (Plenum, New York, 1991), p. 109; D. R. Strongin and G. A. Somorjai, in *ibid.*, p. 1; D. W. Goodman, R. D. Kelly, T. E. Madey, J. T. Yates Jr., *J. Catal.* **63**, 226 (1980); J. Yoshihara and C. T. Campbell, *ibid.* **161**, 776 (1996); G. A. Papapolymerou and L. D. Schmidt, *Langmuir* **1**, 488 (1985); V. P. Zhdanov and B. Kasemo, *Surf. Sci. Rep.* **20**, 111 (1996); S. H. Oh, G. B. Fisher, J. E. Carpenter, D. W. Goodman, *J. Catal.* **100**, 360 (1986).
2. D. A. King, *Stud. Surf. Sci. Catal.* **109**, 79 (1997); J. M. Bradley, A. Hopkinson, D. A. King, *J. Phys. Chem.* **99**, 17032 (1995).
3. J. Rostrup-Nielsen, in *Catalysis, Science and Technology*, J. R. Anderson and M. Boudart, Eds. (Springer, Berlin, 1984), vol. 5, p. 1.
4. ———, *J. Catal.* **85**, 31 (1984); N. T. Andersen, F. Topsøe, I. Alstrup, J. Rostrup-Nielsen, *ibid.* **104**, 454 (1987).
5. J. H. Sinfelt, *Bimetallic Catalysts: Discoveries, Concepts, and Applications* (Wiley, New York, 1983); V. Ponec, *Adv. Catal.* **32**, 149 (1983).
6. G. A. Attard and D. A. King, *Surf. Sci.* **188**, 589 (1987); F. Besenbacher, L. Pleth Nielsen, P. T. Sprunger, in *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, D. A. King and D. P. Woodruff, Eds. (Elsevier, Amsterdam, 1997), vol. 8, chap. 10.
7. L. Pleth Nielsen *et al.*, *Phys. Rev. Lett.* **71**, 754 (1993).
8. M. B. Lee, Q. Y. Yang, S. T. Ceyer, *J. Chem. Phys.* **87**, 2724 (1987).
9. P. Kratzer, B. Hammer, J. K. Nørskov, *ibid.* **105**, 5595 (1996).
10. O. Swang, J. K. Faegri, O. Gropen, U. Wahlgren, P. E. M. Siegbahn, *Chem. Phys.* **156**, 379 (1991); H. Yang and J. L. Whitten, *J. Chem. Phys.* **96**, 5529 (1992); H. Burghgraef, A. P. J. Jansen, R. A. van Santen, *ibid.* **101**, 11012 (1994).
11. T. P. Beebe Jr., D. W. Goodman, B. D. Kay, J. T. Yates, *J. Chem. Phys.* **87**, 2305 (1987); P. M. Holmblad, J. Wambach, I. Chorkendorff, *ibid.* **102**, 8255 (1995).
12. B. Hammer and J. K. Nørskov, *Nature* **376**, 238 (1995).
13. P. M. Holmblad, J. Hvolbœk Larsen, I. Chorkendorff, *J. Chem. Phys.* **104**, 7289 (1996).
14. P. M. Holmblad *et al.*, *Catal. Lett.* **40**, 131 (1996).
15. The calculation is done selfconsistently with ultrasoft pseudopotentials, a slab of three metal layers, and plane waves with kinetic energies up to 25 rydberg at 54 k-points in the first Brillouin zone. Relaxation of the C and the metal atoms in the outermost surface layer is included. Exchange and correlation effects are described within the generalized gradient approximation of J. P. Perdew *et al.* [*Phys. Rev. B.* **46**, 6671 (1992)].
16. We gratefully acknowledge the important preparative work by J. Hyldtoft as well as help and suggestions from I. Alstrup and J. Rostrup-Nielsen. The present work was financed in part by the Danish Research Councils through the Center for Surface Reactivity, DANSYNC, and grant 9501775. We also thank Hasylab for offering beamtime at the ROEMO II EXAFS spectrometer. The Center for Atomic-scale Materials Physics (CAMP) is sponsored by the Danish National Research Foundation. A patent application describing the use of Au/Ni as a steam-reforming catalyst has been submitted [DK patent application 0683/97 (1997)].

26 November 1997; accepted 19 January 1998

The Theropod Ancestry of Birds: New Evidence from the Late Cretaceous of Madagascar

Catherine A. Forster,* Scott D. Sampson, Luis M. Chiappe, David W. Krause

A partial skeleton of a primitive bird, *Rahona ostromi*, gen. et sp. nov., has been discovered from the Late Cretaceous of Madagascar. This specimen, although exhibiting avian features such as a reversed hallux and ulnar papillae, retains characteristics that indicate a theropod ancestry, including a pubic foot and hyposphene-hypantra vertebral articulations. *Rahona* has a robust, hyperextendible second digit on the hind foot that terminates in a sicklelike claw, a unique characteristic of the theropod groups Troodontidae and Dromaeosauridae. A phylogenetic analysis places *Rahona* with *Archaeopteryx*, making *Rahona* one of the most primitive birds yet discovered.

The origin of birds has been debated for more than 100 years, with theropod dinosaurs (*1–6*) and basal archosauriforms (*7, 8*) most frequently hypothesized as their ancestors. Several workers have argued explicitly against the "birds as dinosaurs" theory (*8–12*). We report here a new raven-sized primitive bird that adds new morphological data to the question of bird ancestry. The holotype specimen of this new bird, *Rahona ostromi*, gen. et sp. nov. (*13*), was recovered from a small quarry (site MAD93-18) in Upper Cretaceous rocks in northwestern Madagascar. This quarry has produced a diverse, well-preserved vertebrate fauna, including the primitive bird *Vorona berivotrensis* (*14*).

The skeleton of *Rahona* exhibits a striking mosaic of theropod and derived avian features (Fig. 1). The specimen appears to be adult, based on the complete fusion of neural arches to vertebral centra (Fig. 2). The single camellate cervicodorsal vertebra bears a large hypopophysis and bilateral pneumatic foramina, as in maniraptorans and birds, as well as a large vertebral canal (88% of the centrum height; Fig. 2B). Pneumatic foramina also occur on the dorsal vertebrae, lying within well-developed pneumatic fossae, as in some enantiornithines (Fig. 2A). The vertebral canals are large (42 to 62% of the centrum height), as in birds. The dorsal vertebrae have accessory hyposphene-hypantra articulations, a unique character of theropod and sauropod dinosaurs, retained only in *Patagonykus* (*15*)

C. A. Forster and D. W. Krause, Department of Anatomical Sciences, State University of New York at Stony Brook, Stony Brook, NY 11794, USA.
S. D. Sampson, Department of Anatomy, New York College of Osteopathic Medicine, Old Westbury, NY 11568, USA.
L. M. Chiappe, Department of Ornithology, American Museum of Natural History, 79th Street at Central Park West, New York, NY 10024, USA.

*To whom correspondence should be addressed. E-mail: cforster@mail.som.sunysb.edu