(*9*)—aggravating the vulnerability to catastrophes inherent in the region's geographic subdivision. Species extinctions resulting from human pressures have already struck the West Indies on a massive scale. Of the 197 endemic mammals and birds across the islands (*1*), at least 43 have become extinct over the last 500 years (*10*). This equates to nearly 500 extinctions per year per million species, three orders of magnitude higher than expected given species' lifetimes in the fossil record (*2*). Worse yet, 84 more Caribbean endemic mammals and birds are classified on the Red List as threatened with a high probability of extinction in the medium-term future (*10*). Seen from a gloomy perspective, these species represent an extinction debt—losses already under way after habitat destruction. Worst of all, the remaining habitat patches of the Caribbean are small (and getting smaller), and so, given that the rate of extinction after habitat loss is scale dependent (*6*), these extinctions will probably occur soon.

The studies of Schoener *et al.* and of Ricklefs and Bermingham do, however, cast one ray of hope for conservation of the Caribbean's unique biodiversity. Imagine a conservation vision across the region, with the land- and seascape of surviving habitat fragments connected within a matrix of benign land use by "corridors" (*11*). Such corridors would consist not only of restored habitat and zones of low-impact human activity, but also, as Schoener *et al.* indicate, interdependent systems of tiny, largely pristine, islands. Recall that to reconcile the two studies, we invoke scale dependence in the persistence of the impact of historical catastrophe. If this is correct, then surely the recolonization of tiny habitat fragments across the conservation landscape would be rapid, analogous to the situation illustrated by Schoener *et al.* Obviously, it is too late for groups such as the West Indian macaws, already forced into catastrophic extinction (*12*). For the large portion of Caribbean biodiversity currently threatened with extinction, though, these studies suggest that all is not yet lost—as long as conservation can be implemented on an unprecedented scale across the region.

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PERSPECTIVES: SURFACE SCIENCE

Catalysts Under Pressure

Charles T. Campbell

From car catalysts to petroleum refining, chemical reactions catalyzed by solid surfaces play a major role in our lives today. This knowledge has fostered intensive research in catalysis for many decades, but the need for basic and applied research is stronger than ever. Improved catalysts may, for example, help to reduce the use of fossil fuels by enhancing reaction yields and fuel conversion efficiencies. "Greener" industrial and automotive chemical processes that minimize undesirable side products may be achieved by modifying existing catalysts or developing new ones. Given the correlation between areas with high cancer death rates and those with high densities of pollution sources, this may also help to reduce cancer incidence rates.

To modify existing catalysts or develop new ones, it helps to understand how existing catalysts work. On page 1508 of this issue, Hansen *et al.* (*1*) beautifully demonstrate that structural characterization of a catalyst's surface in the presence of reactive gases can help to clarify how a catalyst modifier—in this case, a barium promoter for ammonia synthesis—promotes the catalyst's activity. The results may help to discover other catalyst promoters.

The authors study the ammonia synthesis reaction

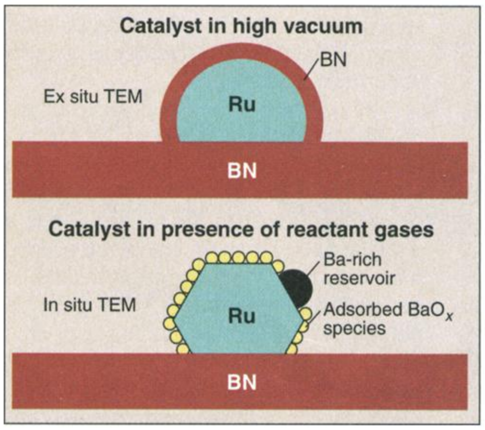
$$N_2 + 3H_2 \rightarrow 2NH_3$$

which provides the essential ingredient for the manufacture of fertilizer. Ever since Haber and Bosch developed the first synthetic process for making ammonia in the early 20th century, this reaction has helped to diminish famine worldwide. It has also been an important prototype reaction for fundamental studies of catalysis.

The difficulty with this reaction is that dinitrogen, N_2, is very unreactive. A transition metal catalyst is therefore required to activate the N_2 reactant. In the best catalysts, the transition metal surfaces are decorated with alkali and/or alkaline earth elements, which promote the reaction, possibly by facilitating N_2 dissociation (*2*).

Many studies have aimed to elucidate the action of the promoters as well as the steps of the reaction mechanism that occur directly on the transition metal surface (*2*–*5*). Many approaches (both experimental and theoretical) widely used today in catalytic research were first developed when studying this prototype reaction (*2*–*4*, *6*). Still, the role of the alkali and alkaline earth promoters has remained elusive.

Hansen *et al.* (*1*) reveal why this has been so and provide important new insights into the role of the barium promoter in enhancing the activity of boron nitride–supported Ru catalysts for ammonia synthesis. The Ba promoter/Ru catalyst system studied by the authors is perhaps the most active catalyst currently known for the ammonia synthesis reaction. Furthermore, ammonia synthesis has long served as a prototype reaction for understanding promotion of catalysts by alkali and alkaline earth elements, which plays an important role in many catalytic reactions.



The value of in situ characterization. The surface structure of a catalyst can change when the gases that make up the reaction mixture are removed, as shown by Hansen *et al.* (*1*) for a BN-supported Ru catalyst with a Ba promoter. At high vacuum, no Ba-rich phases are identified, and the Ru particles seem to be covered with a BN multilayer film. In the presence of reactant gases, this film is not present. Instead, two Ba-rich phases are formed: an adsorbed BaOx species, which acts to electronically promote the Ru surface sites, and Ba-rich particles, which probably act as a reservoir to maintain the surface coverage of BaOx over time.

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Hansen *et al.* (*1*) present beautiful high-resolution transmission electron microscopy (TEM) images obtained in the presence of reactant gases. These images help explain how this important catalytic promoter works. Key to their success is the use of in situ, high-resolution TEM and the correlation of this structural information with kinetic data. The authors show that conventional ex situ TEM (where the sample is studied in high vacuum) fails miserably in this respect because the surface structure of the catalyst is completely different in vacuum.

In the absence of reactant gases, the barium phase does not appear to wet the catalytic Ru particles, which are instead blanketed by several layers of the boron nitride support. When the reactant gases are present at moderate pressure, this boron nitride blanket becomes unstable and disappears, being replaced by an oxygen-containing monolayer surface phase of barium. This structure helps to explain how the Ba promoter enhances the activity of the Ru. The authors argue convincingly that promotion must be due to an electronic effect of the surface Ba phase on the nearby surface Ru sites.

Such an electronic mechanism was proposed previously to explain promotion of catalysts by alkali and alkaline earth elements (*3*, *7*) and is supported by theoretical studies (*6*, *7*). However, it was inconsistent with the surface structure observed with ex situ TEM. In thus clarifying the role of the Ba promoter, Hansen *et al.* solve an important problem in catalysis and reveal how others may be tackled.

The study highlights the importance of in situ catalyst characterization for understanding catalytic processes. Others have demonstrated the importance of in situ electron microscopy (*8*), although not with the atomic resolution achieved by Hansen *et al.* (*1*), who followed the pioneering approach of Gai and Boyes (*9*, *10*).

Many seminal advances in understanding catalysts were made with ex situ surface characterization tools, including important contributions from ex situ TEM to our understanding of ammonia synthesis (*5*) and other catalytic reactions (*11*, *12*). These studies were successful because some details of the catalyst structure did not change upon removal of the reactant gases. However, this will not generally be the case. Just as silver converts from metallic Ag to solid Ag_2O as the oxygen pressure above it increases, so too can we expect that the species present on a catalyst's surface convert between different phases as the pressure of the reactants increases. Such phases can only be characterized with in situ surface characterization.

Many surface characterization tools now allow in situ characterization (that is, in the presence of reactant gases and at high temperatures) (*13*, *14*). Besides the beautiful TEM example discussed above, exciting results have appeared recently using in situ scanning tunneling microscopy, sum frequency generation, and infrared spectroscopy (*15–19*). This promises exciting advances in the next few years in our understanding of catalysis. I look forward to the day when we can continue to improve catalysts while routinely working in the confidence provided by in situ surface characterization.

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PERSPECTIVES: GEOLOGY

Interactions Between Ridges and Plumes

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When geological surveys were limited to continents, geological studies aimed to understand objects such as mountain ranges and sedimentary basins. Plate tectonics provides a well-established theory of volcanism at mid-ocean ridges and subduction zone regions, and is intimately related to large-scale convection in Earth's mantle. In contrast, mantle plumes, which may give rise to intraplate volcanism, have remained enigmatic geological objects. It remains unclear how plumes are formed and whether they act independently from plate tectonics. Earth scientists may learn about the role of plumes in mantle dynamics by studying their interactions with the lithosphere and crust below ridges and the way in which they perturb flow patterns in the uppermost mantle (*1*).

The mantle plume model was first proposed by Morgan (*2*) to explain the systematic northwesterly age progression of volcanoes of the Hawaiian-Emperor chain (*3*). Morgan defined the mantle plume as a temperature anomaly below the overriding plate, but laboratory experimentalists and computer modelers soon gave the plumes a well-defined shape. They envision plumes to consist of narrow tails (plume conduits) and mushroom heads (plume heads) that ascend from a low-viscosity thermal boundary or the transition zone layer (possibly the core-mantle boundary) in the deep mantle.

Plumes transport less than 10% of the total heat from the deep mantle, but their role in geological and biological processes at Earth's surface may be very important. Continental breakup, flood basalt eruptions, mid-ocean ridge formation, and extinction of species may be the result of plume heads impinging upon Earth's lithosphere (*4–7*). Some Earth scientists even claim that plume tectonics might be as fundamental as plate tectonics (*8*). Others relate continental breakup and intraplate volcanism entirely to preexisting weaknesses in oceanic plates and continents and do not see a role for deep mantle plumes (*9*). In these "nonplume" models, edge-driven convection (*10*) is invoked to explain the formation of flood basalts provinces and intraplate volcanism at African and Atlantic hot spots (*11*).

Detections of plumes in geophysical and geochemical data are controversial and trigger vigorous debates. However, measurements of interactions between a plume and a ridge can help to discriminate between plume and nonplume scenarios. Many hot

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