

Probing Catalysts with Water

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Solid acids such as zeolites and the related aluminum phosphates are important catalysts with large-scale use in petrochemical processes. Unlike other acids such as aluminum chloride, they can be easily separated from the gaseous or liquid mixture of reactants and products, which is appealing from the environmental point of view. Understanding the principles that govern their activity and selectivity is prerequisite to tailoring catalysts for applications. To this end, Smith *et al.* (1) report neutron diffraction results on page 799 of this issue that provide detailed information on the acid sites of solid catalysts by examining how water acts when bound to the synthetic catalyst HSAPO-34.

A key question in catalyst research is which molecules get protonated by a particular catalyst and which do not. The ultimate interest is in the fate of hydrocarbon molecules that form the feedstock of many catalytic processes, but for a more fundamental characterization of the acidity of the catalyst, its interactions with simple base molecules such as ammonia, methanol, and water are better suited. When the first infrared spectroscopic (2) and nuclear magnetic resonance (NMR) studies (3) of the interaction of water with protonated zeolites were made, it soon turned out that the interpretation of the signals measured was ambiguous. Even after many spectroscopic studies (4, 5), it was not possible to decide which of the two possible structures was formed: a neutral complex, in which the proton stays at the active site but binds with a water molecule (H_2O), or an ion pair, in which the proton is transferred from the Brønsted site to the water molecule, forming a hydroxonium ion (H_3O^+). While some authors interpreted their results according to either the neutral or the ion pair structures, others assumed an equilibrium between both of them.

In this situation, *ab initio* quantum chemistry, a well-established method for predicting gas-phase acidities, has been called on to help. Two complications arise when dealing with solid acids: (i) zeolites form crystals with many atoms in their repeating cell, and (ii) water and similar molecules bind to the active site by hydrogen bonds. The former makes the calculations very large and models are needed to render the calculations feasible. The latter makes

the results sensitive to the approximations that are inevitable in any practical quantum chemical calculation and requires that electron correlations be included. Early calculations yielded similar energies for both structures (6), but neither the models used nor the methods adopted were fully satisfactory.

Recent developments in computer technology and quantum chemical *ab initio* codes have allowed researchers to overcome such limitations. The interactions of methanol and water with acidic sites of zeolites were studied with state-of-the-art models and methods (7, 8). The potential energy surface obtained shows minima for the neutral complexes only, whereas the ion pair structure proved to be a saddle point (Fig. 1). By predicting the NMR chemical shifts and vibrational spectra, it was possible to show that the assumption of a neutral complex as the only stable structure is consistent with the known experimental data.

The really important finding, however, is that the transition structure (ion pair) is only about 10 kJ/mol higher in energy than the minima. This small energy difference raises the question whether this result could change when small changes on the system are made. The energy difference between both structures decreases as the proton affinity of the adsorbed molecule increases. This can be achieved by adsorbing more than one water molecule per active site,

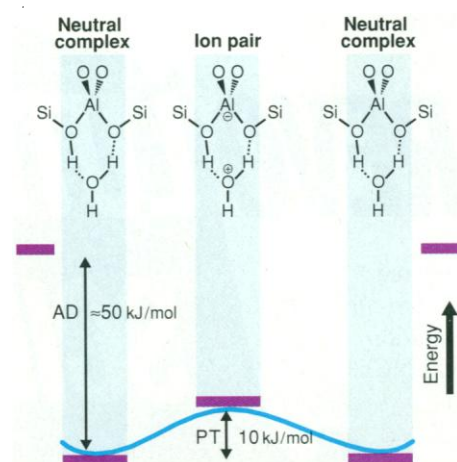


Fig. 1. Calculated potential energy surface for the adsorption of a single water molecule on a zeolitic Brønsted site (surface OH group). Adsorption (AD) and proton transfer (PT) energies are given in kilojoules per mole. Note that the surface hydroxonium is a transition structure, not a minimum, but the energy differences are low. [Adapted from (8)]

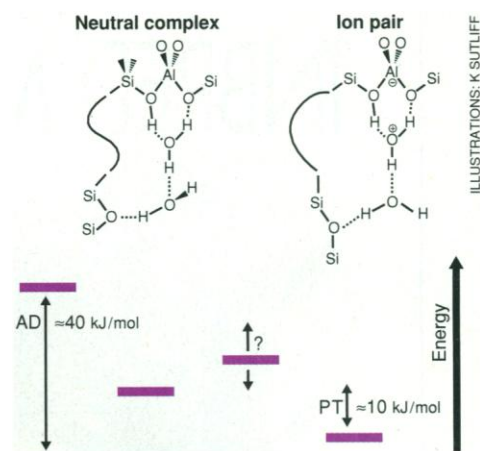


Fig. 2. The surface hydroxonium ion is stabilized by a second water molecule, and both surface species, $(\text{H}_2\text{O})_2$ and $\text{H}_3\text{O}^+\text{H}_2\text{O}$, become stable structures. The transition structure connecting them and its energy are not known. [Adapted from (8)]

that is, by increasing the loading. Indeed, *ab initio* calculations for a loading of two water molecules per zeolitic acid site yielded minima for both structures (Fig. 2), with the ion pair structure slightly more stable than the neutral structure (less than 10 kJ/mol).

Now Smith *et al.* (1) report direct structure information derived from powder neutron diffraction data collected at 10 K, which removes the ambiguity connected with the indirect structure information inferred from spectroscopic experiments. Both hydrogen-bonded neutral water molecules and hydroxonium ions can be identified. On the one hand, this finding supports the conclusions from the latest quantum chemical results, on the other hand, it calls for more theoretical work. What needs to be clarified is the role of different factors that may contribute to the stabilization of the hydroxonium ion: (i) the direct interaction between H_3O^+ and H_2O in the H_5O_2^+ surface species, (ii) the structure of the framework of the catalyst, which provides the possibility of adsorption of H_2O or H_3O^+ in a ring-type structure with stabilization by multisite coordination, and (iii) the long-range electrostatic interaction with the aluminum phosphate framework, which stabilizes the hydroxonium cation more than the neutral water molecule. The models used so far in *ab initio* studies cover only the first of these possible stabilization factors. Larger models or even periodic treatments are necessary to look into the role of the other factors. Such studies are under way by several theoretical groups, for whom the results reported by Smith *et al.* provide a benchmark.

Understanding the cooperation of the active site and its environment in tuning the acidity of the system is a fundamental chemical problem. We are learning more about how

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acidities in solution differ from gas-phase acidities. We also understand how superacidic systems can be created and know that they protonate saturated hydrocarbons and stabilize the carbocations formed. Zeolite catalysts with their vast variety of different compositions and frameworks, but also with their rather well-defined structures, are ideal systems for studying this problem experimentally and computationally. These studies

will also eventually resolve the debate as to whether or not zeolites are superacids (9).

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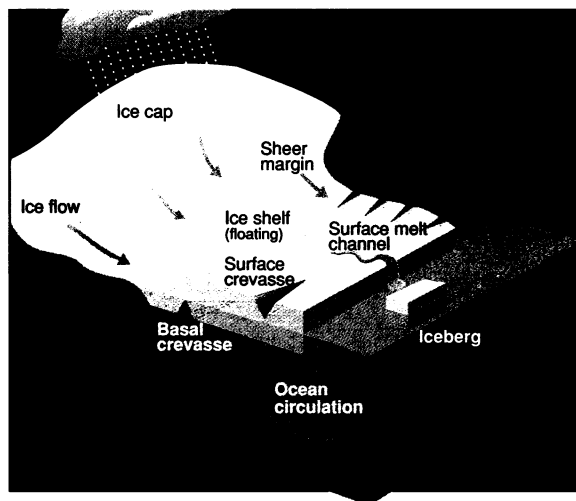
An Ice Shelf Breakup

Mark Fahnestock

Glaciers and ice sheets are controlled by the climate and must change if the conditions that led to their current configurations are changing. These ice masses exist at the interface between the atmosphere, which provides sustaining snowfall and thermal regulation, and the land, which provides a stable base and in many cases the elevation required to reach suitably cold conditions. Ice sheets and glaciers are distributed around the globe and can serve as potential indicators of past climate variability and current climatic trends. Observations of one dramatic kind of change, ice shelf collapse, are reported on page 788 of this issue by Rott *et al.* (1).

Interpretation of the climatic response of a glacier is not easy. The highly variable nature of climatic signals, combined with the wide spectrum of possible delayed responses attributable to complex ice flow, thermal diffusion and advection, and surface melt, produces a system that is in many cases not an optimal recorder of climatic events. Nonetheless, land-based ice promises to tell us about the past, and for hundreds of years in many populated alpine areas, the terminus positions of glaciers have been documented and related to climatic conditions. Satellite imagery has allowed this type of documentation to be expanded into regions that allow only limited access, where changes can go unnoticed for years. We can now study small variations over large areas and can begin to see regional trends in the varied responses of ice masses. Some of what is seen in satellite data is surprising.

Rott *et al.* describe the rapid disintegration of the northern Larsen Ice Shelf, located



Ice shelf dynamics.

ed on the east coast of the Antarctic Peninsula. This event follows the breakup of the Wordie Ice Shelf (2) on the west side of the peninsula and the retreat of ice fronts on both sides (3). The Larsen Ice Shelf breakup was documented with satellite-borne imaging radar, which provided detailed images every few days, unhindered by the cloud cover common to this area. This frequent sampling allowed the authors to show that the main part of the disintegration event occurred over the span of less than a week. This is an extremely short period of time in a field of research that deals with gradual responses to change that take a minimum of a few years and usually require decades to centuries. But the rapidity of the disintegration highlights the difficulties that are inherent in trying to interpret this event in terms of a response to climate: certainly conditions in the area had been changing for years, but how many years, and just what triggered the final breakup? Does this represent a small change in local climate or a much larger, longer term variation?

Ice shelves are floating bodies of ice that are fed mainly by glacier ice flowing off of

land, by snowfall on the surface, and in a few areas by the freezing of seawater (see figure). A typical Antarctic ice shelf is fed by one or more glaciers, fills the space between the coast and a few islands, and ends in an ice cliff that advances for a few to tens of years or longer and periodically calves icebergs, maintaining a stable, though oscillating, ice front position. Approximately half of Antarctica is bordered by ice shelves (4), ranging in size from a few square kilometers to 5×10^5 square kilometers in the case of the Ross and Filchner-Ronne ice shelves, which flank the West Antarctic Ice Sheet.

Ice shelves on the Antarctic Peninsula, which juts out of the continent toward South America, have a connection with the ocean that is shared by coastal glaciers in many regions. With the ocean as a source of moisture, relatively high snowfall in this region of Antarctica helps the balance of glaciers and ice caps. Owing to the influence of the ocean, ice in these coastal areas tends to be closer to the melting point and therefore more sensitive to slight changes in temperature than the cold ice of the interior. The dependence on temperature is especially pronounced for ice shelves (2). Extensive surface melt produces ponds of water and can enhance fracturing, as water-filled cracks can propagate through the entire thickness of the ice. Mercer (5) pointed out that ice shelves did not exist on the western side of the northern tip of the peninsula and showed that this was related to the distribution of monthly average summer temperatures. He went on to predict that the warming over the last few decades measured at stations on the peninsula should push this limit further south, causing the breakup of the northernmost ice shelves.

Extensive ice shelves are restricted to very high latitudes except on the Antarctic Peninsula. Greenland, though similar in size to West Antarctica, has only small ice shelves in the far north (6), and then only where they are supported by rapid discharge of large outlet glaciers. The lack of ice shelves in areas where there is substantial melting at the coast supports the idea that melt-induced changes in structural integrity prevent ice shelves from being stable. At

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