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Characterization of Active Sites in Zeolite Catalysts

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Abstract

This is the final report of a three-year, Laboratory Directed Research and Development (LDRD) project at the Los Alamos National Laboratory (LANL). Atomic-level details of the interaction of adsorbed molecules with active sites in catalysts are urgently needed to facilitate development of more effective and/or environmentally benign catalysts. To this end we have carried out neutron scattering studies combined with theoretical calculations of the dynamics of small molecules inside the cavities of zeolite catalysts. We have developed the use of H₂ as a probe of adsorption sites by observing the hindered rotations of the adsorbed H₂ molecule, and we were able to show that an area near the four-rings is the most likely adsorption site for H₂ in zeolite A while adsorption of H₂ near cations located on six-ring sites decreases in strength as Ni ~ Co > Ca > Zn ~ Na. Vibrational and rotational motions of ethylene and cyclopropane adsorption complexes were used as a measure for zeolite-adsorbate interactions. Preliminary studies of the binding of water, ammonia, and methylamines were carried out in a number of related guest-host materials.

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Background and Research Objectives

Despite the fact that zeolites have been in active use as industrial catalysts for many years their function at a molecular level is still not well understood. These catalysts are extremely important to the petrochemical industry for the conversion of hydrocarbons including, for example, the manufacture of gasoline and isomerization of various molecules. A continuing major effort is therefore directed towards improving these and other catalysts. In addition, environmental concerns and regulations are imposing new requirements on catalysts principally by way of severe restrictions on the types of chemicals that can be produced with or released as side products (e.g., the carcinogen benzene) of catalytic reactions.

For the development of more effective and environmentally benign catalysts a more complete understanding of the catalytic properties of these materials is required. One of the major questions concerning the function of zeolites is the nature of the interaction of the catalytically active sites in that structure with the adsorbed molecules. In the solid acid catalysts such as zeolites¹ these are protons bound to framework oxygen atoms and these can be detached in the catalytic reaction with the adsorbed molecules. Such acid sites have been located directly by neutron powder diffraction, for example, in lanthanum zeolite-Y, which is a commercially important hydrocarbon cracking catalyst. In some other cases molecules adsorbed within the cavities of zeolites have been located by neutron powder diffraction or single crystal x-ray diffraction. However, there has been relatively little detailed work on the dynamical behavior of a molecule adsorbed within the zeolite. Both structural data (such as distortions of the molecule upon adsorption) and molecular vibrational data (frequency shifts of the internal molecular vibrations, guest-host vibrational modes) provide direct information on the interaction of the molecule with the active site, and can be interpreted with the aid of *ab-initio* or other theoretical models. These results can then be utilized in the design of new catalysts with modified activity as required.

Importance to LANL's Science and Technology Base and National R&D Needs

Catalysis plays a fundamental role in the economy, environment, and public health of the nation by providing low-energy pathways for conversion of chemical feedstocks to the building blocks of commerce such as fuels, polymers, plastics, pharmaceuticals, and agrochemicals, and by removing pollutants from combustion and petrochemical processes.

The nation must foster the development of new environmentally benign and economic routes to existing and new products.

Catalysis is a highly interdisciplinary field that requires a wide range of skills: materials design and synthesis, characterization, catalyst evaluation, kinetics modeling, molecular modeling, chemical and reaction engineering, process simulation and evaluation, analytical chemistry, hydrodynamic modeling, molecular dynamics, detailed structural characterization, *in-situ* diagnostics, and process control. Development of a multi-disciplinary competency in catalysis will maintain and strengthen these same areas for the Laboratory. This stronger science base, particularly in the areas of chemical reactivity, interfacial phenomena, materials characterization, and modeling of surfaces and chemical reactions is necessary to attain the goals of the weapons and environmental missions of the Laboratory and DOE complex as well as the more traditional energy research goals. Furthermore, the chemical industry is very interested in partnering with national laboratories, and we are already working with a set of companies interested in working together with us in catalysis.

Scientific Approach and Accomplishments

We have utilized a combination of inelastic neutron scattering (INS) spectroscopy and theoretical modeling, as well as some diffraction studies, to deduce the location of adsorbed molecules in zeolite catalysts and the nature of their interaction with such hosts. This is an extremely powerful combination of techniques since INS spectra are (1) not seriously affected (unlike IR data) by the framework vibrations and are therefore sensitive to vibrational modes of the adsorbate relative to the surface which **directly** reflects this interaction, and (2) are readily calculated (and thus compared with experiment) by several types of theoretical calculations including molecular dynamics (MD) simulation.

We have applied this approach to the adsorption of molecular hydrogen (and in some cases, its isotopomers HD and D₂) in zeolite X and in zeolite A with a wide variety of active sites; i.e., different cations exchanged for the usual Na ions, as well as small molecules (ethylene, cyclopropane) in some of these zeolites. In addition we have carried out a number of preliminary model studies on the dynamics of small molecules in layer compounds where characterization of the guest-host interactions are somewhat easier. The molecules in question, water, ammonia and methylamines, are expected to interact with the zeolite through the formation of hydrogen bonds either with or without transfer of the acid proton to the adsorbate.

INS data on adsorbed H₂ were collected on the IN4 spectrometer at the Institut Laue-Langevin (Grenoble, France), the TOF spectrometer at the National Institute of Standards and Technology (NIST) reactor, and the QENS instrument at the IPNS at Argonne National Laboratory (ANL). Neutron diffraction studies were carried out at the High Flux Beam Reactor at Brookhaven National Laboratory (BNL). All high frequency ($> 50 \text{ cm}^{-1}$) INS spectroscopic data were obtained on the FDS instrument at the Manuel Lujan Jr. Neutron Scattering Center (MLNSC) at LANL. This part of the present project, however, suffered a severe setback in its first year because of an administrative decision not to operate the MLNSC in 1994. As a result, much of the vibrational data was only collected within the last year, and its interpretation is therefore still incomplete at the time of this report.

Hydrogen as a Probe of Adsorption Sites

The study of adsorbed molecular hydrogen by inelastic neutron scattering techniques affords a most sensitive probe of the numbers and types of adsorption sites within the zeolite cavities. The reasons for this are the small size of the hydrogen molecule and its considerable mobility within the cavities and channels of these structures, on the one hand, and the nature of the interaction of neutrons with hydrogen on the other. With inelastic neutron scattering it is possible² to measure the rotational tunnel splitting of the librational ground state of the H₂ molecule. This transition is not directly observable by optical techniques because it requires a change in the total nuclear spin of the molecule. The energy of this transition is extremely sensitive to the rotational barrier because it has an approximately exponential dependence on the barrier height. For a freely rotating H₂ molecule this transition occurs at 14.8 meV and decreases rapidly in energy as an increasing barrier to rotation is applied. In the present case the barrier is provided by the interaction between the H₂ molecule and the framework atoms. These hindered rotations of the H₂ molecule have large amplitudes and therefore good INS intensities. This fact, coupled with the more than one order of magnitude higher neutron-scattering cross section of H compared with that of virtually any other element, makes it possible for INS to be, in fact, a sensitive probe of the dynamics of adsorbed molecules even in the presence of a large amount of scattering from the zeolite itself.

Aluminosilicate zeolites normally contain Na⁺ ions for charge compensation and these have been assumed to be the principal site of catalytic activity for these systems. These can readily be exchanged with a variety of other cations to produce different active sites in the material. Zeolite Na-A consists³ of pairs of sodalite units (cubo-octahedra) that are connected by double four-rings. Four such pairs combine to form the large α -cage in

such a way that its largest openings are eight-rings with an effective diameter of approximately 4.4 Å. In addition there are six-rings that are shared between the α -cage and the sodalite units (β -cage). Cations may then be found in 4-, 6- or 8-rings, either in the plane of the ring or displaced above or below this plane. The 12 Na⁺ ions have been located (Fig. 1) in three different sites: eight of them in 6-ring sites (NaI), three in 8-ring sites (NaII) and one adjacent a 4-ring in the α -cage (NaIII). Two Na⁺ ions can be exchanged by one divalent cation in ion exchange and it is believed that NaIII and NaII types are the first to be replaced. For example, in partially ion-exchanged Ca₄Na₄-A, both the Ca and remaining Na ions are evidently distributed⁴ among the six-ring sites so that all 8 of these sites are occupied either by Na or by Ca. The Ca²⁺ ions are located in the plane of the six-rings whereas Na⁺ ions are displaced into the α -cage. In fully exchanged Ca₆-A all the Ca²⁺ ions are located near the six-rings displaced either into the α -cage or into the β -cage.

At the outset of this project the picture for H₂ adsorption in these zeolites was much like that of dihydrogen coordination in metal complexes;⁵ i.e., the molecules would bind to the cation in side-on fashion essentially in a symmetrical position. For example, for H₂ bound to a cation in the six-ring site, it would be located some distance along the three-fold axis that contains the cation. In addition, it seemed reasonable that a divalent cation would adsorb H₂ more strongly than the monovalent Na. One of the principal results of our studies is a rather different picture of H₂ adsorption which will be described below.

A typical INS spectrum is shown in Fig. 2 for H₂ adsorbed in partially Ca²⁺ exchanged NaA.⁶ There are two strong, broad peaks at 5.62 meV and 3.3 meV as well as a weak shoulder between 7 and 8 meV. An additional well-defined peak is observed at 11 meV in the H₂ spectrum using a different instrument configuration. We chose to load only one H₂ molecule per α -cage with its 8 cations with the hope that all H₂ molecules would prefer just one site over all the others. If so, we would observe just one band in the frequency range shown in Fig. 2. It is, therefore, immediately obvious that several types of adsorption sites are occupied by the molecules which had to be identified.

Our MD simulations⁷ of H₂ in NaA proved to be critical in this process. They show a broad peak in the calculated INS spectrum near 3.6 meV which implies a barrier to a rotation of about 6 kJ/mol. The most likely location for hydrogen found in these studies is near the NaIII and NaII sites. The broad shoulder at 3.3 meV (Fig. 2) can therefore be associated with adsorption near these sites which leaves the strong peak at 5.62 meV as an indicator for adsorption near Ca²⁺. This assignment was confirmed by our experiment on fully exchanged Ca₆-A. The fact that the barrier to rotation experienced by H₂ near the 4-ring site (NaIII) is higher than that near the divalent cation in the six-ring site seemed

surprising. However, this finding is in accord with the electrostatic field calculations by Cohen de Lara, et al.,⁸ and the fact that the 4-ring site has the lowest coordination number. It is also important to note that the effective charges on the cations in the zeolite differ substantially from +1 or +2.

Detailed examination of the INS data collected on H₂ in NaA, ZnNaA (two different Zn²⁺ exchanges), CaNaA, CaA, CuNaA, NiNaA, and CoNaA (from our earlier work)⁹ and comparison with our MD simulation studies⁷ clearly led us to conclude that for a given type of zeolite it is indeed possible to associate a given rotational transition frequency with adsorption in the vicinity of a certain cation. For adsorption at cations located on six-ring sites we also find that the ordering of the rotational barriers for H₂ is Cu ~ Ni ~ Co > Ca > Zn ~ NaI. In addition our simulation studies show that, in contrast to the conventional picture of H₂ absorption in a well-defined coordination geometry with a cation, the H₂ molecule can be found in a large number of positions (and orientations) near a cation or in between two cations. This observation is in qualitative agreement with the failure to locate D₂ molecules in CoNa-A and CaNa-A by powder neutron diffraction,¹⁰ a result that also suggests that the molecules are distributed over a considerable number of sites.

While most of our studies have been concerned with the relatively simple and well-defined zeolite A, we have recently expanded our program to include Faujasite-type zeolites such as NaX. The surprising result of this work is that H₂ seems to interact more strongly with NaX than NaA despite the fact that the geometries of the adsorption sites in the two zeolites are similar. This observation is almost certainly related to the fact that the commercial utility of LiX for O₂/N₂ separation is much greater than that of LiA. The origin of this difference is not clear, and its understanding highly significant. We therefore plan to address this problem in the near future with our combined experimental/theoretical approach.

We have demonstrated that the hindered rotations of the hydrogen molecule adsorbed in zeolites represent a highly sensitive probe of adsorption sites in these systems. Systematic studies of the INS spectra of H₂ in different zeolites can lead to an approximate identification of these sites, something that has, to date, not been possible by diffraction studies. The multitude of INS bands observed and the comparison with the results of MD simulations, however, suggest that the assumption of H₂ adsorption on top of the cations is overly simplistic and that additional information is necessary for a more detailed picture of hydrogen adsorption in zeolites. The adsorption strength of various possible sites in zeolite A for hydrogen evidently does not differ substantially so that even at very low gas loading H₂ does not adsorb at a unique site.

Interactions of Small Molecules with Zeolites

The adsorption of ethylene in zeolites that contain extra-framework cations has been shown¹¹ to occur directly above the cations in contrast to our finding on H₂. This adsorption geometry is similar to the numerous¹² side-on bonded transition metal ethylene complexes that may be viewed as models for the catalytic systems. Coordination of alkenes to transition metals is one step in a number of important catalytic reactions such as hydrogenation, or the polymerization of olefins. The binding of ethylene in such model compounds takes the form of the well known side-on bonded complexes and is accompanied by a wide range of C=C bond activation. Adsorption of ethylene on cationic sites in zeolites has shown similar effects, albeit much weaker effects on ethylene vibrational modes. As in the case of H₂ adsorption described above, the binding of ethylene to a cation in a zeolite will give rise to as many as six "new" external modes that correspond to the whole molecule librating or vibrating with respect to the surface. These modes are readily observed by INS techniques, and can also be calculated by various techniques. Ethylene does thereby serve as an ideal model system of the interactions of alkenes with zeolite catalysts.

INS data on ethylene adsorbed in NaX, ZnNaA, CuNaA, the novel titanosilicate TS-1 and a new¹³ Pt-ethylene complex, Pt(dtbpm)(C₂H₄) where dtbpm = di-*t*-butylphosphinomethane, show a wide range of interactions between the guest molecule and the host. These range from very weak, completely non-site-specific adsorption in TS-1 to extensive C=C bond activation in the Pt complex as expected. Shifts of the internal modes of vibration of the ethylene molecule as a result of adsorption are rather small, typically 5–10 cm⁻¹, but were found to be much larger (up to 100 cm⁻¹) for the Pt-ethylene complex. It is the external modes, however, that are much more sensitive to the interactions of the ethylene molecule with the host. INS spectra of ethylene adsorbed in three of the zeolites we studied are shown in Fig. 3. The frequencies for the three torsions (about the three molecular axes) of C₂H₄ were identified by us at 115, 175 and 210 cm⁻¹ for ethylene in NaX; 187, 250 and 480 cm⁻¹ in CuNaA; and the equivalent internal modes of the Pt-C₂H₄ complex at 235, 590 and 680 cm⁻¹. The results clearly demonstrate the enormous power of INS spectroscopy as a probe for the interactions of small molecules in catalysts. Theoretical modelling of ethylene in zeolites will be carried out as part of the LANL Catalysis initiative. However, our results on C₂H₄ in NaX are the first to test *ab-initio* calculations on adsorbed ethylene and are in good agreement with those obtained by Sauer¹⁴ who finds 96, 184 and 225 cm⁻¹ for the external modes of ethylene in NaX.

One of the most challenging problems at the forefront of industrial catalysis is to carry out selective and catalytic transformation of alkanes, which are notoriously

unreactive. Since alkanes such as cyclopropane are among the weakest electron donors, there has been no example of an isolable metal complex of an intact alkane. The structural characterization and reactivity studies of such an alkane complex would play a crucial role in understanding the mechanism by which the strong C-H σ bonds of alkanes can interact with and eventually break in the proximity of a metal center. Cyclopropane is unique from other alkanes in that its reactivity patterns indicate a marked resemblance between cyclopropane and olefins. Hence it appears that cyclopropane has a significant π character which might allow interaction with transition metal ions. Indeed, the X-ray crystal structures¹⁵ of cyclopropane complexes of Co(II) and Mn(II) ions incorporated into an zeolite A framework have been reported. In both cases, the cyclopropane molecule is very loosely bound to the metal ion in a facial fashion. Vibrational analysis¹⁶ of IR data on adsorbed $c\text{-C}_3\text{H}_6$, however, has been interpreted in terms of side-on binding by one side of the molecule to the cation. We have collected new INS data on $c\text{-C}_3\text{H}_6$ in CuNaA in an effort to resolve this fundamental issue. While detailed analysis of the INS spectra using normal-coordinate analysis of the adsorbate complex is still in progress, initial results do appear to confirm the face-on binding previously observed. In addition, we were able to clearly observe partial isomerization to propylene by means of the three low-frequency internal modes of the latter (188, 428 and 575 cm^{-1}), which have no counterpart in $c\text{-C}_3\text{H}_6$. We point out again that these modes occur in a frequency range that is very difficult to access with IR spectroscopies.

Binding to Acid Sites and Proton Transfer

The interaction with and binding of water molecules in zeolites is of enormous fundamental and practical interest. Of particular importance in this context is to reach a better understanding of Bronstedt acidity, which results from the replacement of a Si atom in the framework by Al to which a proton is added to maintain charge neutrality. In a recent neutron diffraction and IR spectroscopic study¹⁷ of water in H-SAPO-34, the coexistence of two forms of bound water molecules was demonstrated, one by hydrogen-bonding to such an acid site (on the six ring in the chabazite type structure) and the second through proton transfer to form hydronium ions, H_3O^+ , bound to oxygen in the eight-ring channel of the zeolite. The latter result was not predicted by any calculation, although experimental evidence for the formation of hydronium ions had previously been found.

We have been carrying out related work on guest-host systems where such proton transfer can be studied under somewhat more controlled circumstances, namely ammonia and methylamine intercalation compounds of layered dichalcogenides and the binding of water molecules in $\text{Ni}(\text{OH})_2$ from battery plates which also has a layer structure.

While the intercalation of ammonia molecules into TiS_2 is well-known¹⁸ to result in the formation of ammonium ions as it does when adsorbed in acid zeolites, this was not found to occur in the closely related ZrS_2 . The formation of ammonium occurs by way of a redox reaction in TiS_2 whereby the proton is transferred from another ammonia molecule, while in zeolites the proton is derived from the acid sites. When ammonia is co-intercalated with alkali metal or alkaline earth cations¹⁹ in titanium disulfide, it is found to form complexes with the metal ions while some of the ammonia molecules remain unbound. Two energetically distinguishable molecular ammonia species, one weakly bound in the host and the other complexed with alkaline earth cations, were found to coexist with metal and ammonium cations. Vibrational motions associated with complexed ammonia were observed in addition to those from uncomplexed ammonia. INS spectroscopy was crucial in characterizing the nature of the guest species in TiS_2 and provided strong evidence of the existence of distinct molecular ammonia species.

The interaction of methylamines with zeolites is of importance as the latter are used to produce and separate the various methylamines. Our preliminary INS studies of methylamines intercalated in lamellar TiS_2 and ZrS_2 clearly showed the formation of methylammonium in both cases, but to a greater extent in TiS_2 . Analysis of our extensive INS data is currently underway to determine the origin (and resulting products) of the proton transferred to methylamine to form methylammonium. We have carried out single crystal neutron diffraction studies²⁰ of mono- and dimethylamine bulk solids in order to determine the details of the H-bonding networks, which are also critical for understanding the binding of these molecules to hosts. We have also just initiated similar studies of methylamines in acid zeolites as a direct outcome of our extensive work on methylamines in layer compounds and salts.

Our INS studies²¹ of cycled Ni battery plate material have clearly demonstrated two important effects of cycling history: (1) it is apparent that some amount of the $\beta\text{-NiOOH}$ which forms upon oxidation does not convert back to $\beta\text{-Ni(OH)}_2$ upon discharging of the battery and (2) that this amount increases with the number of cycles the battery undergoes. More significantly, however, we have identified vibrational signatures of lattice water and find that the amount of such water increases with KOH concentration used in the cell. Since cells operated at higher KOH concentrations are known to fail after fewer cycles, our INS studies clearly implicate the formation of lattice water as one of the main reasons for this failure. Coordinated water molecules evidently are formed in the Ni(OH)_2 lattice upon oxidation as the remaining proton (NiOOH) is now inserted between two neighboring oxygen atoms by hydrogen bonding. In the following reduction a second proton is attached to one of the O atoms to effectively form a $\text{Ni(H}_2\text{O)}$ complex. INS spectroscopic

signatures of lattice and coordinated water²² are easily recognized because of our extensive experience on such systems.

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Figure 1. Cation sites in zeolite NaA. The twelve Na⁺ ions per unit cell are distributed as follows: 8 type NaI near the 6-rings, 3 type NaII in the plane of the 8-rings and 1 type NaIII near the 4-rings.

Figure 2. Hindered rotational transitions for molecular hydrogen adsorbed in $\text{Ca}_{3.75}\text{Na}_{4.5}\text{A}$. The three components at 3.3, 5.6 and 7.6 meV may be associated with adsorption of H_2 near NaIII, Ca^{2+} in a 6-ring site, and NaI, respectively.

Figure 3. Inelastic neutron scattering vibrational spectra of ethylene adsorbed in CuNaA (top), NaX (middle) and TS-1 (bottom). Peaks in the spectra arise from vibrational and torsional motions of the adsorbed molecule relative to the surface of the zeolite cavity.