

Characterizing the Dealumination of Environmentally Relevant Zeolites Using IR, NMR and Neutron Diffraction Techniques

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Abstract

Results of characterization studies monitoring the sequential chemical bond breaking events, local site symmetry, and long range structural modifications of specific zeolites (H-ZSM-5, TS-1) during hydrothermal treatment of these catalyst materials are described. These characterization techniques include infrared spectroscopy of selected probe molecules, magic angle spinning NMR spectroscopy, and powder neutron diffraction. Information regarding selected examples from each of these techniques is presented and the inherent strengths of each is discussed. The experimental insight into the chemical and structural modifications of high surface area microporous catalyst materials, as a function of deactivation conditions (hydrothermal conditioning) is highlighted.

Introduction

Extensive efforts have been expended on understanding and modifying the stability of zeolite catalysts to high temperature water vapor. Deactivation of zeolite based catalysts is particularly important in novel automotive catalysts which have remarkable catalytic activity in the selective reduction of NO_x from emission sources (3-4). However, high temperatures and water vapor are implicit in automotive exhaust and result in rapid catalyst deactivation. The details of deactivation and methods of circumventing this problem remain a technical challenge. Several mechanistic descriptions have been put forth describing the global deactivation of metal loaded zeolites. Loss of Bronsted sites contributes to loss of ion exchange capacity, increased mobility of entrained metal ions, sintering of metal ions into metal and metal oxide particles, and in extreme conditions loss of framework structural integrity (5,6). Furthermore, the reversible transformation of other framework metal ions such as Ti and V in a steam atmosphere has generated a considerable debate regarding the active state of such species as catalysts of the selective oxidation of alkanes and alkenes (7,8). In this work we examine the role of water vapor in the hydrothermal dealumination and coordination chemistry of the non-siliceous atoms of several zeolites with the MFI structure (e.g., ZSM-5, TS-1) through the use of conventional and non-conventional techniques that include: infrared spectroscopy of adsorbed probe molecules, NMR spectroscopy, and neutron powder diffraction techniques. The purpose of these studies is to exploit the strengths of each technique to arrive at an understanding of the chemistry of water molecules acting on the framework substituted non-siliceous atoms. Central to this concept is an understanding what factors control reversible adsorption (the suggested coordination of water to Ti centers in titanium silicalite-1 (7)) versus bond breaking activity initiated by water molecules in the aluminosilicate zeolite materials.

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Understanding the thermodynamic and kinetic factors underlying the reactivity and deactivation of these materials will certainly aid in the development of novel higher temperature materials more resistant to extreme environments. Furthermore, as part of this effort, we describe and demonstrate a novel in situ neutron diffraction reactor assembly for the first time in examining the structural aspects of steam modification of titanium silicalite-1 (TS-1).

Experimental

Steamed H-ZSM-5 samples were prepared in a shallow bed flow reactor using an H₂O/N₂ gas mixture with 7 Torr H₂O partial pressure at temperatures ranging from 400-850°C. The samples were further characterized by X-ray powder diffraction (XRD) and BET surface area measurements. The BET measurements, carried out using nitrogen as the adsorbent, showed no significant change in the surface area as a result of steaming conditions used in this study. The XRD analysis of the fresh and steamed samples provided no evidence for the collapse of the zeolite framework upon low temperature hydrothermal treatment and only a small extent of structural degradation for the moderate temperature steamed samples with the longest steaming time. TS-1 was prepared according to literature (9) hydrothermal procedures in an autoclave at 175°C. The starting material was characterized by conventional XRD, and diffuse reflectance UV-Vis spectroscopy. Elemental analysis of the H-ZSM-5 and TS-1 was performed using atomic absorption spectroscopy and x-ray fluorescence. The Ti/Si ratio was nominally 0.033 and nonframework Ti was determined to be below our detection limit of 0.002.

Infrared experiments were performed in a turbomolecularly pumped chamber derived from a 2.75" conflat six-way cross. The six-way cross was mounted vertically in the sample compartment of a Mattson Cygnus 100 FTIR spectrometer operated at a typical frequency resolution of either 2 or 4 cm⁻¹. Infrared specific components included an MCT detector, a KBr beam splitter, and CaF vacuum windows. Samples were powders pressed into tungsten wire mesh that was resistively heated using the methodology of Ref. 10. Sample temperatures (-173 to 1273°C) were monitored using a type K thermocouple spot-welded to the center of the tungsten mesh. The sample meshes were supported on specially designed stainless steel mounts attached to a metal to ceramic feed-through mounted on a double wall (1.00" outside diameter) sample manipulator rod. The sample rod was mounted onto a linear motion translator that enabled it to be positioned above and below (in and out of the IR beam) the center portion of the six-way cross. Vacuum integrity was achieved by passing the rod through fixed spring-loaded teflon seals. A complete gas flow manifold with provisions for cleaning of gases and/or mass flow control of gaseous reactants are also attached to the experimental chamber.

The ²⁷Al magic angle spinning (MAS) NMR analyses of aluminum were performed using a Varian Unity 400 NMR spectrometer equipped with a Varian 5 mm MAS probe. The non-framework (octahedral) ²⁷Al NMR signal is very broad and it is difficult to obtain a resonance suitable for analytical integration. Therefore, these analytical determinations were accomplished using the resonance of a small piece of sapphire, inserted in the sample, as an absolute standard for spin counting. The

sapphire resonance is located at approximately 15 ppm, between the resonances at about 0 ppm for octahedral Al and 51 ppm for tetrahedral (framework) Al. The decrease in intensity of the tetrahedral peak as a function of steaming is obtained by analytical reference to the sapphire intensity standard.

In-situ neutron diffraction of zeolite samples was accomplished using a reactor cell specifically designed to fit inside the High Intensity Powder Diffractometer (HIPD) beam line at the Manuel Lujan Neutron Scattering Center at LANL. A more detailed description of the overall neutron diffraction specific instrumentation and technique is contained in Ref 11. The neutron beam source conditions were typically 70 microamps and a diffraction pattern from all four detector banks on a zeolite sample required approximately 4 hours to acquire. The essential elements of the in situ reactor cell are shown in Fig. 1.

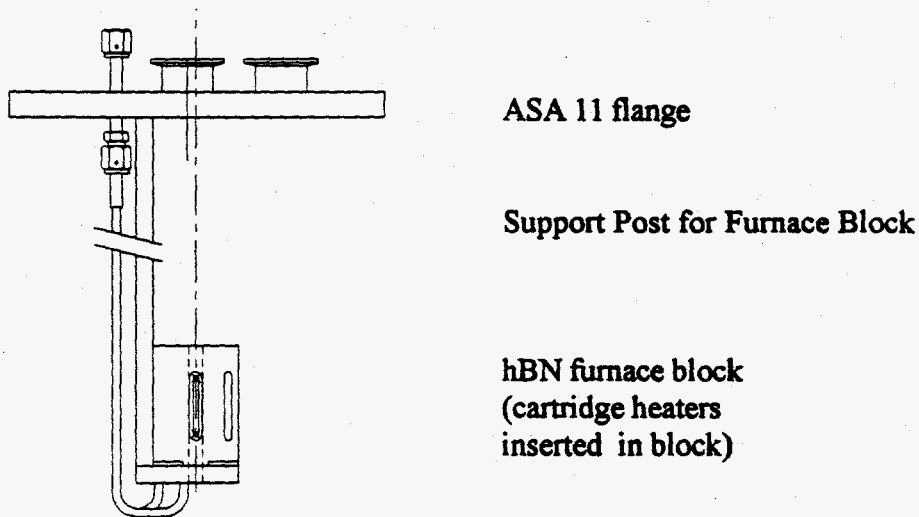


Fig. 1: In Situ Neutron Diffraction Cell; Functional items described in text. Gas, electrical power, and thermocouple feedthrus reside in KF flanges atop the ASA11 flange and are not shown for visual clarity.

The in situ reactor is a conventional plug flow reactor using a thin wall vanadium metal reactor tube (wall thickness 0.015", o.d. 0.375") welded to conventional stainless steel fittings (VCR4 or swagelock). A porous stainless steel frit is captured at the interface between the V and stainless steel and provides a convenient means of positioning the powdered sample in the neutron beam path. Alternatively, a quartz wool plug could be inserted in the bottom of the flow through tube. The V tube reactor was positioned inside an annular boron nitride (hBN) furnace block capable of temperatures to 800°C. The BN furnace block was radially ported to allow neutron beam irradiance, neutron diffraction detector access at $\pm 90^\circ$, $\pm 40^\circ$, and a neutron beam cut out in the back of the reactor (and support rod) to decrease secondary scattering events. In addition, the BN furnace block was drilled to accommodate four 1000W cartridge heaters and six thermocouple wells. The BN furnace block and V tube reactor rests on a Cu pedestal ported for water cooling to reduce the temperature following high temperature excursions. The entire experimental assembly is suspended on a stainless steel post

attached to an ASA 11 flange and is inserted in the vacuum well of the HIPD. The neutron detector elements are entirely contained within this vacuum well. All electrical, gas and water connections were made through KF hardware fittings and in operation vacuum integrity to 10^{-5} Torr was achieved. An additional benefit of the BN furnace block is an extremely low background neutron scattering signal arising from secondary scattering events that are screened by the BN because of the very large absorption cross section of ^{10}B . The technical advantages of the in situ neutron powder diffraction reactor include examining the structural changes occurring in the catalyst under reaction conditions without the necessity of exposing a potentially air sensitive catalyst to atmosphere. In addition, the active state (structure and phase composition) of the catalyst may be substantially different under reactive conditions than in an ex-situ non-reactive environment.

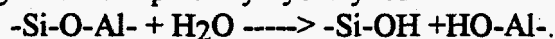
Results and Discussion

In-situ FTIR of CO (and other molecules as site specific probes) was studied on the H-form and hydrothermally treated samples of H-ZSM-5. These results have been more thoroughly reported elsewhere (12) but are summarized here for comparison with experimental data from other techniques. Zeolites have been traditionally examined using infrared spectroscopy of N-containing adsorbates such as ammonia and pyridine to assess Bronsted acidity. The use of weaker Lewis bases allows a more discriminating approach to assessing the strength and quantity of Bronsted sites arising from the partial and sequential dealumination of framework Al in H-ZSM-5.

The spectrum of H-ZSM-5 in the O-H stretching region in the absence of CO displays three absorption features with widely differing intensities. The most intense peak, centered at 3614 cm^{-1} corresponds to the O-H stretching of the bridging Si(OH)Al groups [the Brønsted acid sites of the protonic form of H-ZSM-5 structure]. The sharp feature at 3747 cm^{-1} arises from the O-H stretching of the terminal SiOH groups. Its intensity can qualitatively be used as a measure of the continuity of the zeolite framework. The least intense peak is present only as a shoulder on the high frequency tail of the bridging Si(OH)Al feature and has a frequency of 3665 cm^{-1} . This peak is assigned (13, 14) to AlOH species originating from a certain extent of hydrothermal degradation during the sample calcination process. Upon CO adsorption at low temperature (150K) there are dramatic changes in the O-H stretching region of the IR spectra of H-ZSM-5. The 3614 cm^{-1} peak completely disappears and a new, very broad, intense feature develops with 3310 cm^{-1} frequency at its maximum intensity. This feature arises from the bridging Si(OH)Al groups interacting with CO molecules. The integrated intensity of this peak is several times higher than that of the corresponding OH groups in the absence of CO. This is a direct consequence of the higher polarization of the O-H bond in the presence of CO than in the absence of CO. There is no change in either the peak position or the integrated intensity of either of the other two high frequency O-H features. These observations imply that under the experimental conditions applied ($T > -120^\circ\text{C}$, $P_{\text{CO}} < 200\text{ Torr}$) CO does not adsorb at either the silanol groups or the OH groups of extra-framework Al species, while all the bridging Si(OH)Al groups interacted with CO. Increasing the sample temperature from -120°C to -105°C

results in the desorption of most of the weakly held, physisorbed CO while only a very small amount of CO desorbs from the zeolitic proton sites. Further sample temperature increases result in the complete loss of the feature attributed to physisorbed CO and the gradual decrease of the proton-held CO feature at 2173 cm^{-1} . Concomitantly, the IR features of the zeolite OH groups interacting with CO decrease while the intensity of the CO-free bridging Si(OH)Al feature increases. There is no measurable change in the intensity of either the 2230 or the 2195 cm^{-1} peaks (CO bound at extra framework species) and the intensities of the O-H stretches of the silanol remained unchanged through the experiments.

The effect of steaming on the H-form of ZSM-5 was examined following two steaming temperatures (600 and 850°C). Steaming at 600°C resulted in the appearance of two new, intense IR absorption features in the O-H vibrational region at 3665 and 3785 cm^{-1} . The relative intensity of the very high frequency O-H vibration increases with steaming time while that of the bridging Si(OH)Al hydroxyls decreases. This very high frequency O-H vibration has been observed on Al_2O_3 by Knözinger and Ratnasamy (15) and was attributed to OH groups coordinatively bonded to a single Al cation (-Al-OH). The hydroxyl groups represented by the IR feature at 3665 cm^{-1} are also products of the hydrothermal treatment and are suggested (16) to be Al-OH groups where the Al atoms have not been completely removed from their zeolite framework positions but where the -Si-O-Al- bridge has been partially hydrolyzed:



It is also possible that the 3785 and 3665 cm^{-1} peaks are correlated and they belong to two different kind of hydroxyl groups located on the same Al-containing species $[(\text{OH})_2=\text{Al}=(\text{OH})_2=\text{Al}=(\text{OH})_2]$. For this chemical entity the very high frequency absorption feature would correspond to the terminally bound OH groups while the 3665 cm^{-1} feature would represent bridging OH groups. High temperature steam treatment of the H-form of the ZSM-5 for 2, 4, and 8 hours at 600°C gradually decreased the spectral signature of the bridging Bronsted hydroxyls and resulted in the growth of features corresponding to extraframework alumina and/or Al-OH species which are formed during the hydrolysis of the Si-O-Al bridge but are still in the zeolite framework. The apparent heat of adsorption of CO was measured in the steamed H-ZSM-5 materials and determined to be approximately 4 kJoule mol^{-1} lower than that for the parent H-ZSM-5 zeolite ($32.2\text{ kJoule mol}^{-1}$). The heat of adsorption of CO was noted to be less sensitive to changes (or losses) in the framework Al atoms than the spectral lineshape changes. The extra lattice aluminum is also shown experimentally to transform into stable forms of Al-oxide species under specific hydrothermal conditions as indicated from spectral lineshape shifts. These Al-oxides present in extra-framework positions act as Lewis acid centers for the adsorption of CO.

Zeolites are amenable to extensive characterization by high resolution NMR techniques. In principle, ^{29}Si NMR can give information about framework aluminum and its siting because there are separate peaks for silicon with zero, one, two or more aluminums as next nearest neighbors. Since the MFI structure has 12 or 24 different T sites (depending on the crystalline polymorph) the ^{29}Si MAS NMR spectrum is too broad to obtain quantitative information on framework aluminum. On the other hand,

high resolution ^{27}Al NMR can distinguish between tetrahedral and octahedral aluminum and has been used to characterize dealumination in acid catalysts (17). However, this analysis is not entirely straightforward. If the aluminum "site" is very asymmetric there is extensive second order quadrupolar broadening of the resonance which can cause the signal to vanish. In fact, very dry, H-form zeolites often have a loss in the ^{27}Al NMR intensity because of distortions about the tetrahedral aluminum site. We have developed sample preparation and NMR procedures that allow us to circumvent these difficulties. We are very careful to completely hydrate the samples at room temperature prior to NMR analysis. The octahedral (non-framework) aluminum is comprised of a heterogeneous set of aluminum oxide and hydroxide monomers and oligomers in the pores. These give a very broad NMR signal(s) which cannot be integrated for practical analytical purposes. However, the tetrahedral (framework) aluminum is relatively symmetrical and gives a sharp resonance near 55 ppm (Fig. 2).

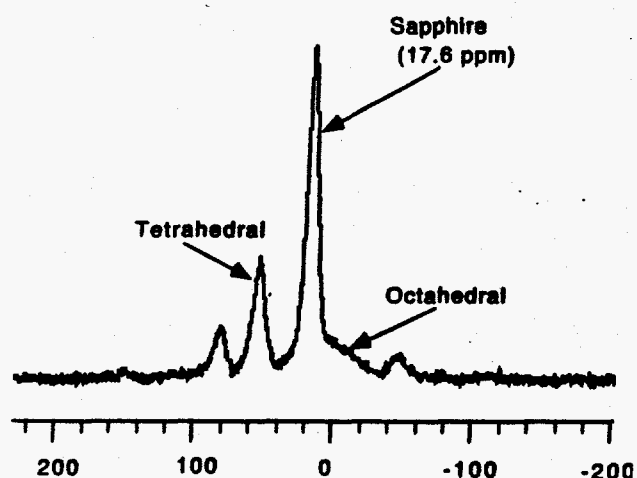


Figure 2: ^{27}Al MAS spectrum of the H-form of ZSM-5 after partial dealumination. The broad signal intensity in the baseline is due to aluminum which has been removed from the structure. The sapphire and tetrahedral (framework) resonances are indicated on the figure.

A calibrated sapphire chip, glued to the cap of our NMR rotor was used as an internal standard. The intensity of the framework aluminum resonance can be integrated relative to the sapphire resonance and the loss of framework aluminum as a function of steam treatment can be followed. From the loss of framework aluminum from samples steamed for different times and temperatures, an estimate of the global energy of activation can be obtained.

In addition to the more conventional methods of examining catalyst deactivation we have examined the effects of hydrothermal conditioning (using D_2O) of TS-1 in the *in situ* neutron powder diffraction cell capable of flow studies described above. The TS-1 sample was steamed using D_2O saturated He at progressively higher temperatures for successive periods of an hour (deuterated solvents are used in place of proto species because of the exceptionally large incoherent cross section and large absorption cross section of H). For brevity we show data recorded after dehydrating the TS-1 sample under a steady flow of dry He and the neutron powder pattern recorded following a 400°C steaming operation (Fig. 3A and B, respectively).

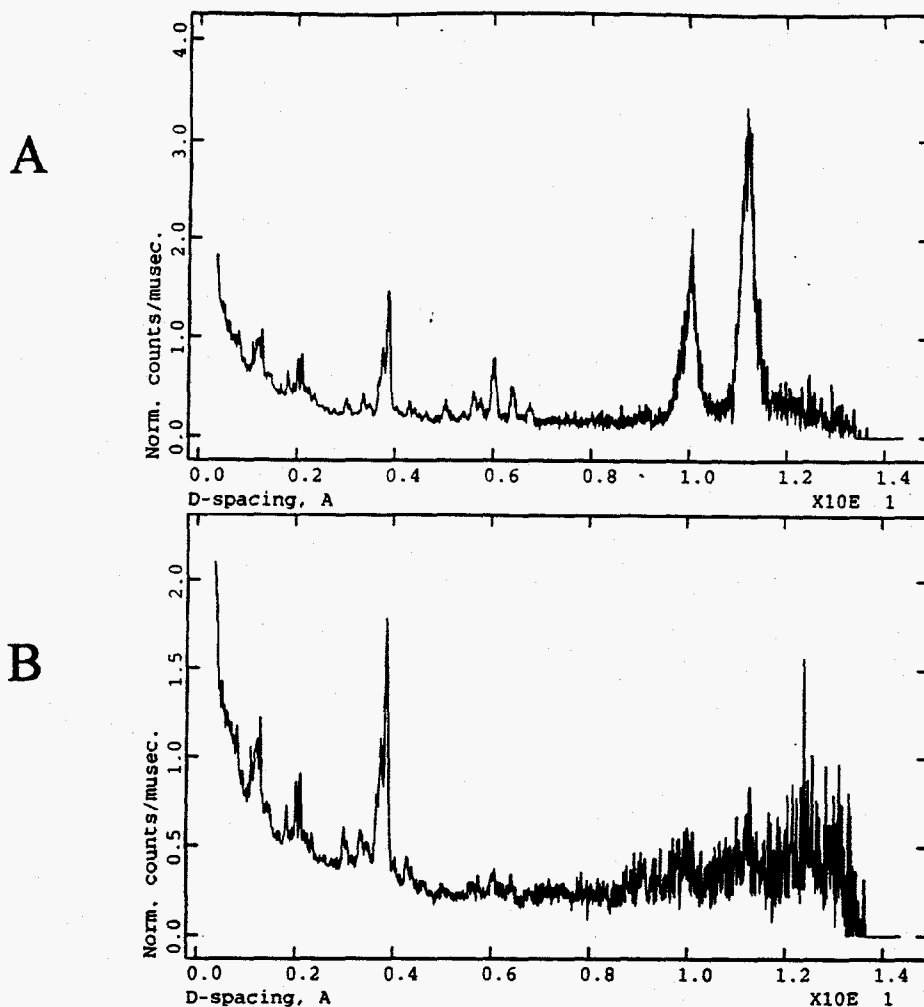


Fig. 3: A) Neutron powder diffraction pattern recorded from TS-1 following dehydration and B) following steaming with D_2O at $400^\circ C$.

The neutron powder spectrum was recorded simultaneously at all four detector banks and for brevity we display the data recorded at the $+40^\circ$ detector bank. The data are displayed as normalized scattering intensity versus d spacing. It is immediately apparent from inspection of the two powder patterns that essentially no structural changes are observed below 5\AA . This implies that the MFI framework of the TS-1 sample remains unchanged. However, very significant changes are observed in the d-spacings of the TS-1 sample following steaming. These include the nearly complete disappearance of the multiple d spacing features centered about 6\AA and loss of the prominent strong reflections occurring at 10.1 and 11.3\AA . A complete description of the structural transformations accounting for these changes is beyond the scope of this article but a preliminary interpretation of the observed differences suggest that the D_2O coordination to Ti centers within TS-1 results in loss of site symmetry within the channel structure. More explicitly stated, substantial adsorption of D_2O within the silicate framework (in addition to the framework Ti centers) upon hydrothermal treatment is indicated from the nearly complete loss of the higher d-spacing reflections of the diffraction patterns shown in Fig. 3. The data display the intrinsic strength of the technique in that both long and short range structural integrity are probed by the technique. The technique does not however probe specific bond making or breaking events or local symmetry about the Ti atom in

this simplistic rendering of the acquired data. More sophisticated structural refinements can, under specific conditions, enable that level of detail to be obtained (21).

Summary

The combination of complementary experimental techniques provides an invaluable understanding of the details of water coordination in several representative zeolite catalyst materials. Specifically, from infrared measurements of weakly coordinated Lewis bases a discrimination in partially dealuminated species can be readily observed in materials that have been progressively dealuminated. From an examination of the both the spectral position, its appearance and shift as a result of coordination versus partial pressure of adsorbate, and the relative change in the integrated band intensity versus the ubiquitous silanol functionalities present in most commercial forms of zeolite a picture of the nature and distribution of the partially framework coordinated species can be determined. Coupled with the ^{27}Al MASNMR measurements that specifically probe the distribution of specific site symmetries within the hydrothermally treated zeolite a detailed picture of chemical species developing within the framework can be corroborated. Finally, the changes in long range order have been demonstrated from a Ti containing structural congener, TS-1, following hydrothermal processing. The emerging picture is that the structural transformations resulting from hydrothermal treatments disrupt site symmetry and order within the long range channels of the zeolite framework and may have a significant impact in utilizing the restrictive site requirements thought to control the very selective catalytic chemistry occurring in such microporous materials.

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