

Acid Catalysis in HZSM-5: The Role of Entropy

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The essential role of Bronsted acid sites (bridging AlOHSi groups) on catalytic reactions of hydrocarbons in zeolites and the existence of a protonation equilibrium with adsorbates related to protonation enthalpies are well established. Various studies focus on the extent of protonation and the docking of molecules at the active site. Deuterium labeling of the zeolite showed that isomerization of alkenes is possible without a complete transfer of the acidic zeolite proton (deuteron).² No H/D exchange was observed during benzene formation from acetylene-*d*₂ on HZSM-5,³ but the formation of cyclohexadienyl radicals from the 1,3- and 1,4-cyclohexadiene radical cations revealed that deprotonation takes place in NaZSM-5,⁴ and H/D exchange was also observed for deuterated benzene on HY.⁵ The temperature dependence of the complexation equilibrium of Bronsted acid sites with unsaturated molecules was studied in HZSM-5.⁶

Organic free radicals which are potential transient intermediates of certain reactions in zeolites may interact with the zeolite in an analogous way as (unsaturated) diamagnetic molecules. The hyperfine splitting patterns of ESR spectra are often characteristic so that radicals are suitable model compounds for protonation studies. Radical cations are formed spontaneously upon adsorption of olefins on activated H-zeolites,⁷ or by radiolysis of alkenes in zeolitic environment.^{3,4} They are often relatively long-lived at room temperature, but some of them deprotonate in reactions with the parent olefin.⁴ The reverse reaction, the protonation of a preformed neutral radical, does not seem to have been observed so far.

The mobility of organic guests is essential for the transport of reactants and products to and from the reaction center, and it is an indicator for the potentially catalytic interaction with the host lattice. For diamagnetic molecules it was probed at different time scales with various NMR methods^{8–13} and neutron scattering.¹⁴

A less conventional magnetic resonance type method, called avoided-level-crossing muon spin resonance (ALC- μ SR), was also successful in characterizing structure and dynamics of radical intermediates in zeolites, notably the reorientation dynamics of

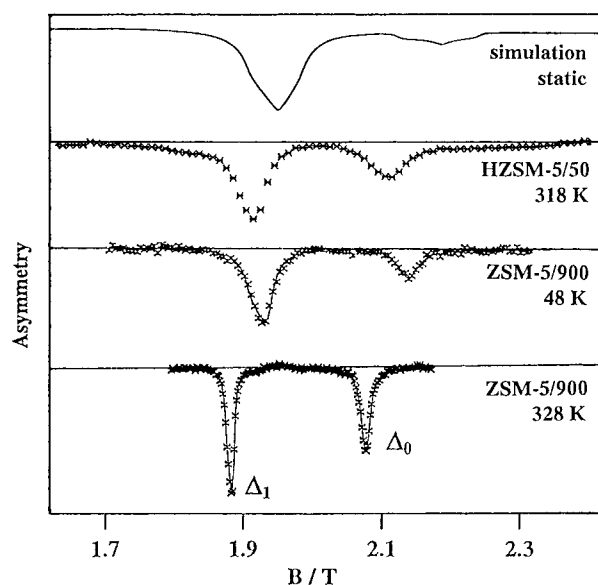
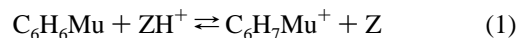


Figure 1. Selected range of ALC- μ SR spectra showing two resonances of the muon-substituted cyclohexadienyl radical in a static simulation,¹⁵ observed with benzene in HZSM-5/50 at 318 K (this work), and in ZSM-5/900 at 48 K and at 328 K.¹⁵ The resonance positions relate to the temperature dependence of the hyperfine couplings.

cyclohexadienyl radicals in high silica ZSM-5¹⁵ and its interaction with copper in ZSM-5 lattices with higher aluminum content.¹⁶ The present work contrasts the behavior in the H-form of ZSM-5 with that in the high silica modification and addresses the question of reorientational mobility of the same radical and its interaction with Bronsted sites.

A sample of HZSM-5/50 (SiO₂/Al₂O₃ ratio of 50) from CU Chemie Uetikon AG was calcined at 770 K, placed into a stainless steel cell, and then evacuated at 570 K. A benzene loading of 1.3 wt % of the dry zeolite, corresponding to approximately one molecule per unit cell, was prepared by adsorbing the benzene at room temperature before sealing the sample. The cell was equilibrated for 2 weeks before measurement, and there was no indication that the results were affected by inhomogeneous distribution of the adsorbate at this low loading.

The main focus of this work concerns the protonation equilibrium between the zeolite acid site (Z) and the adsorbate:



C₆H₆Mu stands for the muonium-substituted cyclohexadienyl radical, the isotopic analogue of C₆H₇, in which the muon, substituted for a proton, acts as a fully polarized spin label. Details of the experimental technique have been given elsewhere.¹⁵

The prominent range of an ALC- μ SR spectrum is compared with analogous spectra obtained in high silica ZSM-5/900 (SiO₂/Al₂O₃: 900) and with a simulation in Figure 1. In HZSM-5/50 at 318 K the resonances are much broader than those observed at a similar temperature (328 K) in the high silica version, but they resemble the ones at 48 K. This immediately tells us that the radical is locked in place and that motional averaging of the hyperfine anisotropy is greatly suppressed by the presence of the Bronsted acid site. In silicalite, on top of a fast rotation about the axis perpendicular to the molecular plane, the radical performs at two-site jump reorientation about a tetrahedral angle.¹⁵ Here,

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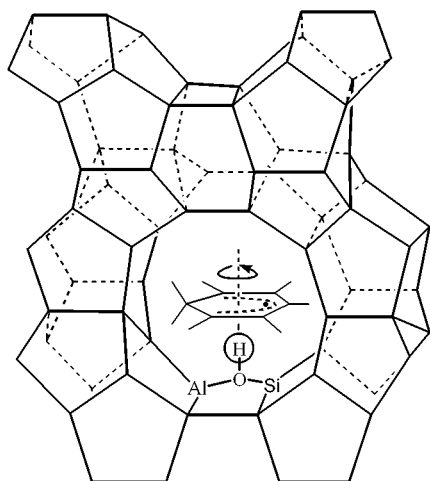


Figure 2. Pictorial view of a possible docking geometry at the HZSM-5 channel intersection.

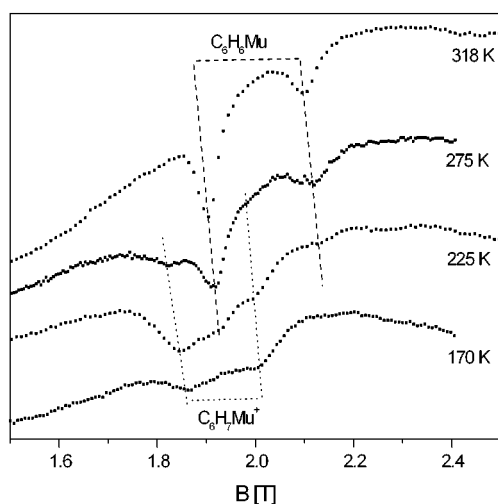


Figure 3. ALC- μ SR spectra obtained with benzene in HZSM-5/50 at various temperatures. The dotted and broken lines indicate how the resonances shift with temperature.

both lines are still narrower than expected for a completely static situation (see simulation; a static behavior was also inferred for NaY where the radical appears to be fully locked to the sodium cation¹⁷), demonstrating limiting motional averaging. The shape of the 1.9 T line (denoted Δ_1 in Figure 1) is characteristic for fast axially anisotropic motion, and the fact that the steep flank is on the high field side of the resonance provides unequivocal evidence that the rotation axis is perpendicular to the molecular plane.¹⁵ This shape and the width thus show that the radical, while it is locked to the acid site, performs a piano-stool type uniaxial rotation (Figure 2). The finding matches the behavior reported by Portsmouth et al. for benzene in HZSM-5.¹¹

Below room temperature, the spectra reveal a quite dramatic change (Figure 3). The two resonances at 1.88 T (corresponding to a muon coupling of 18.3 mT or a proton coupling of 5.74 mT) and at 2.08 T (giving a proton coupling of 4.46 mT), which are pronounced at 318 K, loose intensity, and two new resonances appear at 1.85 T and at 1.99 T (225 K). This indicates the

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formation of a new species that was not observed in silicalite.¹⁵ It is assigned to $C_6H_7\mu^+$, the protonated form of the cyclohexadienyl radical (eq 1). The position of the resonance at 1.85 T relates to a muon hyperfine coupling of 18.0 mT (equivalent to a proton coupling of 5.65 mT), and the 1.99 T resonance requires a proton coupling of 4.71 mT. Both couplings are compatible with a 1,3-cyclohexadiene radical cation, $C_6H_7\mu^+$, arising from protonation of the cyclohexadienyl radical in the ortho position. Shida et al. reported this species in a Freon matrix at 130 K, with 4.24 mT for the two protons in the axial position and <1.5 mT for all the other nuclei.¹⁸ Werst et al. observed it upon γ -irradiation of 1,3-cyclohexadiene in NaZSM-5 and derived couplings of 5.1 mT for the axial protons.⁴ Small proton couplings lead to weaker ALC- μ SR resonances, which escape observation under the present conditions.

The two low-temperature resonances are assigned to the muon and the proton both in axial positions of the 1,3-cyclohexadienyl radical cation. The muon has a strong preference for a conformation in which the C–Mu bond is eclipsed with the p_z -orbital containing the unpaired electron, minimizing its vibrational zero-point energy.¹⁹ Apart from the effect of the larger magnetic moment of the muon its coupling is higher than that of the analogous proton by about 20%, a typical isotope effect between muons and protons in equivalent positions.²⁰ Protonation in the para position would result in the 1,4-cyclohexadiene radical cation for which four equivalent protons with a hyperfine coupling constant of 6.81 mT were reported.¹⁸ This is inconsistent with our observation. Alternatively, one could postulate that the 1,3-cyclohexadiene radical cation forms a chemical bond to the negatively charged zeolite lattice at the deprotonated Bronsted oxygen atom, which would lead to a surface alkoxide radical, akin to the diamagnetic framework-bound alkoxy species which have been detected by NMR.²¹ Such radical species have not yet been detected, and we believe that their hyperfine couplings would be incompatible with the present observation.

Above ca. 250 K, the left-hand side of the protonation equilibrium with the proton residing on the oxygen bridge of the zeolite is favored, below this temperature the radical is protonated. Thus, $\Delta_R G^0 = 0$, and $\Delta_R H^0 = T \Delta_R S^0$ (the index R referring to the protonation reaction) at 250 K. The entropy term dominates the equilibrium at high temperature.

Only a profound quantum chemical analysis will provide the sign of the $\Delta_R S^0$ term. It is thus not possible to conclude that protonation of a molecule in an acid zeolite is generally favored at lower temperatures. Nevertheless, it is remarkable that we probably have the first clear evidence that this *can* be the case. It may explain why acid catalysis is often very efficient at room temperature, and turning the heat up may indeed not always promote it. This possibly counterintuitive finding should encourage theorists to calculate $\Delta_R G^0$ and not only $\Delta_R H^0$ when they evaluate stabilities of products and transition states.

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