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Spin Probes of Chemistry in Zeolites†

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EPR studies in zeolites are reviewed in which radiolysis was used to ionize the zeolite lattice, create reactive intermediates, spin label reaction products and to provide a window onto chemistry and transport of adsorbates and matrix control of chemistry. The review examines reactions of radical cations and the influence of the geometry constraints inside the zeolite, explores how zeolite model systems can be used to learn about energy and charge transfer in solids and illustrates the use of radiolysis and EPR for in situ spectroscopic studies of solid-acid catalysis. The various spin probes created inside the zeolite pores report on properties of the zeolites as well as shed light on radiolytic processes.

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1. INTRODUCTION

In this summary we review several areas of research in which radiolysis was used to provide spin labeling and/or to create reactive species in zeolites. The radiation-induced spins, in the form of defects, trapped charges, and radical ions of impurities, become the indicators for processes of interest by their formation, transformations, reactions with probe molecules, diffusion, and decay. In addition, spin labeling allows in situ chemical identification of intermediates and products of chemical transformations by using EPR spectroscopy.

Zeolite studies are an important component of our effort to better understand the effects of ionizing radiation in the solid state. Four important goals of this research are (1) to provide new information about structure and reactivity of radical cations, (2) to understand and exploit matrix control of radical ion reactions, (3) to develop new ways to probe energy and charge transfer in lattice-type solids, and (4) to elucidate chemical mechanisms and intermediates involved in solid-acid catalysis.

1.1. Radiation Chemistry in Solids. This important counterpart to liquid-phase studies allows us to further investigate the medium effects on charge transfer and energy transfer, the influence of long-range order, heterogeneity, and specific interactions on the reactions and dynamics of reactive intermediates. In the absence of molecular diffusion, modes of charge transfer and energy transfer can become paramount in how chemical energy is stored and dissipated.

Matrix Isolation. In this synopsis we highlight the use of solids for matrix-isolation of reactive intermediates. The use of an inert matrix to trap and stabilize reactive species allows us to augment time-resolved information with the superior structural information available from slow detection techniques such as continuous-wave EPR. Incorporation of guest molecules in interesting solids such as zeolites affords new opportunities to study charge and energy transfer in a well-ordered system, to achieve unprecedented control over reactions of radical cations, and to elucidate zeolite properties and interactions with

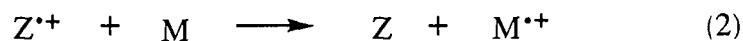
adsorbed species. Finally, extension of our methods to acidic zeolites has afforded a significant new window onto mechanisms of zeolite catalysis.

1.2. Radiolysis/EPR Studies in Zeolites. Our interest in zeolites was initiated by our desire to utilize the constrained spaces of these nanoporous solids to control the chemistry of radical cations. Zeolites are crystalline materials made up of $(\text{SiO}_4)^{4-}$ and $(\text{AlO}_4)^{5-}$ tetrahedra. From these basic building blocks arise myriads of lattice architectures consisting of channels and cages with different types of connectivity. One of these, ZSM5, has a three-dimensional network of intersecting channels with diameters of approximately 5.5 Å. Exchangeable cations are present in stoichiometric amounts to balance the negative charge introduced into the lattice by trivalent aluminum. We have used both the Na^+ and H^+ forms. NaZSM5 is inert while HZSM5 is a strong solid acid.

Zeolite samples were radiolyzed with gamma rays from a Co-60 gamma source or 3 MeV electrons from a Van de Graaff accelerator, and the radiolyzed sample is interrogated using X-band EPR. Variations include pre- and/or post-irradiation exposure to probe molecules, use of more than one probe molecule, sequentially or in mixtures, use of inert diluents, etc. In all of our work, probe molecules were delivered to the zeolite via a glass vacuum manifold and were pre-purified by freeze-pump-thaw cycling. Only dehydrated zeolites were used in the experiments described here. The zeolite powders were first heated to 450°C under vacuum ($<10^{-4}$ torr) for 4 h. Oxygen-free conditions must be maintained if stabilized radical cations are to be detected.

2. RADICAL CATIONS IN ZEOLITES

Radical cations of adsorbed molecules are generated radiolytically and stabilized in zeolites according to eqs (1) and (2). Energy loss from the ionizing particles occurs to the matrix; direct ionization of the guest species is insignificant. Transfer of the positive charge from the lattice (Z^+) to guest species is efficient for a wide range of donor molecules, M.

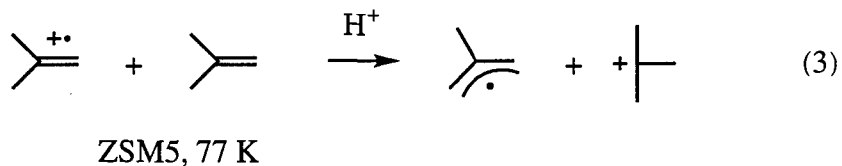


The stabilization of radical cations depends on the ability of the zeolite to trap electrons. These zeolite-trapped electrons in most cases are not detected in the EPR spectrum, one notable exception being the electrons trapped by alkali metal cation clusters in Faujasites [1]. When the zeolite-trapped electrons are not directly detected by EPR, they can be probed by appropriate acceptor molecules. Radical cation stabilization also requires isolation from neutral parent molecules, since encounters are usually reactive, resulting in dimerization, proton transfer or other reactions.

The mechanism depicted by eqs (1) and (2) is directly analogous to that which gives rise to the successful application of molecular solvents such as halocarbons for matrix-isolation of radical cations [2-5]. What sets zeolites apart and lends them new possibilities for studying the chemistry of solids and achieving greater control over reactions of intermediates is their regular channel networks. Zeolites, with their molecular-scale pore dimensions, exert a strongly size-dependent influence on molecular diffusion and add steric constraints on chemical reactions. This is complemented by the ability to carry out experiments over a very wide temperature range in zeolites compared to frozen molecular solvents. By combining temperature control and the molecular sieve effect, one can achieve unprecedented control over encounters between condensed-phase reactant molecules.

We have extensively studied hydrocarbon (alkane, alkene, alkyne and aromatic) radical cations in ZSM5, and to a lesser extent in several other zeolites, such as mordenite, L, BETA and Y [6-15]. Isolation of radical cations from their neutral parent molecules becomes problematic for very small molecules; for example, reaction (3) is observed even at 77 K in ZSM5 [16]. Six- and seven-carbon radical cations, such as benzene^{•+}, tetramethylethylene^{•+}, tetramethylallene^{•+} and cycloheptatriene^{•+} can be stabilized in ZSM5

up to 200 K or above for periods of minutes to hours. The size dependence on diffusion is also reflected by the relative stabilities of neutral radicals, which decay through radical-radical encounters (as opposed to nearest-neighbor encounters as in the case of radical cations). While the tert-butyl radical decays in hours at 77 K in ZSM5 [17], the tropylium (C_7H_7) radical persists for more than a day at room temperature [13].



Radical cation condensation (or complexation) reactions in zeolites exhibit both the steric influence on diffusion and geometric constraints on products. Ion-molecule reaction of acetylene radical cation with neutral acetylene occurs even at 77 K in ZSM5 [14]. Oligomerization proceeds to the trimer stage before any product radical cation is trapped, i.e., benzene⁺. Oligomerization of dimethylacetylene radical cation is halted at the dimer stage in ZSM5 [18]. Larger volume pores, such as those in mordenite, are needed to accommodate the hexamethylbenzene radical cation [19].

Benzene is large enough that it is immobilized at low temperature in a variety of zeolites. Specific electrostatic interactions with the aromatic π system may also be a factor. At any rate, the benzene monomer radical cation has been generated in several zeolites loaded with benzene. In zeolite BETA, the monomer radical cation is stable below 150 K, and at higher temperatures it is irreversibly converted to the dimer radical cation, eq (6) [18]. Dimerization of benzene radical cations is not observed under the tighter steric constraints obtained in ZSM5.

The size-dependent behavior is strong evidence that all of the radical cations that we detect in the EPR experiments are inside the zeolite and not on the external surface. In fact,

when the zeolite is exposed to molecules too large to enter the channels (for example, C_8 and larger hydrocarbons adsorbed on ZSM5), the radical cation signals generated upon radiolysis are very weak to unobservable [16]. Certainly, stabilization of radical cations on surfaces such as silica gel has been demonstrated, but the success of this technique has been mostly limited to simple aromatic hydrocarbons [20,21]. A telling difference between the behavior of benzene radical cation in ZSM5 and on silica gel is that ZSM5 prevents dimerization, whereas formation of the dimer cation is facile on silica gel [21]. This argues that all of the benzene radical cations are confined inside the ZSM5; either benzene radical cations are not stabilized on the external surface, or, more likely, at loadings below saturation none of the benzene remains on the external surface.

Key differences between zeolites and conventional, frozen molecular solvents, such as rare gases and halocarbons, include (1) the molecular sieve property, (2) possible heterogeneity in the guest distribution, and (3) guest-matrix interactions. With regard to the latter, we have shown that the zeolite lattice is a relatively poor acceptor of excess vibronic energy from radical cations [12]. As a result, the exothermicity of charge transfer (>2 eV) is more efficiently channeled into chemical reactions such as isomerization and fragmentation, that are effectively quenched in molecular solvents where energy relaxation via coupling to phonon modes is faster.

2.1. Trap-to-Trap Charge Transfer. Charge transfer represents an important mode of energy transfer in solids where diffusion is ruled out. A fundamental question in solids is how does charge migrate? In doped solids, the question breaks down into two parts: How does charge migrate from the matrix to the trapping sites (donor molecules), and does charge migrate between traps?

A direct way to systematically study trap-to-trap hole transfer is to radiolyze zeolites containing binary mixtures of donors. We carried out such a study using combinations of olefinic donors in ZSM5 [15]. The samples were irradiated at 77 K and the relative concentrations of the two radical cations were deduced from their relative EPR intensities.

Our experiment measured the "final" population of hole traps on the timescale typical of matrix-isolation experiments (minutes to days). The technique allows a wide selection of donor pairs and the ability to tune the thermodynamic driving force for hole transfer. In our experiments the charge transfer exothermicity was varied from negligible to approximately 0.7 eV.

Intertrap charge transfer occurred to a great extent in the zeolite samples containing mixed donors. As expected, the relative radical cation intensities in irradiated, double-loaded zeolites revealed effects of adsorbate heterogeneity, which was more pronounced for larger adsorbates. Measurement of the charge distribution in double-loaded zeolites is a direct way to learn about the effects of coadsorption and to detect spatial heterogeneity. It is straightforward to obtain time-resolved information, for example, by irradiating double-loaded zeolites after variable equilibration times for both donors. Factors such as heterogeneity and differences in site energies probably minimize the role of resonant charge transfer in the zeolite.

2.3. Ion-Molecule Reactions. A significant experimental challenge is to study ion reactions in mixed systems. Also in the gas phase, the difficulty of selectively forming ions in the presence of other reactants precluded such studies before recent technological advances in mass spectrometry, such as flowing afterglow [22], dual-cell FT-ICR [23], resonant-two-photon ionization [24,25] and variations of FTMS [26]. For example, the dual-cell FT-ICR technique allows storage of ions for long periods and transfer of ions from one cell to the other where different reactants can be introduced. Similarly, we have envisioned condensed-phase experiments whereby reactant molecules are contacted with radical cations stored in zeolite matrices.

Our general goal is to deliver reactant or probe molecules from the gas to a solid sample before or after radiolysis in order to probe radiation effects, measure mass transport, study ion-molecule chemistry, vary the environment of radical ions, or analyze gaseous products. To this end, we have assembled in one laboratory the ionization source, X-band

EPR spectrometer with variable-temperature cryostat, and a portable glass vacuum manifold capable of quantitatively delivering gas-phase reactants to the EPR sample tube mounted in the cryostat of the spectrometer. The ionization source is a 3 MeV electron Van de Graaff accelerator. The electron beam can be trained on samples mounted in the cryostat, or alternatively, valved samples can be irradiated at an alternate beam port and transferred to the spectrometer.

Preliminary results for two types of experiment illustrate this approach. In the first, a radical cation, benzene^{•+}, is held in ZSM5 while ethylene is allowed to diffuse in and react. The overall sequence is: (1) adsorb benzene in ZSM5 at room temperature, (2) irradiate sample in liquid nitrogen, (3) transfer sample to cryostat of EPR spectrometer and scan EPR spectrum of benzene^{•+}, (4) transfer ethylene to sample tube, (5) record EPR spectrum as a function of elapsed time and anneal temperature. Disappearance of the benzene radical cation (in less than two minutes at 170 K) upon exposure of the zeolite sample to ethylene, gives evidence for a possible charge transfer reaction concerted with ethylene dimerization and/or reaction with byproducts of ethylene ionization, e.g., vinyl radical [27].

The second type of experiment demonstrates another way the open pore structure of zeolites can be exploited to gain new insights into the reactions and dynamics of reactive intermediates. Just as the zeolite variables (Si/Al ratio, pore size, etc.) can be adjusted to control radical cation reactions, different inert or semi-inert gases can be added to the zeolite to further modify the physical environment of radiolytically generated ions. Through the concoction of different zeolite-plus-buffer gas "solvents", our goal is to control radical cation reactions by modifying the solvation, promoting energy relaxation, or providing a buffer to isolate radical cations from neutrals. In our example, carbon monoxide was added to ZSM5 at room temperature after adsorption of isobutene and the mixture was irradiated at 77 K [27].

The isobutene radical cation is not captured at 77 K in the radiolysis of isobutene in "dry" ZSM5; the proton-loss species, methylallyl ($a(2H) = 13.8$ G, $a(2H) = 14.7$ G, $a(3H)$

= 3.2 G), is the only radical observed [16]. This product is attributed to ion-molecule reaction, eq (3). Owing to its small size, diffusion of isobutene in ZSM5 may not be completely frozen out at 77 K. However, it is difficult to rule out the possibility that a heterogeneous adsorption distribution places isobutene molecules in close proximity in the zeolite; i.e., diffusion is not necessary.

Remarkably, when 1 atm of carbon monoxide was added at room temperature to the EPR tube containing the isobutene-loaded ZSM5 before radiolysis, methylallyl was not observed. Instead, a covalently bound dimer radical cation was formed. Thus we have the very interesting result that carbon monoxide directs the chemistry in a completely different direction. Nonpolar gases, such as nitrogen and hydrogen, did not have the same effect (i.e., methylallyl was still formed). Smaller amounts of CO (less than 50 torr) were not sufficient to redirect the chemistry. A possible role of CO is to stabilize the cation-molecule complex. Carbon monoxide might be needed to solvate the dimer ion, or perhaps it facilitates energy transfer to remove excess internal energy in the ion resulting from the exothermic condensation reaction.

3. ZEOLITE CATALYSIS

Because of its excellent sensitivity and structural specificity, EPR spectroscopy is a strong candidate for *in situ* studies of zeolite catalysis. However, since most intermediates and products in zeolite catalysis are not paramagnetic, the main technical hurdle to overcome is how to label these so that they become visible to EPR. Our solution is to use radiolysis to spin label molecules on zeolite catalysts. This occurs either by one electron oxidation to form radical cations or by H atom addition to form neutral radicals. The chief advantages possessed by the radiolysis/EPR method that are desirable for *in situ* studies of zeolite catalysis are that it can be extended to low temperatures where reactions can be slowed down or quenched and it is capable of unambiguous chemical identification.

The reactions of isobutene on HZSM5 are prototypical of the reactions of simple olefins on acidic zeolites. Even under mild conditions, olefins undergo oligomerization,

isomerization and cracking reactions consistent with carbenium ion chemistry. Such processes rapidly lead to a material composition characteristic of the catalyst and reaction conditions; after many reaction steps memory of the starting material is lost. Isobutene reacts at room temperature or slightly above in a period of hours to yield a hydrocarbon composition which strongly resembles that from any other C₃-C₈ olefin precursor [16].

Experiments with acyclic olefins on HZSM5 at ambient temperature and above were not informative about the elementary sequence of reactions that eventually lead to higher molecular weight products. By conducting experiments at subambient temperatures, we succeeded in arresting the catalytic reactions at earlier stages. For the case of isobutene, we observed four different species, including monomer, two dimers and one cracking product, that preceded the formation of higher polymers [16].

The accurate chemical identification possible with EPR is also an advantage for revealing selectivity in zeolite catalysis. At low temperatures selectivity is enhanced, and subtle structure/reactivity dependences can be more sensitively displayed. Our study of cyclic olefin reactions on HZSM5 and H-mordenite revealed both the dependence on catalyst pore size and structure of the reactant molecule [28]. Reaction of cyclic olefins on HZSM5 below 350 K is mostly limited to unimolecular isomerization. The main process is ring contraction, accompanied by 1,2-hydride and alkyl shifts. For example, our radiolysis/EPR study of a family of seven cyclic olefins with 5-, 6- and 7-member rings and the empirical formula C₇H₁₂ revealed the same dominant product, 1,2-dimethylcyclopentene, in every case.

Under similar conditions on H-mordenite larger products are formed from cyclic olefins, reflecting bimolecular reactions: dimerization and ring expansion [28]. These products, for example, bicyclo[5.5.0]dodecene, are too large to be accommodated inside the ZSM5 channels. These general trends are elaborated by variations in the rates of ring contraction or dimerization with molecular structure. Such examples could provide

interesting test cases to theorists in their attempts to learn about the intimate details of the geometric factors and interactions of the adsorbate with the catalytically active site.

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References:

- [1] P. H. Kasai, R. J. Bishop, Jr., *Zeolite Chemistry and Catalysis*, J. A. Rabo, ed., American Chemical Society, Washington, DC, 1976, Chapter 6.
- [2] T. Shida, E. Haselbach and T. Bally, *Acc. Chem. Res.* **17**, 180 (1984).
- [3] M. Shiotani, *Magnetic Resonance Rev.* **12**, 333 (1987).
- [4] A. Lund, M. Lingren, S. Lunell and J. Maruani, *Molecules in Physics, Chemistry and Biology*, Vol. III, J. Maruani, ed., Kluwer Academic Publishers, Boston 1989, p. 259.
- [5] M. C. R. Symons, *Chem. Soc. Rev.* **13**, 393 (1984).
- [6] X.-Z. Qin and A. D. Trifunac, *J. Phys. Chem.* **94**, 4751 (1990).
- [7] X.-Z. Qin and A. D. Trifunac, *J. Phys. Chem.* **95**, 6466 (1991).
- [8] M. V. Barnabas and A. D. Trifunac, *Chem. Phys. Lett.* **187**, 565 (1991).
- [9] M. V. Barnabas and A. D. Trifunac, *J. Chem. Soc. Chem. Commun.*, 813 (1993).
- [10] M. V. Barnabas, D. W. Werst and A. D. Trifunac, *Chem. Phys. Lett.* **204**, 435 (1993).
- [11] M. V. Barnabas, D. W. Werst and A. D. Trifunac, *Chem. Phys. Lett.* **206**, 21 (1993).
- [12] D. W. Werst, E. E. Tartakovsky, E. A. Piosos and A. D. Trifunac, *J. Phys. Chem.* **98**, 10249 (1994).
- [13] D. W. Werst, E. A. Piosos, E. E. Tartakovsky and A. D. Trifunac, *Chem. Phys. Lett.* **229**, 421 (1994).
- [14] E. A. Piosos, D. W. Werst, A. D. Trifunac and L. A. Eriksson, *J. Phys. Chem.* **100**, 8408 (1996).
- [15] D. W. Werst, P. Han and A. D. Trifunac, *Chem. Phys. Lett.* **269**, 333 (1997).

- [16] E. A. Piocos, P. Han and D. W. Werst, *J. Phys. Chem.* **100**, 7191 (1996).
- [17] P. Han and D. W. Werst, unpublished results.
- [18] D. W. Werst, P. Han and A. D. Trifunac, *Radiat. Phys. Chem.*, in press.
- [19] C. J. Rhodes, *J. Chem. Soc. Faraday Trans.* **87**, 3179 (1991).
- [20] P.-O. Kinell, A. Lund and A. Shimizu, *J. Phys. Chem.* **73**, 1721 (1969).
- [21] R. Erickson, M. Lindgren, A. Lund and L. Sjoqvist, *Colloids Surfaces A* **72**, 207 (1993).
- [22] N. G. Adams and D. Smith, *Techniques for the Study of Ion-Molecule Reactions*, J. M. Farrar and W. H. Saunders, Jr., eds., John Wiley and Sons, NY (1988), Chapter 4.
- [23] K. M. Stirk, L. K. Marjatta Kiminkinen and H. I. Kanttamaa, *Chem. Rev.* **92**, 1649 (1992).
- [24] G. M. Daly, M. Meot-Ner, Y. B. Pithawalla and M. S. El-Shall, *J. Chem. Phys.* **104**, 7965 (1996).
- [25] M. S. El-Shall and Z. Yu, *J. Am. Chem. Soc.* **118**, 13058 (1996).
- [26] D. L. Vollmer, D. L. Rempel and M. L. Gross, *Int. J. Mass Spect. and Ion Proc.* **157/158**, 189 (1996).
- [27] D. W. Werst and A. D. Trifunac, *Mag. Reson. Review*, in press.
- [28] D. W. Werst and P. Han, *Catal. Lett.* **45**, 253 (1997).

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