Zeolite catalysis studied by radiolysis / EPR. Transformations of cyclic olefins *

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The Brønsted acid-catalyzed transformations of cyclic olefins in zeolites HZSM5 and H-mordenite were elucidated by the radiolysis/EPR method. Products of catalytic reactions were spin-labeled by radiolytic means and identified by using EPR spectroscopy. Comparison of reactions on HZSM5 and H-mordenite reveals strong shape selectivity on reactions in these catalysts. The radiolysis/EPR method is a new in situ spectroscopy with excellent sensitivity and structural specificity for the study of reaction mechanisms in zeolite catalysts.

Keywords: radiolysis, EPR, zeolite, catalysis, HZSM5, H-mordenite, in situ spectroscopy

1. Introduction

It has been known for three decades that exposure of easily oxidized compounds, including aromatic and olefinic hydrocarbons, to aluminosilicates can generate paramagnetic species[1–6]. If these can be identified by EPR spectroscopy, they can reveal details about the mechanisms and intermediates involved in solid-acid catalysis. In highly siliceous zeolite catalysts, such as HZSM5 and H-mordenite, normally Brønsted acids, it is possible to generate Lewis acid sites by heating the catalyst in air to 700–900 K [7,8]. After such pretreatment of the zeolite, adsorption of compounds with low ionization potentials can give rise to EPR signals. One usually observes radical cations, which may be due to oxidation of starting material and/or products. Many authors have studied such EPR signals for insights into catalysis mechanisms [1–19]. Unfortunately, this approach is limited by the lack of chemical insight (the observed chemical transformations could be cationic in nature – Brønsted acid-catalyzed – or they could be due to reactions of radical cations) and by the lack of control over the oxidation process.

In order to overcome the inherent limitation of this approach based on Lewis-activated zeolites, radiolysis can be used to convert diamagnetic products to radicals or radical cations [20–24]. This occurs by one-electron oxidation to produce radical cations or by H atom addition to produce neutral H adduct radicals [23]. The radiolytic method of paramagnetic labeling has many advantages. Experiments can be done on catalysts free of Lewis acid sites – there is no self-oxidation. Any species can be labeled (ionization potential is not a limiting factor). Labeling can be done at low temperature; thus catalysis can be studied under very mild conditions. (For an analogous approach using NMR, see ref. [25].) Control of temperature and irradiation dose gives more control over radical cation concentration and thus can lead to improved signal-to-noise. Perhaps most important of all, control experiments can be done on the inert form of the zeolite, e.g., NaZSM5, where no transformations occur prior to radiolysis. This allows one to sort out possible transformations of radical cations from the cationic (Brønsted acid-catalyzed) reactions.

We first demonstrated the radiolysis/EPR method for elucidating acid-catalyzed transformations in a study of acyclic C_3–C_8 olefins on HZSM5 [23]. The primary reaction sequence (dimerization, isomerization and cracking) for isobutene was mapped out in a series of experiments where the reaction time and temperature were varied. The catalysis was halted at various stages by quenching the sample in liquid nitrogen. Radiolysis and EPR detection at cryogenic temperatures allowed the hydrocarbon composition to be interrogated in the absence of ongoing transformations. This systematic approach allowed the first comprehensive and consistent explanation of EPR signals generated from acyclic olefins adsorbed on Lewis-activated zeolites [12–19].

Comparatively less work is found in the literature on radical cations formed from cyclic olefins adsorbed on Lewis-activated zeolites – primarily H-mordenite [6,7,9,26]. Although the early works were flawed, these have largely been corrected by more careful studies [7,9]. In the present paper, we examine the reactions of cyclic olefins on HZSM5 and H-mordenite by the radiolysis/EPR method. Comparison of the major products on HZSM5 and H-mordenite starkly displays the shape selectivity of the zeolite-catalyzed reactions. Our radi-

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olysis/EPR results in H-mordenite are in agreement with results previously obtained on this catalyst by the self-oxidation method. Therefore, similar transformations occur on H-mordenite with or without the generation of Lewis acid sites.

Paramagnetic labeling allows full exploitation of the excellent sensitivity and structural specificity of EPR spectroscopy for investigation of intermediates and products in zeolite catalysis. The radiolysis/EPR technique is a significant new in situ spectroscopy for the study of catalytic reactions.

2. Experimental

The zeolites HZSM5 (Si/Al = 240), NaZSM5 (Si/Al = 170) and H-mordenite (Si/Al = 25) were kindly donated by Chemie Uetikon (Switzerland). All hydrocarbons were purchased from Aldrich or Wiley Organics. These were purified by repeated freeze–pump–thaw cycles using liquid nitrogen.

The zeolite samples were prepared in 4 mm o.d. Suprasil tubes on a glass vacuum manifold. The zeolite powder (50 mg) was activated in vacuum ($< 10^{-4}$ Torr) for 4 h at 450°C. The desired amount of adsorbate was adsorbed/condensed into the sample tube, and the sample tube was sealed under vacuum while the zeolite powder was kept at 77 K. Once the tube was sealed, the zeolite sample was allowed to equilibrate at constant temperature between 295 and 353 K. At the end of the equilibration period the samples were transferred to a liquid-nitrogen storage dewar. No EPR signals were detected in unirradiated samples.

Samples were irradiated at 77 K by ^{60}Co γ-rays to a dose of approximately 3 kGy and then stored in liquid nitrogen. Irradiated samples were transfered to a LTR-3 liquid-helium-transfer cryostat (APD) anchored in the cavity of a Varian E-109 X-band EPR spectrometer operating at the microwave frequency of 9.31 GHz. EPR spectra were collected between 4 K and room temperature. Magnetic field control and data acquisition were accomplished by a LabVIEW (National Instruments) program on a Macintosh II computer.

3. Results

A variety of cyclic olefins with the empirical formula C_7H_{12} were allowed to react on HZSM5 for approximately 16 h (in a few cases up to several days) at temperatures between 295 and 353 K, always with the same outcome. Radiolysis of the zeolite samples at 77 K gave rise to the EPR spectrum shown in figure 1. The dominant signal is the EPR spectrum of the 1,2-dimethylcyclopentene radical cation. Thus all of the molecules in scheme 1 are largely transformed into 1,2-dimethylcyclopentene on HZSM5 under the conditions of the experiment. Included in the test group were molecules with 5-, 6- and 7-member rings and with various alkyl substituents.

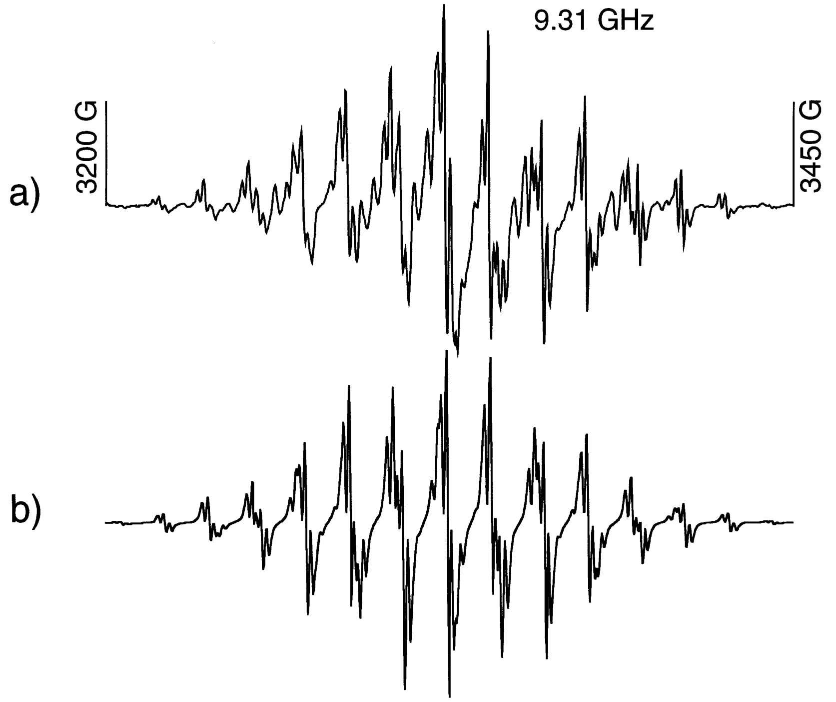
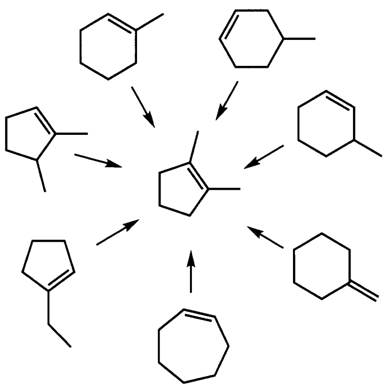


Figure 1. (a) EPR spectrum obtained at 190 K in HZSM5 equilibrated with 120 μmol/g 1,5-dimethylcyclopentene at 318 K. (b) Computer simulation of the EPR spectrum of the 1,2-dimethylcyclopentene radical cation using the hyperfine parameters listed in table 1.



Scheme 1. Transformations of cyclic olefins on HZSM5.

The 1,2-dimethylcyclopentene product developed very slowly (days) from the cycloheptene precursor at 295 K, whereas the conversion was essentially complete after 16 h when cycloheptene was equilibrated at 318 K. There was no evidence that the cycloheptene had significantly adsorbed into the HZSM5 after equilibration at 295 K for 16 h (i.e., no hydrocarbon radical cation EPR signal was obtained upon radiolysis); therefore diffusion through the channels may have been rate limiting.

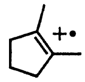
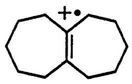
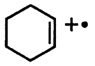
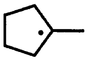
The hyperfine coupling parameters used to simulate the EPR spectrum of the 1,2-dimethylcyclopentene radical cation in HZSM5 are in good agreement with those reported in the CF_3CCl_3 matrix and in H-mordenite (table 1). The γ-hydrogen couplings were not resolved in these two matrices. We likewise obtained a less-resolved EPR spectrum of the 1,2-dimethylcyclopentene radical cation in H-mordenite (when the precursor was 1,5-dimethylcyclopentene) compared to HZSM5.

Reaction of cyclohexene on HZSM5 for 16 h at 295 K resulted in only minimal conversion ($< 10\%$) to 1-methylcyclopentene, most of the EPR intensity in the radiolyzed sample being accounted for by the cyclohexene radical cation. (Formation of 1-methylcyclopentene was indicated by the appearance of the H-adduct radical, 1-methylcyclopentyl. The same radical was generated from 1-methylcyclopentene or methylenecyclopentene on HZSM5 (table 1). The hyperfine coupling constants for the cyclohexene radical cation in HZSM5 are in agreement with those obtained in NaZSM5 and CF_3CCl_3 (table 1). Reaction of cyclohexene for 16 h at 318 K increased the contribution from methylcyclopentyl in the resulting EPR spectrum, but the cyclohexene radical cation still accounted for a significant fraction ($> 50\%$) of the EPR intensity in the radiolyzed sample.

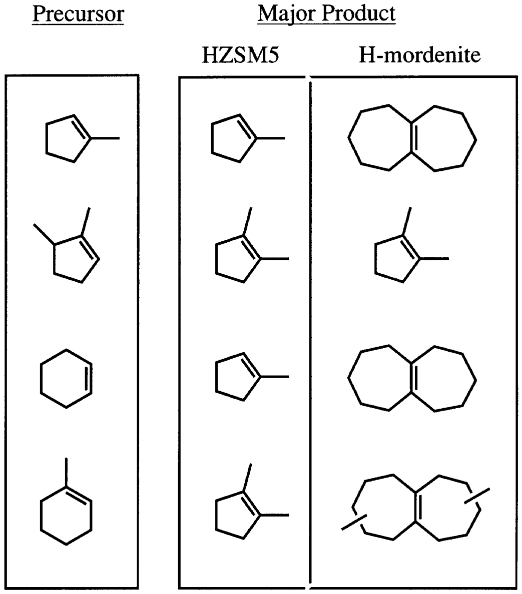
For comparison to the HZSM5 results, 1-methylcyclopentene, cyclohexene, 1,5-dimethylcyclopentene and 1-methylcyclohexene were adsorbed and allowed to react on H-mordenite for 16 h at 295 K. The results are summarized in scheme 2. The EPR spectrum observed

Table 1

Isotropic proton hfcc (G, 1 G = 0.1 mT) of radicals and radical cations in this work

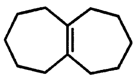
	Matrix	T (K)	hfcc[a]			Ref.
			α	β	γ	
	HZSM5	190		(4H)35.5 (6H)16.1	(2H)2.0	[a]
	CF_3CCl_3	157		(4H)34.2 (6H)16.7		[27]
	H-mordenite	295		(4H)34.2 (6H)16.7		[28]
	H-mordenite	150		(4H)36.2 (4H)14.0		[a]
		120		(4H)35.2 (4H)13.7		[7]
	HZSM5	110	(2H)8.5	(2H)57 (2H)24		[a]
	NaZSM5	110	(2H)8.5	(2H)56 (2H)23.5		[a]
	CF_3CCl_3	140	(2H)9.0	(2H)55.0 (2H)22.0		[29]
	HZSM5	70		(3H)23.5 (2H)24.5 (2H)44.0		[a]
	adamantane	82		(3H)22.6 (2H)24.0 (2H)41.3		[39]

[a] This work.



Scheme 2. Catalytic transformations on HZSM5 and H-mordenite.

after radiolysis of the cyclohexene sample is shown in figure 2. No cyclohexene radical cation was detected. The EPR spectrum is attributed to the radical cation of bicyclo[5.5.0]dodecene, **1**, after the assignment of Crockett and Roduner, who observed the same EPR spectrum upon reaction of cyclohexene on Lewis-activated H-mordenite [7]. Our results for cyclohexene on H-mordenite were the same for loadings of 120 and 500 μmol/g; however, the signal-to-noise ratio was improved at the higher loading.



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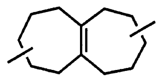


2

Reaction of 1-methylcyclopentene and 1-methylcyclohexene on H-mordenite gave rise to EPR spectra similar to figure 2 upon radiolysis. We assign these signals to the radical cations of **1** and **2**, respectively, in agreement with Crockett and Roduner [7]. In contrast with the other cyclic precursors on H-mordenite, 1,5-dimethylcyclopentene underwent double-bond isomerization but did not undergo dimerization and ring expansion, even when the equilibration temperature was elevated to 318 K (16 h).

It is evident that the observed hydrocarbon transformations are catalyzed by acid sites in HZSM5 and H-mordenite and are not caused by radiolysis. For example, the cyclohexene radical cation was stable in the inert Na^+-exchanged ZSM5 zeolite. Upon warming (> 130 K), ion–molecule reactions converted the cyclohexene radical cation to cyclohexenyl, $C_6H_{11}^{\bullet}$. Radiolysis of NaZSM5 samples loaded with 1-ethylcyclopentene or 1-methylcyclohexene did not give the 1,2-dimethylcyclopentene radical cation. It is presumed that the parent radical cations are produced; however, analysis of the EPR spectra has not been completed. Finally, any indication that the sample equilibration conditions prior to radiolysis control the advancement of the trans-

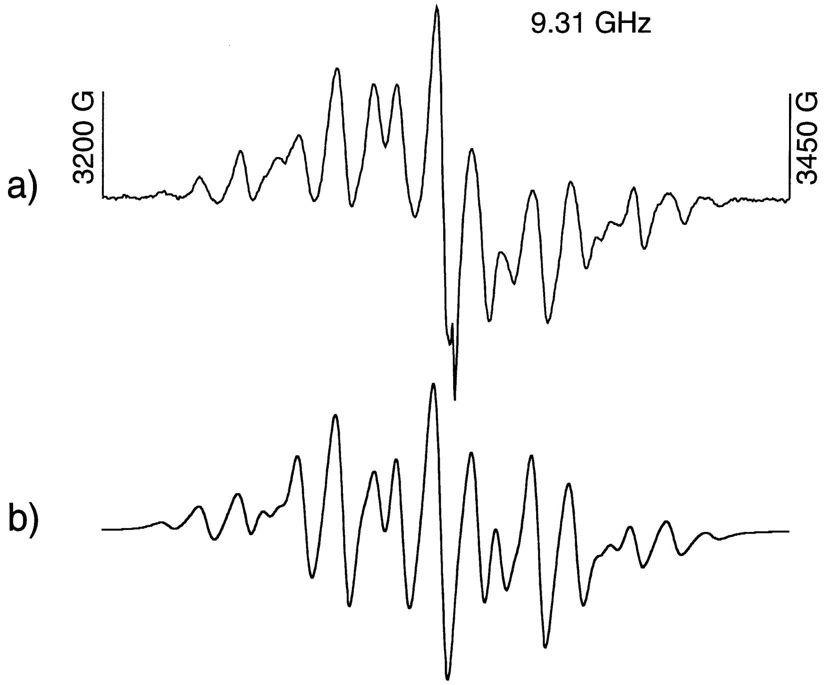


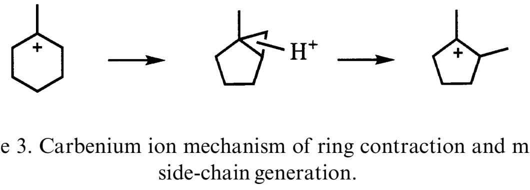
Figure 2. (a) EPR spectrum obtained at 150 K in H-mordenite equilibrated with 500 μmol/g cyclohexene at 295 K. (b) Computer simulation of the EPR spectrum of $\mathbf{1}^{\cdot+}$ using the hyperfine parameters listed in table 1.

formations is further evidence that the chemistry is acid-catalyzed. This was found for HZSM5 samples loaded with cyclohexene, where the relative contributions of cyclohexene radical cation and methylcyclopentyl depended on the pre-radiolysis equilibration temperature.

Some of the precursors that yielded 1,2-dimethylcyclopentene in HZSM5 showed no evidence of adsorbing in NaZSM5 at comparable equilibration temperatures. It has been our experience that HZSM5 is capable of admitting slightly larger molecules than NaZSM5. The acidic hydroxyl groups present a lesser hindrance to molecular diffusion through the channels compared to the sodium cations [40]. Conceivably, diffusion of the hydrocarbon molecules into HZSM5 is also aided by the isomerization process.

4. Discussion

The observed transformations of cyclic olefins on HZSM5 and H-mordenite are of the type expected of Brønsted acid-catalyzed reactions. The classical formalism used to explain such transformations is based on an analogy to the reactions of carbenium ions in superacid solutions, which include 1,2-hydride and alkyl shifts, ring-contraction and ring-expansion reactions, and addition to olefins [30,31]. For example, ring contraction occurs via the mechanism shown in scheme 3, which involves the intermediacy of protonated cyclopropane rings in order to avoid the formation of primary carbenium ion intermediates.



Scheme 3. Carbenium ion mechanism of ring contraction and methyl side-chain generation.

Zeolites derive their Brønsted acidity from hydroxyl groups that bridge between Si- and Al-substituted tetrahedral lattice sites. There is both experimental and theoretical evidence that the acid strength of zeolites is generally not sufficient to form significant equilibrium concentrations of free carbenium ions [32–35]. That is, zeolites are not superacids. Reactive intermediates in zeolite catalysis are probably framework-bonded species in many cases, and theory suggests that catalysis may be bifunctional in nature because of the proximity of neighboring basic oxygen sites [33–35]. The zeolite catalysis can nevertheless involve a transition state with ionic character such that rules governing carbenium ion transformations are obeyed to some degree within the geometry constraints imposed by the zeolite.

The most interesting aspect of our results is the selectivity obtained on the zeolite catalysts. Shape selectivity in zeolite catalysis is commonly divided into three types: shape selectivity on (1) reactants, (2) transition states, and (3) products. A summary of our results, which highlights the differences between HZSM5 and H-mordenite, is shown in scheme 2, and table 2 shows the channel dimensions of these two zeolites. One obvious difference is the absence of the dimerization/ring-expansion process in HZSM5. This would appear to be an example of shape selectivity on the products, **1** and **2** being too large to form inside the channels of HZSM5.

On the other hand, the stability of 1,2-dimethylcyclopentene on H-mordenite suggests that the volume constraint is not the only important factor. Its stability (up to 318 K) contrasts with 1-methylcyclopentene and cyclopentene, which undergo dimerization and ring expansion, the latter at temperatures as low as 210 K [7]. The relative inertness of 1,2-dimethylcyclopentene on H-mordenite is apparently not a case of shape selectivity on products since the other C_7 molecule, 1-methylcyclohexene, reacted to give a dimer product on H-mordenite. Like the case discussed next, reaction of 1,2-dimethylcyclopentene on H-mordenite could be hindered by steric constraints on its interaction with the active site.

Cyclohexene showed greater resistance to ring contraction on HZSM5 than either the methylcyclohexenes or cycloheptene. The carbenium ion-type mechanism does not disfavor the ring contraction in the case of cyclohexene, and the thermodynamic benefit of going from a secondary carbenium ion to a tertiary carbenium ion (methylcyclopentyl) should be a strong driving force for ring contraction. The greater acidity of secondary carbenium ions such as cyclohexyl compared to tertiary ions such as methylcyclohexyl could partly underlie the stability of cyclohexene on HZSM5. However, that suggests that cycloheptene should also be slow to undergo ring contraction, which was not the case. Furthermore, H-mordenite, a weaker acid than HZSM5, is able to activate the conversion of cyclohexene to the dimer product at equally low temperatures.

To explain the relative stability of cyclohexene on HZSM5, we must invoke shape selectivity on the reactant and/or transition state. This selectivity depends, inter alia, on the fit of the reactant molecule in the active site, which is described by the relative geometry of the Brønsted acid group, the neighboring basic sites and the volume of the channel as a whole. A poor fit may not allow the precursor to evolve into the required transition

Table 2
Diameters of elliptical channels in ZSM5 and mordenite (ref. [38])

		Diameter (Å)
ZSM5	10-ring, straight channels	5.3 × 5.6
	10-ring, sinusoidal channels	5.1 × 5.5
mordenite	12-ring	6.5 × 7.0
	8-ring	2.6 × 5.7

state for the isomerization. In any event, the balance of forces is extremely precarious – the mere addition of a methyl group lowers the barrier to reaction.

In conclusion, the radiolysis/EPR technique is a non-intrusive, in situ method for studying mechanisms of zeolite catalysis. EPR surpasses other in situ spectroscopies, such as FTIR and NMR, in sensitivity and structural specificity. The radical cation EPR spectra can lead to the unequivocal identification of the chemical structures of products, whereas inversion of chemical shift spectra to give unique structures is often not achievable.

One weakness of the EPR technique is that hole transfer to lower energy traps creates a detection bias in favor of species with lower ionization potentials [36,37]. Thus one may obtain an artificially narrow view of the product spectrum. This is not a serious drawback. One gains something in selectivity, and those products which are observed can be assured to occur in significant yield. The extent of the charge-transfer bias can be estimated from experiments in double-loaded zeolites as we are beginning to demonstrate [37].

Finally, the present study also shows that the radiolysis/EPR and self-oxidation methods can give compatible results. That is, at least in some cases similar chemistry is observed despite the differences in the manner of pretreatment of the zeolite catalyst. The radiolysis/EPR method is however far more versatile.

Acknowledgement

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