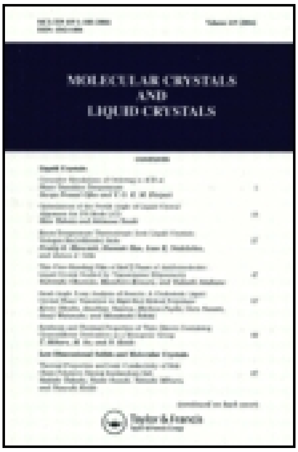

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SOLID STATE NMR AND EPR STUDIES OF INTRACRYSTALLINE VS. EXTERNAL SURFACE ADSORPTION OF PHOTOREACTIVE KETONES IN PENTASIL ZEOLITES

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Abstract It has been shown that the recombination probabilities of radicals generated from photolysis of ketone precursors in pentasil zeolites can be controlled by the distribution of ketones on the internal and external zeolite surfaces as well as by the adsorption siting and sieving attributes of the radical fragments. Here we report the use of magnetic resonance techniques in the elucidation of the adsorption sites of ketone reactants. The techniques employed include solid state ^{29}Si and ^{13}C MAS-NMR to characterize the zeolite frame-work and the ketone adsorbates respectively. EPR spectroscopy of the stable free radical Tempo was also used as a complementary technique to obtain information about the environment of the radical including its interactions with the surface and with the ketones. The latter interactions, when present, result in the broadening and shifting of the ^{13}C NMR signals of the ketone.

Keywords: zeolites, photochemistry, solid-state NMR, dibenzyl ketone, EPR, 2,2,4,4-tetramethyl piperidine N-oxyl (TEMPO)

INTRODUCTION

The last few years have witnessed an increasing interest in photochemical reactivity in organized media and restricted environments.[1] With the potential of controlling complex photochemical processes, zeolites are among the newest organized media systems to be incorporated in the organic photochemistry panorama.[2] One of the most versatile and studied zeolite systems is that given by the pentasil zeolites of which ZSM-5 is the star of the class due to its importance in the catalysis science arena.[3]

The ZSM-5 zeolite and its dealuminated version, silicalite, are composed of structural building blocks (the pentasil unit) arranged to form a periodic lattice that results in an ordered array of two perpendicularly intersecting channel systems (Figure 1).[4] The zeolite LZ-105 also corresponds to the pentasil family and is analogous to ZSM-5. Because of their largely open structure and large internal void volumes, these pentasil zeolites are capable of adsorbing medium-sized organic compounds (~5-6 Å kinetic diameters). Elliptical channels running straight along the ZSM-5 crystal have access dimensions of 5.1 x 5.7 Å, while circular zig-zag channels running in parallel directions have entrance apertures of 5.4 Å diameter (Figure 1).

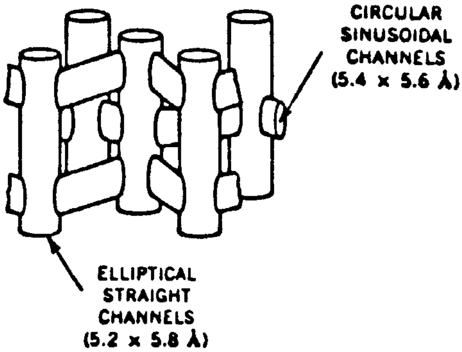


Figure 1. Schematic representation of the channels system in the zeolites ZSM-5, LZ-105 and silicalite.

It has been known for some time that efficient discrimination between closely related isomeric compounds can be carried out by these zeolites based on differences in the molecular dimensions of the adsorbates relative to those of the pore entrances. The term shape-selectivity was coined to refer to this situation[3,5] which has been well studied in the case of the three xylene isomers (ortho, meta and para).[6] It has been well established that because of its relatively small kinetic diameter, p-xylene can diffuse rapidly into the internal channel structure of the ZSM-5 zeolites under conditions where o-xylene diffuses at a much slower rate.[6] Based on these concepts, we recently devised a strategy for controlling the chemistry of radical pairs obtained photochemically from dibenzyl ketone derivatives.[7]

The basic paradigm for the photochemistry on ZSM-5 zeolites consisted of two simple premises: a) the recombination probability of the radicals should depend on whether the precursor ketone resides on the internal or external zeolite surfaces, and, b) a physical separation of the radicals can be achieved due to largely different diffusion rates into the zeolite interior. The compounds selected to test those hypotheses were o-methyl-dibenzyl ketone (oDBK) and p-methyl-dibenzyl ketone (pDBK) which upon photolysis generate o-methyl-benzyl (oBz) and p-methyl-benzyl (pBz) radicals possessing an obvious structural analogy to the corresponding xylene isomers (Scheme 1).

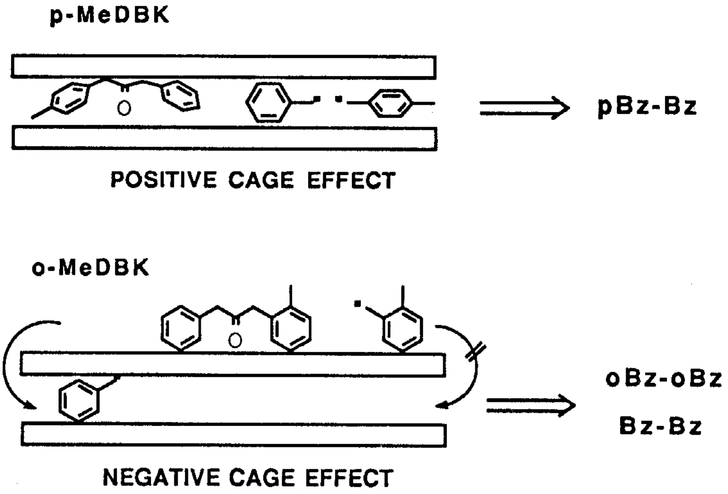
The experimental observations were found to conform to the expectations raised from the structural differences between radicals generated in each case. The recombination probabilities were measured in terms of the cage effect according to the expression:

$$\text{Cage Effect} = AB - (AA+BB) / AB+AA+BB$$

where A and B represent the two radicals formed from the ketones ACOB, and AB, AA and BB represent the corresponding recombination products. Photolysis of pDBK was found to result in the formation of products pBz-Bz (i.e., AB) while oDBK was found to give mainly products Bz-Bz and oBz-oBz (i.e., AA and BB). Application of the cage effect relationship resulted in cage effects large and positive in the case of pDBK and large but negative in the case of oDBK. It was suggested that pDBK and oDBK are photolyzed inside the zeolite channels and the zeolite external surface respectively. Radicals from pDBK being born in the internal surface recombine geminately in the zeolite "cage" to give products pBz-Bz. In contrast, radicals from oDBK generated in the external surface diffuse apart rapidly to form free radicals. The smaller Bz diffuses inside the zeolite channels to give Bz-Bz while the larger oBz is restricted to the external surface to give oBz-oBz.

The model proposed above rests on the possible discrimination of reactants within different domains of the zeolite structure. In this case, the distinction is between the external and internal zeolite surfaces. In this study we have used solid state NMR and EPR techniques to identify and characterize the distribution of ketone molecules in different regions of the zeolite surface. In this paper we present and discuss results based on magnetic resonance measurements carried out with the two ketones (oDBK and pDBK) in the zeolites LZ-105 and silicalite.[8]

Scheme 1



RESULTS AND DISCUSSION

Solid state NMR measurements, using ^{13}C and ^{29}Si at the natural abundance level provided information about the probe and the zeolite medium respectively. Measurements carried out in the presence of the stable free radical 2,2,4,4,-tetramethyl piperidine-N-oxyl (Tempo), which was not expected to diffuse into the zeolite channel system because of its size, provided information regarding the relative location of the free radical and the ketone. Samples containing Tempo were analyzed both by solid state NMR and by EPR.[9] Nitroxide radicals are known to be good EPR probes to analyze gas-solid interfaces as in the present case.[9] EPR spectroscopy may also give direct information about radical localization in different domains of the zeolite surface as well as detailed indications on the mobility of the radical and its environmental polarity.

NMR Measurements

The ^{13}C spectra were recorded with 2 to 4 thousand transients under conditions of single pulse excitation (Bloch decay) with a ^{1}H decoupling field of ca.40 KHz and a recycle delay of 5 s. Spectra were recorded on freshly dried zeolite samples loaded with 5% w/w ketone deposited from isoctane solutions (12 h adsorption time) after the solvent was evaporated first with a gentle argon stream and then by evacuation at 10^{-4} Torr. This loading value represents about a three-fold excess of the maximum uptake to the internal surface in the case of pDBK while all of the sample should be simply deposited on the surface in the case of oDBK. The samples were spun at 3.5 to 5 KHz at the magic angle and chemical shifts were obtained by replacement and comparison with a sample of p-di-*tert*-butyl benzene.

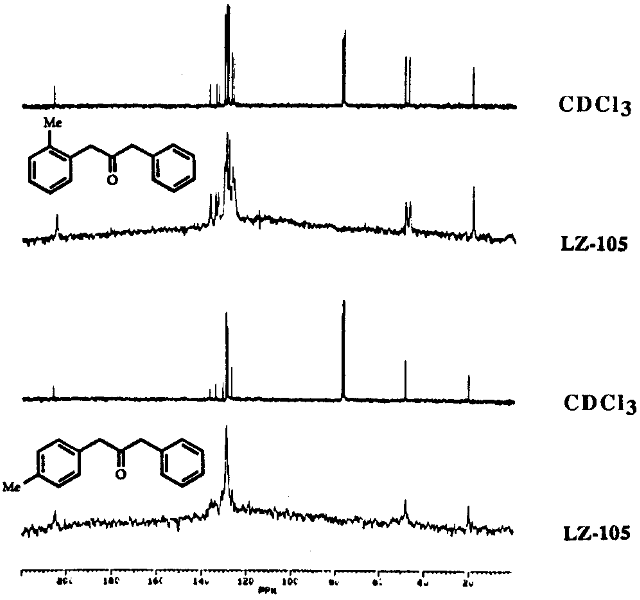


Figure 2. ^{13}C NMR spectra of oDBK and pDBK in $CDCl_3$ solution and adsorbed in LZ-105.

Figure 2 shows the ^{13}C NMR spectra of oDBK and pDBK obtained in LZ-105 along with the spectra measured in $CDCl_3$ solution included for comparison purposes. The signals obtained for each group of carbon nuclei (carbonyl, aromatic, methylene and methyl) were found to present uncorrected chemical shifts comparable to those observed in solution. A slightly better resolution was observed in the case of samples containing oDBK with limitations given by bandwidths of 40-60 Hz.

In order to distinguish possible spectral differences between intracrystalline and external surface-deposited components, the effect of exposure of the above samples to *iso*-octane under conditions of desorption was also investigated. In agreement with previous work suggesting the location of pDBK in the internal channels and of oDBK on the external surface, desorption of the ortho compound was found to be much faster than that of the para isomer. With the same number of transients and acquisition conditions as those employed to obtain the spectra of Figure 2, no signal could be observed after desorption of oDBK while only a ca. 60% decrease in the signal intensity was observed in the case of pDBK. The decrease in signal in the latter experiment was accompanied by changes in spectral appearance such as loss of resolution and line broadening. Under our conditions there is a certain fraction of pDBK on the external surface and these results suggest that the intracrystalline component, perhaps having larger restrictions to molecular mobility, may have longer relaxation times, a larger heterogeneity and consequently a smaller than expected relative intensity.

We reasoned that additional support of the above observations could be obtained by analyzing the interaction between the free radical Tempo and the two ketones. Since the diameter of Tempo is known to be larger than the diameter of the channel entrances,[10] we expected the free radical to reside only in the external surface of the zeolite. The interaction between the ketones and the paramagnetic free radical, under conditions where steric contact between them could be established, was expected to result in line broadening and shifts of the resonance positions. Such turned out to be the observed result when equimolar amounts of Tempo were deposited onto the zeolite surface after adsorption of the corresponding ketones (Figure 3).

Notably the magnitude of the shifts and broadening observed in the case of oDBK were not the same for all carbon resonances indicating a preferred direction for interaction between the two species. In contrast, only a small reduction in the signal intensities with no paramagnetic or line broadening were observed in the case of pDBK.

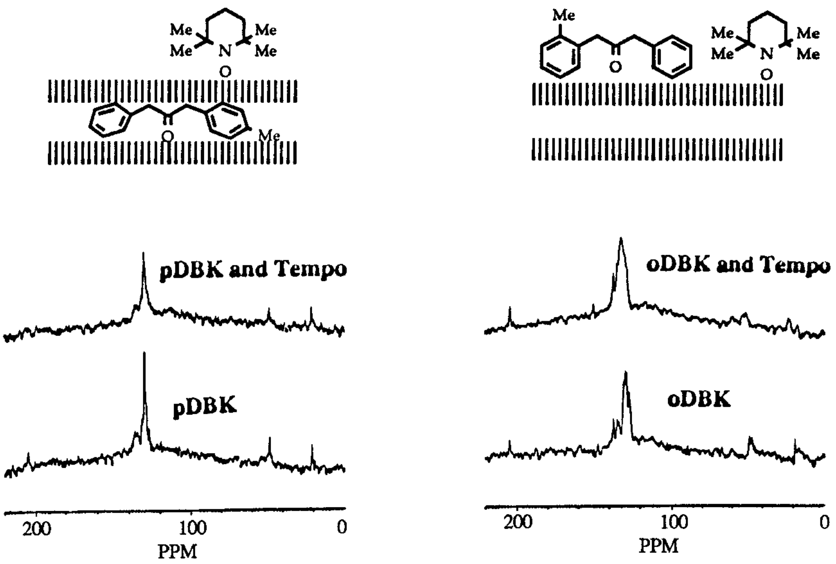
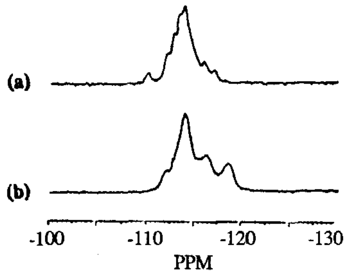


Figure 3. Effect of Tempo on the 13C NMR spectra of pDBK and oDBK adsorbed on LZ-105. A schematic representation of a model accounting for the results is shown at the top of each spectrum.

A further illustration regarding the use of NMR probes to the elucidation of the location of the reactant was obtained by measuring the ^{29}Si MAS NMR spectra of samples of the two ketones in the zeolite silicalite. The choice of this experiment was based on recent observations by Fyfe et. al regarding the sensitivity of the NMR spectra to the presence of additives.[11] Qualitatively, spectral changes are achieved due to subtle structural changes in the zeolite framework.[11] Depending on the resolution obtained in the spectra one may be able to resolve all the crystallographically non-equivalent carbons in the asymmetric unit of the crystal. The resolution observed in commercial samples such as those employed in this study, however, is not sufficient for such a detailed analysis. In spite of this limitation, one can easily observe strong perturbation in the spectra of silicalite with various adsorbates. Our findings with samples containing oDBK and pDBK were consistent with strong structural perturbations only in the case of the former (Figure 4).

Figure 4. ^{29}Si NMR spectra. Samples of silicalite: (a) pure, and (b)with pDBK. The spectrum of silicalite adsorbed with oDBK is identical to the spectrum obtained with pure silicalite.



EPR Analysis

A complementary view of the interaction between the two ketones in their respective environments with the stable free radical Tempo was obtained by EPR spectroscopy. Along with the samples employed for NMR analysis, and in order to carry out a comparison, we also measured the spectrum of Tempo deposited in LZ-105 in the absence of the ketone.

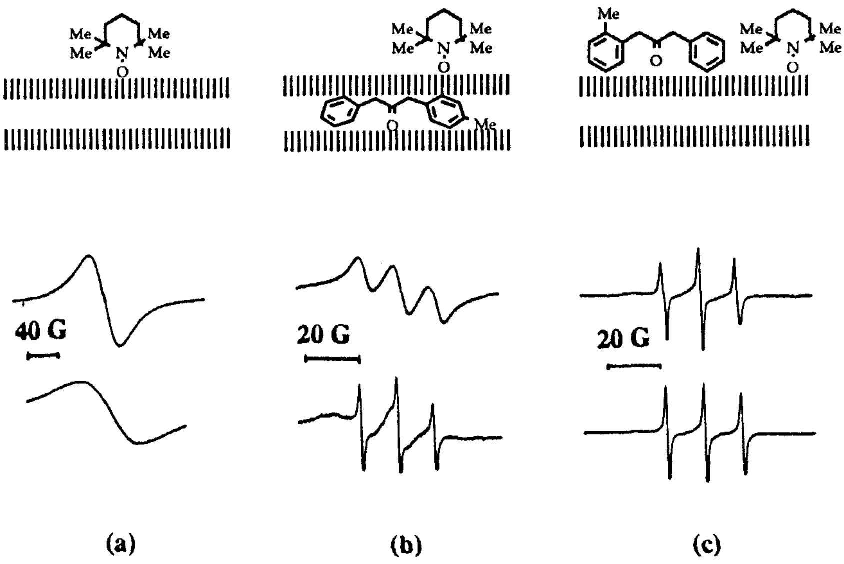


Figure 5. EPR spectra of Tempo radical on the external surface of LZ-105 and its interactions (a) with the zeolite surface alone, (b) with the surface in the presence of pDBK, and, (c) with the surface in the presence of oDBK. Spectra on top are obtained at loadings of 3.5 % Tempo and 5% oDBK and pDBK. Spectra at the bottom are diluted by a factor of 500.

The results shown in Figure 5 indicate striking differences that point out the possible generality of this method in deducing the location of the adsorbate. The spectra of Tempo alone (Figure 5a) indicate a condition of Heisenberg spin exchange[12] which is consistent with a model involving either fast inter-radical encounter or molecular aggregation and clustering on the external surface. The exchange-rate dependence of the spectra of Tempo radicals has been studied in detail by Sache and Marsh and has been shown to result both in line broadening and in variations of the intensity of the three hyperfine lines of the nitroxyl radicals.[12] It is interesting to compare our results with the spectra calculated for different exchange rates of nitroxyl radicals (Figure 6).

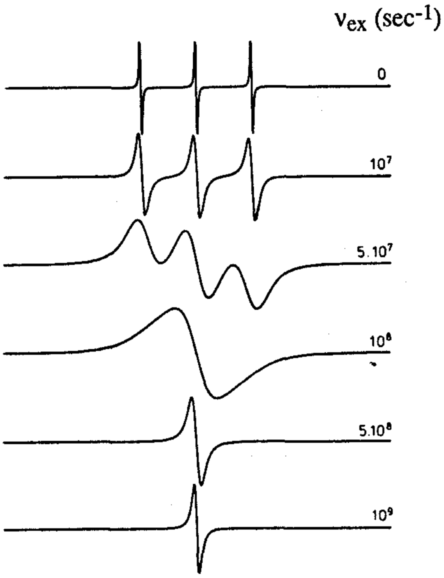


Figure 6. Variation in the first derivative spectra of nitroxyl radicals as a function of the spin-spin exchange rate (adapted from reference 12).

A comparison between the spectra of Tempo covering a loading range between 3.5 % and $7\text{x}10^{-3}$ % w/w indicated a decrease of the spin-spin exchange frequency at the lower radical concentrations. Computation of these spectra by using the Bloch equations including Heisenberg spin-exchange contributions gave[12] $w_{ex} \sim 30$ MHz at 3.5 % w/w and $w_{ex} \sim 15$ MHz at $7\text{x}10^{-3}$ % w/w (DB(-1)=10G, DB(0)=7G, DB(+1)=10G respectively; isotropic hyperfine coupling, $<A_N> = 14.5G$). Changes in the exchange rate as a function of concentration point to a diffusion mechanism but the small variation over the concentration range studied also indicates the participation of radical clustering.

In contrast to the spectra containing only the radical, the spectra obtained in the presence of the externally bound oDBK change drastically and correspond to conditions of radical segregation or dilution (Figure 5c). No spin-spin exchange is noticed under these circumstances even though the same amount of radical is deposited on the surface. The spectrum with 5% oDBK and a ratio oDBK:Tempo = 1:1 is complex in detail as it shows up to three components with different motion conditions. Two of these are characteristic of fast motion ($t \sim 5x10^{11}\ s^{-1}$). The isotropic hyperfine coupling evaluated for these two species (15.0 G and 15.6 G) are consistent with environments of low polarity as expected for radicals surrounded by ketone molecules. The third absorption component is distinctive of slow motion condition ($t \sim 8 \times 10^9\ s^{-1}$) and can be attributed to radicals interacting with the zeolite surface.

At an intermediate stage, the spectrum obtained with 5% pDBK and a molar ratio pDBK:Tempo = 1:1 is still characteristic of spin-spin interactions such as those of the samples containing Tempo alone (Figure 5b). However, both Heisenberg spin exchange and dipolar broadening contribute to the spectral features. By diluting Tempo with respect to the free ketone (pDBK:Tempo = 5%:0.01%) the radical clearly partitions in two different environments. A small percent (~10% as obtained by integration) corresponds to the fast motion contribution. A second component corresponds to radicals in slow motion conditions attributed to the radical interacting with the zeolite surface. These results can be interpreted in terms of a distribution of pDBK between the internal and external zeolite surfaces as expected for the amount of ketone used.

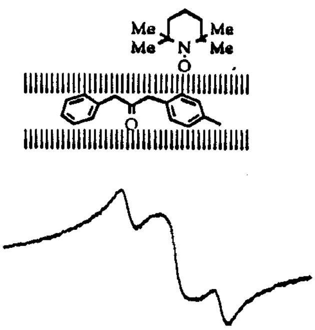


Figure 7. EPR Spectrum of Tempo on LZ-105 saturated with pDBK after desorption of the latter from the external surface.

The spectrum shown in Figure 7 was obtained with a sample of LZ-105 saturated with intracrystalline pDBK and then washed to eliminate the externally bound component. In agreement with our interpretations, the spectral changes observed with this sample are consistent with an increase in the spin-spin exchange rate that results from a smaller ketone occupation on the external surface.

CONCLUSIONS

The partition of molecular adsorbates within the internal and external surfaces can be detected qualitatively both by NMR and EPR spectroscopies. The combined used of these techniques may offer a wealth of information concerning the dynamics and distribution of probes on the zeolite surfaces.

Acknowledgments

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