

Dual Behavior of ZSM-5 as Brønsted Acid and Electron Acceptor in the Adsorption of *N,N'*-Diphenylhydrazine

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Incorporation of *N,N'*-diphenylhydrazine into HZSM-5 led to the formation of azobenzene and aniline (70–80 mol-% mass balance). The formation of azobenzene can be followed by the appearance in diffuse reflectance UV/Vis spectroscopy of a characteristic band ($\lambda_{\text{max}} = 420 \text{ nm}$). IR spectra of the extracted solids indicate that some aniline is retained in the zeolite, probably due to acid-base interaction with active sites. The products are rationalized by two competing mechanisms: the formation of azobenzene by electron

transfer to an oxidizing site, the generation of aniline by proton transfer from a Brønsted acid site. A long-wavelength diffuse-reflectance band ($\lambda_{\text{max}} = 800 \text{ nm}$) in the initial stages of the reaction supports the intermediacy of a radical cation. These results show that acid zeolites can exhibit a dual behavior against basic substrates with low oxidation potential, serving simultaneously as electron acceptor and Brønsted acid.

Introduction

The structures and catalytic properties of zeolites have been extensively investigated as prototypes of acidic industrial catalysts. Zeolites were first introduced as catalysts for large-scale gas-phase reactions in petrochemistry. Compared to conventional liquid acids these materials showed significant advantages for processes such as cracking, aromatic isomerization, or disproportionation because of easy separation of the reaction mixture, reactor design, control of the reaction outcome, shape selectivity, and the possibility to regenerate the catalyst after deactivation.^[1] The results of these gas-phase reactions triggered intense research aimed at developing the potential of zeolites for general acid-catalyzed organic reactions in the liquid phase under batch conditions. During the past two decades an ever-increasing volume of research has been carried out, promoting the use of zeolites as solid catalysts for organic reactions in the liquid phase, e.g. in the production of fine chemicals under environmentally benign conditions. As a result of these studies, heterogeneous catalysis of organic reactions by zeolites is a mature field.^[2–6]

One of the most intriguing properties of acid zeolites is their ability to generate spontaneously organic radical cations upon adsorption of electron-rich organic molecules.^[7] Spontaneous generation of organic radical cations upon adsorption of organic electron-donors into acid zeolites is well documented. Within the pores of the zeolite, the radical cations are protected from reagents that typically would cause

their decay in solution; accordingly, they have increased lifetimes and can be studied by conventional spectroscopic techniques. Furthermore, the limiting geometry of the zeolite pores may manifest itself in two ways: a) it may restrict the geometry of the sequestered intermediates; and b) it may selectively incorporate substrates with suitable geometries. Thus, radiolysis of *n*-hexane and *n*-octane in pentasil zeolite only generated the extended radical cations.^[8] Likewise, diaryl disulfides or diselenides gave rise selectively to “extended” sulfur- or selenium-centered radical cations.^{[9][10]} On the other hand, *trans*-1,2-diphenylcyclopropane was incorporated readily into ZSM-5 (and oxidized within its pores) whereas the *cis* isomer failed to be incorporated.^[11]

The majority of studies in this area are focused on the spectroscopic characterization of the persistent radical cation species; the application of zeolites to trigger electron-transfer (ET) mediated reactions has received comparatively little attention, in contrast to the interest that other chemical and photochemical ET promoters have attracted. For example, the ET reactions of cyanoaromatics,^[12] triphenylpyrylium ion,^[13] or tris(4-bromophenyl)ammonium ion^[14] have been studied in detail.

In one of the few preparative studies on zeolites, Bauld and co-workers found that 1,3-cyclohexadiene undergoes dimerization to the corresponding Diels–Alder adducts in the presence of NaX on a preparative scale.^{[15][16]} 1,3-Cyclohexadiene is an excellent probe molecule to differentiate ET processes since the product distribution changes with the operating reaction mechanism;^{[17][18]} the formation of Diels–Alder (*endo*) adducts is typical for ET-induced dimerization of this substrate. Another recent example of an ET-induced conversion on a zeolite is the dehydrogenation of 4-propylanisole upon adsorption on pentasil zeolite which generates propenylanisole (anethole) radical cation, a process that formally involves the loss of three electrons and two protons.^[19]

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The electron acceptor ability of zeolites has been attributed to the presence of acid sites, although a controversy seems to persist regarding the (Lewis or Brønsted) nature of the active site. Brønsted acid sites are associated with bridged $\equiv\text{Si}(\text{OH})\text{Al}\equiv$ hydroxy groups, whereas Lewis sites are due to octahedral oligomeric and polymeric nonframework positive aluminate clusters of the general composition $\text{Al}_n(\text{OH})_x\text{O}_y^{[3n-x-2y]+}$.^[20] These are generated by migration of tetrahedral framework Al out of the crystal lattice. Therefore, substrates having electron lone pairs as well as a low oxidation potential may have two alternative pathways available, initiated by electron or proton transfer. However, examples showing the simultaneous operation of these two pathways are scarce.^{[21][22]}

In this paper we report the conversion of *N,N'*-diphenylhydrazine (DPH) to azobenzene (AB) upon adsorption onto acid H-ZSM-5; herein, the dehydrogenation product is accompanied by a reduced bond-cleavage product, aniline (AN). Diffuse reflectance optical spectroscopic results lead us to suggest that $\text{DPH}^{+\bullet}$ is an intermediate in the formation of AB.

Results

Inclusion of DPH into H-ZSM-5 was carried out by adsorption from organic solutions or by heating a mixture of solid DPH and hydrated H-ZSM-5 progressively to 150°C. With both procedures, the zeolite turned yellow, indicating that a chemical reaction was taking place. The inclusion of DPH from solution was essentially complete, judging by the depletion of DPH in the supernatant solution. This conclusion was confirmed by combustion analyses of the dried, filtered, and degassed zeolite: The C/N ratio corresponded to that of DPH. Exhaustive solid-liquid extraction of the yellow solids yielded a reaction mixture consisting of AB and AN accompanied by minor amounts of unchanged starting material (70–80 mol-% recovery; Table 1).

Table 1. Products obtained by liquid extraction of HZSM-5 after incorporation of DPH

Method of loading	Mass balance ^[a] [%]	Product distribution ^[b]		
		DPH	AB	AN
Solution	70	—	30	70
Solid phase	75	13	59	23

^[a] $\Sigma[\text{DPH} + \text{AB} + (\text{AN}/2)]/\text{DPH}_0$, where DPH, AB and AN are the molar quantities of each product in the extract and DPH_0 is the initial quantity of DPH. The product distribution was corrected to take into account the initial amount of 12% AB in the commercial sample of DPH used in this work. — ^[b] Product yield = mass balance $\times$ percentage in the product distribution.

Diffuse reflectance UV/Vis spectroscopy (DR) of the yellow loaded zeolite samples showed a new band, $\lambda_{\text{max}} = 420 \text{ nm}$ (Figure 1) which coincides with that of AB in dichloromethane; apparently, AB is formed within the zeolite. While this band is ultimately observed regardless of the in-

clusion procedure, the solid mixture of the reagents showed an additional DR band, $\lambda_{\text{max}} = 800 \text{ nm}$, at an intermediate stage, which disappeared upon further heating (Figure 1).

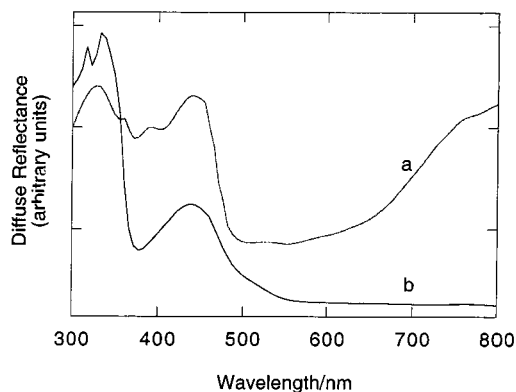


Figure 1. Diffuse reflectance spectra (plotted as the inverse of reflectance, $1/R$) of HZSM-5 zeolite after incorporating *N,N'*-diphenylhydrazine (b) and in the early phase of heating the two solids (a) ground together in a mortar

A complete mass balance is vital to determine the true product distribution of a chemical reaction in a heterogeneous medium; products retained in the solid (and not accounted for) can distort or veil the true outcome of the reaction. Determining mass balances in zeolites has inherent inaccuracies. However, in the case of DPH, the fraction of material not recovered by solid-liquid extraction far exceeds any experimental error (Table 1). A significant amount of organic material is retained in the solid. IR spectra of the solid after degassing (Figure 2, b) showed bands ($1638, 1618, 1583 \text{ cm}^{-1}$) characteristic for AN (Figure 2, c). The presence of DPH (spectrum not shown) or benzidine (bands at $1608, 1537 \text{ cm}^{-1}$)^[21] are clearly ruled out. Apparently, extraction of the zeolite recovers AB almost completely whereas a significant portion of AN is retained by the acid zeolite sites. The preferential retention of AN reflects its greater basicity compared to the azo compound.

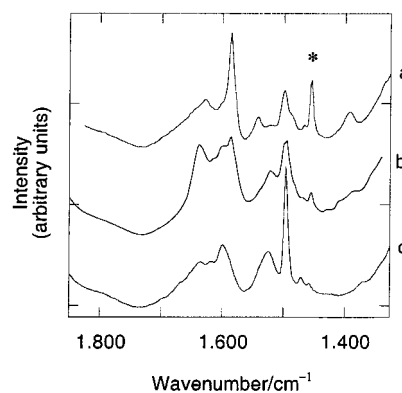
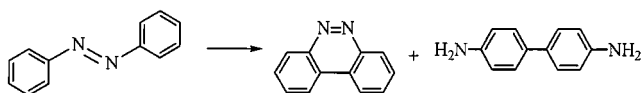


Figure 2. IR spectra of HZSM-5 samples after adsorption of *N,N'*-diphenylhydrazine on HZSM-5 (a), after exhaustive solid-liquid extraction (b), and of pure aniline (c), respectively, adsorbed on HZSM-5; the most characteristic band corresponding to AB (spectrum not shown) is indicated with an asterisk

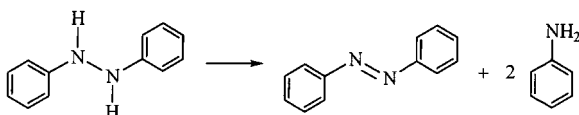
Discussion

The fate of DPH upon incorporation into the zeolite may at first appear surprising because strong acids are known to cause rearrangement of DPH to benzidine,^[23] and HZSM-5 is a solid acid whose acid strength at room temperature is comparable to 75% aqueous solution of H₂SO₄.^[20] The benzidine rearrangement may have been expected also because benzidine was obtained previously as a product of AB in an acid zeolite.^[21] Irradiation of *cis*-AB sequestered in HY-100 faujasite pores resulted in cyclization/dehydrogenation to benzocinnoline and reduction/rearrangement to benzidine.^[21] On the other hand, the limited size of the pentasil zeolite channels (straight elliptical, $5.2 \times 5.7 \text{ \AA}^2$, or sinusoidal channels with nearly circular diameter, ca. $5.5 \times 5.5 \text{ \AA}^2$)^[24] may prevent the “folding” of protonated DPH, which is a prerequisite of the rearrangement. In fact, irradiation of *cis*-AB in the more limiting HZSM-5 did not generate benzidine.^[21] In view of these considerations it is not surprising that the reaction of DPH on HZSM-5 took an alternative course, generating AB (revealed by the 420 nm DR band and product analysis) and AN (supported by product analysis and IR spectroscopy). Benzidine clearly can be eliminated as a product retained in the zeolite by comparison with the IR spectrum of an authentic sample of benzidine adsorbed on HZSM-5.^[21]



Scheme 1. Products obtained upon irradiation of *cis*-azobenzene in HY-100 faujasite

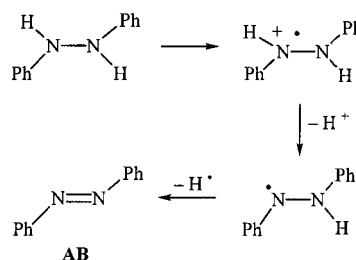
Similar to the irradiation of *cis*-AB in HY-100 faujasite the products isolated from incorporation of DPH into HZSM-5 formally correspond to a disproportionation reaction. However, the recovered product distribution (Table 1) does not support the required stoichiometry; the molar ratio, AN/AB, falls short of the required value of 2, even when taking into account the incomplete material recovery and assuming that AN is the only product retained in the zeolite. To account for the excess AB (Table 1) a competing oxidation mechanism is required, at least to some extent.



Scheme 2. Products obtained upon incorporation of *N,N'*-diphenylhydrazine into HZSM-5

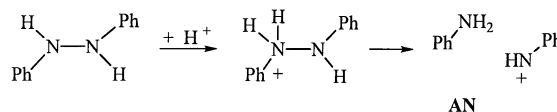
Alternatively, the two products, AB and AN, could be explained by two competing primary reactions. For the formation of AB we envisage electron transfer from DPH to the Lewis sites of HZSM-5. The intermediacy of the resulting radical cation, $\text{DPH}^{\bullet+}$, in the oxidation/dehydrogenation reaction is supported by a transient DR band at 800 nm in the initial stages of the reaction (Figure 1, a); the appearance of long-wavelength absorptions in the visible or

near-IR is typical for radical cations as a consequence of their open shell configuration.^[25] The radical cation, $\text{DPH}^{\bullet+}$, can be deprotonated and the resulting free radical generate AB by loss of an additional hydrogen atom (Scheme 3). There is ample evidence that acid sites in HZSM-5 can function as single electron acceptors;^[9–11,19,26–28] dehydrogenation in zeolites likewise has precedent.^[9,11,19,28] At the low loading levels typical for these experiments, the transfer of the electron, proton, or the hydrogen atom to the ZSM-5 matrix does not cause any noticeable changes in the zeolite. The electron will deactivate the Lewis sites by reducing the nonframework aluminates clusters, $\text{Al}_n(\text{OH})_x\text{O}_y^{[3n-x-2y]+}$ which are characterized only indirectly (vide infra).



Scheme 3. Mechanism proposed to rationalize formation of azobenzene from *N,N'*-diphenylhydrazine in HZSM-5

The competing pathway leading to AN may proceed by proton transfer from the Brønsted acid sites of the zeolite ($\equiv\text{Si}(\text{OH})\text{Al}\equiv$) to DPH. The resulting hydrazonium ion may undergo N–N bond cleavage. Formation of a dication, the key intermediate of the benzidine rearrangement in solution, is less likely. The low density of Brønsted acid sites within the zeolite (Si/Al ratio 34) does not appear to favor double protonation. Moreover, even if the dication were formed, the restrictive environment of ZSM-5 would likely frustrate the “folding” required for the benzidine rearrangement (vide supra). These considerations suggest that bond cleavage may be preferred.



Scheme 4. Mechanism proposed to rationalize formation of aniline from *N,N'*-diphenylhydrazine in HZSM-5

The mechanism proposed here, competing mechanisms with two different primary intermediates generated at two types of active sites, readily account for all observed features. In media other than zeolites, there is ample precedent for the quantitative oxidation of DPH to AB using various mild oxidizing agents, including atmospheric oxygen;^[28] the converse reductive N–N cleavage is less common.

In the context of competing mechanisms in zeolites, the photoreaction of *cis*-AB was discussed as a formal disproportionation.^[21] This reaction generated benzocinnoline, a (cyclized) dehydrogenated product, along with benzidine, a hydrogenated one. On the other hand, the zeolite-induced

conversion of 1,1-diphenylethylene was ascribed to dual pathways initiated at different sites.^[22]

The conclusion that the divergent products are generated by different ZSM-5 sites suggests the interesting experiment to determine the product distribution obtained with a series of ZSM-5 samples containing exclusively Brønsted or exclusively Lewis sites. However, this intriguing experiment has not been possible to date. Although ZSM-5 is a synthetic zeolite and considerable progress has been achieved in the control of its synthesis, all zeolite batches characterized to date contain both Brønsted and Lewis sites.

Conclusion

Adsorption of DPH onto HZSM-5 generates AB and AN. Although these products are formally compatible with disproportionation, they are ascribed to two competing processes, involving electron transfer from DPH to the oxidizing sites of HZSM-5 and proton transfer from Brønsted acid sites to DPH. DR spectroscopy provides sound evidence for the initial ET. Dehydrogenation with formation of C=C bonds had been observed previously upon adsorption of *p*-(*n*-propylanisole) in acid zeolites.^[19]

Experimental Section

General Remarks: A commercial sample of DPH (Aldrich) was used as received; this sample contained an initial amount of 12% of AB. H-ZSM-5 was obtained by deep-bed calcination (600°C, air stream) of an as-synthesized tetra-*n*-propylammonium pentasil zeolite (*n*Pr₄N-ZSM-5) prepared according to the patent literature.^[30] Degradation of the quaternary ammonium ion readily affords the protonated form of ZSM-5 (Brønsted acid sites); however, this type of thermal treatment also generates Lewis acid sites arising from partial framework dealumination. The H-ZSM-5 batch used in the present work was characterized by chemical analysis and by the pyridine adsorption-desorption method. The chemical analysis showed a Si/Al ratio of 34:1; the IR-spectroscopic analysis of pyridine-loaded zeolite samples may identify Brønsted as well as Lewis acid sites by the presence of aromatic bands distinctive of the protonated (pyridinium ion, ca. 1550 cm⁻¹) or Lewis adduct (coordinated Lewis adduct, ca. 1450 cm⁻¹). The relative intensity of these bands can serve to quantify the population of each type of site, whereas the decrease in their intensity with increasing desorption temperature serves to determine their relative acidity.^[20,31–33] The IR analysis (Figure 3) shows the presence of strong Brønsted as well as Lewis sites in the H-ZSM-5 batch used in the present work.

Adsorption Procedure: Two alternative procedures were used to incorporate DPH into H-ZSM-5, either adsorption from isooctane or dichloromethane solution (50°C) onto thermally dehydrated zeolite (500°C, overnight) or heating a mixture of solid DPH and hydrated H-ZSM-5, grinding together in a mortar, progressively to 150°C under nitrogen for 30 min.

Combustion analysis of the loaded zeolite indicated that no solvent was retained in the solid. The loaded zeolite was extracted with dichloromethane in a micro-Soxhlet apparatus and the extract analyzed by GC (Hewlett-Packard 5890, 25 m capillary column of 5% phenylmethylsilicone) and GC-MS (Varian Saturn II). The solvent

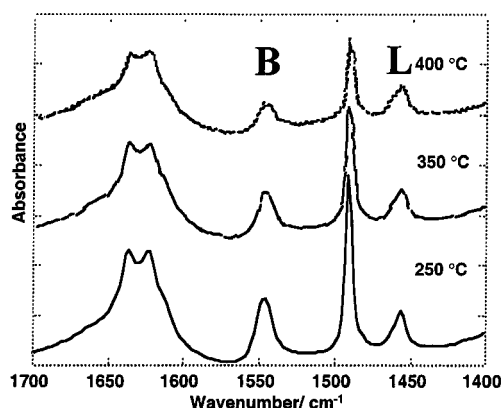


Figure 3. FT-IR spectra of pyridine retained after vapor-phase adsorption at room temperature onto dehydrated H-ZSM-5 and subsequent desorption by heating successively at 250, 350, and 400°C under 10⁻¹ Pa for 1-h periods; the bands characteristic for Brønsted and Lewis sites are designated by letters B and L, respectively

was removed under reduced pressure, the residue weighed, and the product distribution quantified by integration of the corresponding ¹H-NMR signals (Varian Gemini 300 MHz, CDCl₃; TMS as internal standard). DR spectra of the solids were recorded with a Cary 5G spectrophotometer using a praying mantis attachment. IR spectra of self-supported wafers (10 mg, prepared by compressing zeolite powders at 1 Ton × cm⁻²) were recorded with a Nicolet 710 FTIR spectrophotometer using a greaseless cell with CaF₂ windows. The samples were degassed under 10⁻² Pa for successive 1-h periods at 25, 100, 200 and 300°C before recording the IR spectra at ambient temperature.

Acknowledgments

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