

Electrochemical Evidence for an Impeded Attack of Water at Anthracene and Thianthrene Radical Ions Located on the Outermost Layers of Zeolites

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Received December 28, 1998

Introduction

Reactive organic intermediates incorporated within the voids of microporous solids may undergo a remarkable stabilization, increasing enormously their persistence.^{1–4} The increased lifetime of these reactive species is rationalized as arising from the geometrical restrictions caused by the tight fit of the organic species adsorbed inside the zeolite pores. The rigid, inert reaction cavity provided by the zeolite structure is thought to protect the organic guest, impeding the approach of external reagents in the appropriate direction to interact effectively with the reactive centers of the adsorbed species.^{3,4}

This rationalization generally assumes that the guests are completely embedded inside the zeolite particle. However, the question of the specific reactivity of the fraction of guests that are deposited on the cracks and crevices of the external surface or located at the entrances of the pores partially penetrating inside the particle is frequently not addressed.

In the present work we report that the electrochemical oxidation and reduction of anthracene (AN) and thianthrene (TH) incorporated within pentasil and mordenite zeolites in the presence of H₂O shows a distinctive pattern, indicating that the electrochemically generated radical ions located at the outermost layers of the zeolite particles experience an effective protection against the attack of external reagents.

Results and Discussion

Electrochemical techniques specifically probe the fraction of electroactive guests located at the external or at the outermost internal surface of the particles.^{5,6} Owing to the comparatively slow intracrystalline diffusion of the electrolytes with respect to the fast electrochemical measurement, it is known that the population of adsorbed

guests that have penetrated deeply within the pores cannot be tested in the electrochemical experiments. Therefore, electrochemistry of zeolite-modified electrodes (ZMEs) is a valuable tool to gather information exclusively about the particular reactivity of those guest molecules located at the very shallow boundary between the external and internal surfaces.

It should be noted that adsorption of AN and TH in ZSM-5 and mordenite is expected to lead to a statistical distribution of adsorbates among the external and internal (channels and cavities) surfaces. Previous reports showing that AN and TH can be adsorbed inside the pores of ZSM-5 and mordenite can be found in the literature.^{7–10} However, the electrochemically active guests would be solely those located at the cracks and crevices of the external surface plus those others which are fully inside the voids but not far from the entrance (i.e. those that can be reached by the electrolyte during the time scale of the experiment).

Electrochemical oxidation of AN and TH in solution are among the most comprehensively studied in classical organic electrochemistry.^{11,12} Both AN and TH have in essence a common behavior. In aprotic solvents under strict anhydrous conditions cyclic voltammetry (CV) exhibits two reversible monoelectronic waves. The first oxidation peak corresponds to the generation of radical cations which at higher potentials undergo a second monoelectronic oxidation to form their dication (Scheme 1). However, the presence of water or other nucleophiles in the solvent intercepts the primary AN^{•+} or TH^{•+} radical cations, giving rise to hydroxylated AN–OH[•] or TH–OH[•] radicals (Scheme 1), which eventually would form AN=O and TH=O oxides as final products. Therefore, the CVs change in the presence of water and a single oxidation peak involving two or more electrons is recorded. This is the case of the CV of AN and TH in DMF/H₂O (98/2), wherein a single oxidation wave indicative of the trapping of the radical cations by H₂O is recorded (Figure 1, plot A). As the result of this trapping, AN=O is electrochemically generated during the anodic part of the scan, giving rise subsequently to the appearance of a reversible cathodic peak observed at –0.25 V vs SCE.

In contrast to the CV for the homogeneous phase, the electrochemical response of the zeolite-modified electrodes (ZMEs) containing AN under the same conditions gives two separate anodic waves (Figure 1B). All the ZMEs containing AN exhibit the same behavior independent of the zeolite tested, and no relevant variations in the potentials and relative peak intensity were observed (Table 1). The apparent lack of influence of the Si/Al ratio and pore size of the zeolite could be anticipated, considering that in the present electrochemical study the zeolites are playing a passive role, providing a rigid microporous matrix in which the electroactive

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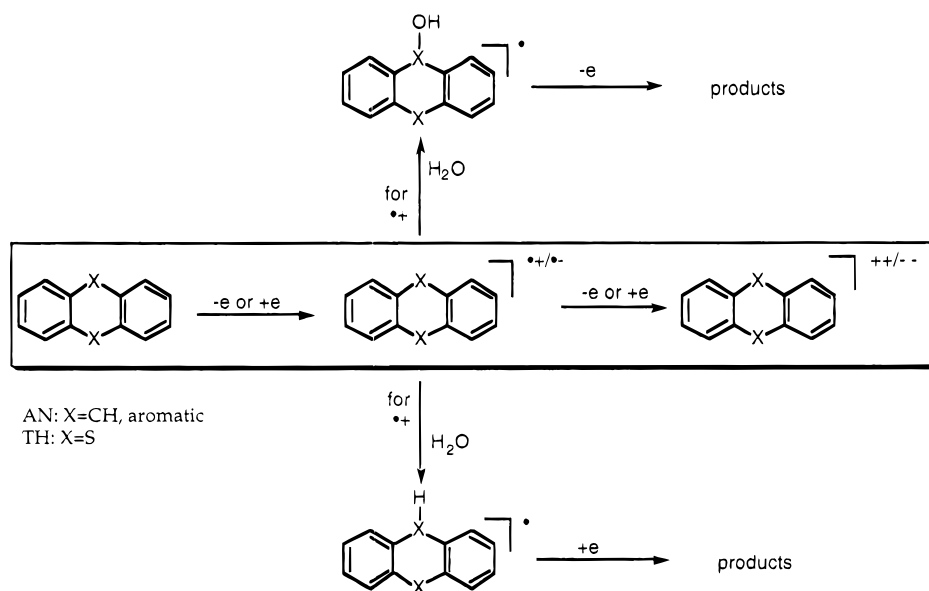
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Scheme 1. Simplified Scheme for the Oxidative and Reductive Processes of AN and TH^a

^a The pathways highlighted inside the frame take place when H₂O does not quench the corresponding radical ions; they appear in CV as two consecutive mono-electronic steps.

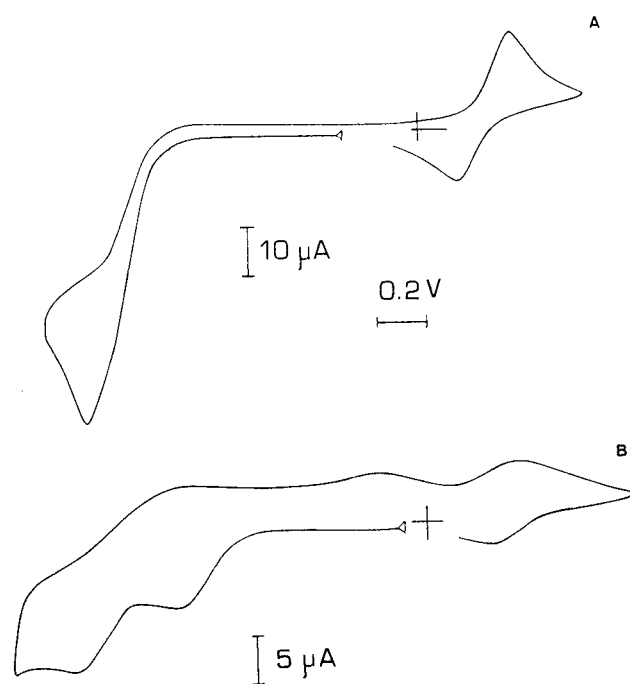


Figure 1. CVs corresponding to AN in DMF/H₂O (98:2) using *n*-Bu₄NPF₆ (0.10 M) as the supporting electrolyte: (A) AN in homogeneous solution (1.5 mM); (B) carbon-paste ZME of AN adsorbed in mordenite. The scan rate was 150 mV s⁻¹.

guests are accommodated but not participating actively in the electron-transfer process.^{13–15}

The appearance and oxidation potentials of the anodic part of the CV of ZMEs correspond to those recorded in anhydrous solution. Therefore, we interpret this result as indicating that at least a portion of the AN located at

Table 1. Oxidation Potentials from DPV Data for AN and TH Measured in Solution and in Polymer Film ZME in Contact with DMF Using Et₄NClO₄ (0.10 M) as Electrolyte^a

sample	<i>E_p</i> anodic ^b (mV vs SCE)	
	neutral → (•+)	(•+) → (2+)
AN solution	+1165	+1500
AN-mordenite	+1170	+1615
AN-ZSM-5	+1175	+1600
TH solution	+1175	+1690
TH-mordenite	+1185	+1710
TH-ZSM-5	+1180	+1685

^a Conditions: potential scan rate, 20 mV s⁻¹; pulse width, 10 mV. ^b The presence of water gives rise to the appearance of additional oxidation peaks; two in the case of AN appearing around +1700 and +1900 mV vs SCE and one at about +1890 mV vs SCE for TH.

the outermost layers of the zeolite grains are not trapped by H₂O at this concentration and undergoes two consecutive mono-electronic oxidations to form AN^{•+} and AN²⁺, respectively (Scheme 1). However, in the cathodic part of the CV following the initial oxidation of AN, two peaks appear, indicating that some byproducts have been generated by H₂O trapping during the oxidation steps.¹⁶ In agreement with this interpretation, Figure 2 shows that when the CVs of ZMEs containing AN are recorded in pure H₂O, a single oxidation wave (analogous to that shown in Figure 1A for the DMF/H₂O solution) is then observed. This electrochemical experiment in pure water indicates that the generated AN^{•+} is not perfectly protected from the H₂O attack, although this attack is, however, notably more impeded on the zeolite surface than in solution.

(13) For previous reports showing that the acid sites of the zeolites can play an active role in the oxidation of TH, see ref 14 and 15.

(14) Corma, A.; Fornés, V.; García, H.; Martí, V.; Miranda, M. A. *Chem. Mater.* **1995**, *7*, 2136–2143.

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(16) The equilibrium potentials of the cathodic peaks appearing after the initial oxidation of AN adsorbed in zeolites and the subsequent trapping with water were measured at +0.30 and -0.25 V vs SCE (Figure 1B). The latter peak can be assigned to the reduction of AN=O on the basis of comparison of the potential with that observed for AN=O in solution (Figure 1A). However, the reduction occurring at +0.30 V vs SCE is not observed in solution and has to correspond to a process exclusively occurring at the zeolite surface.

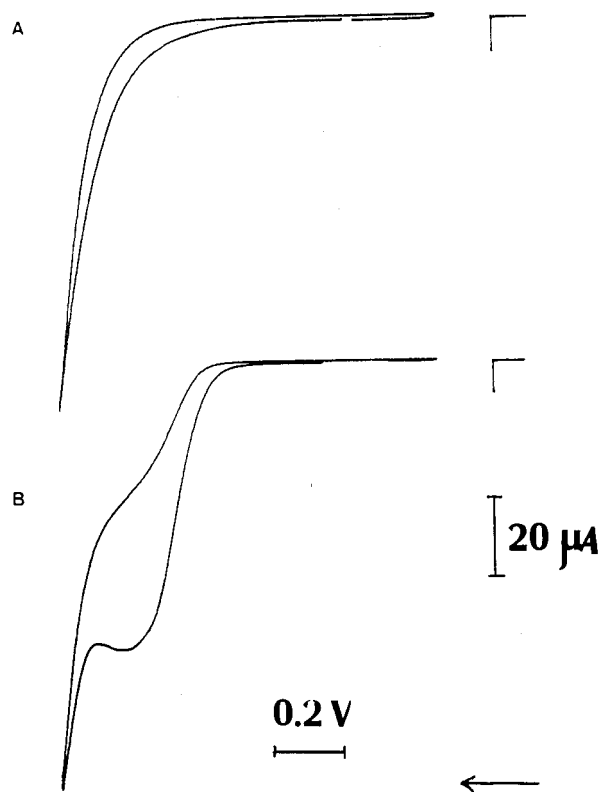


Figure 2. CVs for a carbon-paste ZME immersed in a 0.15 M aqueous solution of NaClO_4 : (A) baseline of the carbon-paste ZME electrode; (B) electrochemical response of the same type of electrode but containing AN incorporated in mordenite.

Blank controls were undertaken to prove that the observed electrochemical response corresponds to guest molecules located on the zeolite particles and not to those molecules that could have migrated into the graphite paste or the electrolyte solution. Thus, the electrochemistry of solid AN and TH (no zeolite) used as modifiers of carbon-paste and polymer-film electrodes or directly deposited on the basal glassy-carbon electrode is almost identical with that recorded in solution.

Two pieces of evidence support the notion that the CV experiments of ZMEs report on the fraction of AN located at the outermost layers of the zeolite grains and that they experience a certain degree of spatial constraint. First, the maximum Coulombic charge uptake in these experiments (estimated from the peak area in the CV of ZME at 20 mV s^{-1} scan rate) was 1.24×10^{-9} mol of electrons, which is a minor fraction of the total 1.1×10^{-6} mol of AN present in the ZME. Second, the electrochemical response of the AN/NaZSM-5 sample decreases 1 order of magnitude when tetrabutylammonium instead of tetraethylammonium is used as the supporting electrolyte. The influence of the supporting electrolyte cation size on the CV of ZME is generally interpreted as indicating that the electrochemical process is subject to some spatial restriction.⁵

The electrochemistry of TH parallels that of AN. Thus, in strictly anhydrous aprotic solvents the electrochemical oxidation of TH occurs in two consecutive one-electron steps, corresponding to the formation of TH^+ radical cation and TH^{2+} dication, respectively (Scheme 1). This behavior is illustrated by the differential pulse voltammetry (DPV) shown in Figure 3A corresponding to an acetonitrile solution of TH in the presence of alumina,

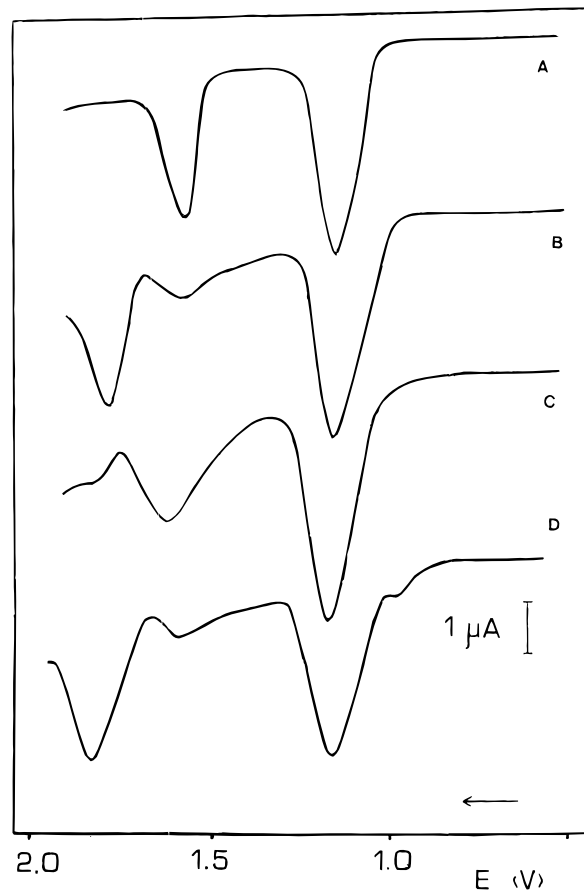


Figure 3. DPVs of a TH solution (1.0 mM) in acetonitrile using Et_4NClO_4 (0.10 M): (A) in the presence of alumina; (B) same as (A) but in the absence of alumina using routinely dried acetonitrile containing minor amounts of residual water; (C) Paraloid film ZME containing TH adsorbed in mordenite immersed in a $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ (98:2) solution having Et_4NClO_4 (0.10 M) as electrolyte; (D) solid TH (no zeolite) deposited on the glassy-carbon electrode under conditions identical with those in (C). The potential scan rate was 20 mV s^{-1} and the pulse width 10 mV.

wherein two anodic peaks at +1.18 and +1.68 V vs SCE can be seen. In the presence of water or other nucleophiles, trapping of electrochemically generated intermediates derived from TH distorts this electrochemical response. Thus, minor amounts of residual water existing in not completely anhydrous solvents are sufficient to react rapidly with most of the TH^+ to form $\text{TH}=\text{O}$, which subsequently oxidizes at a more positive potential. The effect of water can be seen in Figure 3B, where the anodic peak at +1.68 V vs SCE is replaced almost completely by a peak at +1.82 V vs SCE, indicative of the formation of $\text{TH}=\text{O}$. These DPV experiments in solution are fully consistent with the results reported in the literature.¹⁷

In contrast, upon immersion of ZMEs containing TH into wet acetonitrile solutions, the voltammetric DPV pattern resembles closely that recorded in solution under strictly anhydrous conditions (Figure 3C). Thus, even in the presence of water, the very intense anodic peak at +1.65 V vs SCE indicates that the $\text{TH}^+ \rightarrow \text{TH}^{2+}$ oxidation is still the predominant process on the particle surface. Therefore, it can be concluded that TH on the zeolite

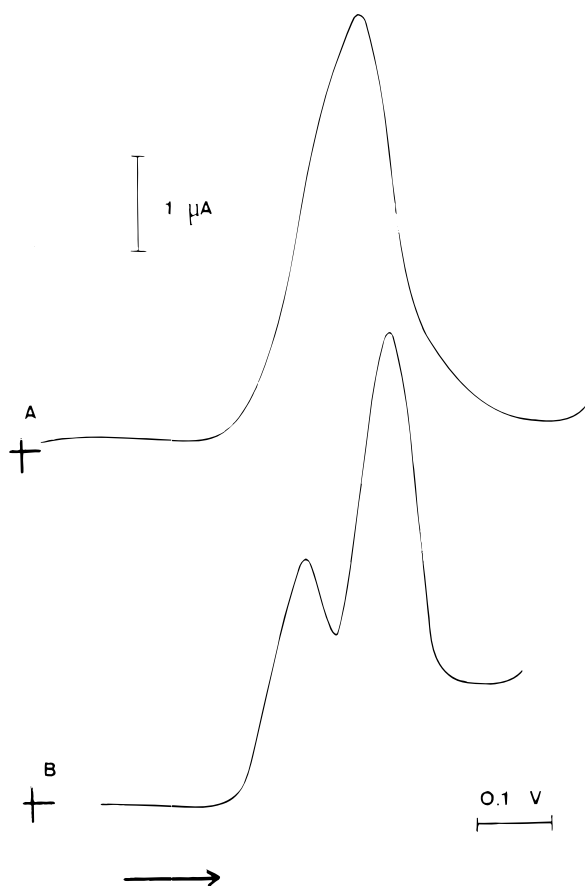


Figure 4. DPVs measured in DMF/H₂O (98:2) using Et₄NClO₄ (0.10 M) as electrolyte: (A) TH in the solution phase (2.0 mM); (B) Paraloid film ZME containing TH incorporated in mordenite.

external surface is experiencing an effective protection against the attack of water.

To provide further support to this conclusion, the electrochemistry of modified electrodes of zeolites not containing AN or TH, but immersed in AN or TH solutions, was also investigated. As shown in Figure 3D, the electrochemical response of this control experiment is similar to that obtained in solution (without any zeolite in the electrodes) but clearly differs from that recorded for ZMEs containing AN or TH previously incorporated within the zeolite (Figure 3C).

To complete our study, the electrochemical reductions of ZMEs containing AN and TH were also carried out. In strictly anhydrous aprotic solvents, the electrochemical reduction pathways of AN and TH parallel that of the oxidation. Thus, we observe two consecutive reversible mono-electronic peaks corresponding to the primary generation of AN^{•-} or TH^{•-} and their subsequent reduction to the AN²⁻ or TH²⁻ dianion, respectively. The presence of protic solvents causes protonation of the radical anions, resulting in the formation of neutral AN-H[•] and TH-H[•] free radicals, whose reduction potential is close to that of the neutral arene (Scheme 1), thus, merging in a single peak. As a result, in aprotic solvents containing water only one reduction peak is observed near to -1 V vs SCE. This can be seen in the DPV of Figure 4A, corresponding to a solution of TH in DMF/H₂O (98/2). In contrast, using the same solvent and conditions, the DPV of a ZME containing TH exhibits two separated cathodic peaks

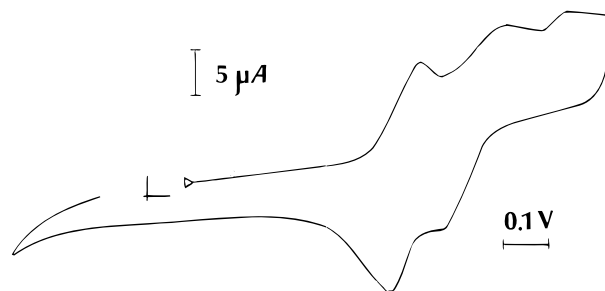


Figure 5. CV of a carbon-paste ZME containing AN adsorbed in ZSM-5 using NaClO₄ (0.15 M) as the supporting electrolyte. The potential scan rate was 150 mV s⁻¹.

(Figure 4B). As expected, a ZME containing AN shows the same electrochemical pattern as TH for the reduction.^{18,19}

Our data indicate that the proton transfer resulting from the attack of water on surface-confined AN^{•-} and TH^{•-} radical anions generated electrochemically is sufficiently slow in the time scale of the electrochemical experiments to allow quasi-reversible electrochemical reduction processes. This behavior occurs even when the ZMEs are in contact with pure water. This fact sharply contrasts with solution electrochemistry where the quenching of the radical anions by water is complete under these conditions. Thus, Figure 5 shows the CV of a AN-containing ZME immersed in an aqueous solution, wherein two reversible couples at -0.75 and -0.95 V vs SCE equilibrium potentials can be clearly seen.

In conclusion, the electrochemical data presented for the oxidation and reduction of AN and TH under conditions in which trapping of radical ions by H₂O occurs in solution indicates that even those probe molecules located at the shallow boundary between the exterior and interior of the zeolite particles are partially protected from the attack of external reagents. This effect probably arises from some degree of spatial constraints experienced by the guests adsorbed on the surface of microporous solids, suggesting that they are most likely partially penetrating through the pore entrances.

Experimental Section

For the present work, two different zeolites were used. Mordenite in its Na⁺ form was a commercial sample (P.Q. Industries). ZSM-5 was obtained by hydrothermal crystallization of silica and alumina gels using tetrapropylammonium as the structure-directing agent according to the patent literature.²⁰ The as-synthesized ZSM-5 sample was deep-bed calcined under an air stream up to 550 °C for 16 h to decompose the organic template. The resulting sample was then submitted to exhaustive ion exchange procedures using a 0.4–0.6 M aqueous solution of Na₂CO₃. The crystallinity and phase purity of the used ZSM-5 material were determined by X-ray diffraction using Cu Kα radiation. The SiO₂/Al₂O₃ ratios of the Na-mordenite and Na-ZSM-5 were 26 and 54, respectively, as measured by quantitative atomic absorption spectroscopy. The absence of residual Brønsted acid sites was assessed by room-temperature FT-IR measurements of the zeolites after exhaustive outgassing at 400 °C

(18) Owing to the negative charge of the zeolite framework, negatively charged species adsorbed on zeolites are very rare. However, some previous examples can be found in the literature. For a precedent in the photochemical generation of an organic radical anion, see ref 19.

(19) Scaiano, J. C.; Garcia, S.; Garcia, H. *Tetrahedron Lett.* **1997**, *38*, 5929–5932.

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under 10^{-2} Pa, where the lack of the characteristic vibration band at $\sim 3600\text{ cm}^{-1}$ corresponding to bridging hydroxyl groups was observed.¹⁴

Incorporation of AN (Aldrich, recrystallized from ethanol) or TH (Aldrich, used as received) within the zeolites after thermal dehydration ($500\text{ }^{\circ}\text{C}$, overnight) was accomplished by stirring the corresponding zeolite magnetically at room temperature with a CH_2Cl_2 solution (15 mL) of AN or TH (20 mg) for 30 min. The suspensions were then filtered and the solids dried at room temperature under reduced pressure for 2 h.

Two different types of ZMEs were used in this work. The first type, zeolite-modified carbon-paste electrodes, was prepared according to the procedure reported in the literature²¹ by mixing the zeolite powder (10 mg) containing AN or TH with graphite powder (10 mg) using paraffin oil (40 wt %) as a binder. The paste was placed onto the tip of a glassy-carbon electrode holder (3 mm diameter). For control experiments, modified electrodes containing AN and TH (no zeolite) were prepared by hand-mixing 5 mg of the organic solids with the carbon paste. Additional control measurements were carried out with modified carbon-paste electrodes of pristine zeolite (without AN or TH) soaked with and without an acetonitrile solution of AN or TH.

Alternatively, ZMEs were prepared as a polymer film. These polymer-film electrodes were obtained as originally reported by

(22) Ghosh, P. K.; Mau, A. W.-H.; Bard, A. J. *J. Electroanal. Chem. Interfacial Electrochem.* **1984**, *169*, 315.

(23) Kauffmann, J. M.; Montenez, T.; Vandenbalck, J. L.; Patriarche, G. I. *Mikrochim. Acta I* **1984**, 95–105.

Bard and co-workers.²² A few microliters of a dispersion of the zeolite in acetone (2 mg mL^{-1}) was deposited onto the surface of a freshly polished glassy-carbon electrode, allowing the coating to dry in air at room temperature. Then, 1 drop of a solution of Paraloid B72 (Rohm & Haas) in acetone (0.5 wt %) was added and the electrode was surface-dried. Paraloid provides a uniform thin film having good adherence and mechanical resistance.²³ For blank controls, modified polymer-film electrodes containing solid AN or TH without zeolite were prepared from a suspension of these arenes in ethanol.

CVs and DPVs were recorded using a conventional three-electrode cell under an Ar atmosphere. Experiments in aqueous solution were carried out with a saturated calomel reference electrode (SCE) in NaClO_4 (0.15 M). Experiments in nonaqueous media (acetonitrile, DMF) used *n*- Bu_4NPF_6 (0.10 M) and Et_4NClO_4 (0.10 M) as supporting electrolytes. To ensure strictly anhydrous conditions when required, the electrochemical measurements were performed in the presence of alumina (BASF, surface area $160\text{ m}^2\text{ g}^{-1}$). A platinum pseudo-reference electrode ($E = 0.02\text{ V vs SCE}$) was used. ZMEs were used as working electrodes, and a Pt wire was employed as the auxiliary electrode.

CVs were measured with a Newtronics 200P triangular wave generator and a HQ 101 potentiostat. DPVs were obtained with a Metrohm E506 Polarecord. The potential scan rate was varied from 10 to 500 mV s^{-1} , and pulse widths were varied from 5 to 20 mV.

JO9825153