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Prevalence of the external surface over the internal pores in the spontaneous generation of tetrathiafulvalene radical cation incorporated in the novel delaminated ITQ-2 zeolite

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Received 20th November 2000, Accepted 15th January 2001 First published as an Advance Article on the web 9th February 2001

ITQ-2 is a novel delaminated zeolite whose crystalline sheets (2.5 nm depth) define a large external surface $(\sim 720 \text{ m}^2 \text{ g}^{-1})$ having 12-membered ring (MR) open cups together with a reduced microporosity due to a 10 MR channel system. This feature is the reverse of that of classical zeolites (*i.e.*, much larger internal area compared to the external surface). Herein, we have used tetrathiafulvalene and triphenylamine to probe the capability of layered ITQ-2 zeolite to generate persistent organic radical cations compared to conventional Y, mordenite and ZSM-5 zeolites as well as to Al/MCM-41 (3.2 nm diameter) and amorphous silica–alumina. By selective silylation of the external cups, it has been found that formation of a significant concentration of persistent organic radical cations in ITQ-2 is a property that occurs within the open cups of the external surface rather than inside the 10 MR pores.

Introduction

The ability of acid zeolites to act as single electron acceptors and spontaneously generate significant amounts of radical cations upon adsorption of low oxidation potential organic compounds is well documented.¹⁻¹⁷ Although it is known that the oxidizing sites are related to the presence of Al and acid sites, their exact structure and location still remains to be fully understood. Both Brönsted and Lewis acid sites have been proposed as the electron acceptor sites of the zeolite. The activation treatment of the zeolite may play a role in the creation of these acid sites. In this regard, the higher ability of zeolites to generate persistent (sometimes indefinitely longlived) organic radical cations compared to amorphous silicaalumina and mesoporous MCM-41 has been suggested to be related to the microporous structure of zeolites and to the internal location of the generated radical cations.13,14 It has been proposed that the tight fit between the zeolite framework and the radical cation is the major factor responsible for the remarkable stability of these otherwise highly reactive species.14 When the host/guest dimensions are very close, the rigid zeolite framework protects the radical cation from the attack of oxygen, water or any external reagent.⁷ In this regard, zeolites will share with other solid acids the ability to spontaneously generate organic radical cations, but they will be unique in stabilizing these species by embedding them into their micropores.

Zeolites are widely used as solid acids in some important processes of the petrochemical industry and are being increasingly introduced for the production of specialty and fine chemicals.^{18,19} Furthermore, the use of zeolites as heterogeneous catalysts in general organic reactions is an active area of research.^{20,21} However, one of the major limitations that restricts the use of zeolites in catalysis is the narrow range of available pore sizes. Zeolites are classified as small,

medium, large and extra-large pore size depending on whether the number of TO_4 (T = Si or Al) of the smallest ring aperture is 8, 10, 12 or more, respectively.²² However, even for extralarge pore zeolites (over 12 TO₄ aperture) the pore dimension is below the nm range and obviously there are still numerous reagents and products that are too large to diffuse through their internal voids.

This has motivated an intense search for zeolitic materials that can overcome the pore size limitations of conventional microporous zeolites. In this regard, the synthesis of mesoporous MCM aluminosilicates has constituted a significant breakthrough.^{23–25} However, the poor hydrothermal stability $^{26-29}$ and the weak strength of the acid sites³⁰ have been two important drawbacks against the widespread use of mesoporous MCM aluminosilicates as catalysts. Recently, we have reported the preparation of a layered zeolitic material termed ITQ-2, obtained by delamination of the layered precursor of MCM-22 zeolite.31,32 ITQ-2 encompasses a large well structured accessible external surface area above 700 m² g^{-1} formed by 12 MR open cups, with a microporous system formed with a residual microporosity and small internal surface by a sinusoidal 10-membered ring channel (ca. 0.55 nm in diameter) parallel to the main plane of the layer (Fig. 1).

Obviously, the reports on the ability to generate organic radical cations are limited to the classical zeolitic families and they focus on the characterization, persistence and reactivity of the embedded organic radical cation. The aim of this article is to determine if the external surface of this material with 0.7×8.2 nm cups represents a well of potential and whether molecules adsorbed there can generate organic radical cations analogously to their generation in the channels of zeolites. The behavior of ITQ-2 has been compared with that of Y, mordenite MCM-22 and ZSM-5 zeolites as well as mesoporous Al/MCM-41 (3.2 nm diameter) and amorphous silica– alumina (25 wt.%). We have found compelling evidence for

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Fig. 1 Crystal structure of ITQ-2 showing the 2.5 nm layered structure encompassing open cups and the 10-membered ring channels running between the major planes of the layer.

the prevalence of accessible open cups on the external surface over internal micropores in the generation of persistent organic radical cations, provided that the organic donor can experience the presence of these potential wells.

Results and discussion

The main analytical and textural characteristics of the solids used in this work are collected in Table 1. Given that ITQ-2 micropores are 10-membered rings (~ 5.4 Å diameter), in this work we have used small tetrathiafulvalene (TTF) and large triphenylamine (TPA) as probe molecules. TTF would experience the electron acceptor sites located either in the channels or in the open cups. On the other hand, TPA (~ 12 Å) cannot be accommodated within the cups and, therefore, TPA would probe the external surface of ITQ-2 as a "flat" surface without potential wells and experience only a loose interaction.

TTF (E_{ox} ca. 0.5 V vs. SCE in acetonitrile) has been extensively used as the electron donor in numerous charge transfer complexes³³⁻³⁹ and in some of them the corresponding TTF⁺⁺ radical cation has been characterized by EPR and optical spectroscopy.^{33,40} However, in spite of this, as far as we know, this is the first report that uses TTF to probe the oxidizing sites in zeolites. Upon incorporation of TTF from dichloromethane solutions into thermally dehydrated mordenite, ZSM-5 and MCM-22 zeolites in their H⁺-form, the solids become brownish red. Diffuse reflectance UV-Vis spectroscopy of the powders after filtration indicates the formation of a new species characterized by two absorption bands at 440 and 580 nm (Fig. 2). This species was identified as monomeric

Table 1 Some relevant physicochemical parameters of the solid acids used in this work

	Si/Al ratio	BET surface area/m ² g ⁻¹	Crystal size /µm	Micropore volume /cm ³ g ⁻¹
ZSM-5	≈40	386	0.5–1	0.111
H-mordenite	10	423	0.05-0.3	0.170
Na-mordenite	6.5	356	0.1-0.5	0.155
NaY	2.6	654	0.2–1	0.303
HY	2.6	554	0.2–1	0.240
Al/MCM-41	13	874	0.1-0.3	0.46
SiO ₂ /Al ₂ O ₃	2.5	289	_	0.059
ITO-2	58	806 ^a	< 0.5	0.009
MCM-22	50	400^{b}	≈1	0.121

^a External surface area measured by N₂ isotherm adsorption of 706 $m^2 \ g^{-1} . \ ^b$ External surface area measured by N_2 isotherm adsorption of 82 $m^2 \ g^{-1} .$



Fig. 2 Diffuse reflectance UV-Vis spectra (plotted as the inverse of the reflectance, R) of zeolite ZSM-5 (a), mordenite (b) and HY (c) after incorporation of TTF by stirring a dichloromethane solution at reflux temperature for 2 h.

TTF'+ radical cation, based on the coincidence with the reported characteristic optical spectrum of this radical cation in solution.⁴⁰ The formation of dimeric species reported in other media and conditions was conclusively ruled out by the absence of a significant absorption at 715 nm that is characteristic of this dimer.40

Interestingly, in the case of HY zeolite, even though the solids developed a light colour during the incorporation procedure, the colour immediately vanished upon filtration of the solids. This observation suggests that some TTF⁺ could have been formed in this tridirectional, large pore zeolite imparting its characteristic colour, but apparently it is not persistent enough to survive exposure to the ambient. Analysis of the organic material by GC after incorporation in HY indicates that TTF has remained unaltered and no reaction product could be detected. The most reasonable interpretation is that the initial oxidation of TTF to TTF⁺⁺ reverts rapidly back to the neutral molecule in HY zeolite. In support of this is the fact that TTF⁺ generated on medium pore sized, ZSM-5 and MCM-22 exhibits some partial decay over the time that can be conveniently followed by the decrease in the intensity of TTF⁺⁺ characteristic bands in the diffuse reflectance UV-VIS spectra for periods longer than weeks.

An intermediate situation between Y and medium pore zeolites occurs in the case of the large pore mordenite, wherein an intense optical absorbance due to TTF⁺⁺ is initially recorded after the incorporation procedure, but the intensity progressively decreases within hours leading to a residual, stationary diffuse reflectance spectrum attributable to a minor proportion of persistent TTF'+. This decay of TTF'+ radical cation within mordenite can also be adequately followed with a conventional spectrophotometer. The initial disappearance kinetics fits reasonably well to a first-order decay with a halflife under our experimental conditions of 2 h, approximately. The previous observations during TTF adsorption as well as the diffuse reflectance UV-Vis spectra study are compatible with a rationalization in which a spontaneous generation of TTF⁺⁺ due to the acid sites of the solid occurs. Once TTF⁺⁺ is generated by interaction with the solid acid sites its subsequent persistence will be a function of the TTF⁺/zeolite tight fit. This interpretation assumes that TTF⁺ is located totally or predominantly inside the zeolite micropores, wherein geometrical restrictions can apply. We have performed molecular modeling at the semiempirical level of the best docking of TTF'+ inside the straight channels of ZSM-5 that shows that this molecule fits tightly inside the pentasil zeolite pores. As reported in other cases,⁴¹ we have also found here a relationship between the presence of acidity on the solid and its ability to generate TTF'+. Zeolite Y and mordenite in its neutral Na⁺-form give negligible absorption bands at λ_{max} 460 and 540 nm and thus TTF⁺, if formed (see below

for EPR quantification), has to be in very low amounts compared to the almost quantitative generation from TTF observed for the H⁺-exchanged zeolites (compare IR presented in Fig. 3). Given the lower strength of the acid sites of Al/MCM-41 and silica–aluminas compared to acid zeolites, these two solids should exhibit an ability to generate TTF⁺⁺ intermediate between that of H⁺ and Na⁺ zeolites, as was indeed observed.

The results presented so far for TTF fit nicely with the current paradigm of radical cation persistence in zeolites and related microporous materials. The next step was to test the behavior of ITQ-2 and compare it with those of MCM-22 (same 10-membered ring channel system, external surface negligible) and Al/MCM-41 and SiO₂-Al₂O₃ (large external surface, no cups or microporous channel system). Diffuse reflectance UV–Vis spectroscopy shows that TTF⁺⁺ radical cation was generated upon adsorption of TTF on ITQ-2 from CH₂Cl₂ or cyclohexane solutions.

At the loading studied $(10-20 \text{ mg TTF } (\text{g zeolite})^{-1})$ and immediately after preparation essentially all the TTF was oxidized to the radical cation. Although diffuse reflectance UV-Vis spectroscopy indicates the formation of TTF⁺⁺ radical cation, it does not give any indication of how much neutral TTF is adsorbed in the solid without being converted into TTF⁺. A quantitative indication that there is not a significant amount of TTF left in the solid could be obtained based on the conclusive information gained by IR spectroscopy. TTF has a characteristic vibration band at about 1520 cm⁻¹ that totally disappears upon incorporation on ZSM-5, MCM-22 or ITQ-2. As an example, Fig. 3 compares the aromatic region of the IR spectrum of pure TTF in KBr disk with that of a self-supported wafer of ITQ-2 after incorporation of TTF. The absence of the 1520 cm⁻¹ band in the IR spectrum of TTF incorporated within zeolite indicates that no neutral TTF is left and that the conversion to TTF'+ is almost quantitative.

Interestingly, adsorption of TTF onto Al/MCM-41 and $SiO_2-Al_2O_3$ also gives rise to the generation of TTF⁺⁺ radical cation, as assessed by diffuse reflectance UV-Vis spectroscopy. The initial intensities of the TTF⁺⁺ adsorption bands on Al/MCM-41 and $SiO_2-Al_2O_3$ are, however, weaker than that on ITQ-2 and exhibit a relative decay with respect to the initial intensity, 15 days after preparation, of 45 and 55% for Al/MCM-41 and $SiO_2-Al_2O_3$, respectively, that is more pronounced that the 20% decrease measured for ITQ-2.

To provide a better comparison of the ability of ITQ-2 and the different solids to generate TTF^{+} , an EPR quantification of the relative number of spins for different samples was carried out. The results are summarized in Table 2. Selected EPR spectra of some of the samples prepared are shown in Fig. 4.

Fig. 3 $1800-1300 \text{ cm}^{-1}$ region of the FTIR spectra of TTF in KBr disk (a) and after incorporation on ITQ-2 (b). Spectrum b was recorded at room temperature after outgassing self-supported zeolite wafers at 200 °C under 10^{-2} Pa for 1 h to avoid interference of coadsorbed water.

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 Table 2
 Normalized relative spin density obtained by double integration of the signal between 3340 and 3420 G observed in the EPR spectra of samples of aluminosilicates containing TTF. The values have been corrected to correspond to the same amount of adsorbed TTF as measured by combustion chemical analyses

Sample	Normalized spin density ^a (%)
ZSM-5	90
ITQ-2	100
Na-mordenite	17
Na-Y	0.1
SiO_2/Al_2O_3	0.6
Al/MCM-41	0.1
⁴ Estimated relative error ± 2	0%.

The most salient data from this Table are that the amounts of TTF⁺⁺ generated on ITQ-2 and ZSM-5 are the same within the experimental error and over two orders of magnitude higher than on Al/MCM-41 and SiO_2 -Al₂O₃. This quantitative study clearly indicates that ITQ-2 behaves like a mediumpore zeolite with respect to its ability to generate radical cations of electron-rich aromatic compounds, which is notably higher than those of silica–alumina and mesoporous solid silicas. This is in spite of the reduced ITQ-2 microporosity compared to conventional medium-pore zeolites. Therefore, we wanted to discover whether TTF⁺⁺ radical cation is generated only within the ITQ-2 channel system (as for MCM-22 and similar to ZSM-5, but with a significantly reduced area) or also on the externally accessible cups.

To address this question, we started from ITQ-2 (Si/Al 50) and proceeded to the selective silylation of the external surface using hexamethyldisilazane. This procedure is analogous to those used in the silylation of MCM-41 and other silicates.^{42,43} In this way a new material ITQ-2sil was obtained in which the external open cups have been blocked by the bulky silyl groups while the channel still remains accessible. Accessibility of the channel system was confirmed by pyridine adsorption and observation by IR that the intensity of pyridinium ions on the ITQ-2 after the silylation is very similar to that recorded prior to the silylation procedure.

Importantly, ITQ-2 loses almost completely the capacity to generate TTF⁺⁺ radical ion upon silylation. The diffuse reflectance UV-Vis spectra of silylated ITQ-2 containing TTF exhibits an intensity of the 440 and 580 nm bands characteristic of the radical cation more than one order of magnitude lower than that of the original ITQ-2 before silylation under the same conditions. This treatment leaves the acid sites and

Fig. 4 EPR spectra recorded at room temperature of TTF^{++} generated upon adsorption of TTF onto ITQ-2 (a), ZSM-5 (b), SiO₂-Al₂O₃ (c) and Al/MCM-41 (d). Spectra c and d have been magnified by a factor of 100.









Fig. 5 Visualization of the best docking of TTF inside the open cups of ITQ-2. The molecular modeling shows that one of the rings of TTF is totally inside the cup and that the sulfur atoms are well protected by the zeolite lattice and they experience the internal electrostatic fields.

the accessibility to the channels unaltered. Based on this result, we propose that TTF^{++} radical cations in ITQ-2 are generated predominantly on the external cups. This is in sharp contrast to the behavior of conventional microporous zeolites. These cups will act as a well of potential energy and will stabilize the encapsulated TTF^{++} . Molecular modeling at the semiempirical level shows that TTF can penetrate partially inside the external cups, and in this way the positive sulfur atom will be protected, like a hand in a glove. A selected visualization of this docking is shown in Fig. 5. The fact that aromatic radical cations on the external surface of zeolites, but partially penetrating inside the pores, are relatively protected from the attack of nucleophiles has been previously assessed by electrochemical studies.

In order to provide some additional support to this novel idea that external nests can protect adsorbed radical ions, triphenylamine (TPA) ($E_{ox} \sim 0.7 vs$. SCE in acetonitrile)^{44,45} was also used as a "rough" probe molecule of the ITQ-2 external surface as if it were a flat surface since there is no possibility of experiencing the cups due to the large TPA molecular size. TPA is also too large (reported molecular diameter of 13 Å) to diffuse inside the channel system of mordenite, ZSM-5 or ITQ-2. Therefore, TPA⁺ (if formed) can only be located on the open layers of ITQ-2 experiencing a loose interaction. Upon stirring a dichloromethane solution of TPA in the presence of dehydrated ITQ-2 at reflux temperature a weak green coloration was developed that fades almost completely upon



Fig. 6 Diffuse reflectance UV-Vis spectra (plotted as the inverse of the reflectance, R) of TPA adsorbed on ITQ-2 (a) or Al/MCM-41 (b). Note that the absorbance at about 800 nm is characteristic of TPA⁺.

filtration of the solid. ZSM-5 exhibits the same behavior as ITQ-2. In contrast, mesoporous Al/MCM-41 can incorporate TPA and it forms a significantly higher concentration of persistent TPA⁺, as seen by diffuse reflectance UV–Vis spectroscopy. Fig. 6 compares the diffuse reflectance UV–Vis spectra of TPA adsorbed onto ITQ-2 or Al/MCM-41. The results observed using TPA as probe combined with those of ITQ-2sil indicate that the major factor in the radical cation generation using zeolite ITQ-2 as host is the ability to experience the potential wells of cups. When the organic electron donor can fit inside the cups, then the novel layered zeolite ITQ-2 behaves like a conventional microporous zeolite.

Experimental

TTF (Aldrich), TPA (Aldrich), SiO₂-Al₂O₃ 25 wt.% (BASF) as well as HY (P.Q.), NaY (P.Q.) and Na⁺ and H⁺mordenites (P.Q.) were commercial samples and used as received. ZSM-5,46 MCM-22,47-49 Al/MCM-4123-25 and ITQ-2^{31,32} were prepared by hydrothermal sol-gel crystallization according to the detailed procedures reported in the literature. The crystal structure of the synthesized aluminosilicates was confirmed by powder X-ray diffraction. Silvlation of ITQ-2 was carried out by stirring a suspension of the dehydrated layered zeolite (1 g) with hexamethyldisilazane (0.5 g) in toluene (25 ml) at reflux temperature for 2 h. After this time, the solid was filtered, exhaustively washed with CH₂Cl₂ and dried.^{42,43} Adsorption of TTF or TPA on the solids was carried out by stirring magnetically, at reflux temperature for 2 h, a suspension of the organic compound (10-20 mg) in CH₂Cl₂ or cyclohexane (20 ml) in the presence of the corresponding solid (1 g) that had been previously dehydrated by heating at 500 °C overnight. The solid was filtered, washed with fresh solvent (20 ml), dried under vacuum and stored in closed vials at the ambient. Diffuse reflectance UV-Vis spectra were recorded using a Cary 5 spectrophotometer adapted with a "praying mantis" diffuse reflectance accessory as reference. FTIR spectra of the zeolites containing TTF were recorded in a Nicolet 710 FT spectrophotometer using greaseless quartz cells having CaF₂ windows and a stopcock valve that allowed them to be sealed under high vacuum. Selfsupported wafers (~10 mg) were prepared by pressing the zeolite powder at 1-3 t cm⁻² for 1-2 min. The samples were outgassed at $100 \,^{\circ}\text{C}$ under 10^{-2} Pa for 1 h before recording the spectra at room temperature. Pyridine vapour at 10^{-1} Pa was admitted at room temperature onto dehydrated ITQ-2 and ITQ-2sil samples placed in the IR cell. The cells were evacuated at 250 °C under 10^{-2} Pa for 1 h and the intensity of the IR spectra corresponding to the residual retained pyridine compared for the two samples. EPR spectra were recorded at -200 °C on a Brucker ER200D spectrometer working at the X band (9.65 GHz) and using DPPH (g = 2.0036) as reference. Semiempirical calculation of the optimized geometry as well as docking and molecular modeling was performed using the Insight II program package working on a Silicon Graphics workstation.

Acknowledgements

Financial support by the Spanish DGES (MAT97—1016-C02-01) is gratefully acknowledged. Dr. Lorenzo Fernández and Dr. Germán Sastre are thanked for their assistance in the molecular modeling calculations.

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