Electron transfer mechanisms of biphenyl sorption in M-ZSM-5 (M = H+, Cu²⁺) zeolites

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The sorption of biphenyl (BP) in dehydrated M-ZSM-5 (M = H+, Cu²⁺) zeolites through solid–gas exchange spontaneously causes ionisation of BP molecules; the radical cation and trapped electron disappear slowly *via* two different electron transfer mechanisms.

Spontaneous generation of long-lived organic cation radicals in porous crystalline aluminosilicates (zeolites) has been known for over three decades.[1–3] The tight fit between the radical cation and the pore size is considered to be the main factor responsible for this stabilisation and it is now accepted that the acid sites of the porous materials are related to their electron acceptor ability.[3,4] The Brönsted acid sites can impart to zeolites a dual behaviour as acid and oxidant. Earlier work has showed that persistent carbocations are formed more readily than radical cations.[5] However, the electron and proton transfer mechanisms are not yet completely understood, particularly the fate of the ejected electron.[3,4,6,7] This gap prompted this work relating to unusual biphenyl sorption behaviour in M-ZSM-5 zeolites with H+ and Cu²⁺ as counterbalancing cations.

UV–VIS, IR, Raman, EPR spectra as well as chemical analysis of calcined zeolites $M_{m/n}(SiO_2)_{96-m}(AlO_2)_m$ ($m = 3, 6$; M = H+, Na+) (24 h, 773 K, O₂, Ar) do not exhibit any detectable impurity (Fig. 1) with X-ray diffraction patterns exhibiting the characteristics of well-crystallised ZSM-5 solids while ²⁹Si MAS NMR spectroscopy revealed the absence of abnormal defect groups. The ²⁷Al MAS NMR spectrum of hydrated H₆ZSM-5 shows only a low amount of six-coordinated non-framework Al.

Exposure under argon or helium atmosphere at room temperature of freshly dehydrated $H_m(SiO_2)_{96-m}(AlO_2)_m$ ($m = 3, 6$) powdered solids to dry biphenyl, turned the powder immediately from white to blue and after one week the solids turned pink. Numerous diffuse reflectance UV–VIS absorption spectra were recorded at different times, immediately after the exposure and until the reaction went to completion over one month at 330 K. The processing data for all the spectra of each sample (Fig. 2), provided evidence of three independent spectra of occluded species in H_m-ZSM-5.[8] The extracted spectrum with main bands around 380 and 666 nm reached a maximum intensity within several minutes and then decreased slowly, and was assigned to the radical cation BP·⁺. It should be noted that this maximum corresponds to *ca.* 10% of BP·⁺ with respect of the BP loading. The extracted spectrum with two prominent features at 468 and 491 nm reached maximum intensity within 20 h and then decreased slowly and was attributed straightforwardly to trapped electrons. The spectrum with two maxima at 250 (sharp) and 505 nm (broad) increased slowly with diffusion of BP in the porous void and reached a maximum within one month and was assigned to non-bonding electronic interactions of BP with protons of the Si–OH–Al framework groups. The EPR spectra recorded immediately after the exposure of H_mZSM-5 samples to BP solid exhibited the sharp features of BP·⁺ at 300 and 77 K. After annealing the sample at 320 K for one week, these sharp features disappeared to give a broad intense signal (77 K) corresponding to both trapped electrons and positive holes. After annealing the sample at 320 K for a month no paramagnetic species were detected. Zeolite samples with loading values from 0.2 to 1 BP per unit cell ($m = 3, 6$) exhibited similar behaviour.

The exposure of dehydrated $M_m(SiO_2)_{96-m}(AlO_2)_m$ ($m = 3, 6$, M = Li+, Na+, K+, Rb+, Cs+) to solid BP led to no colour change and BP was found to be sorbed as an intact molecule.[9]

Photolysis at 248 nm of BP occluded in M-ZSM-5 (M = Li+, Na+, K+, Rb+, Cs+) generated persistent UV–VIS spectra analogous to that generated spontaneously through BP sorption in $H_m(SiO_2)_{96-m}(AlO_2)_m$ without photolysis.[9] EPR spectroscopy provided evidence of paramagnetic species, namely trapped electrons and positive holes, after the disappearance of BP·⁺.[9] Exposure of dehydrated $M_{m/2}(SiO_2)_{96-m}(AlO_2)_m$ ($m = 6$, M = Zn²⁺, Cd²⁺) to solid BP also led to no colour change and BP was found to be sorbed without any ionisation.
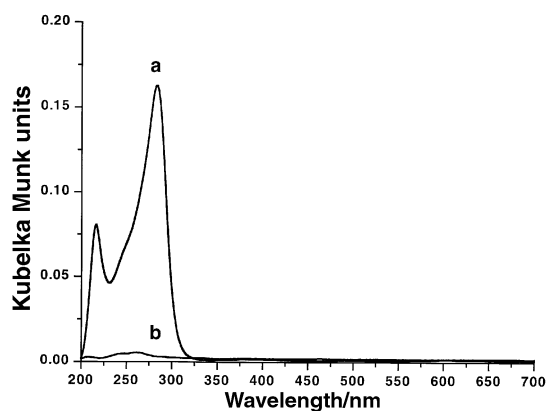
Fig. 1 Diffuse reflectance UV–VIS absorption spectra (Kubelka-Munk units) recorded (a) before thermal treatment of (NH₄)₆ZSM-5 zeolite (NH₄)₆(SiO₂)₉₀(AlO₂)₆ and (b) after thermal treatment (24 h, 773 K, O₂).
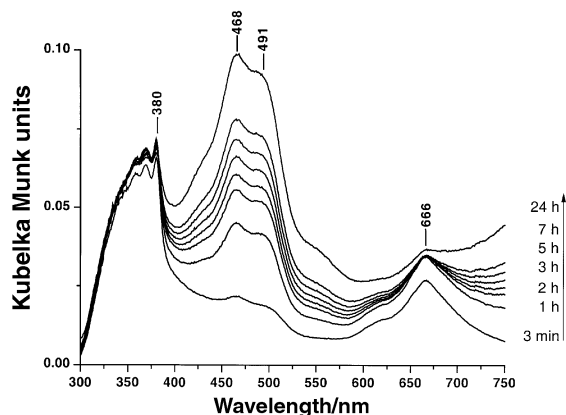
Fig. 2 Diffuse reflectance UV–VIS absorption spectra (Kubelka-Munk units) recorded during the sorption of biphenyl into H₆ZSM-5 zeolite [1BP/ H₆(SiO₂)₉₀(AlO₂)₆]. The spectra were recorded at room temperature at different times.

Exposure of $Cu_3(SiO_2)_{90}(AlO_2)_6$ after thermal treatment (24 h, 773 K, O_2) to solid BP under argon generated persistent $BP^{\cdot+}$ and trapped electrons as evidenced through data processing of the UV–VIS spectra. Surprisingly, Cu(II) does not appear to be a preferred electron trapping site.

Diffuse reflectance IR absorption spectra of dehydrated $H_m(SiO_2)_{96-m}(AlO_2)_m$ samples ($m = 3, 6$) exhibited two sharp OH stretching bands at 3611 and 3745 cm^{-1}. These bands were assigned to acidic (Si–OH–Al) hydroxy groups and (Si–OH) silanol groups, respectively.[10] After BP sorption was complete, the 3611 cm^{-1} band decreased in intensity and a new broad band appeared at 3300 cm^{-1}. The dehydrated $M_{m/n}$ZSM-5 (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$, Zn^{2+}, Cd^{2+}) exchanged zeolites (24 h, 773 K, O_2) did not exhibit any intense OH stretching band at 3611 cm^{-1}. In contrast, the O_2-calcined Cu$_3$-ZSM-5 sample DRIFT spectrum showed an intense band at 3661 cm^{-1}.[11] It is tempting to attribute the spontaneous BP ionisation to the acidic properties of the O_2-calcined Cu$_3$-ZSM-5 sample. The most prominent mid-IR absorption bands (1485, 1432 cm^{-1}) of BP occluded in H_mZSM-5 do not differ from those recorded for Na$_m$ZSM-5 (1485, 1432 cm^{-1}) or for the bulk solid (1480, 1430 cm^{-1}). ^{13}C CP-MS NMR spectra of BP occluded in H_mZSM-5 and Na$_m$ZSM-5 were found to be very similar. Thus, in spite of the high basicity of BP (proton affinity = 814 kJ mol^{-1}), proton transfer from H-ZSM-5 to BP does not occur at room temperature.

The FT-Raman spectra (1.06 μm excitation) of occluded BP in M_mZSM-5 (M = Li$^+$, Na$^+$, K$^+$, Rb$^+$, Cs$^+$) were found to be similar in frequencies and relative intensities with the Raman spectrum of BP in solution. However, the relative intensities of the Raman bands of occluded BP in $M_{m/n}$ZSM-5 (M = H$^+$, Zn^{2+}, Cd^{2+}, Cu^{2+}) differed markedly from BP in solution and provided significant evidence of local BP symmetry lowering and electrostatic interactions between BP and the extraframework cations M^{n+}.

Spontaneous ionisation phenomena upon sorption into H_mZSM-5 has been observed for several aromatics such as biphenyl, naphthalene and anthracene which have relatively low ionisation energies (ca. 8 eV in the gas phase). The formation of radical cations occurs by electron detachment mediated by the combined effects of radical cation stabilisation and the electron trapping ability of the host. It should be noted that for BP, the ratio $BP^{\cdot+}$/BP is < 0.1, but for anthracene, the ionisation yield approaches unity. It appears that acid sites, either Brönsted or Lewis in nature, are necessary for this reaction to occur at room temperature. The zeolites behave both as electron acceptors to electron donor aromatics and as electron donors to electron deficient radical cations. The role of possible undetectable impurities, such as low extraframework Al content, may be ruled out, since the Na$^+$ exchanged ZSM-5 sample did not exhibit any spontaneous charge separation; however, the role of defect groups cannot be excluded.[6] The exact chemical nature of the electron trapping sites as well as the positive holes within the ZSM-5 zeolites is not unequivocally identified from the present spectroscopic data. Evidence for charge separation arises from electronic and EPR spectra. In addition, it is possible that the ionisation occurs at the pore openings of the zeolite microcrystals.[12] From the relationship between the zeolite Al content and the stabilisation of the charge separation, it appears that Al is directly involved in the electron trapping sites. However, the presence of nearest Si–OH–Al Brönsted sites appears to be necessary to induce the spontaneous phenomenon at room temperature since H$^+$–Na$^+$ exchange of samples with analogous Lewis sites inhibited this effect.[13] A recent model of the interaction of trapped electrons in sodalite cage sheds some light on the possible environment of the trapped electron.[14] The frame atoms for the electron can be provided by five-member ringed containing Al and bridging OH. The radical cation or the positive hole ($R^{\cdot+}$) counterbalances the negative charge in $[H(AlO_2)(SiO_2)_4 \; e] \; R^{\cdot+}$. A concerted mechanism in the void space of ZSM-5 zeolites between the occluded aromatic, the proton interactions and the nearest efficient trapping site can lower the ionisation activation energy and can lead to thermally durable charge separation.

Notes and references

1 D. N. Stamires and J. Turkevich, *J. Am. Chem. Soc.*, 1964, **86**, 749.
2 F. R. Chen and J. J. Fripiat, *J. Phys. Chem.*, 1993, **97**, 5796.
3 F. L. Cozens, R. Bogdanova, M. Régimbald, H. Garcia, V. Marti and J. C. Scaino, *J. Phys. Chem. B*, 1997, **101**, 6921.
4 V. Ramamurthy, P. Lakshminarasimhan, C. P. Grey and L. J. Johnston, *Chem. Commun.*, 1998, 2411.
5 V. J. Rao, N. Prevost, V. Ramamurthy, M. Kojima and L. J. Johnston, *Chem. Commun.*, 1997, 2209.
6 J. K. Thomas, *Chem. Rev.*, 1993, **93**, 301.
7 K. B.Yoon, *Chem. Rev.*, 1993, **93**, 321.
8 W. Windig, *Chemom. Intell. Lab. Syst.*, 1994, **23**, 71.
9 I. Gener, G. Buntinx and C. Brémard, *Angew. Chem., Int. Ed.*, 1999, **182**, 278.
10 S. Kotrel, M. P. Rosynek and J. H. Lunsford, *J. Catal.*, 1999, **182**, 278.
11 J. Sárkány, *Phys. Chem. Chem. Phys.*, 1999, **1**, 5251.
12 K. K. Iu, X. Liu and J. K. Thomas, *J. Photochem. Photobiol. A: Chem.*, 1994, **79**, 103.
13 M. L. Cano, A. Corma, V. Fornes and H. Garcia, *J. Phys. Chem.*, 1995, **99**, 4241.
14 N. P. Blake and H. Metiu, *J. Chem. Phys.*, 1995, **103**, 4455.