

## Communications to the Editor

### Catalytic Structure Sensitivity: The Effect of Pore Size on the Oxygen Quenching of Excited Aromatic Molecules Adsorbed on Silica Surfaces

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The performance of a catalyst reflects a complex interplay between chemical and geometrical parameters of the surface.<sup>1</sup> Much attention has been devoted to structure sensitivity in the case of metal catalysts for which specific crystal planes were found to affect catalytic activity.<sup>2</sup> Considerably less understood is the effect of average pore size (aps) as a purely geometrical parameter controlling catalytic processes. On several metal surfaces the increase in activity with decrease of pore size was attributed to the accompanying increase in surface area.<sup>3</sup> The fast progress in the application of zeolites to catalytic processes<sup>4</sup> has drawn renewed attention to pore size as a key geometrical parameter in catalytic surface reactions. However, a thorough study of this parameter requires the ability to control and to vary it gradually. This is difficult in the case of zeolites which are characterized by a fixed pore size per chemical composition.<sup>5</sup> A convenient family of materials, which allows changes in the average pore size without changing the chemical composition, is that of porous silica gels,<sup>6</sup> e.g., as recently applied by Turro et al. in the investigation of the photodecomposition of aryl ketones, for which a surface-cage effect was found.<sup>7</sup>

In this study we wish to report some preliminary observations indicative of a new surface catalytic effect associated with an increase in activity per *unit area* by decreasing the average pore size, in contradistinction to an increase in activity which follows an increase in total surface area by decreasing the particle size<sup>8</sup> or the aps.<sup>9</sup>

Four aromatic molecules, pyrene, pyrene-1-butyrac acid, coronene, and Ru(bpy)<sub>3</sub><sup>2+</sup>, exhibiting luminescence lifetimes in the 10<sup>-7</sup>-10<sup>-6</sup>-s range, were adsorbed on porous silica at a fixed low surface coverage ( $\theta = 0.01$ -0.02). As shown in Table I, steady-state experiments indicate that in the case of the polycyclic molecule, quenching by exposure to dry air on a 60-Å aps surface (Si-60, Merck or Woelm Products, N<sub>2</sub>-BET surface area ~550 m<sup>2</sup>/g) is effective by more than 1 order of magnitude as compared to a 1000-Å aps silica (Si-1000, a Fractosil-1000 Merck product, N<sub>2</sub>-BET area 20 m<sup>2</sup>/g). Table I and Figure 1 also present the observations in terms of the corresponding lifetimes measured as

Table I. Pore Size Effects on the O<sub>2</sub> Quenching Efficiency of Excited Aromatic Molecules Adsorbed on Porous Silicas

probe molecule	I(N <sub>2</sub> )/I(O <sub>2</sub> ) <sup>a</sup>		Si-1000 <sup>b</sup>		Si-60 <sup>b</sup>	
	Si-1000	Si-60	$\tau_{1/2}$ (N <sub>2</sub> )	$\tau_{1/2}$ (O <sub>2</sub> )	$\tau_{1/2}$ (N <sub>2</sub> )	$\tau_{1/2}$ (O <sub>2</sub> )
pyrene	3	30	35/60	18/28	60/90	2/2
pyrene-1-butyrac acid	3	30	25/45	13/20	30/65	1.5/1.5
coronene	2	25	40/50	29/45	25/60	3.5/4
Ru(bpy) <sub>3</sub> <sup>2+</sup>	4	15	530/760	130/170	340/470	34/44

<sup>a</sup>Steady-state fluorescence intensities (*I*) were measured with a Perkin-Elmer LS-5 spectrofluorimeter. The pyrene-coated silica was obtained by a solution evaporation procedure as described elsewhere.<sup>19</sup> Parameters denoted by (N<sub>2</sub>) were measured under vacuum or under N<sub>2</sub>. Those denoted by (O<sub>2</sub>) were obtained by flushing the Si samples with dry air. <sup>b</sup>Fluorescence half-lives ( $\tau_{1/2}$ ) were recorded using a homemade blumlein transmission line (atmospheric pressure) N<sub>2</sub> laser (for more details see ref 20). The  $\tau$  values reported are in nanoseconds and refer to the first and second half-life, respectively.

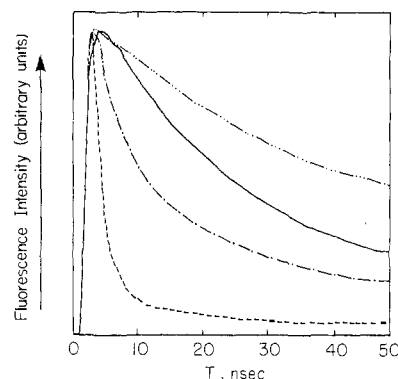


Figure 1. Decay curves of pyrene fluorescence on silica gel: On Si 60: (----) in N<sub>2</sub>; (---) in air. On Fracto-sil 1000: (—) in N<sub>2</sub>; (---) in air.

previously described.<sup>10</sup> Since the decay of adsorbed aromatics on silica is frequently multiexponential,<sup>11</sup> the first two half-lives ( $\tau_{1/2}$ ) on the fluorescence decay are reported. It is evident that the O<sub>2</sub>-sensitivity of  $\tau_{1/2}$  shows a trend analogous to that of the steady-state intensities, *I*. In other words, the O<sub>2</sub> quenching mechanism is dynamic in nature. A complete analysis of the oxygen effect on the lifetimes is limited by the time resolution of our apparatus (~0.5 ns). However, the observation that the O<sub>2</sub> effect on *I* is somewhat stronger than on the corresponding  $\tau_{1/2}$  values (see Table I) is indicative of contributions from kinetically unresolved components of  $\tau_{1/2}$ (O<sub>2</sub>) in the nanosecond range.

We note that Ru(bpy)<sub>3</sub><sup>2+</sup> exhibits  $\tau_{1/2}$ (O<sub>2</sub>) values which are higher by approximately 1 order of magnitude as compared to those of the three polycyclics. This is qualitatively in keeping with the lower O<sub>2</sub> quenching efficiency of Ru(bpy)<sub>3</sub><sup>2+</sup> in solution (~4 × 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup><sup>12</sup>) as compared to ~4 × 10<sup>10</sup> M<sup>-1</sup> s<sup>-1</sup> for the latter molecules.<sup>13</sup>

Preliminary mechanistic considerations should interpret these observations in terms of mechanisms for gas-surface reactions in the range between two extremes: gas-phase bombardment

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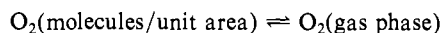
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mechanisms (Rideal-type processes<sup>14a</sup>) and diffusion of the reactants on the surface (Langmuir-Hinshelwood-type processes).<sup>14b</sup> The complexity of mechanisms between these two extremes may be substantial, especially with geometrically and energetically heterogeneous surfaces where reaction pathways are not necessarily associated with pure gas-phase bombardment or with pure surface diffusion, i.e., molecular motions can be a combination of both, involving jumps from wall to wall and from one crest to another. It seems to us, however, that a pure gas-phase bombardment mechanism can be excluded, even at this early stage. Thus, the number of collisions of gaseous molecules per unit time and unit surface of a spherical pore is only a function of pressure and not of pore diameter; i.e., a bombardment mechanism will not exhibit a dependence on pore size. (We note that the pore system in silica is open and interconnected, allowing for efficient O<sub>2</sub> equilibration between pores during the 10<sup>-6</sup>-10<sup>-7</sup>-s lifetime of the excited adsorbate). This conclusion is in keeping with that of Gafney et al., who excluded gas-phase bombardment in the case of quenching of Ru(bpy)<sub>3</sub><sup>2+</sup> on vycor glasses by O<sub>2</sub>, SO<sub>2</sub>, and NO<sub>2</sub>.<sup>15</sup>

At present, we thus tend to favor the alternative explanation, based on a nonhomogeneous coadsorption quenching mechanism according to the following considerations: At low  $\theta$  values both probe and O<sub>2</sub> will be preferentially adsorbed on surface zones which originate in the low-diameter tail of the pore-size distribution curve. This is not only due to energetic factors (the number of adsorption sites/unit area in small, concave pores is higher than the average) but also due to the simple fact that most of the surface area is concentrated in narrow pores.<sup>16</sup> Thus, in narrow pores the equilibrium



is shifted to the left relative to wide pores, resulting in a higher local oxygen concentration. Consequently, a higher quenching efficiency via a short-range surface diffusion mechanism is observed. In larger apertures, where the relative amount of narrow pores decreases, long-range (surface) diffusion pathways, as well as gas-phase collisions, may prevail, leading to diminished quenching rates.

Preliminary O<sub>2</sub> quenching experiments were also carried out with some other silicas with varying psd. A general behavior similar to that of Si-60 was observed in the case of Merck Si-200 and Si-500 while Si-2500 exhibited O<sub>2</sub>-quenching efficiencies similar to Si-1000.

Finally, it should be noted that a number of investigators have observed profound differences between solution and surface quenching behavior of excited singlet and triplet state by gaseous quenchers.<sup>17</sup> It cannot be excluded that in some of these systems the enhanced quenching process may be attributed to high local quencher concentrations associated with surface geometry features, e.g., trapping in very narrow pores. Similarly, Casal and Scaiano<sup>18</sup> have observed deviations from Stern-Volmer plots in the O<sub>2</sub> quenching of triplet ketones adsorbed on silicalite. They interpreted their observations as due to site inhomogeneities in this zeolite. Again, it is plausible that these inhomogeneities are associated with geometrical factors such as zeolitic structural imperfections.

Further work (e.g., dependence on O<sub>2</sub> pressure, probe concentration, presence of coadsorbates) is in progress in our laboratory aiming at obtaining a quantitative model for the struc-

ture-sensitive catalytic effect reported here.

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**Registry No.** Ru(bpy)<sub>3</sub><sup>2+</sup>, 15158-62-0; SiO<sub>2</sub>, 7631-86-9; O<sub>2</sub>, 7782-44-7; pyrene, 129-00-0; pyrene-1-butyl acid, 3443-45-6; coronene, 191-07-1.

## Stereocontrolled [m + n] Annulation Reactions. 2. A [3 + 3] Route to Chiral, Nonracemic 1,2-Cyclohexanediols

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As part of an ongoing program initiated to generate stereocontrolled approaches to a variety of carbocyclic ring systems,<sup>2</sup> we sought to develop a [3 + 3] annulation strategy utilizing three carbon dielectrophilic synthons in conjunction with 3-iodo-2-[(trimethylsilyl)methyl]propene<sup>3</sup>/SnF<sub>2</sub><sup>4</sup> as a trimethylenemethane dianionic synthon. Few [3 + 3] approaches to six-membered rings utilizing dianion/dielectrophile strategies have been reported.<sup>5</sup> While highly effective in generating functionalized ring systems, existing approaches do not address the important problems of controlling relative and absolute stereochemistry in construction of functionalized carbocycles.

We sought strategies that would allow control of stereochemistry at several stereocenters and, furthermore, permit straightforward generation of chiral, nonracemic cyclization products. Efforts therefore focused on use of  $\alpha,\beta$ -epoxy aldehydes as the dielectrophilic partner in the [3 + 3] process. Epoxy aldehydes are extremely attractive substrates since they are readily accessible in high enantiomeric excess from appropriate allylic alcohols by Sharpless asymmetric epoxidation<sup>6</sup> followed by Swern oxidation<sup>7</sup> of the resulting epoxy alcohols, as well as by other techniques.<sup>8</sup>

In the [3 + 3] annulation process envisioned, addition of allyl tin trihalide (generated in situ) to the carbonyl of the epoxy aldehyde was expected to occur with good diastereofacial selectivity in the Felkin-Ahn sense as reported previously for a number of related substrates.<sup>4c,f</sup> The combination of intramolecular Sn<sup>4+</sup> Lewis acid

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