in this case is better described as the formation of a solid solution rather than attachment to a two-dimensional surface.

Klafter and co-workers have examined trapping and reaction processes on fractal surfaces.[20] They found that the density of trapping sites is governed by the fractal dimension. Since platinum islands on the TiO_2 particles efficiently accumulate electrons,[21] surface irregularities are likely sites for hole trapping. If the rate of interfacial hole transfer is proportional to the density of active surface sites, the transfer efficiency for excitation carriers will be greatest for surfaces with $D = 3.00$. The high fractal dimension of the synthesized oxidized TiO_2, along with the presence of platinum deposits, should represent an optimum surface topography for charge transfer in these systems.

The incident monochromatic photon-to-product efficiencies that are reported here represent a lower limit to the actual absorbed photon-to-product efficiency because the scattering of the incident light is not considered in the calculation. In addition, the reactions that employed the synthesized powders were by necessity run to high conversions. Under these conditions competitive absorption of acetophenone to active sites on the particle surface may lead to a reduction in the reaction efficiency.

Conclusion

We have shown that surface factors play an important role in determining the IMPP efficiency for the oxidation of α-methylstyrene to acetophenone in nonaqueous media using platinized TiO_2 photocatalysts. The high roughness factor of the synthesized oxidized powders gives rise to dramatic improvements in the product yields when compared with commercial powders that possess smoother surfaces. Surface analysis of the synthesized powders indicates a high level of self-similarity. A fractal dimension that approaches the theoretical value of 3.0 was measured for the synthesized oxidized TiO_2 powders. This represents an optimum surface topography for interfacial charge transfer in these systems.

Surface modification of the synthesized powders with an *n*-octyl group further increases photoefficiencies through enhanced adsorption of the solution-phase hole acceptor. Preliminary experiments suggest that additional improvements in the IMPP efficiency can be realized through optimization of solution-phase parameters such as the concentration of dissolved electrolyte and the powder-to-substrate ratio. Also, we have observed that specific surface interactions can affect the course of reaction with regard to product distribution. These results will be reported in a future publication.

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Bromide/Chloride Counterion Exchange at the Surfaces of Dioctadecyldimethylammonium Vesicles

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The exchange between bromide and chloride counterions at the surfaces of dioctadecyldimethylammonium vesicles has been examined through fluorescence quenching experiments. The quenching of the fluorescence of vesicle-incorporated naphthalene derivatives by bromide counterions has been studied under different experimental conditions. The data are analyzed by following the pseudophase ion-exchange model and assuming that the observed quenching is a direct function of the local quencher concentration at the vesicle surfaces. The fluorescence quenching behavior is found to be accounted for by the ion-exchange formalism when experiments are performed on vesicles having the same ionic composition for the contacting solution at both the outer and inner aqueous pseudophases. From this type of experiment, a bromide/chloride counterion exchange constant equal to 4 ∓ 1 is obtained. Experiments performed by addition of a vesicle solution containing a single counterion (chloride) to an isotonic solution containing a mixture of bromide and chloride allow an evaluation of the ability of the vesicles to exchange the counterions at the outer surface while maintaining a single counterion at the inner surface. An analysis of the quenching data obtained by extrapolation to time zero indicates that the ability of the outer surface to exchange counterions under these conditions is lower than that predicted by the exchange model. The luminescence observed decreases with time in a manner that is indicative of fast diffusion of bromide across the vesicle bilayers. These results are interpreted in terms of the strain imposed on the bilayer by the asymmetrical counterion distribution, strain that can be relaxed by an increased rate of surfactant flip-flop leading to a thermodynamically stable state.

Introduction

Exchange of counterions at the surface of ionic micelles has been widely investigated. Most of the data obtained in this type of study can be rationalized in terms of the ion-exchange formalism.[4,5] This simple model allows for a quantitative treatment of micellar effects on chemical reactions and equilibria[4-8] and intramicellar photochemical processes.[9-14] Furthermore, counterion-exchange constants which can be obtained by following the

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ion-exchange formalism account for counterion effects on basic micellar properties such as degrees of ionization,[15] critical micelle concentrations,[12,16] and sphere–rod transitions.[17,18]

Ionic unilamellar vesicles can also concentrate and exchange counterions[19-22] at both the inner and outer faces. However, for these systems, there have been few studies directed toward the determination of exchange constants or to assess the ability of both interfaces to exchange counterions.[23] In the present paper, we report results bearing on the concentration and exchange of bromide and chloride counterions at the surfaces of dioctadecyldimethylammonium vesicles. These data were obtained from an analysis of the effect of counterion composition on the fluorescence emission of vesicle-incorporated naphthalene derivatives.

Experimental Section

Dioctadecyldimethylammonium chloride (DODAC) (Herga Industria Quimica Brasil) was purified as previously described.[24] Dioctadecyldimethylammonium bromide (DODAB) (Eastman Kodak) was purified by repeated recrystallizations from acetone. Sodium chloride (Merck) and sodium bromide (Baker Analyzed) were analytical grade. All solutions were prepared in deionized doubly distilled water. Two fluorescent probes were employed: dodecyl-α-naphthyl acetate (DNA) and 1-laurylnaphthalene (LN). DNA was synthesized from α-naphthylacetyl chloride and dodecanol in benzene. LN was prepared by Friedel–Crafts acylation of naphthalene with dodecanoyl chloride and subsequent reduction of the ketone following the Huang–Minlon method.[25] Both compounds were purified by column chromatography and their purity checked by NMR and elemental analysis. Both probes were excited at 290 nm and the fluorescence emission recorded at 340 nm.

Vesicles were prepared from DODAC and/or DODAB following either injection with simultaneous vaporization of the solvent (large vesicle) or sonication (small vesicles) methods.[26]

Three type of experiments were carried out:

Method I. Fluorescent probe matched solutions of DODAC and DODAB vesicles, prepared at the same ionic strength, were mixed and the resulting fluorescence compared with that obtained from the initial solutions before mixing.

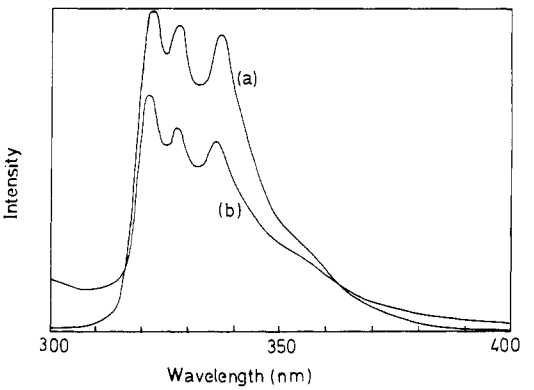

Figure 1. Fluorescence spectra of LN in benzene (a) and in a 0.2 mM solution of DODAC (large) vesicles in 2 mM NaCl (b). Excitation at 290 nm; probe concentration = 1×10^{-6} M.

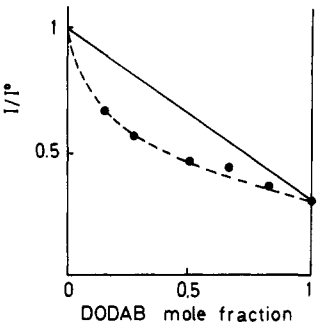

Figure 2. Relative fluorescence intensity of DNA from mixtures of DODAC and DODAB vesicles (large) plotted as a function of DODAB mole fraction. Total surfactant concentration, 0.2 mM. The solid line represents the behavior expected in the absence of counterion exchange.

Method II. Mixed (with chloride and bromide as counterions) vesicles were prepared either by injection of the surfactant into a mixture of NaCl and NaBr or by sonication of a mixture of surfactant and both salts. Fluorescent probes were added prior to injection or sonication.

Method III. A solution of the fluorescent probe containing vesicles, prepared at a given ionic strength with a single counterion, was added to a given NaBr/NaCl mixture of the same ionic strength.

Probe to surfactant mole ratios employed were below 3×10^{-4}. All experiments were carried out at surfactant concentration 0.2 mM with the total added salt concentrations below 5 mM in order to minimize vesicle fusion.[27] Freshly (daily) prepared solutions were employed. For some of the vesicle (large) solutions employed the particle size was measured by dynamic light scattering (using a Malvern PCS 100 spectrophotometer). Only a single molecular size distribution was detected, indicating only unilamellar vesicles are present.[26] An average diameter of 0.55 ± 0.08 μm (range 0.2–1.4 μm) was obtained, which is in agreement with the reported size of large DODAC vesicles.[26] The scatter-absorption spectra of all solutions employed were in accordance with a value of 300 M^{-1} cm^{-1} for the absorptivity at 400 nm.[26] All experiments were done in the low-temperature phase[28] at 22 °C.

The microprobe of a Braunsonic 1510 sonicator (operated at 70 W) was used for the preparation of small vesicles. Absorption spectra were recorded on either a Hewlett Packard 8541 or a Shimadzu 160 spectrophotometer. Fluorescence spectra and intensities were recorded on either a Perkin Elmer LS5 luminescence spectrometer or a Spex 111-CM fluorimeter. Fluorescence lifetimes were measured on a PRA single-photon counter and the data analyzed on a PDP-11 computer.

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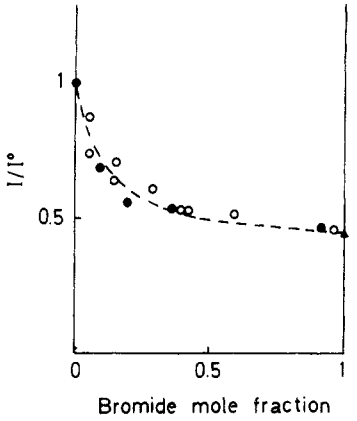

Figure 3. Relative fluorescence intensity of LN from vesicles prepared by injection of DODAC (final concentration 0.2 mM) into mixtures of NaCl and NaBr plotted as a function of bromide mole fraction: (○) total counterion concentration, 5.2 mM; (●) total counterion concentration, 2.2 mM; (▲) DODAB (0.2 mM) in NaBr 2 mM.

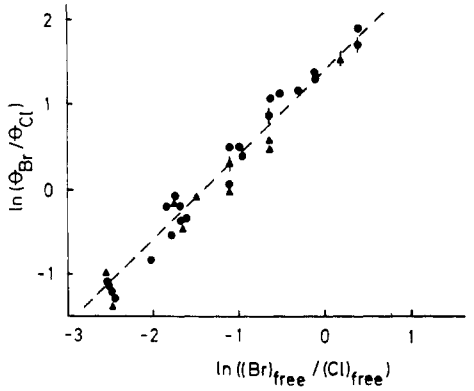

Figure 4. Plot of ln $(\theta_{Br}/\theta_{Cl})$ vs ln $[(Br)_{free}/(Cl)_{free}]$. The ratios $(\theta_{Br}/\theta_{Cl})$ (eq 1 and 3 and $[(Br)_{free}/(Cl)_{free}]$ (eq 4 and 5) were calculated from the fluorescence quenching data obtained in experiments type II (see Experimental Section). (●) Large (injected) vesicles. LN as probe. (▲) Small (sonicated) vesicles. LN as probe. (●) Large vesicles. DNA as probe. (▲) Small vesicles. DNA as probe.

Results and Discussion

The fluorescence spectra of 1-laurylnaphthalene (LN) in benzene and in a 0.2 mM solution of DODAC (large) vesicles in 2 mM NaCl are shown in Figure 1 (similar spectra were obtained in all the vesicle solutions employed). The close correspondence between these spectra (peak maxima at 321, 327, and 336 nm) indicate that scattering by the vesicles is negligible under the experimental conditions employed and make clear the fluorescence quenching experiments. The emission spectra of dodecyl-α-naphthyl acetate (DNA) were very similar to those of LN in either benzene or the vesicle solutions.

(A) Fluorescence Measurements in Mixtures of DODAC and DODAB Vesicles (Experimental Method I). Values of I/I^0 for DNA (where I is the fluorescence intensity measured in a given surfactant mixture 15 s after mixing matched DODAC and DODAB vesicle solutions, and I^0 is the value obtained in DODAC at the same probe absorbance) are given in Figure 2 plotted as a function of DODAB mole fraction. These data indicate that the probe fluorescence is efficiently quenched by bromide counterions. Furthermore, since the fluorescence intensity readings were taken 15 s after mixing both solutions, the data of Figure 2 also indicate that there exists a ready exchange of counterions between the vesicles (I/I^0 values expected in the absence of counterion exchange are shown by the solid line in Figure 2).

An interesting feature of the data obtained after mixing matched solutions of DODAC and DODAB at the same concentration (0.2 mM) in the absence of added salt is that the fluorescence intensity steadily decreases with time (up to 15% in 10 min). This effect, which can be due either to a displacement of the probe towards DODAB vesicles or, more likely, to a slow counterion exchange, will be discussed in the following sections.

(B) Fluorescence Measurements in Mixed Vesicles (Experimental Method II). The fluorescence intensity depends on the percentage of bromide present as counterion. Typical data obtained in vesicles prepared by injection of DODAC (final concentration 0.2 mM, LN as probe) into mixtures of NaCl and NaBr are given in Figure 3. From this type of data it is possible to obtain the value for the counterion-exchange constants $K_{Br/Cl}$ following a procedure similar to that employed previously for the exchange at the surface of cetyltrimethylammonium micelles.[9] In order to apply this procedure, it was assumed that the observed fluorescence quenching can be fit to a simple Stern–Volmer relationship in terms of the average bromide fractional counterion coverage (θ_{Br})

$$I^0/I = 1 + K_{SV}\theta_{Br} \quad (1)$$

Here K_{SV} is defined by

$$(I^0/I_{DODAB}) - 1 = K_{SV} \quad (2)$$

where I_{DODAB} stands for the fluorescence intensity emitted under matched conditions in DODAB vesicles. This treatment assumes that the probe solubilized either at the inner or at the outer interfaces is equally quenched by the bromide counterions. In order to apply mass balances to obtain θ_{Cl}, $(Br)_{free}$, and $(Cl)_{free}$ from the total amount of added electrolyte and the θ_{Br} values, the amount of free surfactant and the counterion dissociation degrees were neglected. This is a reasonable assumption due to the fact that added electrolyte was more than 10 times the surfactant concentration and since the surfactant concentration employed (0.2 mM) is considerably higher than the critical vesicle concentration.[29]

With these assumptions, the following equations hold:

$$\theta_{Cl} = 1 - \theta_{Br} \quad (3)$$

$$(Br)_{free} = (Br)_{total} - (DoDAC)\theta_{Br} \quad (4)$$

$$(Cl)_{free} = (Cl)_{total} - (DODAC)\theta_{Cl} \quad (5)$$

The bromide/chloride counterion exchange constant is defined by

$$K_{Br/Cl} = \frac{\theta_{Br}(Cl)_{free}}{\theta_{Cl}(Br)_{free}} \quad (6)$$

According to eq 6, a plot of ln $(\theta_{Br}/\theta_{Cl})$ vs ln $[(Br)_{free}/(Cl)_{free}]$ must be linear, with a slope equal to 1 and intercept equal to ln $(K_{Br/Cl})$. The plot obtained for θ_{Br} values between 0.2 and 0.75 is shown in Figure 4. These data indicate that for both sonicated (small) and injected (large) vesicles $K_{Br/Cl} = 4 \mp 1$, a value closely similar to that reported for micellar systems formed from tetraalkylammonium surfactants.[8,9] This is the expected result if counterion binding is mainly determined by a localized adsorption driven by the micellar surface potential.[30]

(C) Counterion Exchange after Vesicle Preparation (Experimental Method III). These experiments were performed by addition of a solution of fluorescent probe containing DODAC vesicles to NaCl/NaBr mixtures.[31] It was expected that, due to the fast counterion exchange taking place at the outer interface (see subsection A) and the slow bromide diffusion through the bilayer, only the outer interface counterions would be exchanged. Two types of experiments were carried out: (i) 0.5 cm^3 of DODAC (1 mM) in NaCl (0.4 mM) was added to 2 cm^3 of a NaCl–NaBr solution of total concentration 0.4 mM, and (ii) 0.25

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(31) DODAB vesicles prepared in Br^- buffer were added to solutions of Cl^- (total added [salt] < 5 mM); this leads to an increase in fluorescence intensity indicative of a partial displacement of Br^-. Nevertheless, (due to the larger affinity of bromide counterions) the observed increase is too small to merit a quantitative treatment. Addition of DODAB vesicles to higher concentration of Cl^- was not attempted since under these conditions vesicle fusion cannot be disregarded.[27]

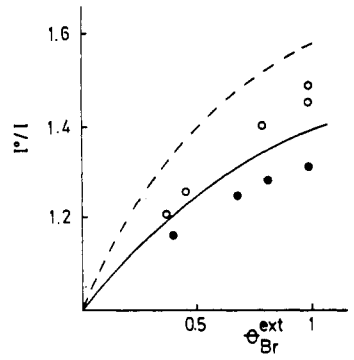

Figure 5. Relative fluorescence intensity values obtained by extrapolation to $t = 0$ plotted against θ_{Br}^{ext} according to eq 8. LN as probe: (●) experimental data; (—) calculated curve (large vesicles). DNA as probe: (○) experimental data; (---) calculated curve (large vesicles).

cm³ of DODAC (2 mM) in NaCl (2 mM) was added to 2.25 cm³ of a mixture of NaCl and NaBr of total concentration 2 mM. The addition of DODAC vesicles to isotonic NaCl and the addition of DODAB vesicles to isotonic NaBr were taken as references.

A general feature of all the data obtained with both probes is that, when a solution of DODAC vesicles is added to a isotonic solution containing bromide ions, the fluorescence intensity steadily decreases with time. We shall discuss briefly the values obtained by extrapolation of the fluorescence readings to time $k = 0$, and, afterwards, the meaning of the change of the fluorescence intensity with time. On the assumption that the outer/inner surfactant ratio in the vesicles is 1 in the large vesicles,[32] we shall consider that 50% of the light is emitted from the outer interface (i.e., is "quenchable" by external ions) and 50% is emitted from the inner interface. We shall further assume that, at $t = 0$, counterions of the external interface are exchanged with $K_{Br/Cl} = 4$.

The values of θ_{Br}^{ext} at the outer interface are related to I^0/I by the equation

$$\frac{I^0}{I} = \frac{1 + K_{SV}\theta_{Br}^{ext}}{\alpha + (1 + K_{SV}\theta_{Br}^{ext})(1 - \alpha)} \tag{7}$$

where α is the fraction of the light emitted from the probe at the outer interface. For $\alpha = 0.5$, eq 7 reduces to

$$\frac{I^0}{I} = \frac{1 + K_{SV}\theta_{Br}^{ext}}{1 + 0.5K_{SV}\theta_{Br}^{ext}} \tag{8}$$

The values of θ_{Br}^{ext} can be evaluated from the external electrolyte composition and the $K_{Br/Cl}$. Experimental values of I^0/I obtained from both fluorescent probes employed and the theoretical curves calculated from eq 8 are shown in Figure 5. K_{SV} values employed were 1.4 and 2.8 for LN and DNA, respectively. The difference in the K_{SV} values is not due to different fluorescence lifetimes. The fluorescence decay curves measured in benzene solution were monoexponential, with an almost equal decay parameter for both probes employed. Values measured in oxygen-free (argon purged) benzene solutions were 60.8 ns for LN and 61.2 ns for DNA, which are in agreement with the lifetimes of similar naphthalene derivatives in hydrocarbon solvents.[33] The decay profiles in the DODAC vesicle solutions were found to show nonexponential decay behavior. The emission decay curves showed contributions from short-lived and long-lived components. The short-lived component could not be excluded[34] and is believed to arise from scattered light. However, the later part of the decay

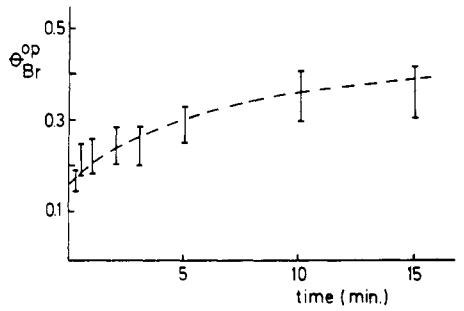

Figure 6. Plot of θ_{Br}^{op} against time after addition of fluorescent probe containing DODAC (large) vesicles to isotonic NaBr solutions. DODAC concentration after addition, 0.2 mM. Total external counterion concentration, 0.4 mM. Fraction of bromide ions in the external aqueous phase 0.8. Probe, LN.

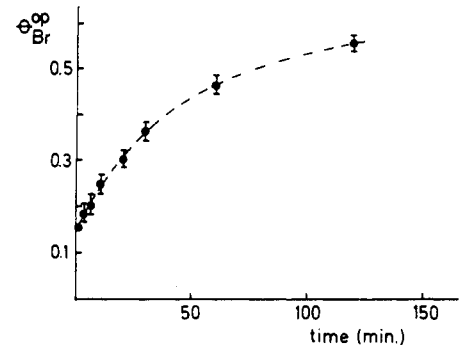

Figure 7. Plot of θ_{Br}^{op} against time after addition of fluorescent probe containing DODAC (large) vesicles to isotonic NaBr solutions. DODAC concentration after addition, 0.2 mM. Total external counterion concentration, 2 mM. Fraction of bromide counterions in the external aqueous phase, 0.9. Probe, LN.

curves could be fit for monoexponential decay and the lifetimes obtained from this treatment in DODAC vesicles were 32 ns for LN and 34 ns for DNA (in air-saturated solutions). The different K_{SV} values for the naphthalene derivatives can probably be best attributed to different locations for the naphthalene moieties at the vesicle interfaces, the more hydrophilic DNA being more exposed to bromide and hence, experiencing a higher susceptibility to quenching by the bromide counterions.[28]

The data of Figure 5 show that, even though the experimental data follow the pattern predicted by eq 8, they are lower than the theoretical values. This must imply (i) a rather slow exchange (kinetic effect), or, (ii) lower $K_{Br/Cl}$ values when only the external ions are being exchanged (thermodynamic effect). If we accept that, as in the micelles, the average distance between surfactant heads is different for bromide than for chloride counterions[18] (a closer packing being obtained when bromide ions are the counterions), changing only the counterions of one side of the bilayer must be a less favorable process than changing simultaneously the ionic composition of both sides ("thermodynamic" effect). Similarly, exchange of the counterions at one side can require surfactant rearrangements that could take longer times than those over which the measurements are being carried out (15 s) ("kinetic" factor).

The fluorescence intensity for both probes steadily decreases with time after addition of fluorescent probe-containing DODAC vesicles to an isotonic solution containing bromide ions. Operationally, a parameter θ_{Br}^{op}, can be simply defined by eq 9 where

$$\theta_{Br}^{op} = \frac{(I^0/I) - 1}{K_{SV}} \tag{9}$$

I^0 is the emission intensity when the DODAC vesicles are added to a isotonic solution containing only NaCl, and I is the intensity measured at time t after addition to a solution containing bromide ions.

Changes in θ_{Br}^{op} with time for LN obtained after addition of 0.5 cm³ of (DODAC (1 mM) in 0.4 mM NaCl) to 2 cm³ of 0.4

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(34) (a) Careful purification of the surfactant employed gave the same result. (b) It was taken into consideration that part of the short component emitted light intensity was due to self-quenching of naphthalene chromophores. However, no decay signals appeared when recorded at 400–450 nm and no naphthalene excimer emission was observed in the steady state of fluorescence spectra.

mM NaBr are shown in Figure 6. It can be seen that θ_{Br}^{op} steadily increases with time. This result can be explained either by a displacement of the probe toward the outer interface and/or by bromide penetration through the bilayer. Figure 7 shows data obtained for LN with a larger excess of bromide ions. In these experiments, total added electrolyte is 2 mM and 0.25 cm^3 of (DODAC (2 mM) in 2 mM NaCl) are added to 2.25 cm^3 of 2 mM NaBr. After 15 h, θ_{Br}^{op} reaches a value of 0.87. These data can only be explained in terms of a steady penetration of bromide ions through the bilayer. Permeation of ions through simple tetraalkylammonium ionic vesicles has been extensively studied by Moss et al.[35-39] In particular, these authors found that dioctadecyldimethylammonium vesicles are remarkably efficient in avoiding anion permeation through the bilayer.[39] For example, Ellman's anion and *o*-iodosobenzoate can be separately entrapped in DODAC vesicles and maintained in the same aqueous solution for many hours with minimal reaction, even though they react within 10 s when free.[39] Nevertheless, the data shown in Figures 6 and 7 imply a rather fast rearrangement of counterions in the asymmetric vesicle having different counterion composition at the outer and inner surfaces. The ability of a bilayer to avoid ion diffusion is determined by the packing of the alkyl chains, and permeability increases notably when this order is reduced, i.e., when the vesicles are heated above the phase transition temperature,[39-41] or when divalent cations (i.e., Ca^{2+}) are added which can disturb the bilayer structure (for example, with didodecyl phosphate bilayer membranes.[41] We consider that the most likely explanation of the increased permeation observed in the asymmetric bilayer is that changing the outer counterions imposes on the bilayer a tension that reduces the order and promotes rearrangement, most probably by enhancing the "flip-flop" movement, to achieve a thermodynamically stable state. Both effects, the reduced order of the bilayer and the increased flip-flop movement, can enhance the counterion permeation. Although, the driving force in this case is surely different, the results presented here provide another of a growing number of cases where the transit of impermeable of nearly impermeable ions across a bilayer is mediated by subtle changes in the external environment.[42-45]

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Effects of Palladium Particle Size and Palladium Silicide Formation on Fourier Transform Infrared Spectra of CO Adsorbed on Pd/SiO_2 Catalysts

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Two major modes of CO adsorption on SiO_2-supported Pd reflect different extents of back-donation, which is, at least in part, controlled by the local electron density at the adsorption site. The fraction of CO in the bridging mode (B) increases and that of the linear mode (L) decreases, with increasing size of the Pd particles, indicating high electron density at Pd atoms in terraces of close-packed crystal faces, in agreement with Smoluchowski's classical model.[1] For samples reduced at 300 °C our data points and those of other authors are located on a common curve of B/L vs metal dispersion. Extensive reduction at 600 °C results in significantly lower B/L values, attributed to the incipient formation of a palladium silicide. Oxidation followed by reduction at 300 °C destroys the silicide, and the B/L value returns to the original curve.

Introduction

Reduction of oxide-supported transition metals (e.g., Pt/Al_2O_3, Rh/TiO_2, or Pd/SiO_2) under severe conditions (e.g., flowing hydrogen at 700 °C) often induces characteristic changes of the adsorptive and catalytic properties of the metal. Previous research has identified two major causes for these changes:

1. Metal particle growth, mainly by migration of primary particles over the support surface, and their coalescence.[2] This results in a change of specific catalytic activity for structure-sensitive reactions.

2. Partial reduction of the supporting oxide, followed by chemical interaction with the metal. Well-documented examples are (a) formation of a PtAl alloy from Pt/Al_2O_3;[3-5] (b) formation of palladium silicide from Pd/SiO_2;[6,7] and (c) partial reduction

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