radicals detected may have resulted from decomposition of a resulting surface species. The remaining oxides (Bi_2O_3, γ-$Bi_2O_3 \cdot MoO_3$, and PbO) probably were incapable of promoting the initial hydrogen atom abstraction; therefore, neither gas-phase vinyl radicals nor a surface radical species were produced.

Lead monoxide (PbO), when heated in the presence of air or oxygen, is easily converted to the mixed oxide $Pb_2(II)Pb(IV)O_4$ (red lead), which behaves chemically as a mixture of PbO and PbO_2.[26] The standard high-temperature oxygen pretreatment used in this work would easily convert PbO to this mixed oxide form, and inspection of these samples (labeled PbO(I)) after pretreatment, and after reaction, confirmed this fact. To eliminate this transformation, PbO samples were examined after only a thermal, vacuum pretreatment and inspection of these samples (labeled PbO(II)), after reaction, indicated that the original form of the oxide had been preserved. Considering this chemistry and the radical amounts observed for the PbO samples, it appears that the sites responsible for hydrogen atom abstraction on these oxides

are most likely lattice O_s^{2-} ions associated with Pb(II) ions, and not Pb(IV).

Conclusions

The results described here clearly demonstrate that the ability of a surface to generate gas-phase hydrocarbon radicals depends upon the bond strength of the weakest C–H bond, the presence of particular radical-forming sites on the surface, and the propensity of the radicals to either desorb or to undergo further surface reactions. The importance of gas-phase radical coupling reactions is evident in the catalytic conversion of propylene to 1,5-hexadiene over Bi_2O_3[27] and the conversion of methane to ethane and ethylene over Li/MgO.[28] Subsequent surface reactions of allyl radicals are responsible for the conversion of propylene to acrolein over the bismuth molybdates.[15,16]

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Integrated Chemical Systems: Photocatalysis at TiO₂ Incorporated into Nafion and Clay

Fu-Ren F. Fan, Hsue-Yang Liu, and Allen J. Bard*

Department of Chemistry, The University of Texas, Austin, Texas 78712 (Received: June 7, 1985)

TiO_2 incorporated into Nafion or clay films has been prepared by treatment with Ti(III) followed by oxidation. Both systems show photocatalytic activity in the reduction of methylviologen (N,N'-dimethyl-4,4'-bipyridinium or MV^{2+}) with oxidation of triethanolamine. The state and the chemical reactivity of titanium species in Nafion were characterized by electron spin resonance (ESR) spectroscopy. The similarity with the solution spectra suggests that Ti(III) ions tumble in solvent-saturated Nafion but do not in the dry film. Oxygen adsorption on a dry Ti(III)-incorporated Nafion membrane gives a strong ESR signal with $g = 2.0095$, which has been assigned as the superoxo complex of Ti(IV).

Introduction

The utilization of integrated chemical systems[1] to carry out a particular process is of current interest. For example, the photogeneration of hydrogen on a p-type semiconductor electrode (e.g., GaAs and Si) is enhanced by the addition to its surface of a viologen-bearing polymer layer containing finely divided Pt and the photogeneration of oxygen or chlorine on an n-type semiconductor electrode (e.g., Si) is facilitated by the addition of RuO_2 to the surface silicide layer.[2] The incorporation of a dispersed semiconductor (e.g., CdS) within a polymer membrane to carry out photocatalytic and photosynthetic processes has also been described.[3] In these systems, suitable relays and catalysts can be added to promote photocatalytic reactions on these membranes. Separation of products may also be feasible in these systems. We report here another system based on titanium-exchanged Nafion

or clay (e.g., hectorite) membranes. TiO_2-based membrane integrated systems are of special interest because of the widespread use of TiO_2 particle dispersions in photocatalytic and photosynthetic studies.[4]

Experimental Section

Consider first the incorporation of Ti(III) into Nafion. A Nafion membrane (type 125, 110 equiv wt, thickness ca. 0.13 mm) was pretreated by boiling it in concentrated HNO_3 until it became clear and transparent. It was then soaked and stored in deionized distilled water. Ti(III)-exchanged Nafion was prepared by immersing a clean and thoroughly washed (with deoxygenated MeOH) Nafion membrane in a 0.1 M $TiCl_3$ (Alfa Products, Danvers, MA) in deoxygenated MeOH solution overnight. The light purple Ti(III)-incorporated Nafion membrane was then washed thoroughly with deoxygenated MeOH. The incorporation of Ti(III) into hectorite membranes was performed in a similar fashion.

The light purple Ti(III)–Nafion membrane (A), when exposed to moisturized air or immersed in air-saturated H_2O, became

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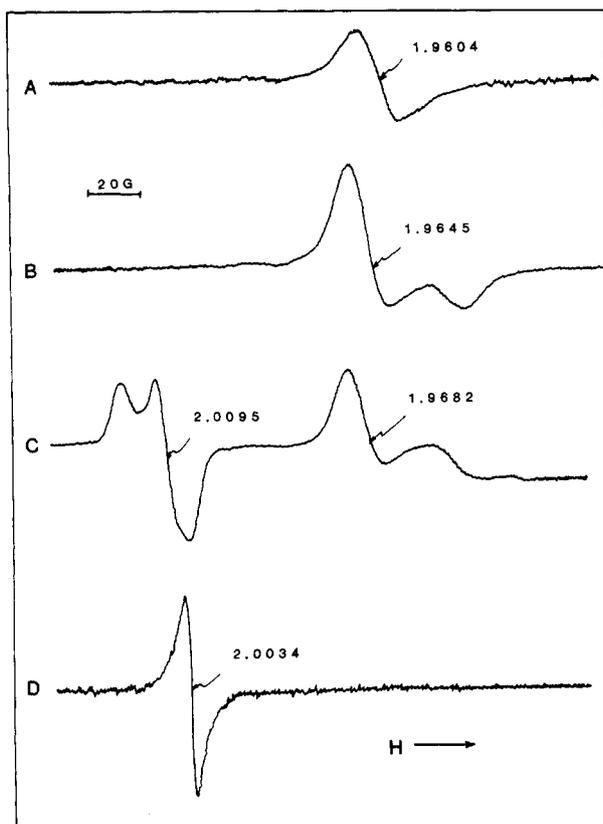
Figure 1. ESR spectra of Ti-incorporated Nafion membranes: (A) fresh Ti(III) in methanol-saturated Nafion membrane under N_2 at room temperature; (B) sample in (A) after evacuation for several hours at 10^{-4} torr in the dark at room temperature; (C) sample in (B) after exposed to dry O_2 in the dark for 10 min at room temperature; (D) sample in (C) after illumination with a 450-W Xe lamp under vacuum. ESR spectroscopy conditions: microwave frequency, 9.297 GHz; microwave power, 30–40 mW; modulation amplitude, 0.16–0.25 G; modulation frequency, 100 kHz; time constant, 0.3 s; receiver gain, (1.6–6.3) × 10^3; measuring temperature, 20 °C.

colorless. Both colorless and purple films when immersed in an acidic solution (pH ca. 0.5) containing excess hydrogen peroxide yielded the orange peroxo Ti(IV) complex (λ_{max} = 405 nm),[5] which confirmed that Ti had been incorporated into the membrane. The clay, Ca–hectorite (San Bernadino, CA), was exchanged to the Na form by repeated treatment with NaCl solution and then washed and dried by standard methods.[6] A clay membrane was then prepared by painting a clay gel (15% clay in H_2O) on a Teflon substrate, followed by drying at room temperature or in an oven (ca. 100 °C). After the Ti(III) was incorporated into the film, the clay membrane was then washed thoroughly with deoxygenated MeOH and again dried in an oven. This dry clay membrane could be peeled off the Teflon substrate quite readily.

A conventional three-electrode, single-compartment cell was used for photocurrent measurement.[7] The light source was an Oriel Corp. (Stamford, CT) 450-W Xe lamp. Instrumentation for photoelectrochemical experiments consisted of a Princeton Applied Research (PAR) Model 173 potentiostat/galvanostat and a PAR Model 179 digital coulometer. Electron spin resonance (ESR) measurements were made with a Varian E-9 X-band spectrometer equipped with a TE_{102} dual-sample cavity.

All chemicals were reagent grade and were used without further purification. Deionized distilled water for all experiments was from a Millipore water reagent system.

Results and Discussion

Electron Spin Resonance Studies. The light purple Nafion membrane A containing incorporated Ti(III) exhibits a nearly isotropic ESR spectrum, I, with a g value of 1.9604 and a line width of 16 G at room temperature (Figure 1A). Since the ESR spectrum of the Ti(III) ion in Nafion is readily observable at room temperature, the configuration of ligands around Ti(III) in Nafion clearly deviates from a species with perfect octahedral symmetry, which is ESR-inactive due to very rapid spin relaxation.[8] Evacuation of the Nafion membrane at 10^{-4} torr at room temperature for several hours yields a two-line ESR signal, II, which is much stronger than that observed before evacuation (Figure 1B). The line shape and g value (1.9682) in the dry film are very similar to those observed with an immobilized Ti(III)–porphyrin (Ti(F)(TPP)) crystal,[9] Ti(III) in MgO,[10] or Ti(III) in CH_3OD at low temperature.[11] The variation in the line shape and in the intensity with the state of solvation indicates that Ti(III) ions in solvent-saturated Nafion are capable of tumbling and that they lose this capability when the Nafion membrane is dry. Evidence of rapid tumbling of a paramagnetic ion ($MV^+\cdot$) in solvent-saturated Nafion has recently been reported.[12]

The admission of dry oxygen in the dark at room temperature and atmospheric pressure to the evacuated Ti(III)–Nafion system yields a new ESR signal, III (Figure 1C), at lower field (g = 2.0095), while the resonance of II decreases in intensity. Long-term exposure of the Ti(III)–Nafion membrane leads to a complete loss of signal II and yields an intense signal III, which will persist, if the membrane is kept in the dark under vacuum.

The line shape and g value of signal III are very similar to those observed for the dioxygen adduct of Ti(F)(TPP) which has been assigned to a superoxo Ti(IV) formalism.[9] Thus, we assign signal III in this titanium–Nafion system, B, to the formation of a superoxo Ti(IV) complex. Upon exposure of the Ti–Nafion system B to moisture, signal III gradually loses its intensity, presumably because of a spontaneous dismutation with the formation of a diamagnetic Ti(IV) peroxo or oxo compound. Illumination of the dry-oxygen-exposed Ti–Nafion membrane B under vacuum produced an intense, isotropic ESR signal, IV, at g = 2.0034 with a line width of 4.5 G (see Figure 1D). The identity of signal IV is still not clear but might be related to the photogenerated species responsible for the photoreduction of methylviologen, MV^{2+}, as illustrated below. There have been many studies of the ESR of different types of TiO_2 samples.[13] A signal with characteristics similar to that seen upon irradiation has been attributed to trapped electrons.

MV^{2+} Incorporation and Photocatalysis. Both colorless and orange Ti-incorporated Nafion membranes show additional cation-exchange sites for the incorporation of a cationic relay, such as MV^{2+}. If this membrane containing MV^{2+} and Ti is now immersed in a deaerated 0.1 M NaOH solution and irradiated with a 450-W Xe lamp coupled with a water filter, the membrane slowly turns purple. The addition of 50 mM triethanolamine as a sacrificial donor into the solution accelerates the rate of photoreduction of MV^{2+}. Within 1 s, an intense purple spot can easily be seen at the location where the membrane is illuminated. When the membrane is exposed to air, the dark purple spot gradually disappears. Such a coloring/bleaching cycle can be repeated many times. The reactions occurring under irradiation are probably the same as those at particulate suspensions of TiO_2,[14] i.e.,

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electron–hole pair formation followed by reaction of holes with triethanolamine (or water) and reaction of electrons with MV^{2+} yielding the blue $MV^{+}\cdot$. Similar $MV^{+}\cdot$ formation was observed with the CdS–Nafion system.[3b] Without the co-incorporation of Ti(III), a MV^{2+}–Nafion system fails to show photocoloration under the same experimental conditions. These results clearly demonstrate the photoactivity of a Ti–Nafion membrane and its ability to incorporate suitable redox relays. Ti(III) can also be incorporated into hectorite clay membranes. These show similar photoactivity toward the photoreduction of MV^{2+}. However, the clay membranes were mechanically much less stable than Nafion when immersed in water.

A SnO_2 electrode coated with Ti-incorporated Nafion immersed in 0.1 M NaOH solution containing 1.0 mM MV^{2+} and held at

–0.4 V vs. SCE shows a small photocurrent (ca. 1 $\mu A/cm^2$) under illumination with a 450-W Xe lamp. The addition of 50 mM triethanolamine into the solution as a hole scavenger, as expected, enhances the photocurrent (ca. 10 $\mu A/cm^2$). A bare SnO_2 electrode only shows a very small photocurrent (< 1 $\mu A/cm^2$) under the same experimental conditions.

To photoreduce water more efficiently through the mediator MV^{2+}, Pt or another hydrogen evolution catalyst needs to be incorporated into the membrane.[2b] By use of the technique employed for the incorporation of Pt into the CdS–MV^{2+}–Nafion system,[3b] incorporation of Pt into the Ti–Nafion or Ti–clay system appears possible. Extension of these systems for the photooxidation of water also appears feasible. These experiments are currently in progress.

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The Silicon/Aluminum Ratio of Single Crystals of Zeolite A Used for Crystal Structure Analysis

C. Scott Blackwell,*

Central Scientific Laboratory, Union Carbide Corporation, Tarrytown, New York 10591

Joseph J. Pluth, and Joseph V. Smith

Geophysical Sciences and Materials Research Laboratory, The University of Chicago, Chicago, Illinois 60637
(Received: June 18, 1985)

A magic-angle-spinning nuclear magnetic resonance spectrum of ^{29}Si in single crysals of as-synthesized zeolite A shows three peaks with the following chemical shifts, normalized integrals, and widths: –89.4 ppm, 89.3%, 73 Hz; –94.3 ppm, 9.2%, 171 Hz; –109.9 ppm, 1.5%, 49 Hz. The assignments of nearest tetrahedral neighbors are 4 Al, 3 Al + 1 Si, and 4 Si + 0 Al. The presence of the two weak peaks was confirmed by two more runs. The mean spectrum is consistent with occupancy by Si of ~1.5% (±0.5% precision) of the Al positions in an ideal framework with strict alternation of Si and Al. The NMR-derived Si/Al ratio of 1.03 ± 0.01 is consistent with the electron microprobe analyses and X-ray structure determinations by Pluth and Smith, and 1.04 ± 0.01 is consistent with a proton probe analysis by Hanson, Jones, and Smith. These observations rule out the arguments of Seff and Mellum for strict alternation of Si and Al in single crystals used for X-ray structural analysis.

Introduction

Determination of the Si/Al ratio is crucial to the interpretation of the crystal structure of zeolite A and ion-exchanged derivatives. Aliquots of the same batch of single crystals prepared by G. T. Kokotailo (Mobil Corp.) were used by K. Seff and students and by J. J. Pluth and J. V. Smith. The latter scientists concluded that the Si/Al ratio is greater than unity because of electron microprobe analyses and because of population refinements of exchangeable cations in as-synthesized zeolite A and various ion-exchanged derivatives: both techniques indicated a bulk Si/Al ratio near 1.03.[1] It should be emphasized that crystal structure analyses of dehydrated varieties which had been ion exchanged with *divalent* cations showed an aluminum oxide complex inside the sodalite unit and tetrahedral distances in the framework corresponding to alternation of Si and $Al_{0.9}Si_{0.1}$ over the tetrahedral sites.[2–4] Seff and Mellum[5] dispute these items of evidence and

claim that the Si/Al ratio of the crystals is unity. Furthermore, they incorrectly quote the statements by Pluth and Smith about the Si/Al ratio of the framework of the material exchanged by divalent cations.

Experimental Section

Figure 1 shows three magic-angle-spinning nuclear magnetic resonance spectra of ^{29}Si nuclei in as-synthesized zeolite A crystals from which Pluth and Smith selected their single crystals. Spectrum a was taken on an aliquot of about 0.3 g which was then analyzed with a proton probe in the Department of Applied Sciences, Brookhaven National Laboratory. It shows a strong peak with an isotropic chemical shift at –89.4 ppm, a broad shoulder near –94 ppm, and a weak peak at –110 ppm. After completion of the proton probe analysis, spectrum b was taken to check the reproducibility. A third spectrum (c) was taken as an additional check. The experimental conditions follow those in ref 6: Bruker CXP-200 instrument observing ^{29}Si at 39.74

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