Journal of Solid State Chemistry **144,** 349–353 (1999)
Article ID jssc.1999.8164, available online at http://www.idealibrary.com on IDEAL®

Copper Precursor Effect on Reducibility and Titania Phases Concentration of Sol–Gel Cu/TiO$_2$ Catalyst

X. Bokhimi[1] and O. Novaro[2]

Institute of Physics, The National University of Mexico (UNAM), A. P. 20-364, 01000 Mexico, D. F., Mexico

R. D. Gonzalez

Department of Chemical Engineering, Tulane University, New Orleans, Lovisiana 70118

and

T. López, O. Chimal, A. Asomoza, and R. Gómez

Department of Chemistry, Universidad Autónoma Metropolitana-I, A. P. 55-534, 09340 México, D.F., Mexico

Received June 8, 1998; in revised form January 6, 1999; accepted January 20, 1999

Cu/TiO$_2$ catalyst was synthesized by cogelling CuSO$_4$, or CuCl$_2$, with titanium ethoxide. Samples were nanocrystalline with titania phase concentration that depended on copper precursor and sample annealing temperature. Phase quantitative analysis was performed by refining crystalline structure. The fresh samples prepared with CuSO$_4$ contained almost amorphous rutile with an average crystallite size of 1.4(1) nm. Average crystallite sizes correlated well to BET areas, which were large for fresh samples and for those calcined at 400°C, and only a few square meters per gram for those calcined at 800°C. Hydrogen consumption of the samples prepared with CuSO$_4$ was 20 times larger than in those prepared with CuCl$_2$. Reduction temperature and hydrogen consumption, which are determined by copper–titania interaction, can be explained in terms of the main defects found in nanocrystalline titania phases: titanium vacancies and hydroxyls in their crystalline structure. © 1999 Academic Press

Key Words: ***Cu*/TiO$_2$ catalyst; copper oxide reduction; nanocrystalline titania; copper titania interaction; amorphous rutile.**

INTRODUCTION

The low cost and availability of copper and its activity as a catalyst for decomposition of nitrogen oxides (NO$_x$) make it very attractive to substitute for noble metals in this kind of reaction (1–6); copper also enhances hydrogen activation (7). To be used as a catalyst, copper is supported on oxides, which determine its dispersion and active surface area. From them, titania is one of the most used oxides (1, 8–10).

Copper supported on titania (Cu/TiO$_2$) has been mainly used to selectively reduce nitrogen oxides (11–13). These oxides bring down stratosphere's ozone concentration, and, together with sulfur oxides, represent the predominantly undesirable components responsible for atmospheric contamination (14). Titania is also a good catalyst support, because it has a high resistance to sulfur poisoning (7, 9, 15–16).

Titania crystallizes in different phases, brookite, anatase, and rutile. The stable phases at low sample calcining temperatures are brookite and anatase (17), which transform into rutile when they are annealed at higher temperatures. Brookite and anatase, however, can be stabilized at high temperatures by the ions present in the synthesis (18–20), which inhibit their transformation into rutile. Therefore, to understand Cu/TiO$_2$ catalyst behavior, it is necessary to analyze its titania phases and their transformations between each other.

When copper is supported on titania, the different copper oxidation–reduction cycles determine the stability of the metallic phases responsible for the catalytic behavior. Therefore, these cycles should be analyzed in detail, for example, by studying copper oxide reduction as a function of temperature and titania phases concentration. Catalyst thermal treatment, copper precursor, and synthesis method also have an enormous effect on its catalytic properties (8).

One of the best techniques to study copper reduction is the temperature programmed reduction (TPR). Here, catalysts are exposed to a reducing gas stream (for example H$_2$) while temperature is linearly increased. This technique provides the temperature at which reduction takes place, and

---

[1] To whom correspondence should be addressed.
[2] Member of El Colegio Nacional, Mexico.

0022-4596/99 $30.00

the H_2 amount consumed during reduction process. Under certain conditions, H_2 consumption can be correlated to the amount of reduced metal. In general, TPR results provide information about metallic dispersion, metal–support interactions, and catalytic activity and selectivity.

For the present study, TPR technique was used to analyze the reduction of Cu/TiO_2 catalyst prepared by using the sol–gel method with two different copper precursors. Reduction results were correlated with the titania phase concentrations and their average crystallite size, both determined by using X-ray diffraction and crystalline structure refinement.

EXPERIMENTAL

Cu/ TiO$_2$ (1.0 wt% Copper) Synthesis

Copper precursor, $CuSO_4 \cdot 5H_2O$ (Baker 99.9%) or $CuCl_2$ (Baker 99%), was dissolved in deionized water; sulfuric acid (Baker 98%) or hydrochloric acid was added until obtaining pH 3. To this solution, refluxed and stabilized at 70°C, titanium tetraethoxide (Alfa Products 99%) dissolved in absolute ethanol was dropped, stirring and refluxing continuously until gelling.

Fresh samples were dried at 70°C; thereafter, they were calcined in air at 400 or 800°C during 4 h.

TPR Analysis

TPR experiments we performed by using a TPD/TPR Micromeritics 2900 equipment with a thermal conductivity detector. About 30 mg of the sample previously annealed at the desired temperature was put in a quartz container. To stabilize the basis line, the gas mixture (Linde UHP) containing 30% nitrogen in helium was fluxed through the sample; thereafter, this gas mixture was substituted for the reducing gas (Linde UHP, 9.97% hydrogen in argon). Reduction was analyzed from room temperature to 650°C at 20°C/min.

X-Ray Diffraction

X-ray diffraction analysis was performed at room temperature with Cu$K\alpha$ radiation in specimens prepared by packing sample powders in a glass holder. Intensity was measured by step scanning in the 2θ range between 20 and 110°, with a 2θ step of 0.02° and a measuring time of 2 s per point. Crystalline structures were refined with the Rietveld technique by using DBWS-9411 (21) and WYRIET (22) programs. To determine average crystallite size, peak profiles were modeled with the pseudo-Voigt function modified by Thompson *et al.* (23), which has average crystallite size as one of the profile-breadth fitting parameters (24). Standard deviations, showing numbers of last figures variation, are given in parentheses. When they correspond to parameters obtained from the refinement, their estimated values are not estimates of the total probable error, but only of minimum possible probable errors based on their normal distribution (25).

BET Specific Surface Area

Specific surface areas were determined with an ASAP 2000 equipment that has nitrogen as adsorptive. BET areas were calculated from the nitrogen isotherms, from which mean pore size was also obtained by using the BJH method.

RESULTS AND DISCUSSION

Samples were crystalline with phase concentrations that depended on copper precursor and sample annealing temperature (Figs. 1 and 2). For their quantitative analysis, the different titania phases and tenorite (CuO) were modeled. Brookite was modeled with an orthorhombic unit cell described by space group *Pbca*; anatase was modeled with a tetragonal given by space group $14_1/amd$. Rutile was also modeled with a tetragonal unit cell but with the symmetry described by space group $P4_2/mnm$. Tenorite was modeled with a monoclinic unit cell that had the symmetry of space

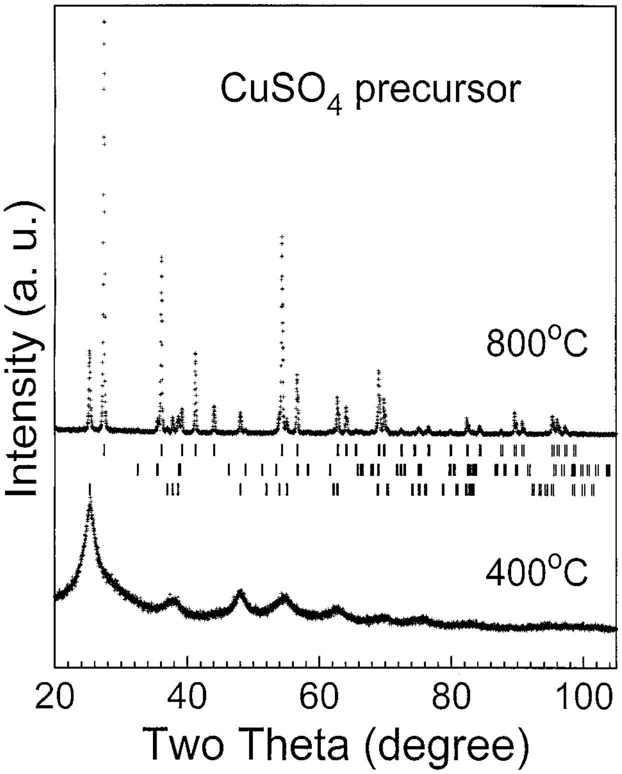

FIG. 1. Temperature dependence of X-ray powder diffraction patterns of the samples prepared with $CuSO_4$. Upper tick marks correspond to rutile, middle marks, to tenorite, and lower marks to anatase.

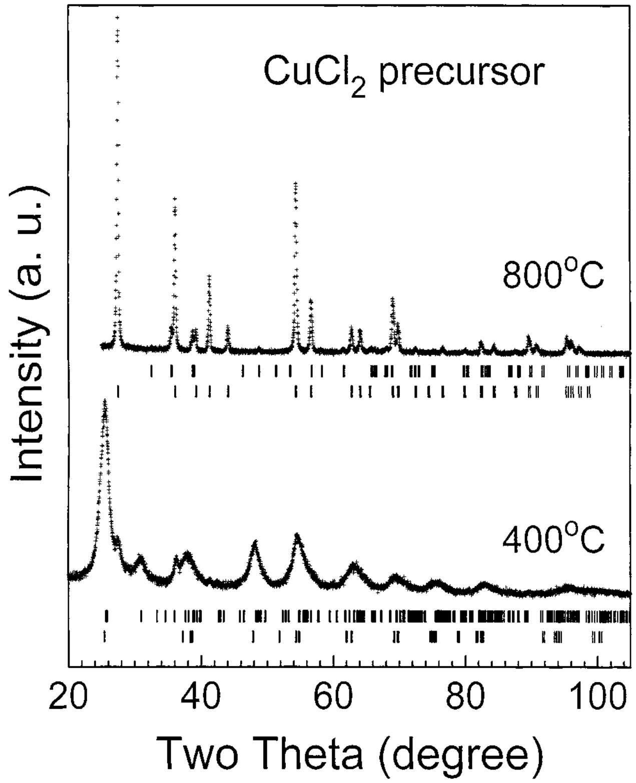

FIG. 2. Temperature dependence of X-ray powder diffraction patterns of the samples prepared with CuCl$_2$. Below the samples annealed at 800°C, the upper tick marks correspond to tenorite, the lower marks to rutile. Below the diffractogram of the sample calcined at 400°C, the upper tick marks correspond to brookite and the lower marks to anatase.

group *C*2*c*. Atom positions in the unit cell of titania phases were obtained from Bokhimi *et al.* (17).

For CuSO$_4$ precursor (Fig. 1), the fresh samples and those calcined at 400°C contained 58.0(5) wt% anatase (Table 1) with an average crystallite size of 3.5(1) nm (Table 2), and 42(1) wt% rutile with an average crystallite size of 1.4(1) nm (it was almost amorphous). BET area of these samples was 219 m^2/g (Table 3) showing that they were composed of single-crystal particles that produced pores with a mean diameter of 7.7 nm. When samples were calcined at 800°C, anatase was partially transformed into rutile with an average crystallite size of 128(3) nm, which gave rise to a BET area of only 5 m^2/g and a low hydrogen consumption (Table 3). The nontransformed anatase, which had an average crystallite size of 65(5) nm, was stabilized by the sulfate ions in the sample (20).

TABLE 1
Concentration of Titania Phases as a Function of Calcining Temperature

Sample	*T* (°C)	Brookite (wt%)	Anatase (wt%)	Rutile (wt%)
Prepared with CuSO$_4$	70	—	58.0 (5)	42 (1)
	400	—	58.0 (5)	42 (1)
	800	—	16.2 (9)	83.8 (9)
Prepared with CuCl$_2$	70	45.3 (8)	52.7 (5)	2.0 (2)
	400	46.7 (7)	46.8 (5)	6.5 (2)
	800	—	—	100

TABLE 2
Average Crystallite Size of Titania Phases as a Function of Calcining Temperature

Sample	*T* (°C)	Brookite (nm)	Anatase (nm)	Rutile (nm)
Prepared with CuSO$_4$	70	—	3.5 (1)	1.4 (1)
	400	—	3.5 (1)	1.4 (1)
	800	—	65 (5)	128 (3)
Prepared with CuCl$_2$	70	4.4 (2)	4.6 (3)	12 (2)
	400	5.2 (3)	5.9 (4)	12 (2)
	800	—	—	56 (2)

The samples prepared with CuCl$_2$ and calcined at 70°C were a mixture of brookite, anatase, and rutile (Fig. 2). Titania phase concentrations did not change when samples were annealed at 400°C (Table 1). Brookite and anatase, the main phases, had average crystallite sizes of 4.4(2) and 4.6(3) nm respectively, which, together with the BET area of 85.5 m^2/g (Table 4), indicate that these samples were also composed of single-crystal particles. When samples were calcined at 800°C, brookite and anatase were transformed into rutile with an average crystallite size of 56(2) nm, reducing sample BET area to only 4.6 m^2/g.

In the X-ray analysis, tenorite (CuO) was detected only when samples were calcined at 800°C (Figs. 1 and 2). This technique did not identify copper oxide in the samples annealed at lower temperatures. Since copper oxide reduces around 400°C, a better technique to identify it and its transformations at these temperatures is the thermo-programmed reduction.

To analyze the reduction of copper supported on titania, the reduction profile of pure tenorite was used as a base reference. Its TPR curve had a single maximum centred at 371°C (Fig. 3), which is in accordance with reported literature (26). In this temperature range, pure titania does not absorb hydrogen.

When samples were prepared with CuSO$_4$, the TPR curve of fresh and calcined samples at 400°C had a single reduction maximum (Figs. 3a and 3b), which were at 535 and 495°C respectively. They occurred at higher temperatures than in pure CuO, evidencing an interaction between CuO and titania. The samples calcined at this temperature contained similar concentrations of nanocrystalline anatase

TABLE 3
TPR Data of CuO and the Catalysts Prepared with $CuSO_4$ and Calcined at Different Temperatures

Sample	Temperature of reduction maxima (°C), and partial H_2 consumption (mmol H_2/g of Cu)	Total H_2 consumption (mmol H_2/g of Cu)	BET area (m^2/g)	Mean pore diameter (nm)
CuO	371 (18.63)	18.63	—	—
Calcined at 70°C	535 (19.20)	19.20	—	—
Calcined at 400°C	495 (13.64)	13.64	219.5	7.7
Calcined at 800°C	217 (0.032), 396 (0.836)	0.87	5.0	9.9

and rutile (Table 1). The small crystallite sizes favored a strong interaction between copper and titania.

Although anatase and rutile concentrations for both calcining temperatures (70 and 400°C) were almost the same, the reducing temperature was different, 535 and 495°C, respectively. This difference can be explained by taking into account the fact that hydroxyl concentration in sol–gel titania depends on its calcining temperature (17). The concentration in the samples calcined at 70°C is higher than in those calcined at 400°C. Therefore, if we assume that hydroxyls promote the interaction between titania and CuO, this interaction will be stronger in the samples calcined at 70°C. Consequently, they should have a higher reduction temperature.

The TPR curve of the samples calcined at 800°C had two reduction peaks (Fig. 3c); the main peak was broad with its maximum at 396°C. Since the samples calcined at this temperature were a mixture of anatase and rutile with very different average crystallite sizes, each reduction peak can be associated to one crystallite size.

Large crystallite sizes diminished the interaction between CuO and titania. This reduction can be explained in two ways. First, titania phases have titanium vacancy concentration that decreases as crystal size increases (17). A high vacancy concentration would favor the interaction of copper oxide with titania support. Second, hydroxyl concentration in titania crystalline structure decreases as crystallite size increases (17). If hydroxyls favor the interaction between copper and titania, this interaction would be weaker at higher crystallite sizes.

Hydrogen consumption depended on sample annealing temperature and copper precursor (Tables 3 and 4). Hydrogen consumption per gram of copper was 19.20 mmol H_2 for fresh samples, 13.64 mmol H_2 when they were calcined at 400°C, and 0.836 mmol H_2 when calcining temperature was 800°C. The large reduction of hydrogen consumption for this last temperature can be explained by assuming that titania partially covered the copper.

The samples prepared with $CuCl_2$ absorbed 20 times less hydrogen than when they were prepared with $CuSO_4$ (Tables 3 and 4). Hydrogen consumption varied between 0.44 and 0.65 mmol H_2 per gram of copper. This suggests that copper strongly interacted with titania.

TPR curves of the samples prepared with $CuCl_2$ and calcined at 70 and 400°C had three reduction maxima (Fig. 4). The peak a 274°C, which corresponds to a weak interaction, should correspond to the phase with the largest average crystallite size (Table 2), rutile. In the samples calcined at 400°C, the TPR maxima at 525 and 328°C can be associated to copper in the phases with the smaller average crystallite size, brookite and anatase, respectively. The absorption peak at 205°C corresponds to the interaction of copper with the crystallites of larger size, rutilie crystals. The shift of these peaks and the change in intensities, compared to fresh samples, could be produced by the difference in hydroxyl concentration in the samples.

TPR curves of the samples calcined at 800°C, which only contained rutile (Fig. 2 and Table 1), had one reduction peak at 413°C and another at 613°C (Fig. 4c). The peak at

TABLE 4
TPR Data of Catalysts Prepared with $CuCl_2$ and Annealed at Different Temperatures

Annealing temperture (°C)	Temperature of reduction maxima (°C), and partial H_2 consumption (mmol H_2/g of Cu)	Total H_2 consumption (mmol H_2/g of Cu)	BET area (m^2/g)	Mean pore diameter (nm)
70	274 (0.05), 417 (0.03) 497 (0.53)	0.61	—	—
400	205 (0.37), 328 (0.11), 525 (0.16)	0.65	85.5	3.4
800	413 (0.42), 617 (0.02)	0.44	4.6	5.5

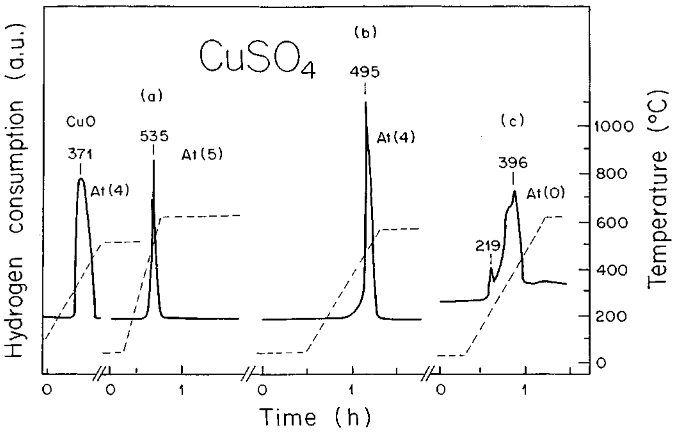

FIG. 3. TPR curves of the samples prepared with CuSO$_4$ and calcined at different temperatures: (a) 70°C, (b) 400°C, (c) 800°C. CuO is shown as a reference. At( ) represents attenuation factor; At(0) = 1.0.

613°C could indicate either a strong interaction between copper and titanium oxide or rutile partial reduction.

CONCLUSIONS

The titania phases formed in fresh Cu/TiO$_2$ catalyst depend on copper precursor. When it was CuSO$_4$, anatase and rutile were present with similar concentrations; rutile was almost amorphous. For the CuCl$_2$ precursor, brookite and anatase were the main phases having similar concentrations; rutile was an impurity.

Fresh samples were nanocrystalline, with single-crystal particles that gave rise to large BET areas and high hydrogen consumption. Hydrogen consumption and reduction temperatures were determined by the interaction between copper and titania phases. Since these phases are titanium deficient and have hydroxyls in their structure, this interaction was strongly affected by these defects.

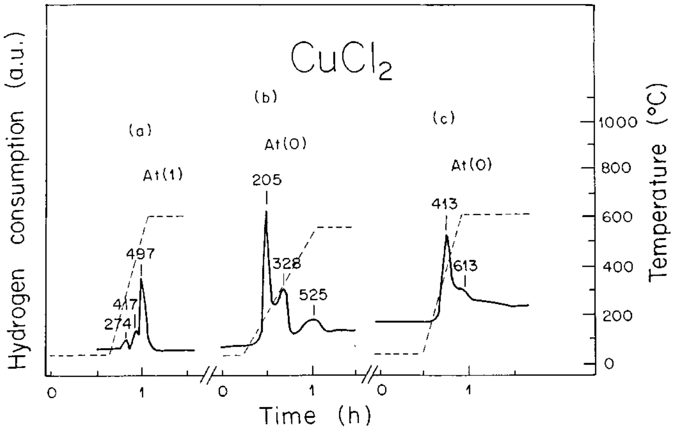

FIG. 4. TPR curves of the samples prepared with CuCl$_2$ and calcined at different temperatures: (a) 70°C, (b) 400°C, (c) 800°C. At( ) represents attenuation factor; At(0) = 1.0.

Hydrogen consumption of the samples prepared with CuSO$_4$ was 20 times larger than in those prepared with CuCl$_2$. This suggests that copper titania interaction is stronger in the samples prepared with this last precursor. It is expected that the catalytic properties of Cu/TiO$_2$ would also depend on the copper precursor.

ACKNOWLEDGMENTS

We thank Mr. A. Morales and Mr. A. Aguilar for technical assistance, and CONACYT, and FIES–IMP grant, Mexico, NSF–USA, and CNRS–France, for financial support.

REFERENCES

1. A. Wölner, F. Lange, H. Schmelz, and H. Knözinger, *Appl. Catal. A* **94,** 181 (1993).
2. H. Chen and R. B. Anderson, *J. Catal.* **43,** 200 (1976).
3. G. Ertl, R. Hierl, H. Knözinger, N. Thiele, and H. P. Urbach, *Appl. Surface Sci.* **5,** 49 (1980).
4. Y. A. Lokhov, L. N. Morozov, A. A. Davydov and V. V. Kostrov, *Kinet. Katal.* **21,** 943 (1980).
5. R. Liu, B. Tesche, and H. Knözinger, *J. Catal.* **129,** 402 (1991).
6. M. C. Schoenmarker-Stolk, J. M. Verwijs, and J. F. Scholten, *Appl. Catal.* **30,** 339 (1987).
7. H.-W. Chen, J. M. White, and J. G. Ekedt, *J. Catal.* **99,** 293 (1986).
8. M. del Arco, A. Caballero, P. Malet, and V. Rives, *J. Catal.* **113,** 120 (1988).
9. F. S. Delk II and A. Vavere, *J. Catal.* **85,** 380 (1984).
10. F. Boccuzzi, E. Guglielminotti, G. Martra, and G. Cerrato, *J. Catal.* **146,** 449 (1994).
11. K. C. Taylor, *Catal. Rev. Sci. Eng.* **35,** 457 (1993).
12. G. Centri and S. Perathoner, *Appl. Catal. A* **132,** 179 (1995).
13. K. M. Minachev, G. V. Aiitoshin, Y. A. Yusifov, and E. S. Shapiro, *ACS Symp Series* **40,** 559 (1977).
14. T. W. Danii, K. H. Schulz, M. Manii, and M. Collings, *Appl. Catal. B* **6,** 1 (1995).
15. M. del Arco and V. Rives, *React. Kinet. Catal. Lett.* **31,** 239 (1986).
16. P. A. Sermon, K. Rollins, P. N. Reyes, S. A. Lawrence, M. A. Luengo, and M. J. Davies, *J. Chem. Soc. Faraday Trans. 1* **83,** 1347 (1987).
17. Bokhimi, A. Morales, O. Novaro, T. López, E. Sánchez, and R. Gómez, *J. Mater. Res.* **10,** 2788 (1995).
18. E. Sánchez, T. López, R. Gómez, Bokhimi, A. Morales, and O. Novaro, *J. Solid State Chem.* **122,** 309 (1996).
19. R. D. Shannon and J. A. Pask, *J. Am. Ceram. Soc.* **48,** 391 (1965).
20. V. T. Zaspalis, W. Van Praag, K. Keizer, J. R. H. Ross, and A. J. Burggraaf, *J. Mater. Sci.* **27,** 1023 (1992).
21. R. A. Young, A. Saktivel, T. S. Moss, and C. O. Paiva-Santos, *J. Appl. Crystallogr.* **28,** 366 (1995).
22. Margarita Schneider. EDV-Vertrieb, Pöcking, Germany, 1992.
23. P. Thompson, D. E. Cox, and J. B. Hastings, *J. Appl. Crystallogr.* **20,** 79 (1987).
24. R. A. Young and P. Desai, *Arch. Nauki Mat.* **10,** 71 (1989).
25. E. Prince, *J. Appl. Crystallogr.* **14,** 157 (1981).
26. S. J. Gentry, N. W. Hurst, and A. Jones, *J. Chem. Soc. Faraday Trans. 1* **77,** 603 (1981).