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fine particles prepared at room temperature.

The total surface area of Pt–Ru/C was 1800 m^2 g^{-1} as determined from the nitrogen BET. The percent distribution of Pt, Ru, and Pt–Ru on carbon was found to be 77, 27, and 129, respectively. (The percent distribution is 100 times the ratio of the surface atoms of the catalyst, as estimated by hydrogen chemisorption, to the total number of atoms actually deposited onto a carbon support.) Maximum dispersion for Pt–Ru may be accounted for by the hydrogen spillover phenomenon. Robell et al.,[51] Boudart et al.,[52] and Bagotzky and Skundin[53] have also reported hydrogen spillover for Pt on carbon.

The 50–50 Ni–Ti alloy gave an X-ray diffraction pattern similar to that of Cr–Fe. The structure of this alloy changes with small departures from stoichiometry, and the stability of the alloy in the working electrolyte is only ensured at the 50–50 Ni–Ti composition. We therefore may assume that the surface composition is similar to that in the bulk.

Conclusions

Anticipation of a net charge transfer from the more electropositive to the more electronegative partner of a binary alloy is supported by spectroscopic evidence from the Pt–Ru system. Moreover, straightforward—though qualitative—arguments based on such a charge transfer are able to account satisfactorily for several features of the synergistic enhancement of activity on Pt–Ru alloys of three important fuel cell reactions. However, a relatively strong 3d-electron transfer from Ti to Ni, which is reponsible for the stabilization of Ni–Ti in acid, binds surface species won from the electrolyte too strongly to permit fuel cell reactants access to the surface. Therefore, as anticipated, fuel cell reactions are suppressed at a Ni–Ti electrode. On the other hand, electrolytic reactions proceed normally—and stably in acid—on a Ni–Ti alloy, but the onset potentials and exchange-current densities are shifted by the bias fields introduced by charge transfer within the alloy.

These preliminary results must encourage the exploration of other alloy systems tailored to promote specific catalytic reactions.

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Registry No. Pt–Ru, 12779-05-4; O_2, 7782-44-7; H_2, 1333-74-0; CH_2OH, 67-56-1; C, 7440-44-0; 50–50 Ni–Ti, 11110-85-3; 75–25 Pt–Ru, 37258-16-5; 40–60 Pt–Ru, 42615-02-1; 55–45 Pt–Ru, 50954-06-8; 70–30 Pt–Ru, 63627-81-6; 25–75 Pt–Ru, 121232-02-8; polyethylene, 9002-88-4.

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Formation of Particulate Opaque Silica Gels from Highly Acidic Solutions of Tetramethoxysilane

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The gelation behavior of highly acidic solutions of tetramethoxysilane (TMOS) of molar compositions $TMOS:H_2O:CH_3OH:HCl = 1:1.44–2.00:2:0.01–0.40$ has been studied. The most weakly acidic solutions (HCl/TMOS = 0.01) turned into spinnable sols and then transformed into transparent gel fragments, whereas solutions of higher HCl content did not show spinnability and lost their transparency before gelation. The gels derived from highly acidic solutions were of a particulate nature, consisting of distinct large particles. A gel monolith consisting of 5-μm particles was obtained from the solution of $TMOS:H_2O:CH_3OH:HCl = 1:1.53:2:0.40$.

Introduction

Synthesis of silica glass by the sol–gel method consists of (1) gel formation through hydrolysis and polycondensation reaction of silicon alkoxide, (2) drying of the wet gel, and (3) transformation of the dried gel into silica glass by sintering. This route for preparing silica glass is attractive since this makes it possible to prepare shaped silica glasses at low temperatures without melting. To make bulk silica gel, precursor for bulk silica glass, fracture of the gel during the drying process should be avoided. Crack formation during drying may be caused by the stress generated in the gel due to capillary forces, and hence it is assumed that the fracture may be suppressed by making gels having continuous pores of large size. Rabinovich et al.[1,2] have prepared gels with a two-mode pore-size distribution, one maximum in the region 1–8 μm and the other in the region 13–20 nm, by dispersing dense gels in water with a high-shear device. Scherer and Luong[3] have prepared silica particles of 60–100 nm in diameter by flame oxidation of $SiCl_4$ and dispersed them in organic liquids with the additions of alcohol, producing gelation by adding amines or ammonia. Prassas et al.[4] have prepared gels with a porous microstructure by heating sols in the autoclave prior to gelation. Another method for making crack-free

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Table I. Compositions and Properties of $Si(OCH_3)_4$ Solutions

compositions								
H_2O/TMOS	HCl/TMOS	CH_3OH/TMOS	sedimentation	appearance at gelation	appearance of dried gels	gelling time, h	spinnability	wt loss, %
2.00	0.01	2	no	transparent	transparent	12.6	yes	
2.00	0.40	2	no	transparent	transparent	0.6	no	3
1.70	0.01	2	no	transparent	transparent	13.4	yes	33
1.70	0.40	2	no	opalescent	opalescent	1.0	no	3
1.53	0.01	2	no	transparent	transparent	14.5	yes	39
1.53	0.15	2	no	opalescent	opaque	3.6	no	10
1.53	0.20	2	no	opalescent	opaque	2.9	no	7
1.53	0.25	2	no	opaque	opaque	2.5	no	7
1.53	0.30	2	no	opaque	opaque	1.9	no	7
1.53	0.35	2	yes	opaque[a]	opaque	(1.6)[b]	no	5
1.53	0.40	2	yes	opaque[a]	opaque	(1.3)[b]	no	4
1.44	0.01	2	no	transparent	transparent	17.2	yes	41
1.44	0.40	2	yes	opalescent[a]	opaque	(1.4)[b]	yes[c]	

[a] With liquid phase left on the gel at gelation. [b] No clear determination was made, since gelation occurred during sedimentation. [c] Sedimentary layer showed spinnability.

silica gel is to use solvents of low surface tension and low volatility; Adachi and Sakka[5-8] have used *N,N*-dimethylformamide as a DCCA (drying control chemical additive) and made a dried gel rod of 12 mm in diameter and 12 cm in length.

We[9,10] have found that monolithic opaque gels composed of large silica particles in the micrometer size range are obtained from tetramethoxysilane solutions, when a small amount of water (H_2O/TMOS < 2) and a large amount of hydrochloric acid (HCl/TMOS > 0.1) are used for hydrolysis. Because of the large pores, crack formation during drying can be suppressed easily. Formation of a crack-free opaque gel plate of 21 cm × 17 cm × 0.9 cm was possible.[10] This is a new method for making monolithic opaque silica gel and unique in that the process is very simple and the silica particle size, and accordingly the pore size, can be drastically changed by controlling the amount of hydrochloric acid.

In general, round-shaped silica particles are believed to be formed from alkoxide solution when a large amount of water or basic conditions are used for hydrolysis, whereas linear particles or polymers are formed with addition of a small amount of water under acidic conditions.[11]

In the present study, effects of the amount of water and acid on gelation behavior of tetramethoxysilane solution are investigated.

Experimental Section

Tetramethoxysilane $Si(OCH_3)_4$ (TMOS, Chisso Co. Ltd.), 99.6% methanol (CH_3OH, Wako Pure Chemical Ind., Ltd.), 36% hydrochloric acid (Wako Pure Chemical Ind., Ltd.), and ion-exchanged water were used as the starting materials. Alkoxide solutions having the mole ratio of TMOS:H_2O:CH_3OH:HCl = 1:1.44–2.00:2:0.01–0.40 were prepared by mixing the reagents under vigorous stirring at room temperature: 50 mL of the alkoxide solutions were kept at 40 °C in an uncovered 100-mL beaker 50 mm in inner diameter and 70 mm in height.

To study the spinnability of the sols, a glass rod was immersed in the sol and pulled up. Fracture surfaces of the dried gels were observed by Hitachi S-450 scanning electron microscope. Raman spectra of the alkoxide solutions were measured with Nippon Bunko Co. Model JASCO NR-1000S laser Raman spectrometer using Ar^+ laser operating at 250 mW of power at 5145 Å.

Results

Gel Formation. Initially, all the starting solutions were transparent. It was found, however, that the solutions of higher HCl and lower H_2O contents have a higher tendency of turning opalescent or translucent before gelation. This effect of the composition can be clearly seen in the appearance of the gels at gelation shown in Table I. In the series of constant H_2O content at H_2O/TMOS = 1.53, transparent gels were obtained for the lowest HCl content at HCl/TMOS = 0.01, opalescent gels at HCl/TMOS = 0.15–0.20, and opaque gels at HCl/TMOS > 0.20. On the other hand, for the series of constant HCl content at HCl/TMOS = 0.40, formation of a transparent gel is found only for the solution of the highest H_2O content at H_2O/TMOS = 2.00.

In the solutions having the highest HCl and the lowest H_2O contents at HCl/TMOS = 0.35 or 0.40 and H_2O/TMOS = 1.44 or 1.53, occurrence of slow sedimentation of particles was observed before gelation. For the solutions of the composition of H_2O/TMOS = 1.53 and HCl/TMOS = 0.40, gelation took place as sedimentation proceeded, leaving a liquid phase of less than 10% of the total volume above the gel. For the solution having a still lower H_2O content at H_2O/TMOS = 1.44 and the same HCl content at HCl/TMOS = 0.40, more evident tendency for sedimentation was found; a sedimentary layer of about 20% of the total volume gelled at the bottom of the container.

Figure 1 shows the dependence of the gelling time and the time for occurrence of opalescence on the HCl and H_2O content. As seen in Figure 1, top, the solutions having an H_2O content of H_2O/TMOS = 1.53 turn opalescent for HCl/TMOS $\geqslant$ 0.15 and are gelled at 0.5–1 h after disappearance of the transparency. Gelation and disappearance of the transparency occur faster for solutions of higher HCl contents. For the series of the solutions having constant HCl contents at HCl/TMOS = 0.01 and 0.40, the gelling time is shortened as the H_2O content increases as shown in Figure 1, bottom.

Spinnability of the Sols. As shown in Table I, gel fiber drawing from the viscous sol was possible for all the solutions having the lowest HCl content at HCl/TMOS = 0.01, gelation of which was accompanied by 30–40% weight loss due to vaporization of the solvent, leading to the formation of concentrated, transparent sols. In contrast to this, spinnability was not seen in the nontransparent sols, that is, the sols derived from the solutions of higher HCl contents. Gelation of these nonspinnable sols was

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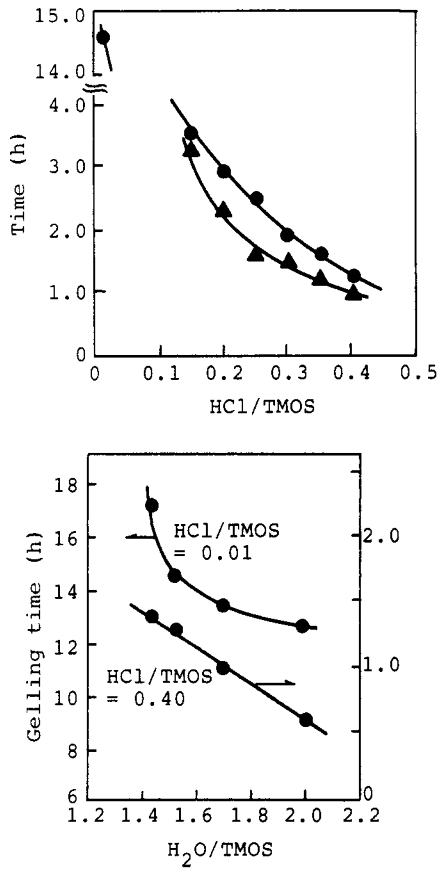


Figure 1. Dependence of gelation time (●) and time for appearance of opalescence (▲) on HCl/TMOS ratio and H_2O/TMOS ratio: (top) H_2O/TMOS = 1.53; (bottom) HCl/TMOS = 0.01 and 0.40.

accompanied by less than 10% weight loss of the solvent. It should be noticed, however, that in the solution of the highest HCl content at HCl/TMOS = 0.40 but the lowest H_2O content at H_2O/TMOS = 1.44, the sedimentary layer mentioned above was viscous and showed spinnability before gelation.

Appearance of the Dried Gel. Figure 2 shows the appearance of the dried gels. In the series of the solutions having a constant H_2O content at H_2O/TMOS = 1.53 (Figure 2a–c), the transparency of the gel and the tendency for crack formation in the gel decreases as the HCl content increases. Totally crack-free opaque gel was formed from the solution of HCl/TMOS = 0.40 and H_2O/TMOS = 1.53 (Figure 2c).

On the other hand, in the series of the solutions having a constant HCl content at HCl/TMOS = 0.40 (Figure 2c–e), the transparency and the tendency for crack formation decrease with decreasing amount of H_2O from H_2O/TMOS = 2.00 to 1.53. In the solution of the lowest H_2O content at H_2O/TMOS = 1.44, however, the sedimentation layer transformed into opaque gel fragments as shown in Figure 2f.

SEM Observations. Figure 3 shows the scanning electron micrographs of the fracture surfaces of the dried gels. In the series of constant H_2O content at H_2O/TMOS = 1.53, particulate texture is seen in the gels derived from the solutions of higher HCl content at HCl/TMOS = 0.15 and 0.40 (Figure 3b,c), which are opaque in appearance, whereas no distinct microstructure can be seen in the transparent gels from the solution having the least HCl content at HCl/TMOS = 0.01 (Figure 3a). Connected round-shaped particles are clearly seen in the photograph of the gel prepared from the solution of HCl/TMOS = 0.40 (Figure 3c), indicating that the particles build up the gel skeleton. Dependence of the particle size determined by the SEM observation on the HCl content for this series is shown in Figure 4, where the bulk density of the dried gels is also shown as a function of the HCl content. The particle size increases up to about 5 μm with increasing HCl content, and the bulk density of the dried gel decreases with increasing HCl content. That is, gels composed of larger particles have smaller bulk density.

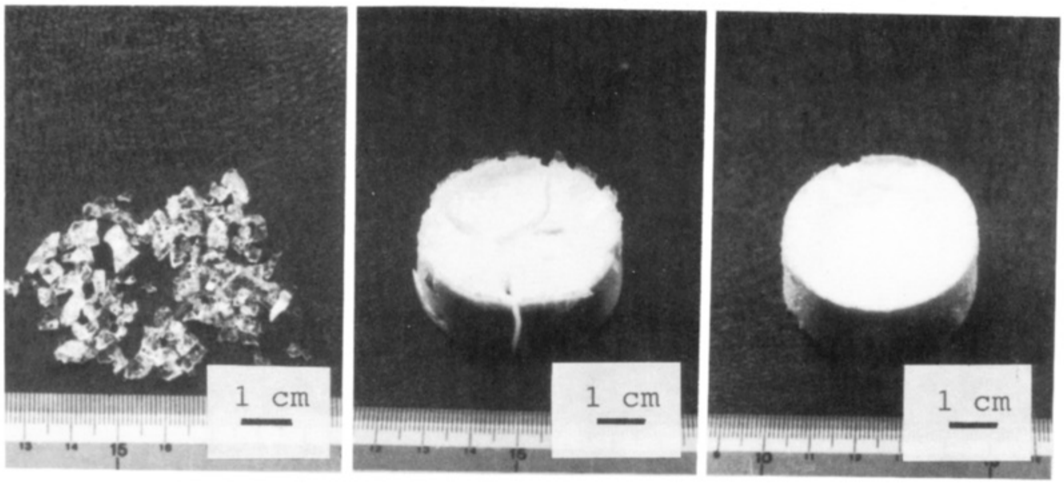
In the series of a constant HCl content at HCl/TMOS = 0.40 (Figure 3c–g), particulate configuration is seen for H_2O/TMOS > 1.50. The particle size increases with decreasing H_2O/TMOS ratio from 2.00 to 1.53, corresponding to the decrease in the transparency of the dried gels. Still lower H_2O contents, however, are found to provide a higher degree of particle coagulation. As shown in Figure 3f, the gel obtained from the solution of H_2O/TMOS = 1.50 has no distinct particulate configuration, in some part due to the high degree of particle coagulation. In the gel derived from the solution of the lowest H_2O content at H_2O/TMOS = 1.44 (Figure 3g), the voids between the particles transform into closed pores and particulate configuration completely disappears. Vaporization of the solvent in the closed pores causes fracture of the gel during drying (see Figure 2f).

It should be noticed that particulate nature is not seen in the gels formed from spinnable sols, that is, in the gels derived from the solution of the lowest HCl content at HCl/TMOS = 0.01 and from the solution of the highest HCl content at HCl/TMOS = 0.40 and the lowest H_2O content at H_2O/TMOS = 1.44 (Figure 3 a and g).

Raman Spectra. Figure 5 shows the Raman spectra of the solution of molar composition TMOS:H_2O:HCl:CH_3OH = 1:1.53:0.40:2, which turns opaque at 1.1 h after preparation, transforming into an opaque gel composed of particles 5 μm in diameter. Spectra of TMOS and CH_3OH are also shown. It can be seen that just after mixing the reagents, unhydrolyzed TMOS molecules disappear, indicating that all the alkoxide molecules are attacked by water in the initial stage of the reaction.

Gelation under Centrifugation and Effects of Addition of Organics. Centrifugation was performed for the solution of molar composition TMOS:H_2O:HCl:CH_3OH = 1:1.53:0.40:2, aged at 40 °C for 45 min, which corresponds to the time just before the occurrence of opalescence, beyond the gelation. The rate of centrifugation was 3000 rpm and was performed at room temperature. Figure 6a shows the SEM of the fracture surface of the resultant dried gel. For comparison, the micrograph of the gel obtained by keeping the same solution at room temperature after aging at 40 °C for 45 min is also taken (Figure 6b). Closed pores are observed in the gel obtained through centrifugation, whereas particulate structure is seen in the gel without centrifugation.

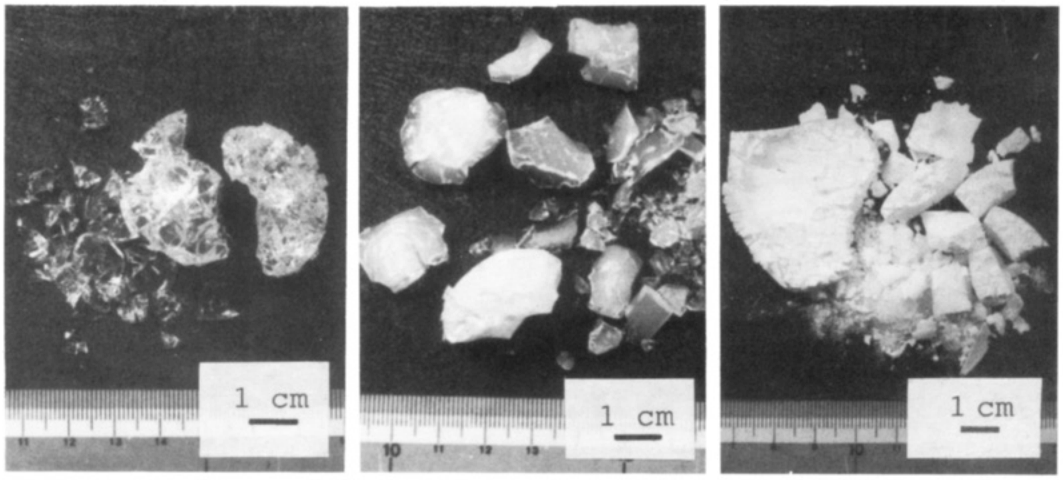
Benzene (20 mL) was added to a 25-mL solution of the above composition after aging at 40 °C for 50 min, when the opalescence of the sol appeared. It was found that the sol turned transparent by the addition and mixing. After addition of benzene, the transparent sol was kept 40 °C in an air-sealed beaker. The scanning electron micrograph of the resultant dried gel is shown in Figure 7a, where particles much smaller than those observed in the gel prepared without addition of such organics are seen. It is not the effect of the dilution of the sol; to confirm this, 20 mL of CH_3OH, the solvent, was added to 25 mL of sol under the same condition, and after that the sol was converted to gel in the same manner. The microstructure of the resultant gel is shown in Figure 7b, where microme-



HCl/TMOS = 0.01
H_2O/TMOS = 1.53
(a)

HCl/TMOS = 0.15
H_2O/TMOS = 1.53
(b)

HCl/TMOS = 0.40
H_2O/TMOS = 1.53
(c)



HCl/TMOS = 0.40
H_2O/TMOS = 2.00
(d)

HCl/TMOS = 0.40
H_2O/TMOS = 1.70
(e)

HCl/TMOS = 0.40
H_2O/TMOS = 1.44
(f)

Figure 2. Appearance of the dried gels. Constant H_2O/TMOS series (a–c) and constant HCl/TMOS series (c–f).

ter-sized particles are clearly observed.

Discussion

Initial Stage of the Reaction. The present study has shown that round-shaped particles are formed even in acidic solutions containing a small amount of water, and spinnability of sols is not likely to be observed when the amount of HCl increases.

Sakka and Kamiya have shown that one-dimensional polymers or particles are formed in TEOS solutions when a limited amount of water ($H_2O/TEOS < 4$) and a small amount of acid ($HCl/TEOS = 0.01$) are used for the hydrolysis.[11] Recently, however, Orgaz and Rawson[12] have referred to the formation of round-shaped particles in highly acidic TEOS solutions, and Kamiya and Yoko[13] have found that gel fiber drawing is difficult for highly acidic solutions of tetraethoxysilane (TEOS), probably due to the formation of round-shaped particles. Thus, round-shaped particles are likely to be formed under highly acidic conditions, but the mechanism of the formation of such particles is not yet clear.

Generally, the shape and the nature of polymerized species formed in the alkoxide solutions depend on the kind of catalysts and the amount of water used for the hydrolysis reaction. Under acidic conditions, polymerized species with a less cross-linked structure are formed when the amount of water is small, leading to formation of spinnable sols.[11] On the basis of a previous Raman spectroscopic study[9] on $TMOS:H_2O:HCl:CH_3OH$ solutions, it was found that under acidic conditions unhydrolyzed TMOS molecules disappear in the initial stages of the reaction even in the solutions having a H_2O/TMOS ratio less than 2, indicating that the probability of the hydrolysis reaction is equal for all alkoxide monomers. This results in formation of partially hydrolyzed alkoxide molecules in the solution when the amount of water added is small. Since the number of sites that can undergo condensation is limited under such conditions, less cross-linked polymers are formed. When the amount of water is large, however, the number of sites hydrolyzed is so large, even under acidic conditions, that highly cross-linked polymers may

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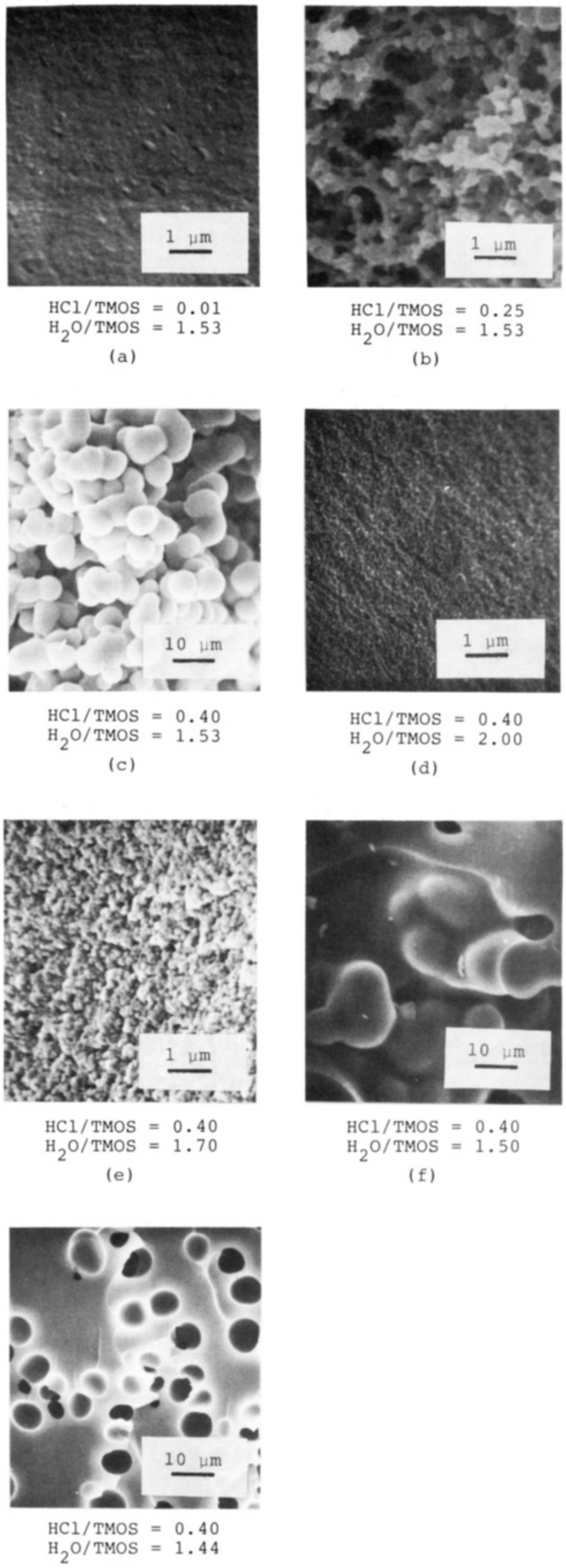

$HCl/TMOS = 0.01$
$H_2O/TMOS = 1.53$
(a)

$HCl/TMOS = 0.25$
$H_2O/TMOS = 1.53$
(b)

$HCl/TMOS = 0.40$
$H_2O/TMOS = 1.53$
(c)

$HCl/TMOS = 0.40$
$H_2O/TMOS = 2.00$
(d)

$HCl/TMOS = 0.40$
$H_2O/TMOS = 1.70$
(e)

$HCl/TMOS = 0.40$
$H_2O/TMOS = 1.50$
(f)

$HCl/TMOS = 0.40$
$H_2O/TMOS = 1.44$
(g)

Figure 3. Scanning electron micrographs of the fracture surfaces of the dried gels. Constant $H_2O/TMOS$ series (a–c) and constant HCl/TMOS series (c–g).

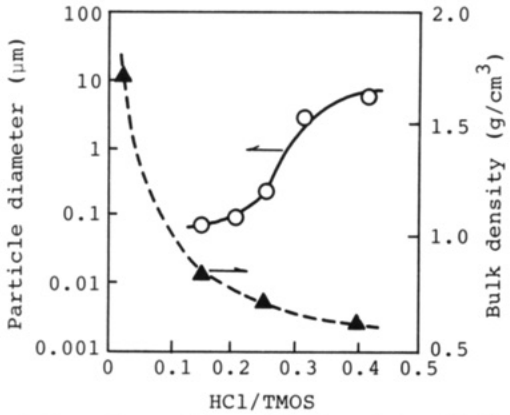

Figure 4. Dependence of the particle size and the gel bulk density on HCl/TMOS ratio; $H_2O/TMOS = 1.53$.

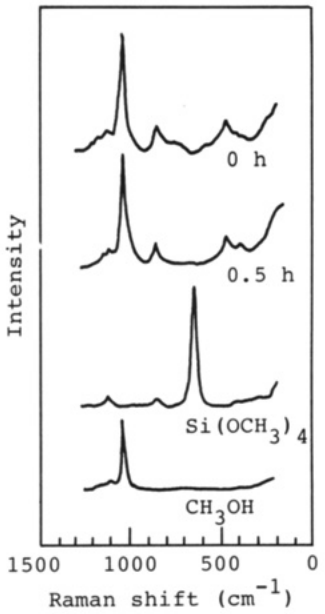

Figure 5. Raman spectra of the alkoxide solution of $HCl/TMOS = 0.40$ and $H_2O/TMOS = 1.53$, tetramethoxysilane, and methanol. The alkoxide solution becomes opaque at 1.1 h, just before gelation.

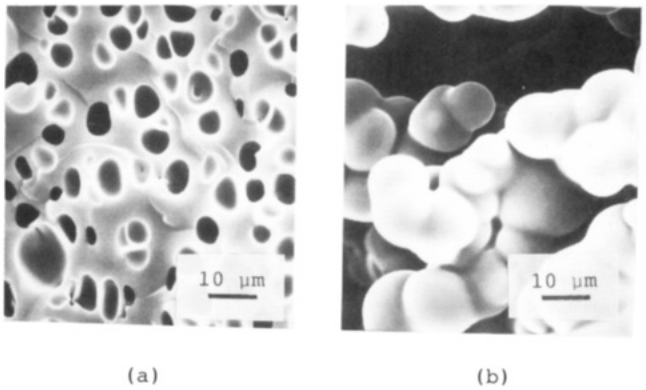

Figure 6. Scanning electron micrographs of the fracture surface of the dried gels obtained with centrifugation (a) and without centrifugation (b).

be generated, leading to formation of round-shaped particles and nonspinnable sols.

On the other hand, under basic conditions, the probability of the hydrolysis reaction does not appear to be equal for all of the alkoxide molecules, especially when the amount of water is limited.[9] The rate of hydrolysis is higher for partially hydrolyzed species than for non-

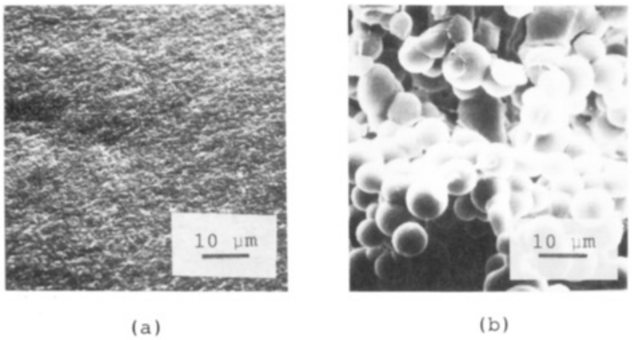

Figure 7. Scanning electron micrographs of the fracture surface of the dried gels derived from the solution to which benzene was added (a) and methanol was added (b) after the occurrence of opalescence.

hydrolyzed species, which allows formation of completely hydrolyzed $Si(OH)_4$ monomer, even when the water content is small. As a result, highly hydrolyzed species are formed, and the condensation reaction occurs between these species, which provides highly cross-linked polymers and round-shaped particles. Solutions containing such polymerized species do not show spinnability.

The mechanism of formation of round-shaped particles under highly acidic conditions with a limited water content seems to be different from that for basic conditions, in which a part of $Si(OCH_3)_4$ molecules are hydrolyzed to $Si(OH)_4$, while the rest remains unreacted. Raman spectra of the highly acidic solution (Figure 5) have shown that unhydrolyzed alkoxide molecules disappear in the initial stage of the reaction as is observed in the weakly acidic solution. Considering that the H_2O/TMOS ratio is limited to 1.53, it is possible that every alkoxide molecule is subjected to hydrolysis, leading to formation of partially hydrolyzed alkoxide molecules. Hence, formation of highly cross-linked polymers, as is observed under basic conditions, is not expected to take place.

Formation of the Round-Shaped Particles. Because of the small amount of water used in the hydrolysis reaction, a large amount of unhydrolyzed alkoxy groups, which are lipophilic in nature, are expected to be left on the polymerized species. It is also assumed that a larger portion of methanol may be protonated and the ionic nature of the solvent may increase as the HCl content increases, resulting in a decrease in solubility of alkoxy groups in the solution. It might be possible that under such conditions linearly polymerized primary particles form round-shaped secondary particles by folding themselves into a micellar structure, leaving hydrolyzed groups on the surface of a secondary particle and unhydrolyzed groups inside the particle.

The assumption that the micrometer-sized particles are secondary particles is supported by the pore-size distribution curve of the dried gel. Small pores less than 100 Å in size may be the voids between the primary particles.[14] This assumption is supported by the experimental fact that a translucent solution of HCl/TMOS = 0.40 and H_2O/TMOS = 1.53 turns transparent when benzene is added before gelation. Such disappearance of the translucence by adding a nonpolar organic solvent would not be expected for colloidal sols. This means that the origin of the translucence resides not in stable silica particles insoluble in nonpolar organic solvents but in secondary particles or droplets composed of polymers or primary particles that are soluble in such solvents. This is suggested by the fact that nonparticulate nature was found in the gels obtained through centrifugation; if the micrometer-sized particles are stable silica particles, such a structure is not expected to be formed.

The fact that the sedimentary layer formed in the solution of HCl/TMOS = 0.40 and H_2O/TMOS = 1.44 is viscous and shows spinnability before gelation suggests that especially when the amount of water added is quite small, the sedimentary particles consist of weakly cross-linked, flexible polymers that provide spinnability but not highly cross-linked, rigid silica particles.

Effect of the Composition on Gelation. It is known[15,16] that the rate of hydrolysis and polycondensation of silicon alkoxide increases as the pH of the solution decreases in the range pH < 2. Hence, it is expected that larger polymerized species are formed under highly acidic conditions. This is reflected in the formation of larger particles, presumably composed of larger primary species, and the shorter gelling time observed for the solutions of higher HCl content in the present study.

In a previous study,[17] we have shown that the translucence of the gels decreases when alcohols having longer carbon chains are used as solvents. This can be attributed partly to the higher solubility of the nonhydrolyzed methoxy groups in the alcohols having longer carbon chains and partly to a decrease in the reaction rate, which is caused by the ligand exchange between the methoxide and the alcohol. We have also found that the tendency of sedimentation or occurrence of opalescence increases as the dissociation constant of an acid used as a catalyst increases.[17] This may be due to an increase in the reaction rate by the lowering of the pH, which may provide larger primary particles, and to an increase in the ionic strength of the solution.

Thus, the formation of round-shaped particles in highly acidic alkoxide solutions is considered to take place for the composition that provides a high rate of chemical reaction, lipophilic nature of the linearly polymerized species, and ionic strength of the solvent.

Formation of Nonspinnable Sols. Spinnability of the sols is not likely to occur in the sols derived from highly acidic TMOS solutions. It has already been shown by viscosity measurements[11] that concentrated sols composed of linear particles or polymers exhibit spinnability at a viscosity range of 10–100 P, whereas sols composed of round-shaped particles do not show spinnability. In the highly acidic TMOS solutions, round-shaped secondary particles are formed, which makes the sol nonspinnable, although the primary particles are thought to be linearly polymerized species. When the water content is limited to H_2O/TMOS = 1.44, however, the sedimentary layer showed spinnability even for the high HCl content of HCl/TMOS = 0.40. In this case, the sedimentary layer is assumed to be composed of linearly polymerized sol particles, which do not form round-shaped secondary particles because of the limited number of hydrolyzed sites.

Conclusions

The gelation behavior of TMOS solutions of molar composition $TMOS:H_2O:CH_3OH:HCl$ = 1:1.44–2.00:2:0.01–0.40 has been investigated as functions of HCl and H_2O content in the starting solutions. Gels composed of secondary round-shaped particles were found to be formed under highly acidic conditions, where the particle size increases with increasing HCl and decreasing

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H_2O content in the starting solutions. Larger amounts of HCl in the starting solution gave rise to the formation of monolithic opaque gels with larger particles and accordingly larger open pores. It was argued that particles in the solutions do not form rigid, highly cross-linked polymers as in base-catalyzed solutions but form round-shaped secondary particles composed of linearly polymerized primary particles.

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A New Amorphous Magnetic Material: $Fe_5(InTe_4)_2$

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A new ternary Zintl material of the formula K_5InTe_4 has been prepared. This material undergoes a metathesis reaction with ferrous chloride in aqueous solution to produce the alloy $Fe_5(InTe_4)_2$. The dc magnetic susceptibility of $Fe_5(InTe_4)_2$ is reported and is consistent with a spin glass having a freezing temperature of $T_f = 15$ K. The isothermal and thermal remanent magnetization experiments are also described. The ac magnetic susceptibility has been measured as a function of frequency and temperature and exhibits a broad maximum with two humps occurring at 15 and 32 K.

Introduction

Zintl phases are combinations of metals and/or metalloids in which large differences in electronegativity result in a substantial amount of ionic character in the bonds.[2,3] A ternary Zintl material K_4SnTe_4 has been prepared[4] and has been shown to react with divalent transition-metal cations in methanolic solution to produce amorphous alloys of the formula M_2SnTe_4, M = Cr, Mn, Fe, Co, and Ni. Recent studies of these alloys have shown them to exhibit spin glass behavior,[5-9] unusual photomagnetic effects,[10] a wide range of electrical resistivities,[11] and form thin films on polyimide plastics.[12,13]

We have now prepared a new ternary Zintl phase material, K_5InTe_4. The ionic character of K_5InTe_4 permits the Zintl phase to form an ionic solution in polar solvents such as water and liquid ammonia, as shown in (1).

$$K_5InTe_4(s) \xrightarrow{H_2O \text{ or } NH_3} 5K^+ + InTe_4^{5-} \qquad (1)$$

In the presence of a transition-metal cation of sufficient electron affinity, this material will form an insoluble metallic alloy of formula M_nInTe_4 due to the redistribution of charge between the $InTe_4^{5-}$ anion and the metal cation following reaction 2, where the stoichiometric coefficient

$$M^{\delta+} + InTe_4^{5-} \rightarrow M_nInTe_4(s) \qquad (2)$$

n is determined by the charge δ on the metal cation as well as other reduction characteristics of the solution. In this report, we describe the synthesis and characterization of a new amorphous magnetic material, $Fe_5(InTe_4)_2$, which forms from the reaction of the Zintl phase material, K_5InTe_4, with $FeCl_2$ in an aqueous solution.

Experimental Section

Synthesis. Due to the extreme sensitivity of these compounds, all manipulations were carried out in an argon-filled glovebox containing less than 1 ppm of oxygen.

K_5InTe_4. The binary Zintl phase K_5In_8 was prepared by mixing molten potassium with molten indium in a stoichiometric ratio in a quartz crucible to give the K_5In_8 shiny black powder. Then the K_5In_8 powder was mixed with tellurium powder in the molecular ratio of 1 to 4 and heated at 550 °C for 4 h in a furnace. The resulting solid was dissolved in the water and filtered to remove the excess solid indium metal, while the ternary Zintl phase, K_5InTe_4, remained in solution. The percentage yield of K_5InTe_4 was greater than 95%. The growth of single crystal of this Zintl phase from an aqueous solution has not been successful due to its extremely large solubility. Attempts to grow single crystals in liquid ammonia, ethylenediamine solution, or in the molten phase are in progress. Elemental analysis (Schwarzkopf Analytical Labs, NY) gave the following empirical formula: $K_{4.92}InTe_{3.83}$.

$Fe_5(InTe_4)_2$. The ferrous indium telluride was prepared by the reaction of aqueous solutions of K_5InTe_4 and $FeCl_2$. In a typical preparation, while stirring the $FeCl_2$ solution (40 mL, 0.05 M), a stoichiometric quantity of the K_5InTe_4 solution (50 mL, 0.1 M) was slowly added. A fine black precipitate was immediately formed, separated by suction filtration, washed with water and acetone, and dried overnight under vacuum. Elemental analysis (Schwarzkopf Analytical Labs, NY) gave the following empirical formula: $Fe_{2.97}InTe_{3.86}$. The analysis indicates that the material is slightly iron rich; however, previous analyses of transition metals in related alloys (e.g., M_2SnTe_4[11,12]) commonly give higher apparent

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