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Characterization of di-phasic nanoscale composites derived from xerogels

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Di-phasic xerogel-derived composites, such as SiO_2–AgCl, SiO_2–$AlPO_4$, SiO_2–$CePO_4$, SiO_2–Nd_2O_3, SiO_2–CdS, SiO_2–$CrPO_4$, SiO_2–$BaSO_4$ and SiO_2–$PbCrO_4$ have been characterized in detail by X-ray powder diffraction (XRD), transmission electron microscopy (TEM) and selected-area electron diffraction (SAED) techniques. The SiO_2–AgCl photochromic composites with small amounts of AgCl did not show any crystallinity either by XRD or by SAED. Thin edges of these SiO_2–AgCl composites did not reveal discrete AgCl particles because these are too small to be resolved even by TEM and are expected to be in the range 1.5 to 2.5 nm in size based on the pore size of silica gel. A few large AgCl–Ag particles precipitated on the outside of silica gel were, however, detected by TEM–SAED in silica gels with higher concentrations of AgCl. The SiO_2–$AlPO_4$ and SiO_2–Nd_2O_3 composites are noncrystalline and did not show any periodic structure by TEM and SAED. Heat treatments to 400 or 600° C did not crystallize the $AlPO_4$ or Nd_2O_3 phases. On the other hand, SiO_2–$CePO_4$ and SiO_2–CdS composites showed lath-like particles of $CePO_4$ and irregular particles of presumably CdS on the surfaces of silica gels. The SiO_2–$BaSO_4$ and SiO_2–$PbCrO_4$ composites showed crystals of $BaSO_4$ and $PbCrO_4$ which are too large to be incorporated in the silica gel pores. These results show that the size and crystallinity of a second phase within silica gels can be controlled by the appropriate manipulation of the different parameters, and to do so is an important advantage for this new class of diphasic nanoscale composite xerogel materials.

1. Introduction

Beginning with our original development of the concept in 1948, the extensive sol–gel research done in the fifties and sixties was based on the common goal of making maximally homogeneous ceramics and glasses [1–3]. The revived interest in sol–gel science and technology is still based on this same ability to achieve homogeneity on an atomic scale via the sol–gel route. In 1982, in our sol–gel work, we embarked upon a radically different goal: making heterogeneous crystalline and noncrystalline ceramics – with the very special boundary condition that the heterogeneity be on a nanoscale, i.e. with the phases in the 1 to 10 nm range. One part of this endeavour has been the preparation of two-phase ceramic–metal composites by reducing one of the components of mixed oxide (or hydroxide) with H_2–N_2 at the desiccation stage. Ni–Al_2O_3, Co–Al_2O_3, Fe–Al_2O_3, etc., composites with submicrometre metal particles have all been prepared [4] and this class of materials could obviously be important in the catalytic materials area. We use the terms "diphasic" or "composite" xerogels, to describe these materials heterogeneous on a nanoscale. A sol–gel process has been described by us for the preparation of diphasic composite materials [5] and a special case of this diphasic composite resulted in photochromic xerogels [6]. This technique represents a far more versatile approach to making nanoscale compositionally diphasic materials than does, say, precipitation out of a glass. In addition, the diphasic xerogels are expected to store more metastable energy than the single-phase xerogels [7] or glasses. The objective of the present investigation was to characterize these diphasic materials, which constitute a new class of materials, in some more detail. Transmission electron microscopy (TEM), selected-area electron diffraction (SAED) and X-ray diffraction (XRD) were used in the present study.

2. Experimental procedure

The procedure for preparation of the diphasic materials used in this study (Table I) has already been described in detail elsewhere [5, 6]. Briefly, the method of preparation involves soaking pre-formed silica gel in metal nitrate solutions followed by the precipitation of the metals in gel pores with selected anions, and subsequent densification by drying. The parameters for preparation of different diphasic materials are given in Table I. In the case of SiO_2–AgCl diphasic systems, the silica gels were washed after soaking in $AgNO_3$ and the amount of silver remaining in solutions was determined to calculate the amounts of silver incorporated in silica gels as AgCl. The solutions were analysed for silver by atomic emission

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TABLE I Parameters for the precipitation of a second phase into 5 cm^3 silica gel

No.	Diphasic system	Source of cation	Source of anion
1	SiO_2–AgCl	1.0 mg $AgNO_3$ in 25 ml H_2O	0.5 M HCl
2	SiO_2–AgCl	4.0 mg $AgNO_3$ in 25 ml H_2O	0.5 M HCl
3	SiO_2–AgCl	10 mg $AgNO_3$ in 25 ml H_2O	0.5 M HCl
4	SiO_2–AgCl	20 mg $AgNO_3$ in 25 ml H_2O	0.5 M HCl
5	SiO_2–AgCl	250 mg $AgNO_3$ in 25 ml H_2O	0.5 M HCl
6	SiO_2–AgCl	300 mg $AgNO_3$ in 25 ml H_2O	0.5 M HCl
7	SiO_2–AgCl	400 mg $AgNO_3$ in 25 ml H_2O	0.5 M HCl
8	SiO_2–AgCl	500 mg $AgNO_3$ in 25 ml H_2O	0.5 M HCl
9	SiO_2–$AlPO_4$	500 mg $Al(NO_3)_3 \cdot 9H_2O$ in 50 ml H_2O	0.5 M H_3PO_4
10	SiO_2–$CePO_4$	2330 mg $Ce(NO_3)_3$ in 50 ml H_2O	0.5 M H_3PO_4
11	SiO_2–Nd_2O_3	1320 mg $Nd(NO_3)_3$ in 20 ml H_2O	None used
12	SiO_2–CdS	4730 mg $Cd(NO_3)_2$ in 20 ml H_2O	1 M $Na_2S_2O_4$ at 65° C
13	SiO_2–$CrPO_4$	400 mg $Cr(NO_3)_3 \cdot 6H_2O$ in 25 ml H_2O	0.5 M H_3PO_4
14	SiO_2–$BaSO_4$	100 mg $Ba(NO_3)_2$ in 25 ml H_2O	0.5 M H_2SO_4
15	SiO_2–$PbCrO_4$	1000 mg $Pb(NO_3)_2$ in 20 ml H_2O	0.5 M chromic acid

spectroscopy (AES) with d.c. plasma using a Spectra-Metrics SpectraSpan III instrument. Transmission electron microscopy and SAED of the various diphasic materials was carried out with a Philips 420 electron microscope. All the as-prepared diphasic materials were characterized by XRD. Crystallization of the diphasic materials upon heat treatment at 400 and 600° C for 4 h was investigated by XRD with a Philips APD-3600 X-ray diffractometer which uses graphite monochromated Cu*K*α radiation.

3. Results

3.1. Diphasic SiO_2–AgCl composites

Diphasic SiO_2–AgCl composites were shown to be photochromic [6] and hence a detailed investigation of these composites was undertaken here by XRD and TEM–SAED to determine the size of the colloidal silver halide within the silica gel matrix. Silica gels with different amounts of AgCl loadings (Table II) were studied. Table II presents the actual amounts of AgCl precipitated within the silica gels and shows that 88.6 to 92.8% of the added $AgNO_3$ was precipitated in these gels. XRD analysis did not reveal the presence of an AgCl phase below the 4 mg $AgNO_3$ treatment (Table I) because the amount of AgCl is too small to be detected by XRD. Tranmission electron microscopy coupled with SAED also did not reveal the presence of a separate AgCl phase in the dispersion (Figs. 1a and b) at *low* AgCl loadings (below 4 mg $AgNO_3/5\,cm^3$ silica gel, see Table I). However, at higher $AgNO_3$ loadings some crystals could be detected on the outside of the silica gel and these are of the order of 6 to 60 nm in size (Figs. 1c and e). SAED showed these to be a mixture of AgCl and Ag phases (Fig. 1d). These crystals appear to have precipated on the outer surfaces of the silica gel since the true gel pores are too small [8] to accommodate such large crystals. Thin edges of the somewhat honeycomb-shaped silica gel matrix did not reveal any discrete colloidal particles and SAED showed only an amorphous nature (Fig. 1f). Presumably the silver chloride colloids are too small to be detected by TEM and SAED. These results are consistent with the silica gel structure, i.e. silica gels have pores of the order of only 2 to 8 nm in size [8] and hence the AgCl precipitated in the gel pores will be about this size or smaller. Reversible photochromic glasses contain silver halide crystals of the order of about 5 nm in size [9] which also suggests that the silver halide crystal size is about the same in these SiO_2–AgCl composites since these latter also exhibit reversible photochromicity when the AgCl concentration is small [6].

3.2. Diphasic SiO_2–$AlPO_4$ composite

No crystalline phases could be detected by XRD in this composite at room temperature or after heat treatment to 400° C (Table III). However, in samples which had been heated at 600° C, a $Si_3(PO_4)_4$ phase was detected. TEM observations did not resolve any discrete phase in the silica gel matrix (Fig. 2a) and SAED showed that the as-prepared composite is truly amorphous (Fig. 2b).

3.3. Diphasic SiO_2–$CePO_4$ composite

XRD of the as-prepared composite and of the composite heated to 400° C revealed the presence of a

TABLE II Analyses of solutions to determine the extent of Ag precipitation as AgCl and its detection by XRD

SiO_2–AgCl system	Amount of $AgNO_3$ added to Si gel (mg)	% Ag in solution	% Ag precipitated	XRD Analysis
1	1	11.3	88.7	Amorphous
2	4	11.4	88.6	Amorphous
3	10	8.7	91.3	Semicrystalline AgCl
4	20	8.3	91.7	AgCl
5	250	7.2	92.8	AgCl
6	300	7.3	92.7	AgCl
7	400	7.5	92.5	AgCl
8	500	7.4	92.6	AgCl

TABLE III X-ray diffraction and SAED analyses of diphasic composites

Diphasic system	SAED of unheated samples	X-ray diffraction analyses		
		Unheated	Heated at 400° C	Heated at 600° C
SiO_2–$AlPO_4$	Amorphous	Amorphous	$Si_3(PO_4)_4$	$Si_3(PO_4)_4$
SiO_2–$CePO_4$	$CePO_4$	$CePO_4$	$CePO_4$	$Si_3(PO_4)_4$ + $CePO_4$
SiO_2–Nd_2O_3	Amorphous	Amorphous	Amorphous	Amorphous
SiO_2–CdS	*	Amorphous	Amorphous	Amorphous
SiO_2–$CrPO_4$	†	Amorphous	$Si_3(PO_4)_4$	$Si_3(PO_4)_4$
SiO_2–$BaSO_4$	$BaSO_4$	$BaSO_4$	$BaSO_4$	$BaSO_4$
SiO_2–$PbCrO_4$	$PbCrO_4$	$PbCrO_4$	$PbCrO_4$	$PbCrO_4$

*Unidentified crystalline phase with *d*-spacings at 0.329, 0.230, 0.206, 0.199, 0.174, 0.1636, 0.1186 and 0.1124 nm.
†Possibly $Cr_3H(P_3O_{10})_2 \cdot 24\ H_2O$.

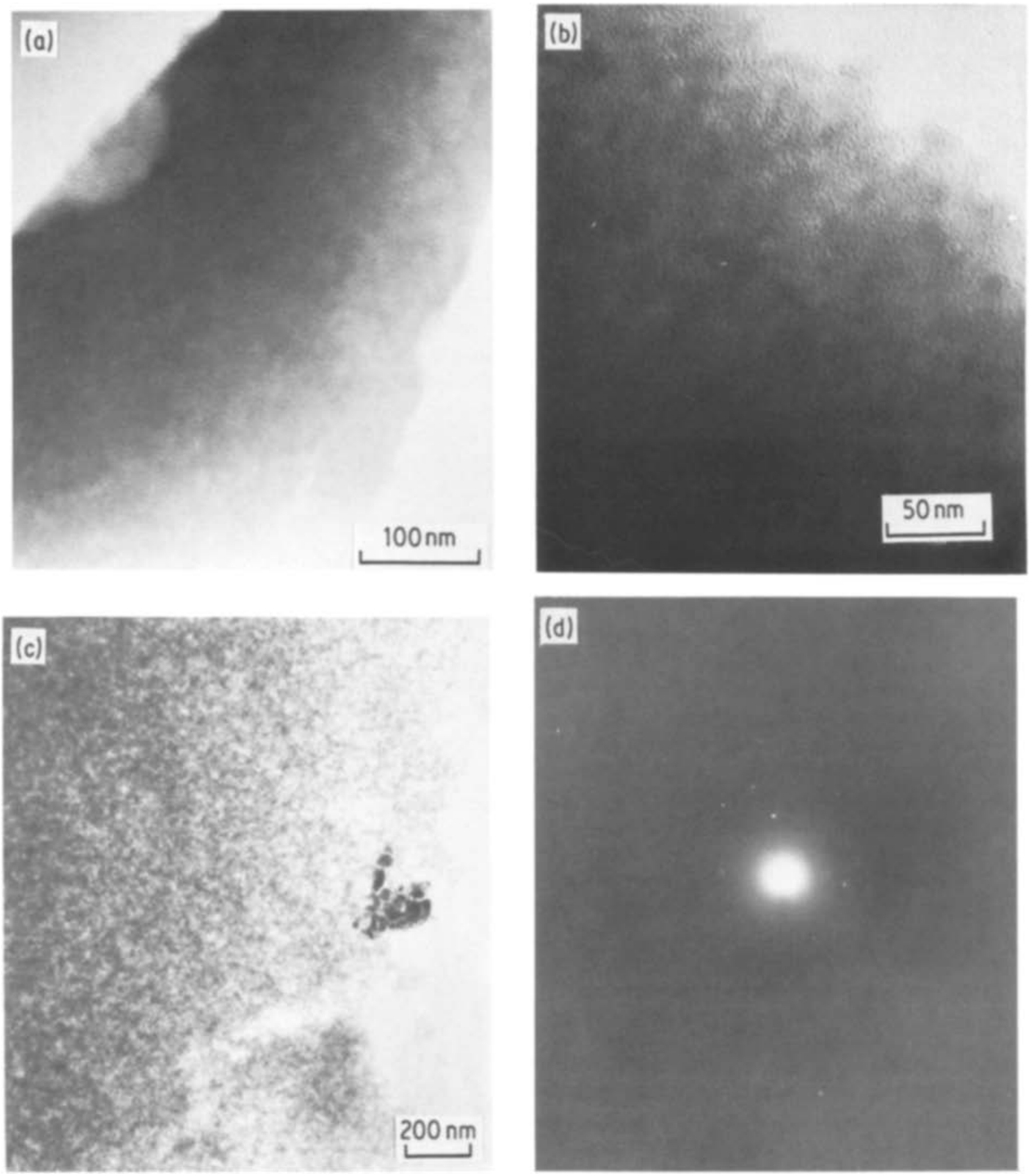
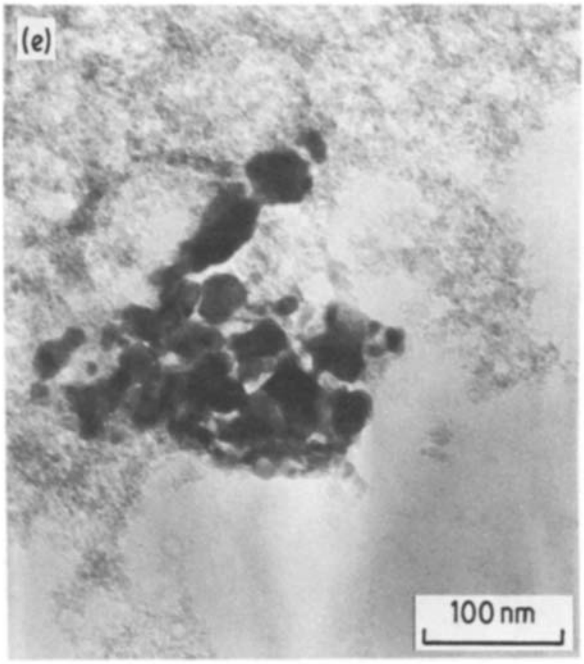


Figure 1 Transmission electron micrographs and SAED patterns of SiO_2–AgCl composites: (a), (b) Samples with 1.0 mg $AgNO_3$ (precipitated as AgCl) showing no discrete AgCl at very high magnification. (c) Sample with 250 mg $AgNO_3$ (precipitated as AgCl) showing large black crystals on the edges. (d) SAED of these crystals shows AgCl + Ag. (e) Same as (c) showing thin edges of silica gel with no discrete AgCl. (f) SAED of thin edges in (e) showing no crystallinity.



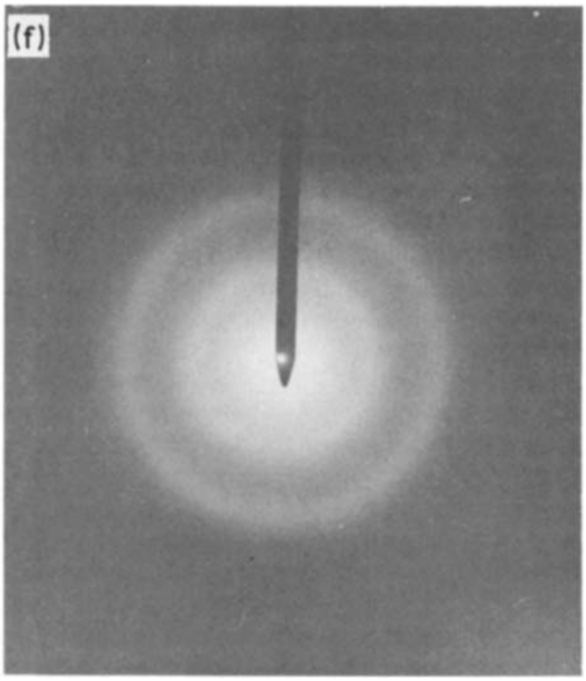


Figure 1 continued.

crystalline $CePO_4$ phase (Figs. 3 and 4). Further heat treatment to 600° C showed both $Si_3(PO_4)_4$ and $CePO_4$ (Fig. 3) which indicates the reaction of the gel matrix with $CePO_4$ to form $Si_3(PO_4)_4$. Transmission electron microscopy showed a lath-like phase on the outer surfaces of silica gel (Fig. 4a) and this phase was found by SAED to be crystalline $CePO_4$. The lath-like $CePO_4$ phase could be detected only on the outer surfaces and the laths are too large to be present within the silica gel pores.

3.4. Diphasic SiO_2–Nd_2O_3 and SiO_2–CdS composites

These two composites did not show any crystallinity by XRD but the latter showed some crystallinity by SAED (Fig. 5). The SiO_2–Nd_2O_3 composite appears to be truly amorphous and could not be differentiated morphologically from the silica gel (Fig. 5a). However, the SiO_2–CdS composite showed some irregular dark grains of about 10 to 20 nm (Figs. 5b and c) on the silica gel and this composite gave a crystalline SAED pattern (Fig. 5d). This crystalline phase could not be identified and the *d*-spacings are listed in Table III. Heat treatments of these composites to 400 and 600° C also failed to crystallize the Nd_2O_3 or CdS phases as determined by XRD (Table III).

3.5. SiO_2–$CrPO_4$ composite

X-ray powder pattern did not show any crystallinity, but SAED showed a hydrated chromium phosphate

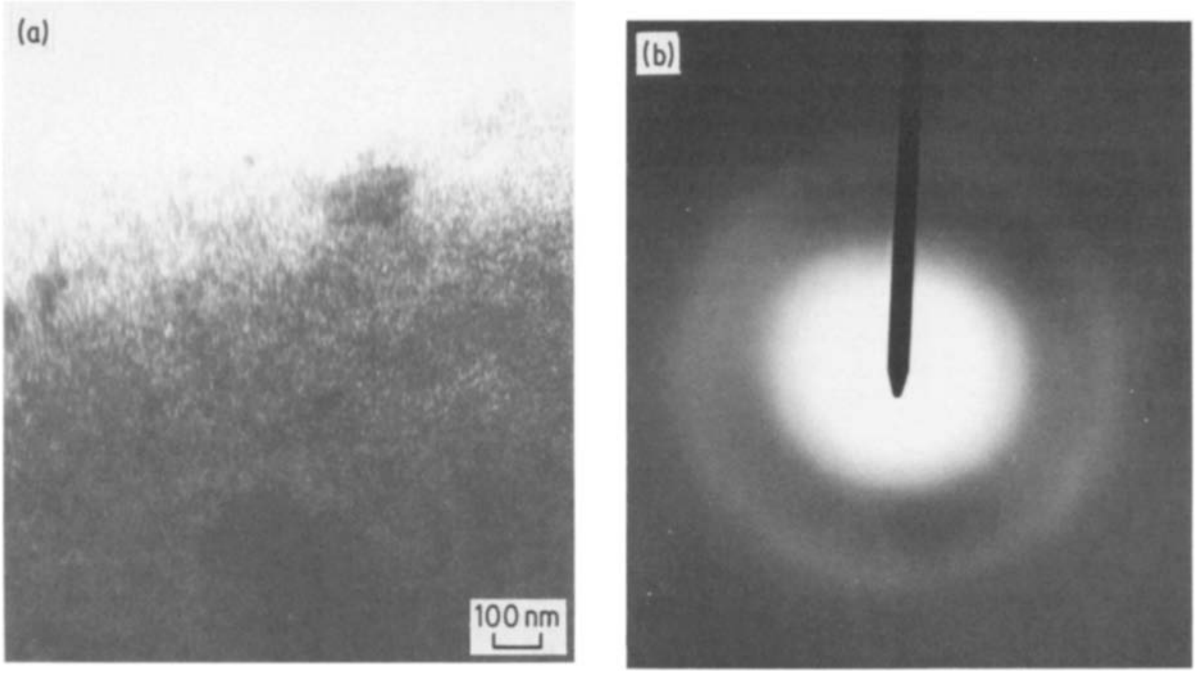


Figure 2 TEM photograph and SAED of SiO_2–$AlPO_4$ composite (a) Silica gel showing no discrete $AlPO_4$. (b) SAED shows amorphous nature.

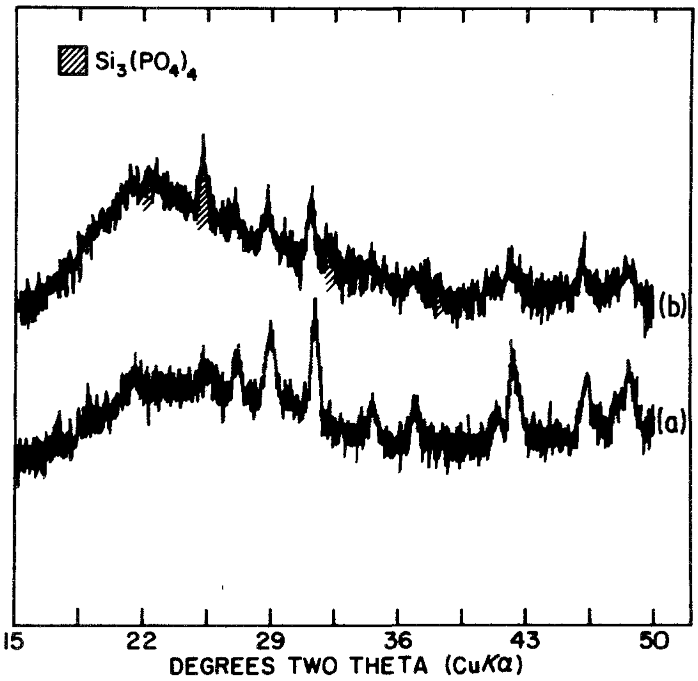


Figure 3 X-ray diffractograms of SiO_2–$CePO_4$ composites. (a) Heated at 400° C showing $CePO_4$. (b) Heated at 600° C showing $CePO_4$ + $Si_3(PO_4)_4$.

phase (Table III) which did not exhibit any morphological distinction from silica gel (TEM pictures not shown). Heat treatments of this composite at 400 and 600° C formed the $Si_3(PO_4)_4$ phase by the reaction of the matrix with the hydrated chromium phosphate phase.

3.6. SiO_2–$BaSO_4$ and SiO_2–$PbCrO_4$ composites

These two composites showed the $BaSO_4$ and $PbCrO_4$ phases at room temperature and after treatments at 400 and 600° C by X-ray powder diffraction. TEM–SAED studies of these two composites showed small and large crystals of barite (Figs. 6a and b) and large crystals of $PbCrO_4$ (Fig. 6c), presumably in gel cracks as well as on the outer surface. These crystals are too large to be accommodated in the gel pores. The presence of extremely small crystals within the gel pores, however, could not be discerned with the TEM–SAED studies.

4. Discussion

The diphasic composites are a new class of materials heterogeneous on a nanoscale as characterized in this study. The introduction of second phases into preexisting gel pores is a novel idea since the dispersion of a second phase (metal or ceramic) in the gel (matrix) pores can be controlled. The results presented here show that the precipitated second phases are of the order of a few nanometres conforming to the size of silica gel pores. This type of metal dispersion of a few nanometres size can be very useful in the catalytic materials area because of the possibility of achieving extremely high surface areas for these particulates

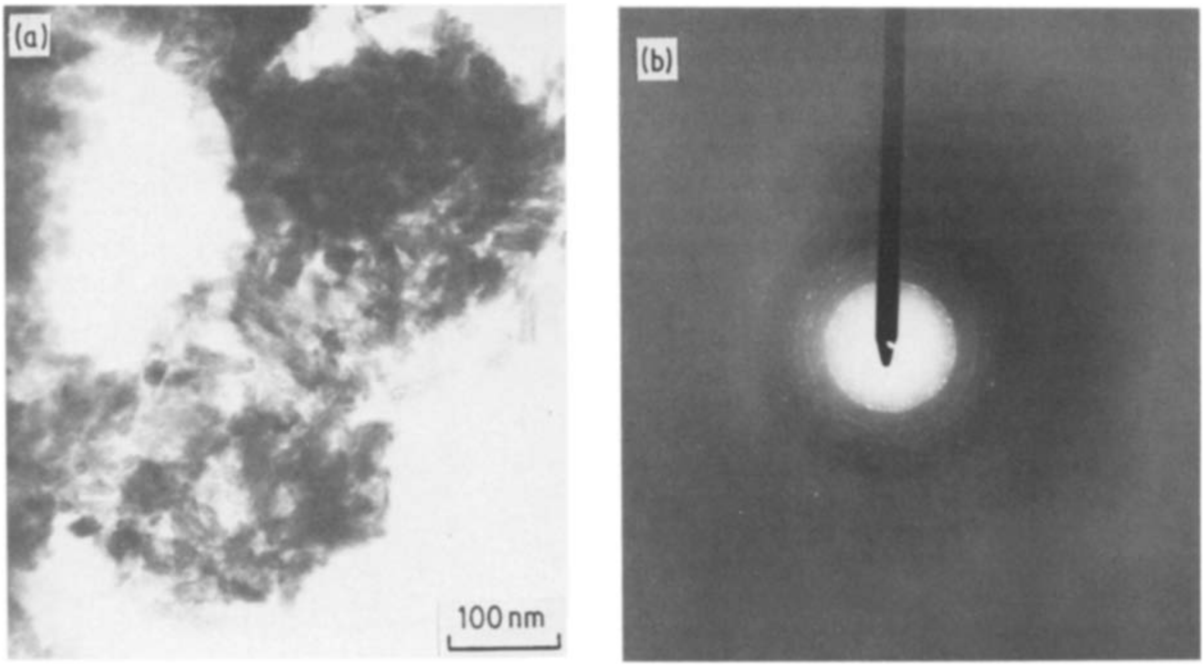


Figure 4 Transmission electron micrograph and SAED of SiO_2–$CePO_4$. (a) Lath-like $CePO_4$ phase. (b) SAED shows crystalline $CePO_4$.

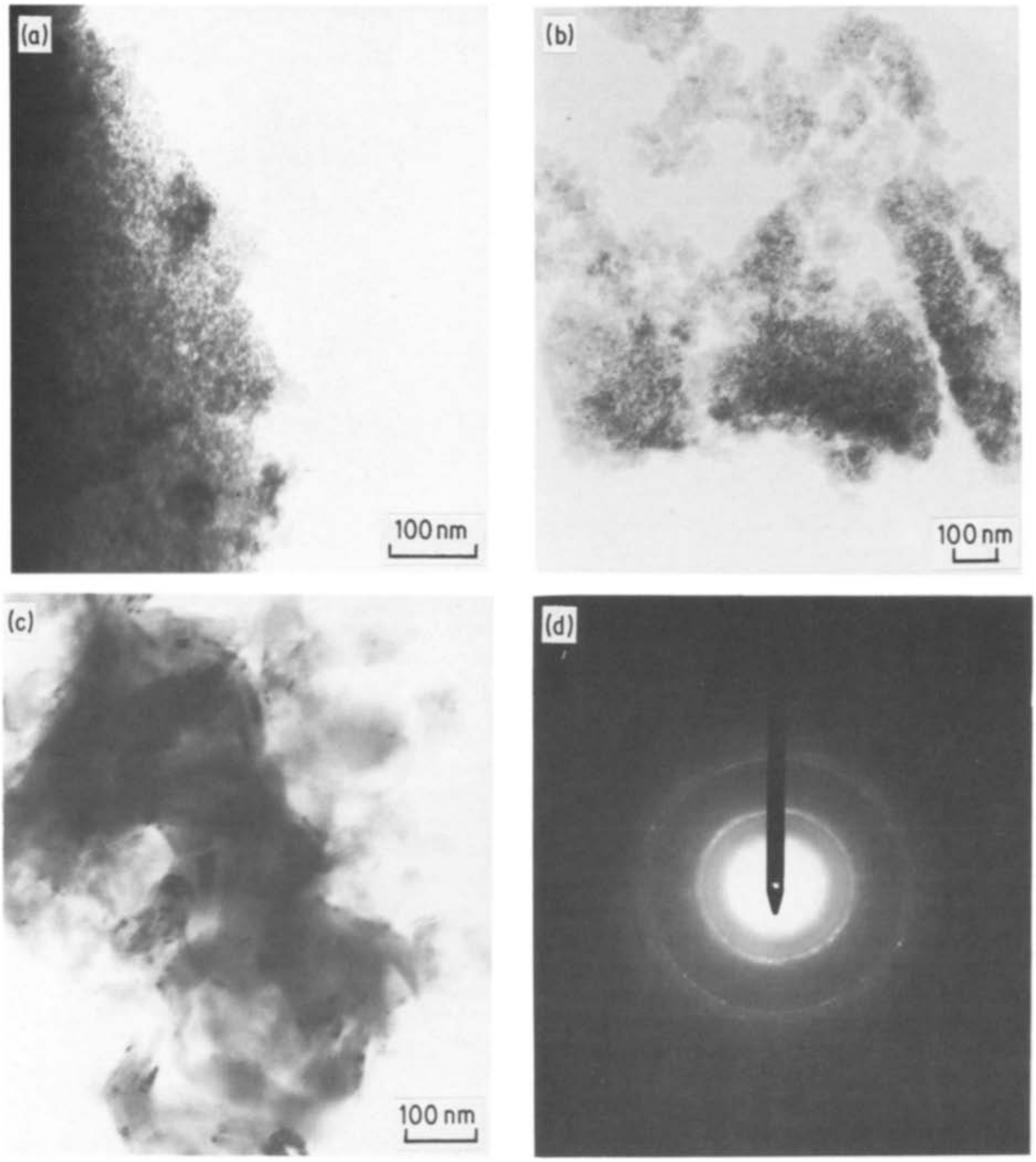


Figure 5 Transmission electron micrographs and SAED patterns. (a) SiO_2–Nd_2O_3 composite showing no discrete Nd_2O_3 phase in silica gel. (b) SiO_2–CdS composite showing black grains on the silica gel surface. (c) Same as (b) at a higher magnification. (d) SAED shows crystallinity of unidentified phase.

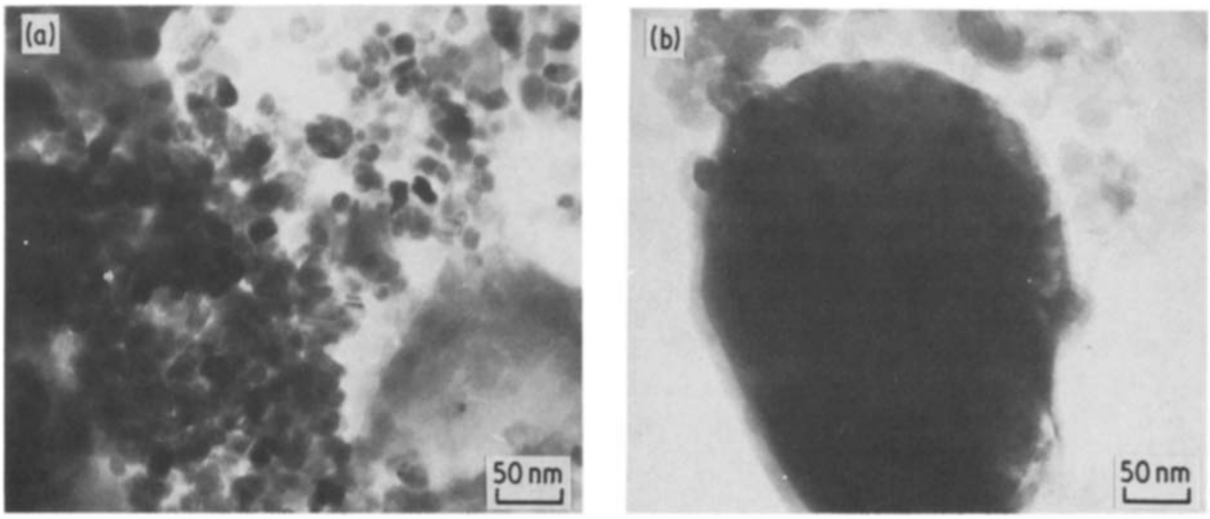


Figure 6 Transmission electron micrographs. (a) SiO_2–$BaSO_4$ composite showing small discrete barite crystals. (b) SiO_2–$BaSO_4$ composite showing large barite crystal. (c) SiO_2–$PbCrO_4$ composite showing large $PbCrO_4$ crystals on silica gel surface.

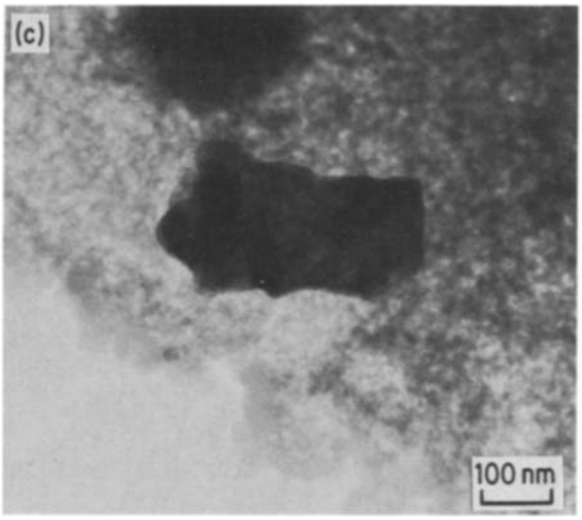


Figure 6 continued.

upon reduction to metals. The results presented here show that the second phases which are precipitated in the gel pores are indeed small and their size can be controlled by manipulating the various parameters rather easily.

Acknowledgements

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