

The role of N,N-dimethylaniline in the formation of titania gel monolith by sol-gel method

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Our investigation on the rheological aspects such as gelling time, specific density, fluidity, viscosity and surface tension of the sol derived from titanium-tetra-isopropoxide (TTIP), water and isopropanol (i-PrOH) has been reviewed in the presence of n,n-dimethylaniline (DMA) as a drying control chemical agent (DCCA). Dry gels derived from DMA stabilized sol were found to be crack free with a larger surface area. The titania gel monolith obtained in the presence of DMA could be processed into rutile at much lower temperatures.

1. Introduction

Since TiO_2 is a major constituent in many electronic devices, a lot of attention has been focused on monodisperse TiO_2 powders prepared by different chemical routes [1-4]. In particular, sol-gel chemistry of titanium alkoxides for the synthesis of monolith titania gels has been investigated by several workers [5-8]. Sol-gel synthesis is advantageous in not only producing morphologically controlled particles, but also in having compositional and microstructural control with low processing temperatures. Sol-gel synthesis involves hydrolysis of metal alkoxides by water which proceeds through a complex polymerization reaction leading to metal oxides or hydrated oxides. Conditions such as water/alkoxide ratio, solvent, catalyst, reaction temperature, and nature of alkyl groups in the alkoxide are all known to affect the kinetics of hydrolysis reactions and in turn modify the structural and physical characteristics of the final material obtained by thermal treatment. Unlike zirconia [9, 10], there is only limited data available on the sol-gel chemistry of titanium alkoxides in producing monolith gels.

A major problem encountered in producing gel monoliths through the sol-gel process is fracture and crack formation taking place during the conversion of the wet gel to dry gel [11-13]. Drying control chemical additives (henceforth referred to as DCCA) are known to overcome this problem [11]. Chemical composition also greatly influences the microstructure of gels such as rheological behaviour of sol, sol-gel transformation, drying and shrinkage of gels, calcination of dried gels and its sintering behaviour. In this paper we present our study on the different sol to gel transformation for the preparation of monodisperse TiO_2 powders and investigate the influence of n,n-dimethyl aniline (DMA) on the structure, sol-gel transitions and rheological behaviour such as specific

density, viscosity and surface tension of sol. To our knowledge there is no report on the use of DMA as a drying control chemical agent for titanium alkoxide sol.

2. Experimental

Commercially extra pure grade titanium-tetra-isopropoxide (TTIP), isopropanol (i-PrOH) and n,n-dimethyl aniline (DMA) were used as starting materials without further purification. Distilled water was used for hydrolysis. The preparative schedule for titania sol is summarized in Fig. 1. A known amount of TTIP was dissolved in i-PrOH. The solution was stirred at room temperature for about 20 min. A suitable amount of DMA was added to it and stirred for 2 h so that complete dispersion of DMA occurred. Water solution with i-PrOH was added dropwise to TTIP solution with continuous stirring.

Two series of samples were prepared. The sol composition in series I contained TTIP = 1 mole, Water/TTIP molar ratio = 1, i-PrOH/TTIP molar ratio = 13.75 and different concentrations of DMA (DMA/TTIP molar ratio = 0 to 4). While series II contained a different concentration of water (Water/TTIP molar ratio 1 to 4) at fixed concentration of DMA (DMA/TTIP molar ratio = 1).

The density of the sol was determined by weighing 10 ml of sol at 25°C until it became a gel. The time of flow and viscosity of the alkoxide solution were measured at 25°C using an Ostwald type viscometer. The surface tension of different sol was measured by a Stalagmometer using the drop count method at 25°C. BET surface area measurements were made on gels with different DMA concentration. The surface of the fresh and calcined gel was studied using transmission electron microscopy (Model Jeol-200 CX).

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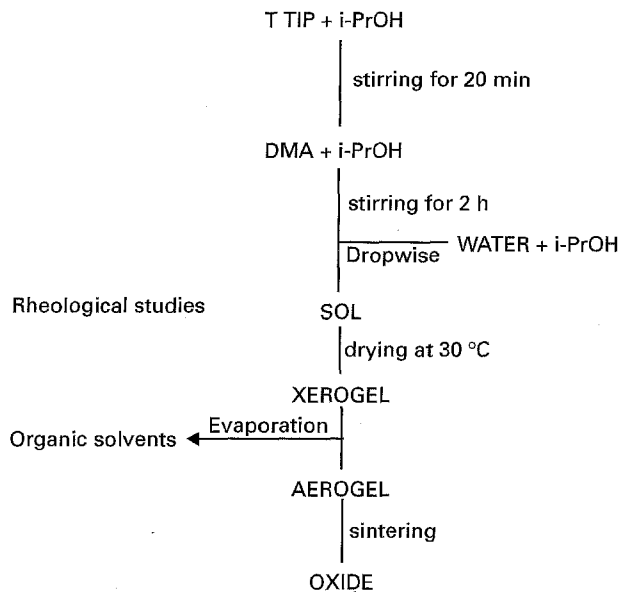


Figure 1 Schematic diagram for the preparation of titania sol.

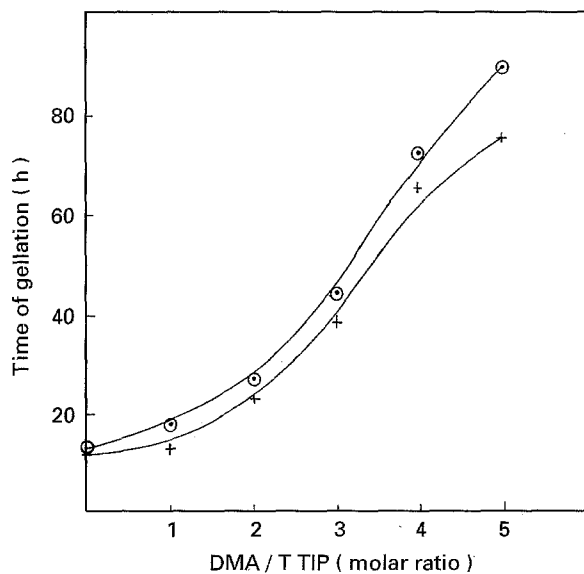


Figure 2 Effect of DMA on the gelation time of the sol containing TTIP:Water (+) 1:1 and (O) 1:0 molar ratio.

3. Results and discussion

3.1. Time of gelation and specific density

It can be seen from Fig. 2 that the time of gelation of the sol increases with increase in concentration of DMA at a particular concentration of water. It is obvious from Fig. 3 that in the presence of DMA, excess water can be added to the solution without precipitation. But when the concentration of TTIP was changed from 1 to 5 at a given concentration of DMA the trend was reversed. Also, the increase in concentration of TTIP allowed a smaller quantity of water and shorter time of gelation to give a clear sol as shown in Figs 4 and 5. While the ageing time increases, the sol gets converted into a gel leading to an increase in specific density as is noted in Fig. 6. The increase in densities of the sol are in accordance with the expectation due to the formation of polymers as a result of polycondensation with ageing.

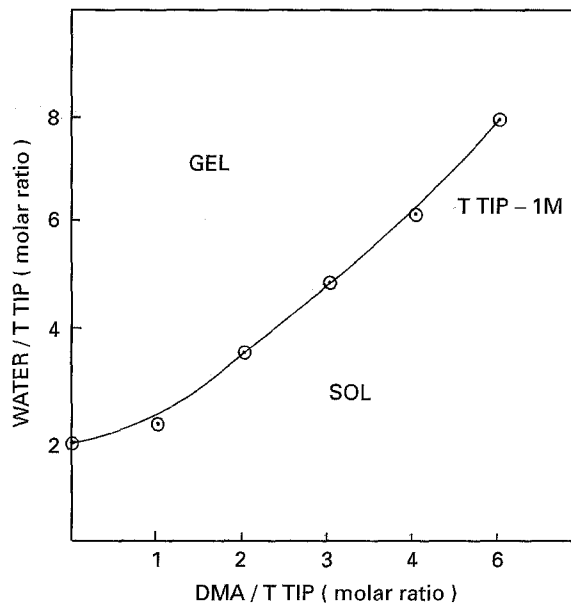


Figure 3 Effect of DMA on addition of water to the sol containing TTIP = 1 M.

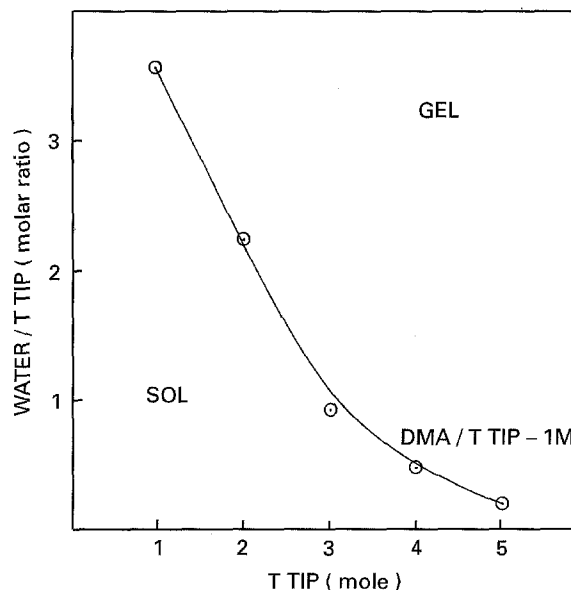


Figure 4 Effect of TTIP on addition of water to the sol containing DMA/TTIP = 1 molar ratio.

3.2. Variation of viscosity of titania sol with time

The relative viscosity of different sets of TTIP solutions containing varying concentrations of DMA are shown as a function of time in Fig. 7. The difference in viscosity between the initial solutions (at $t = 0$, the degree of polymerization is negligible) are essentially due to variation in the composition between the solutions. Our results also showed that the sol became viscous and gel in a shorter time when the concentration of DMA was lower. The variation of viscosity of the sol increased with ageing is also shown in Fig. 7. The viscosity of the sol increased with ageing at a particular concentration of DMA because of enhancement in the degree of hydrolysis of TTIP and subsequent condensation.

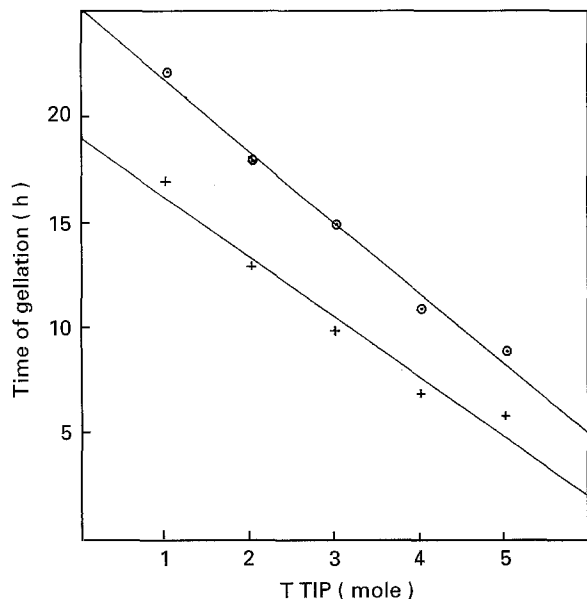


Figure 5 Effect of TTIP on the gelation time of the sol containing DMA:Water (○) 1:1 and (+) 1:2 molar ratio.

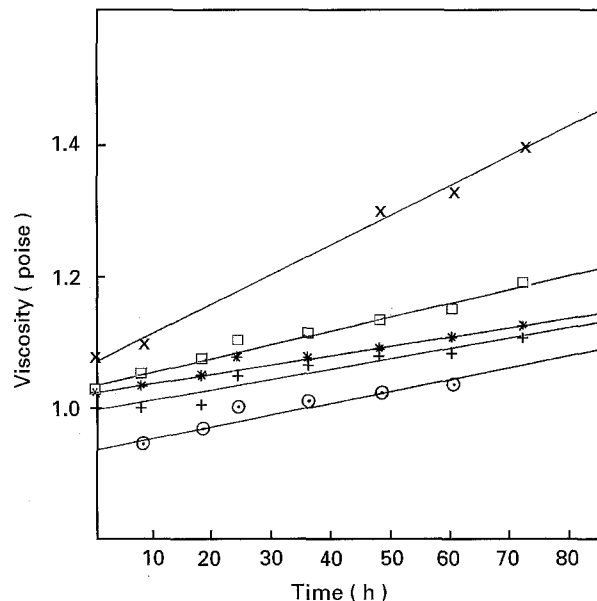


Figure 7 Effect of DMA on the viscosity of the sol containing TTIP:Water:DMA (○) 1:1:1, (+) 1:1:2, (*) 1:1:3, (□) 1:1:4 and (X) 1:1:5.

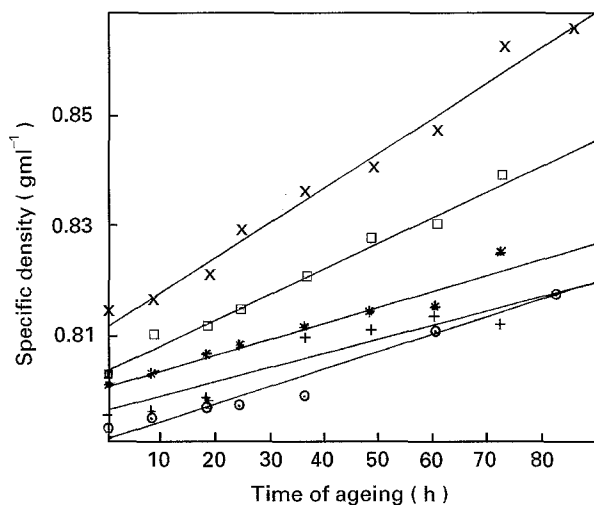


Figure 6 Effect of ageing on specific density of the sol containing TTIP:Water:DMA (○) 1:1:1, (+) 1:1:2, (*) 1:1:3, (□) 1:1:4 and (X) 1:1:5.

3.3. Crack formation and microstructure in dried titania gel

The presence or absence of cracks observed in dry gels is shown in Table I. We found that dry gels without cracks can be produced when the starting solutions contained DMA while severe cracks were noticed during drying in the absence of DCCA. We observed the crack formation in five out of eight samples in which the starting solution contained more water and less DMA. Ray *et al.* [9] have made a similar observation in zirconium alkoxide sol and attributed the crack formation to the possible capillary forces exerted on the microstructure made of metal oxides/hydroxides by the liquid remaining in the pores. The value of the capillary force depends on the pore size and the surface tension of the solution as given by the relation $\Delta p = 2\gamma \cos \theta / r$ where the capillary pressure Δp is proportional to the surface tension and inversely proportional to the pore radius r . On the basis of this relation

TABLE I Effect of DMA on the nature of gel

DMA (mol/mol)	Water (mol/mol)	Nature of gel
1	1	cracked
1	2	cracked
1	3	cracked
1	4	cracked
0	1	cracked
1	1	cracked
2	1	crack-free
3	1	crack-free
4	1	crack-free

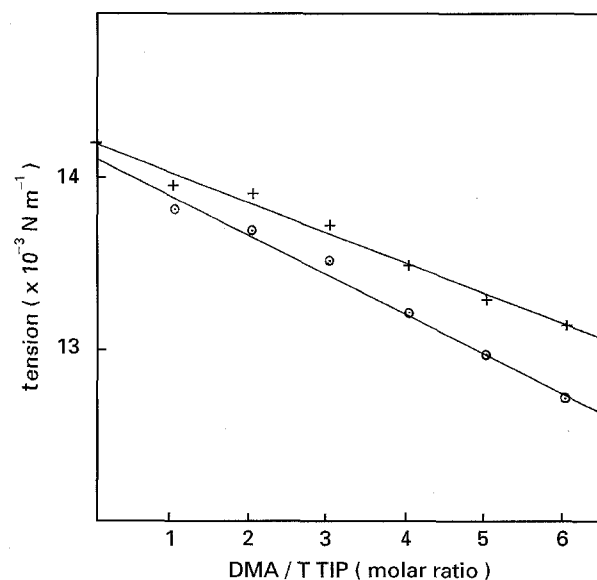


Figure 8 Effect of DMA on surface tension of the sol containing Water:TTIP (○) 1:1 and (+) 1:2.

an organic additive which decreases the surface tension of the sol and increases the pore size of the gel favours crack-free gels [11]. It can be seen from Fig. 8 that surface tension of the sol decreases with

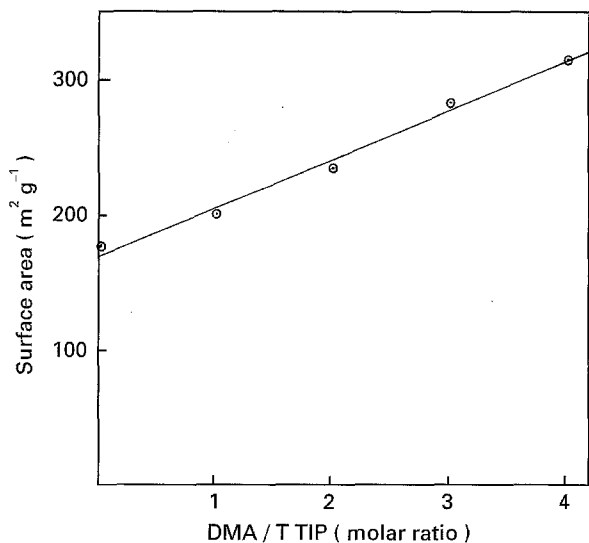


Figure 9 Effect of DMA on surface area of the dried gel derived from the sol containing TTIP:Water, 1:1.

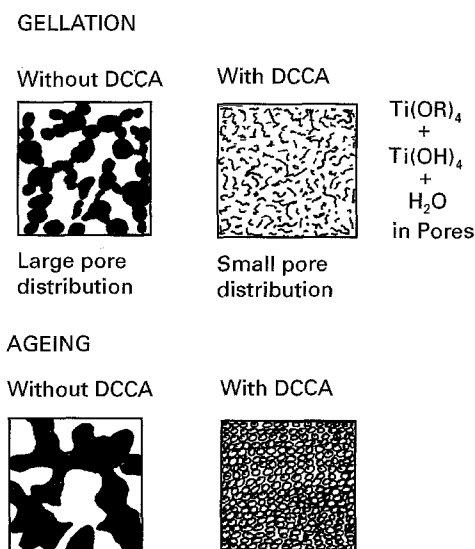


Figure 10 Pore size control of titania gel with DCCA.

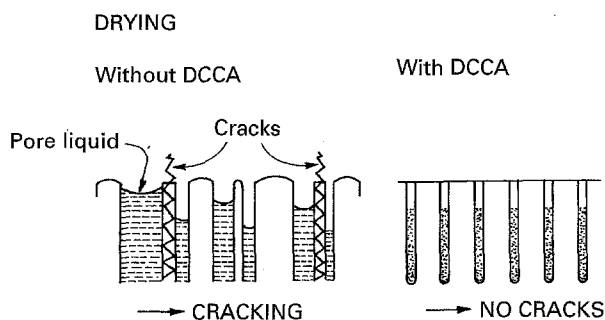


Figure 11 Schematic diagram for crack formation during drying.

increase in concentration of DMA at a given concentration of TTIP. Also, increasing concentration of DMA has increased the surface area of the gel (Fig. 9), i.e. it increases the pore radius of the gel and thereby decreases the capillary pressure on the pores in conformity with the above relation [11, 14].

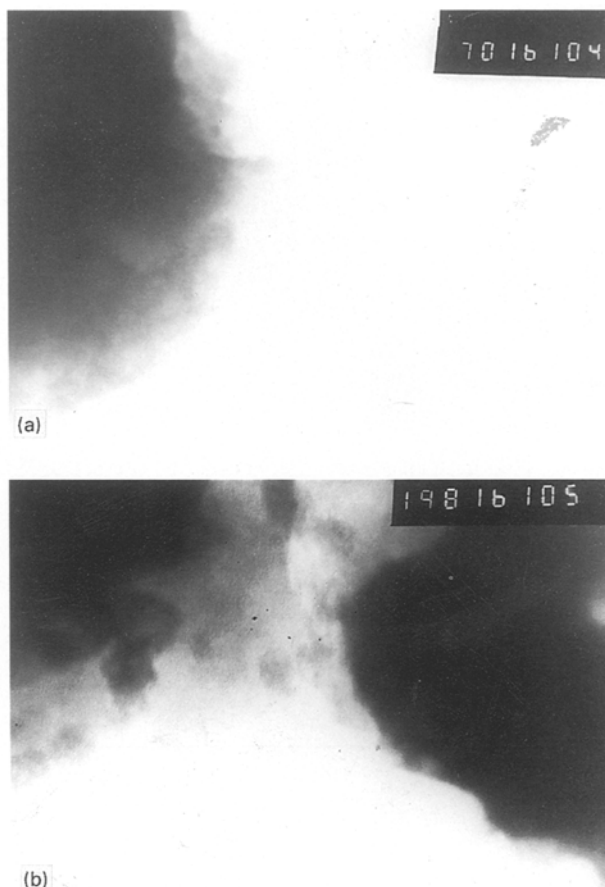


Figure 12 TEM micrograph of titania gels dried at room temperature from sol containing (a) DMA/TTIP = 0 and (b) DMA/TTIP = 1.

Figs 10 and 11 show diagrammatically how organic DCCA such as DMA control the sol-gel chemistry of titania particles. The DCCA possibly minimize differential drying stresses by reducing differential rates of evaporation and ensure a uniform thickness of solid [15, 16]. Fig. 12a is the transmission electron microscopy (TEM) micrograph of the gel derived from the sol containing DEA/TTIP = 0 molar ratio and Water/TTIP = 1 molar ratio. It is obvious from this figure that there is agglomeration of particles which is due to uncontrolled hydrolysis in the absence of DMA. Fig. 12b is the TEM micrograph of the gel containing DMA/TTIP = 1 molar ratio and Water/TTIP = 1 molar ratio. This figure shows the segregation of the particles forming large pores in between. This also supports our data that the surface area of the gel increases from 175 to 200 m² g⁻¹ when the DMA concentration changes from 0 to 1 molar ratio (refer to Fig. 9). Fig. 13a shows a TEM micrograph of the gel calcined at 400 °C together with a selective area electron diffraction pattern (Fig. 13b). The results show that we have indeed obtained well-developed TiO₂ crystals (anatase) as a result of controlled hydrolysis in the presence of DMA. Preliminary X-ray diffraction studies have shown that gels prepared in this study could be converted into rutile form at much lower temperatures (around 650 °C) than reported so far. The detailed results will be described elsewhere [17].

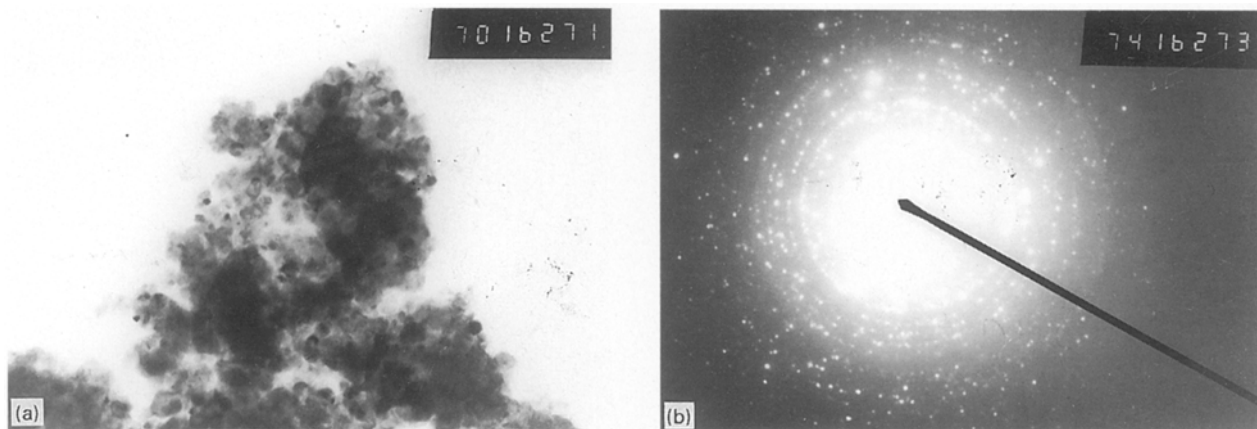


Figure 13 TEM of titania gels from a solution with DMA/TTIP = 1 after heating to 400 °C: (a) TEM images and (b) selective-area electron diffraction pattern.

4. Conclusions

Rheological properties of TTIP derived titania sol were investigated in the presence of DMA. During ageing, sol underwent transitions in flow behaviour and converted into gel. Model experiments have been carried out to investigate the hydrolysis and polycondensation process by gelation time, density, flow and viscosity. Our study has shown that a larger concentration of DMA favours a higher gelation time. Also the addition of a large amount of water to metal alkoxide in the presence of DMA results in a monolithic titania gel.

Acknowledgements

We thank DST for financial support. PKS thanks the Indian Institute of Technology, New Delhi for the award of a research fellowship. Our thanks are due to Mr F. V. Verghese for help with surface area measurements and Dr G. N. Subbanna, Indian Institute of Science, Bangalore for help with the electron microscopy analysis.

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Received 3 June 1994

and accepted 5 April 1995