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The role of the DCCAs in the preparation of crack-free Xerogel

ABSTRACT

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Sol–gel chemistry is an efficient tool to control the morphology and reactivity of solids. Drying is the crucial step due to the capillary forces exerted during the classic ambient drying process, which induces the collapse of the wet gel porosity. The use of N, N-dimethylformamide (DMF), a newly found DCCA were found to be effective in the sol–gel synthesis of crack-free silica gel monolith from tetraethoxysilane (TEOS) via acid catalyzed. We investigate the effect of N, N- dimethylformamide as DCCAs in simple inorganic silica obtained from tetraethoxysilane (TEOS) and the effects drying control chemical additives (DCCA) on gelatin time and physical properties of the dry gel were examined in an acidic silica sol-gel process.

Keywords: *Sol-gel processing; Crack-free xerogel; Synthesis; Porosity; N, N-dimethylformamide(DMF).*

INTRODUCTION

Sol-gel technology provides an alternative method to the production of ceramics, glasses and coatings from the hydrolysis of tetraethoxysilane (TEOS) [1]. The overall process evolves hydrolysis and polycondensation reactions leading to the growth of clusters that eventually collide together to form a gel. The structure and properties of the final product have been found to be strongly dependent on the initial conditions of preparation. Since water and TEOS are immiscible, a mutual solvent such as ethanol is usually employed as a homogenizing medium in the conventional sol–gel method. Silica gels have been considered as appropriated matrices for the preparation of complex-center doped materials for a variety of metallic ions [2-3] and for encapsulation of a variety of organics [4-6] and inorganic compounds [7-8], with interesting optical and/or electronic properties.

It is difficult to obtain a large amorphous silica monolith by directly drying a wet silica gel which is made through a sol-gel process due to intensive cracking during drying.

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The origin of the cracking has been attributed to capillary pressure generated in micropores in the gel during the drying process. Hench [9] proposed addition of drying control chemical additives (DCCAs) to the solvent in order to decrease surface tension. They concluded that the DCCA had a role in increasing the pore radius, since the dry gel obtained had larger and more uniform pore radii than those in a DCCA-free gel. To favor obtaining of monolithic pieces of dried gels, some drying control chemical additives (DCCA) have been recognized, which can really act as structure modifiers. N,N-dimethylformamide has been considered as a basic DCCA structure modifier [10] because its relative low surface tension and its ability to form strong hydrogen bonds with the silanol groups of the silica gel. We investigated the chemical effect of DCCA and final properties of silica xerogels, the DCCA: silicon alkoxide ratio was varied from 0.2 to 2 in this study.

EXPERIMENTAL

Sol-Gel Preparation

The molar composition of the synthesis mixture was corresponds to an Initial ethanol: water: TEOS: 0.07N hydrochloric acid mole ratio of thick 11:5:1:0.004, respectively, and the molar ratio of DCCA/TEOS were varied from 0.2, 0.5, 1 and 2, after stirred for 15 minute. The mixture was refluxed for 90 minute.

Sols were cast in plastic cylinder of 1 cm diameter and 4.8 cm in length. Dried xerogel obtained by exposure of the sols to laboratory condition until a constant weight was reached. In order to understand the role played by the DMF in the final properties of the material, another xerogels were synthesized according to the typical process described above, but without adding DMF. We obtained crack-free xerogels from the sols synthesized in the presence DMF with the mole ratios of the 1TEOS/1DMF. Other samples were not measured because of cracking (Figure 1).

Characterization procedures

Powder X-ray diffraction (XRD) was measured on a Bruker D8 advance diffract meter equipped with Cu tube X-ray and using Cu kα

radiation. The bulk density was determined by measuring the weight and volume of the sample. The gelation time was defined as the period from adding catalyst to the time at which the flow stopped in the tubes when tilted, Scanning electron microscopy (SEM) measurement was performed with a Jcxa-733 instrument operated at an accelerating voltage of 20 kV. FTIR spectrum was recorded on a Thermo Nicolet Nexus 670 spectrometer with samples pressed into KBr pellets. The nitrogen adsorption–desorption isotherms were determined on a Quantachrome NOVA instrument. The BET surface area was calculated from the linear part of the BET plot [11]. Pore size distribution was calculated from desorption branch data according to the BJH method [12] in addition by nitrogen sorption at 77 K surface area of the microspores and the external surface area (t-plot [13]) was evaluated. Thermogravimetric and differential thermal analyses (TGA and DTA) were performed Perkin-Elmer (Wellesley, MA) Pyris instrument in the temperature range of 35–700 °C in flowing Nitrogen at a heating rate 20 °C/min.
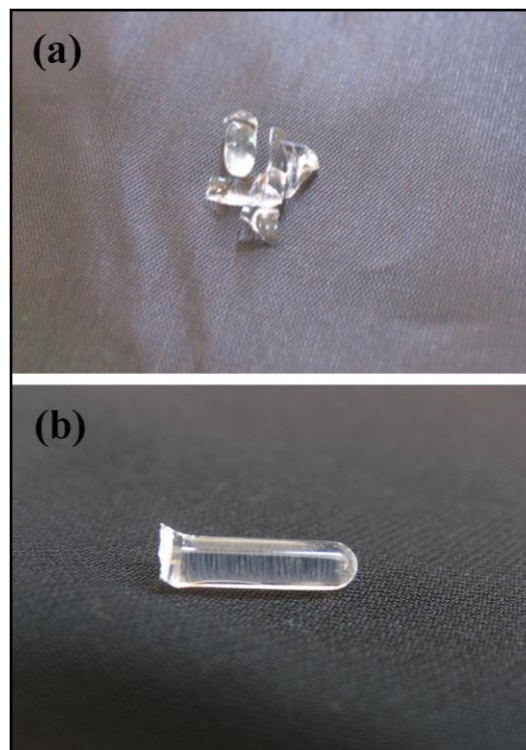

Fig. 1. (a) silica xerogel from TEOS without DMF (b) xerogel from TEOS in the presence DMF with the mole ratios of the 1TEOS/1 DMF

RESULTS AND DISCUSSION

Table 1 shows the values measured for density and gelation time of the xerogels and the effect of DMF on the time.

Table 1. Physical properties of samples

DMF/ TEOS	ρ (g cm^{-3})	T_G(day)
0	1.66	10
0.2	1.48	7
0.5	1.35	6
1	1.28	5
2	1.21	3

Gelation time shows the relation between the gelation time and DCCA addition. Addition of DMF decreased the gelation time, In the case of the TEOS sol prepared without DCCAs, the gel time was significantly longer, around 10 days. This shows that the DCCA promotes silica condensation; gelation is faster In the presence of DCCAs. We obtained optically transport and crack-free xerogels from the sols synthesized using DMF with 1 molar rate. The XRD spectra of silica produced using DMF with 1 molar rate is shown in Figure 2. A broad peak centered at 2θ angle of 22 confirmed the amorphous nature of the silica without any detectable ordered structure (Kalapathyetal, 2000 a).

The specific surface areas of xerogels were determined from the BET (Brunauer, Emmett and Teller) multipoint method [14] and the pore size distribution was obtained using the BJH (Barret, Joyner and Halenda) method [15] Texture properties of the silica xerogel under study were determined from nitrogen adsorption-desorption isotherm.

Some of the key physical properties valuated for all the xerogels samples are summarized in Table 2: envelope BET specific surface area (S_{BET}), external surface area (S_{ext}), micropores surface area (S_{mic}), the total specific pore volume (V_{por}) as the cumulative nitrogen volume adsorbed at a point close to the nitrogen saturation pressure at 77 K, micropore volume (V_{mic}) thought *t*-plot method and pore size distribution as obtained from the Kelvin equation and the classical Harkins and Jura model for cylindrical pore [16].
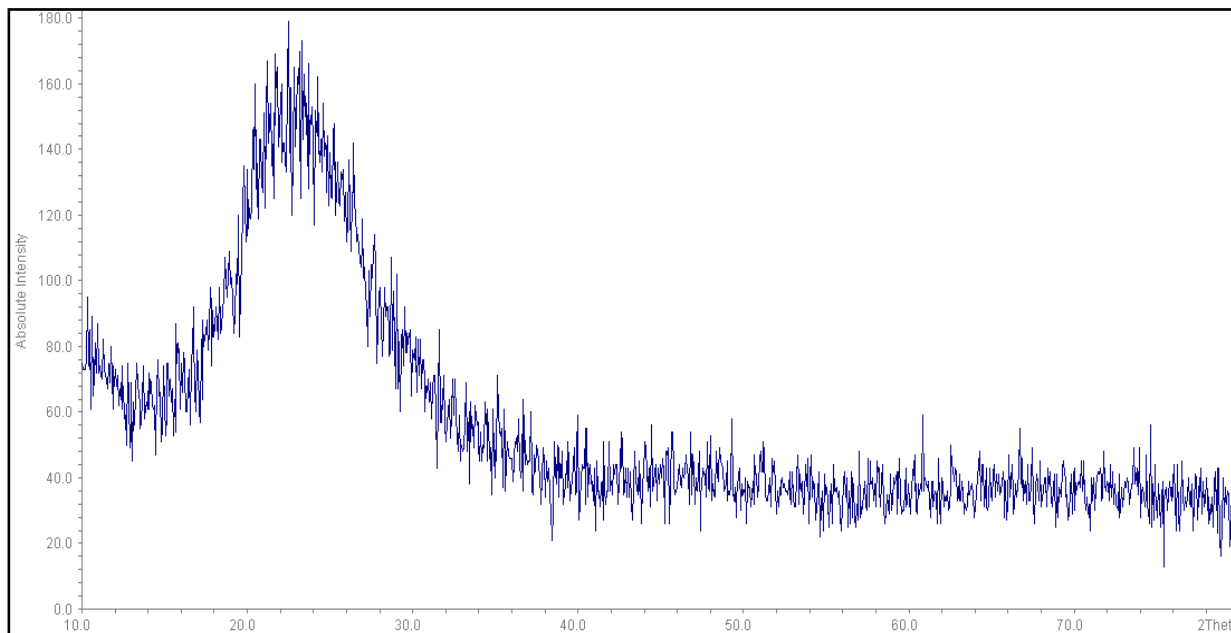

Fig. 2. XRD pattern for the xerogel from TEOS in the presence of DMF

Table 2. Pore characteristics of the samples obtained from the analysis of N2 sorption data

Properties	Free	DMF
BET surface area (m^2/g)	394.7	322.4
Langmuir surface area (m^2/g)	482.4	386
External surface area (m^2/g) [a]	26.26	54.99
Micropore surface area (m^2/g)	368.4	267.4
Total pore volume (cm^3/g)	0.1826	0.1593
Micropore volume (cm^3/g)	0.1592	0.1129
Mesopore volume (cm^3/g)	0.0234	0.0646
Average pore size (nm)	1.851	1.977
Microporosity(V_{MIC}/V_{TOTAL})	0.87	0.71
Mesoporosity(V_{MES}/V_{TOTAL})	0.12	0.29

Figure 3a and 3b shows the N_2 adsorption isotherms for the xerogels. It can be seen that two curves are type I (according to BDDT classification) isotherms, typical of microporous materials [17]. The surface area values obtained for these samples are presented in Table 2. Xerogel without DCCA has BET surface area of 394.7 m²/g. In the case of xerogel prepared in presence of DMF the BET surface area is 322.4 m²/g. The pore size distribution (PSD) curves in Figure 4a and 4b are results from BJH method of N_2 sorption analysis which measured the average pore diameter of the pores and evolution of the cumulative pore volume distributions of xerogels. PSD showing the nanosized pores of typical porous materials prepared by the sol–gel method pore distribution rapidly decreases with increasing pore diameter. silica xerogels prepared without DCCA, and in the presence of DMF xerogel presents a great quantity of pores in the micropore region (pores with diameter an average pore about 2 nm), which is inclusive in agreement with the great micropore volume V_{mic} as determined from t-plot method , the highest value V_{mic} was obtained for sample without DCCA (Table 2 Figure 5), and the xerogel in the presence of in presence of DMF shows a higher pore size distribution, smaller micropore volume V_{mic} (Table 2, Figure 4).

In xerogels the existence of micropores and the measurement of their volume can be obtained from t-plot curves. This method is based on a transformation of the nitrogen adsorption isotherm: the amount of adsorbed nitrogen's expressed as a function of statistical depth of the adsorbed layer of nitrogen. The values are calculated from the Harkins- Jurae equation. The t-plots generated using the N_2 adsorptions are shown in Figure 5a and 5b for samples. It has been suggested that this linear plot can be used to calculate the external surface area of the solid and that the slope of the line drawn from the origin to the "monolayer point" can be used to calculate the surface area of the micropores and the external surface (Table 2) another samples were not measured because of cracking.
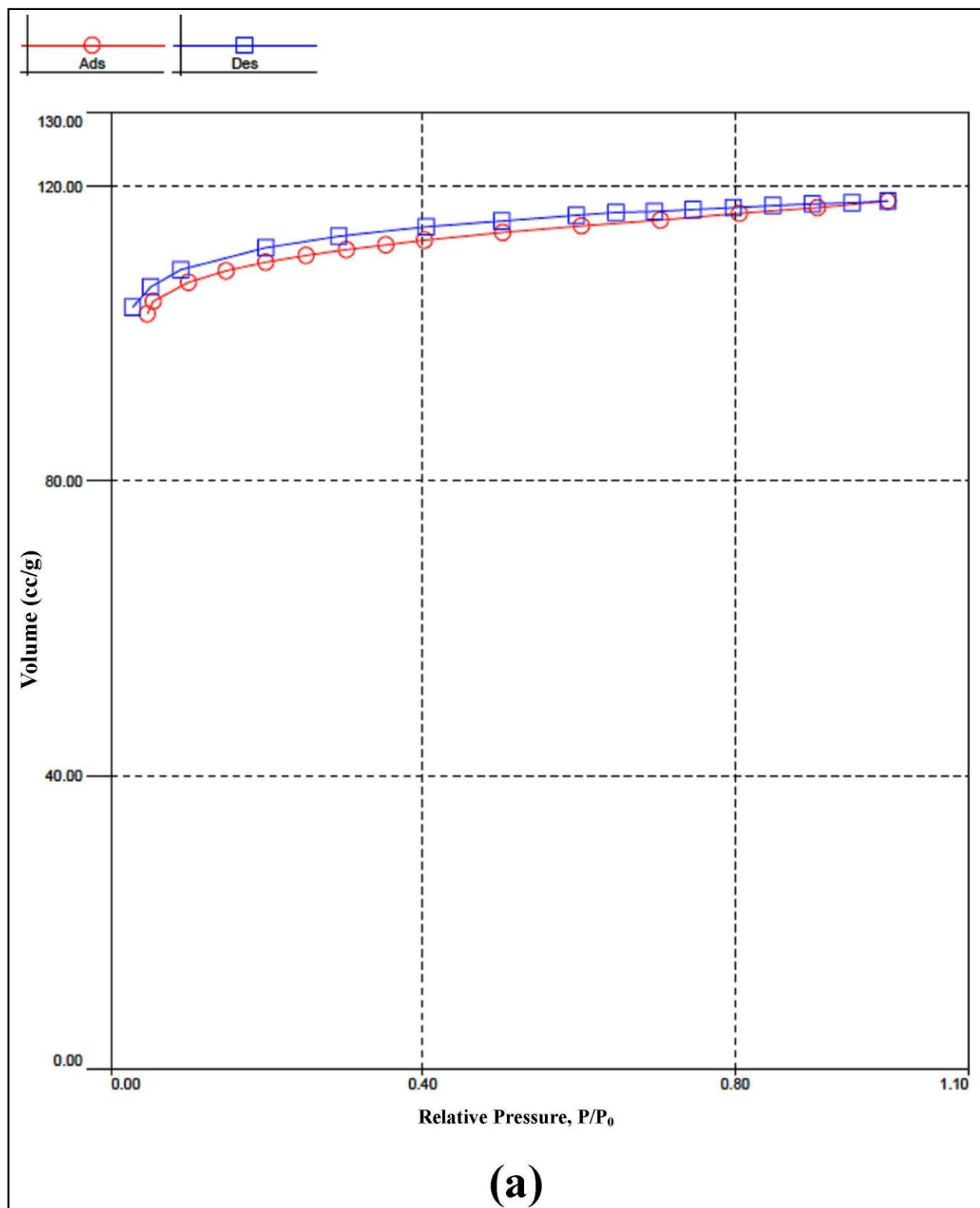
Fig. 3a. Nitrogen adsorption–desorption isotherms of the xerogel from TEOS without DCCA.
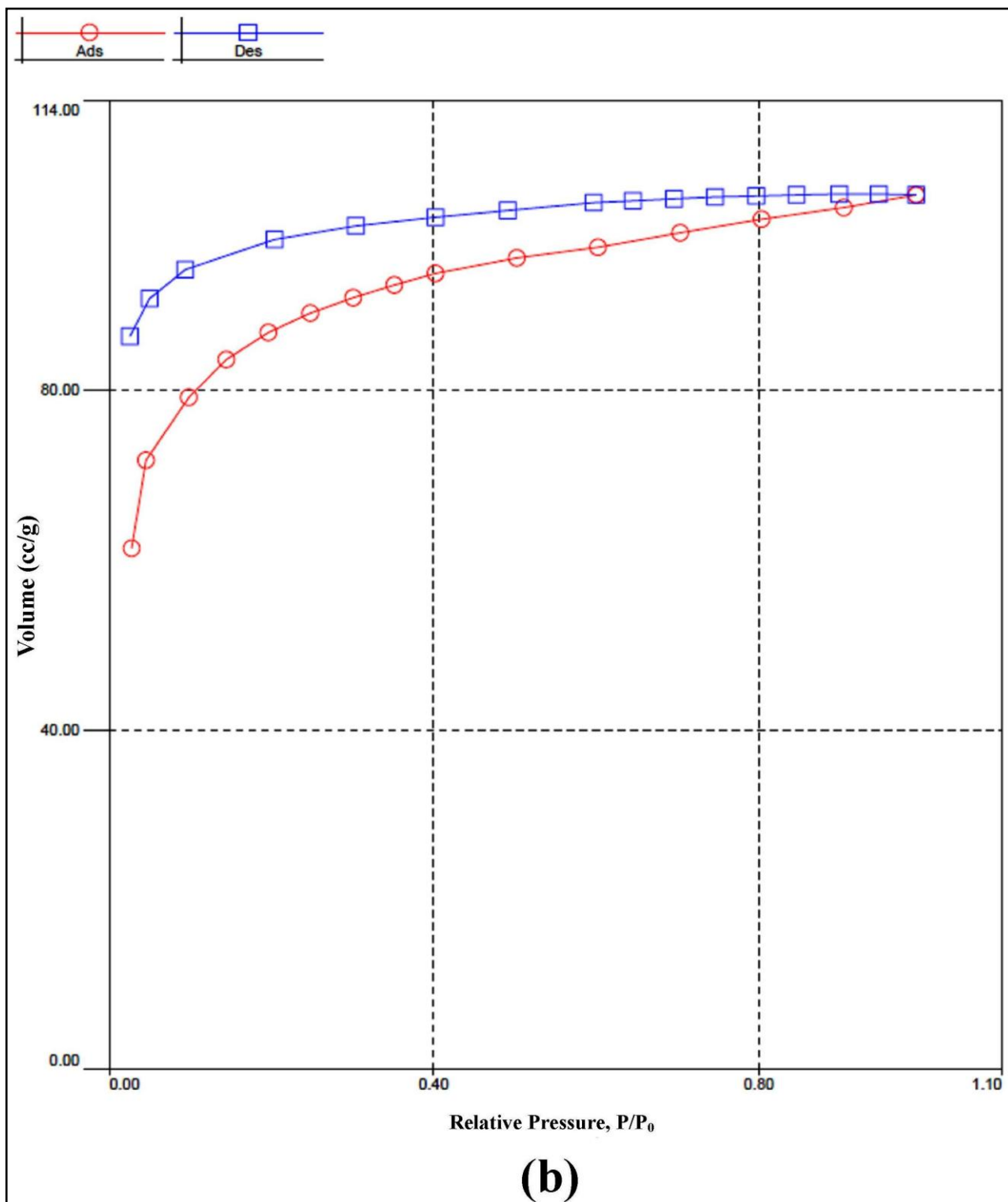
Fig. 3b. Nitrogen adsorption–desorption isotherms of the xerogel from TEOS in the presence of DMF.
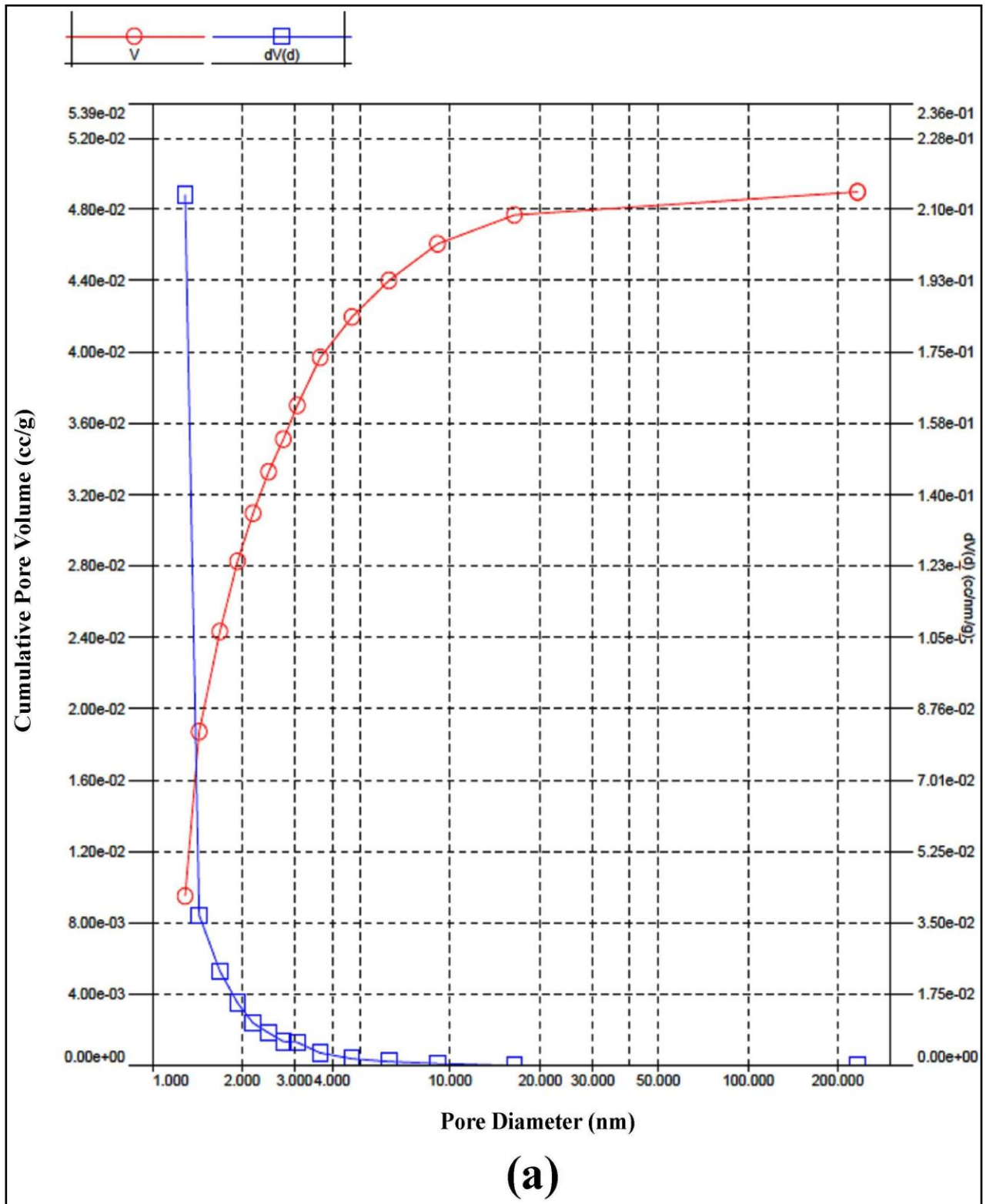
Fig. 4a. Pore size distributions of the xerogels from TEOS without DCCA.
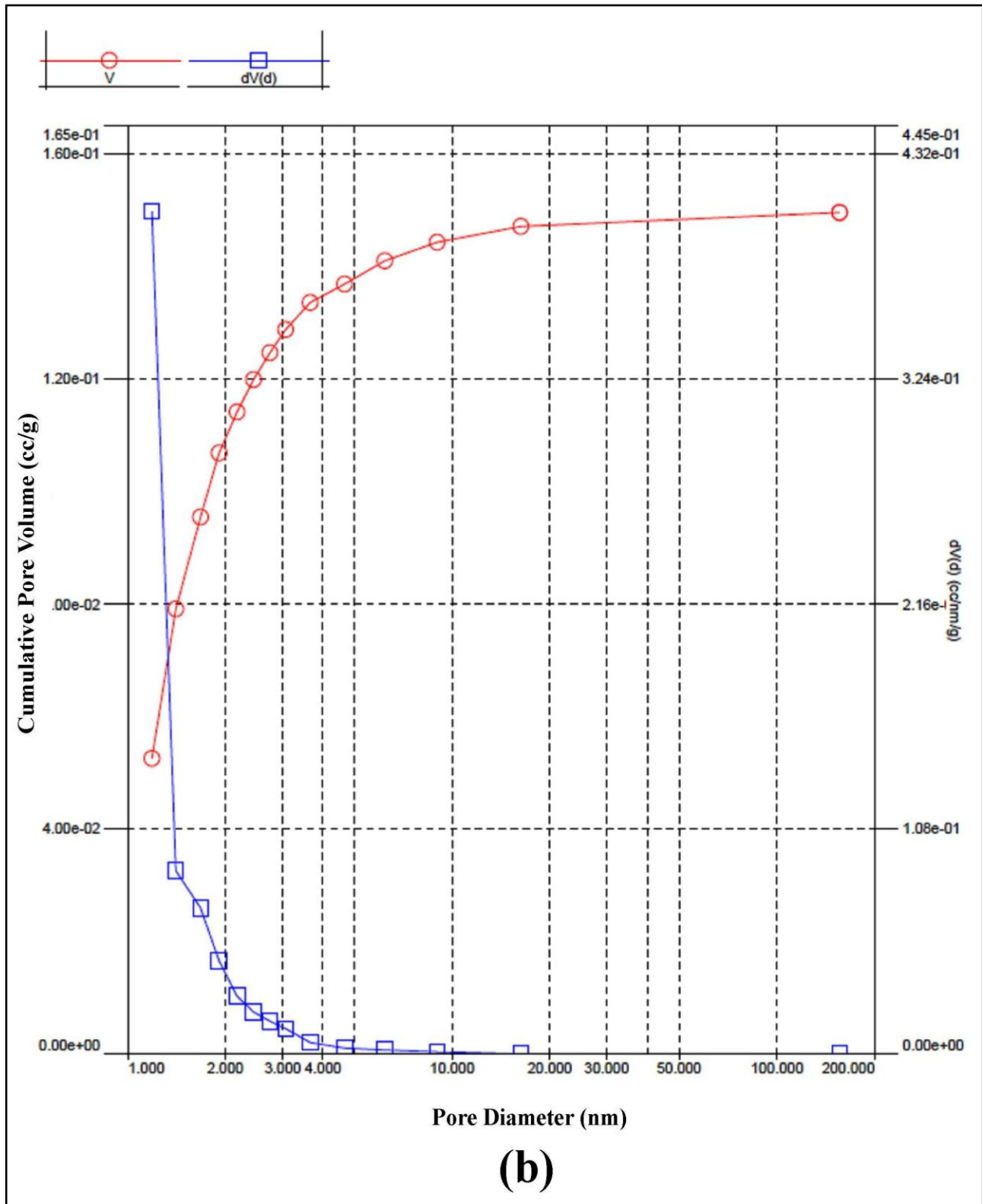
Fig. 4b. Pore size distributions of the xerogels from TEOS in the presence of DMF
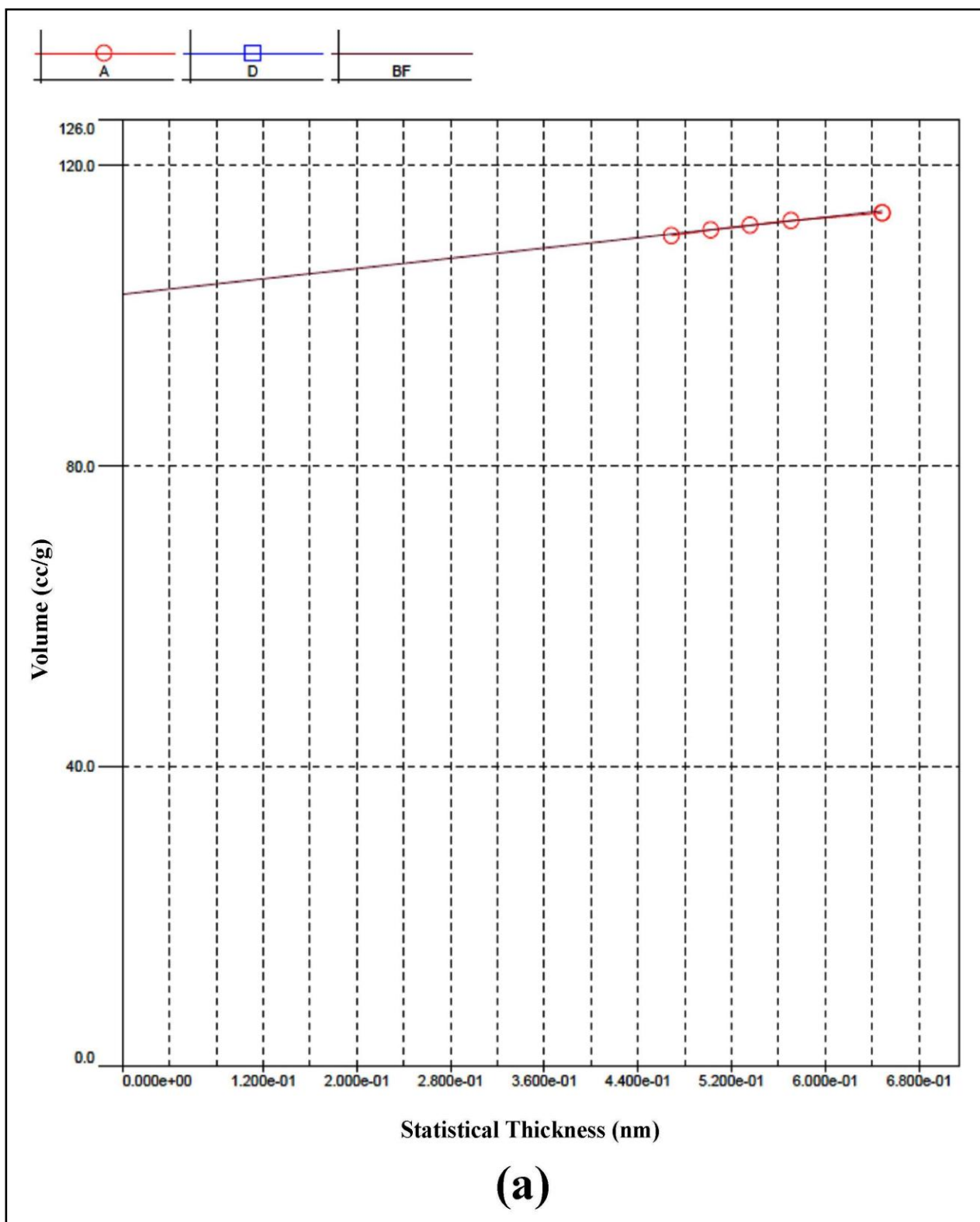
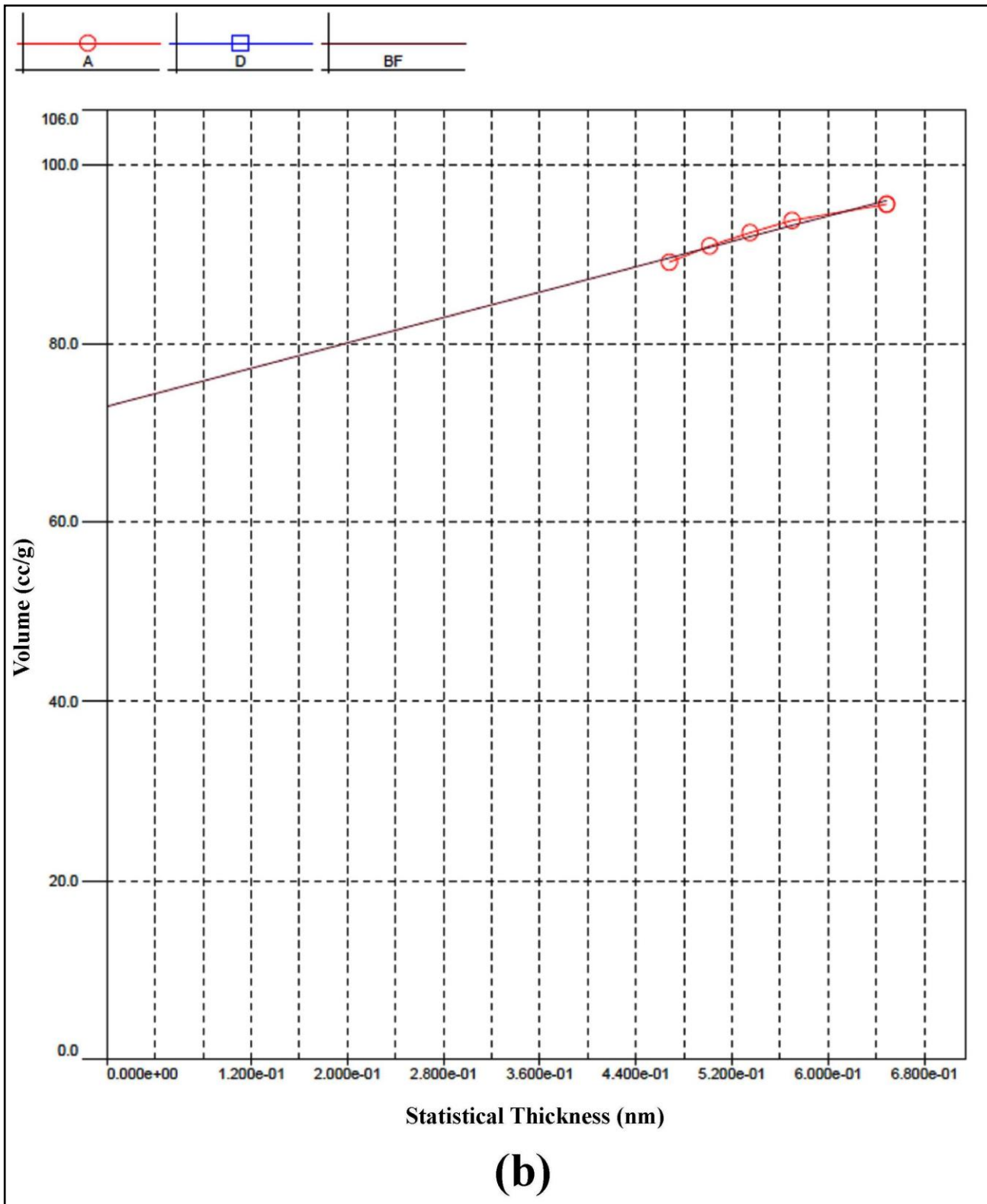**Fig.5a.** t-plot of the xerogels from TEOS without DCCA.

Fig. 5b. t-plot of the xerogels from TEOS in the presence of DMF.

The thermal behaviors of porous monoliths are examined by TGA and DTA to determine the transformation temperature of organic groups and water and weight percent of the residue. Figure 6 shows the differential thermal analysis (DTA) and the derivative of the thermogravimetric (TGA) test data for powder samples of the silica xerogels. The tests were carried out under a heating rate of 20 °C/min. The results show a weight loss in the temperature range around 100 °C due to the loss physically adsorbed water and residual volatile solvents, associated to an exothermic DTA signal.
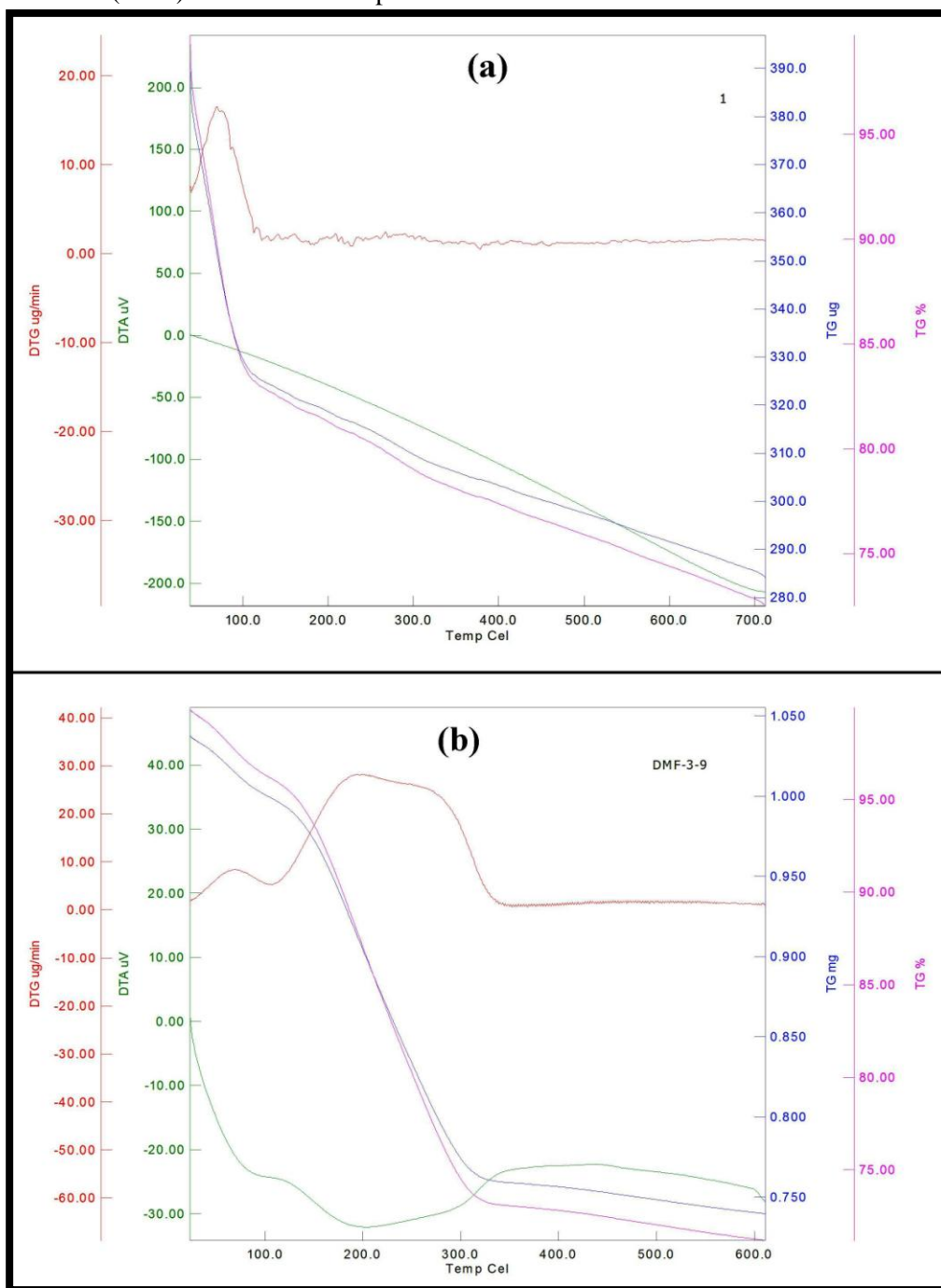

Fig. 6. Thermal analyses of xerogels. DTA and TG were carried out under a heating rate of 20 °C/min (a) without DCCA (b) in the presence of DMF

The second weight loss for sample in presence of DMF observed, DMF may be responsible for the more complex and progressive weight loss recorded in the TGA trace. In particular the weight loss between 200- 250 may be related to the removal of bonded DMF.

Figure 7 shows SEM micrographs of fractured surfaces of xerogels. The inspection of micrometer range morphology was carried out by observing the cross-section structure of the dried gels. Figure 7 displays the SEM images of silica xerogels prepared of (a) without DCCA (b) in the presence of DMF. Porous microstructure is observed for samples The SEM image in presence of DCCA reveals more uniform and globular morphology. Careful observations indicate that the sizes of particles and pores are increased in presence of DMF.
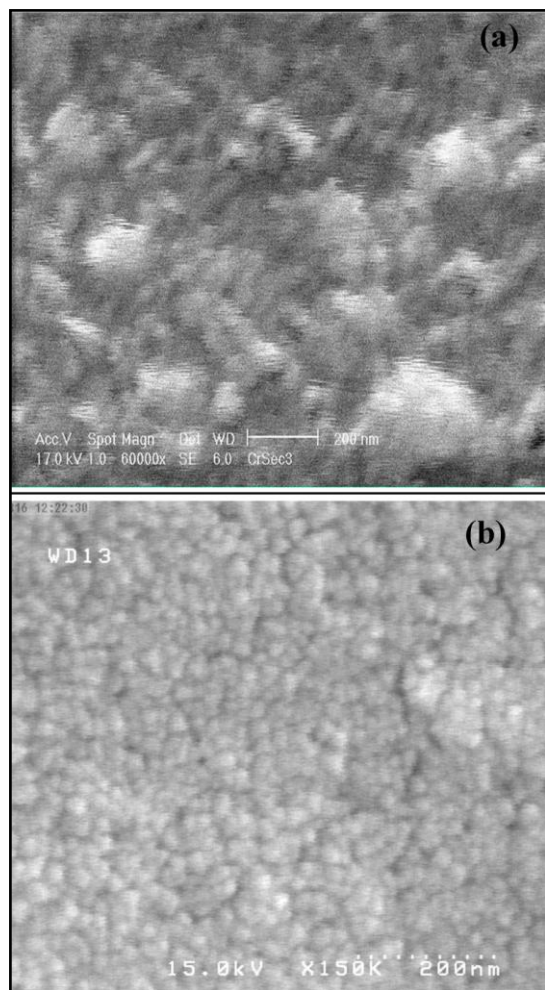
From FTIR results, it is found that the FTIR characteristics of all samples are almost same. The typical FTIR spectra of xerogel (a) without DCCA (b) in the presence of DMF are shown in Figure 8. The peaks at 2970 and 1410 cm^{-1} correspond to the stretching and bending modes of C–H bonds [18]. The peaks at 1270 and 854 cm^{-1} are attributed to the Si–C bonds. The characteristic adsorptions of Si–O–Si skeletal vibrations are shown around 1000 and 780 cm^{-1} [19]. The curve shows very weak peaks of –OH around 3200 and 1640 cm^{-1}, indicating the hydrophobic nature of the sample. All the spectra present the same characteristic bands of silica gel system, with exception of a strong band at about 1690 cm^{-1} characteristic of a C=O bond belonging to N,N-dimethylformamide or amide groups, present in the spectra of sols containing DMF.

Fig. 7. SEM micrographs of the silica xerogels from TEOS (a) without DCCA (b) in the presence of DMF
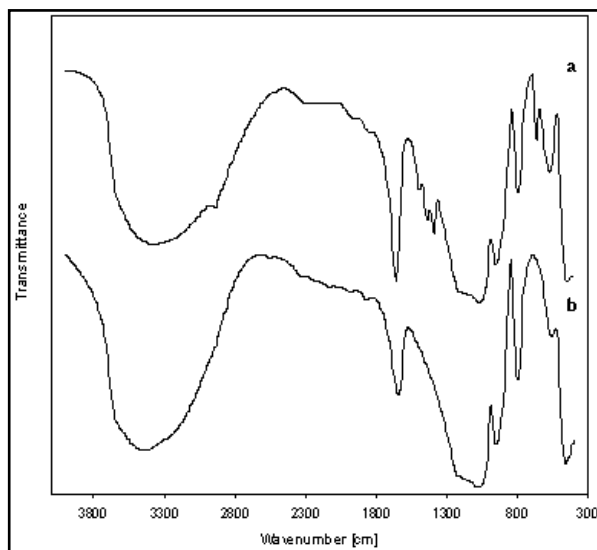

Fig. 8. FT-IR spectra of the silica xerogels under study: silica xerogels from TEOS (a) in the presence of DMF (b) without DCCA

CONCLUSIONS

The chemical effects of DMF as DCCA were examined in a silica sol gel process. Addition of DCCA affected the structure of the obtained silica as seen by means of N_2 adsorption/desorption measurements and SEM images. Use of DCCA in sol-gel silica systems was satisfactory to produce crack-free amorphous silica xerogel, decreasing gelation time and volume micropores in presence of DMF.

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