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A ^{29}Si magic angle spinning NMR and DTA study of thermal crystallization of sphene and zircon gels

J. S. HARTMAN*, R. L. MILLARD*, E. R. VANCE‡§
*Department of Chemistry, Brock University, St Catharines, Ontario L2S 3A1, Canada
and ‡Whiteshell Nuclear Research Establishment, Atomic Energy of Canada Limited,
Pinawa, Manitoba R0E 1L0, Canada

^{29}Si MAS NMR spectra of gels of sphene and zircon stoichiometry show wide variations in local silicon environments at intermediate stages of crystallization, depending on the pH of the starting mixtures. The broad NMR peaks of the calcined gels give way on heating to spectra of varying complexity, including a cristobalite peak which then diminishes in intensity again as the sphene or zircon peak becomes predominant on further heating. Differential thermal analysis as a function of heating rate for selected zircon and sphene gels yields activation energies of crystallization of about 300 kJ mol^{-1}.

1. Introduction

A recent paper [1] addressed thermal crystallization of near-amorphous materials having $CaTiSiO_5$ (sphene, also known as titanite), $ZrSiO_4$ (zircon), and $ThSiO_4$ stoichiometries. These materials were prepared by calcining materials produced by sol–gel methods, by vitrification, and by irradiation of corresponding crystalline material, and were studied by powder X-ray diffraction (XRD), infrared spectroscopy (IR), and differential thermal analysis (DTA). However, considerable uncertainty still remains about the structures of these materials.

The recent development of high-resolution solid state nuclear magnetic resonance (NMR) spectroscopy, using the technique of magic angle spinning (MAS), has provided a new approach to the study of complex solids, as it is directly sensitive to the local environments of the NMR-active nuclei [2, 3]. The initial ^{29}Si MAS NMR work on silicates by Lippmaa *et al.* [4] has been followed by a rapid proliferation of applications of this versatile technique to a wide range of natural and synthetic crystalline and amorphous silicates [5], including studies of aluminium, silicon order–disorder relationships [6, 7]. We have recently applied this technique to monitoring sphene glass ceramic synthesis from gels and from vitreous precursors [8]. We now report solid-state high-resolution ^{29}Si NMR studies on the crystallization of calcined gels of sphene and zircon stoichiometry that have been prepared at the Whiteshell Nuclear Research Establishment, Atomic Energy of Canada Limited, and studied previously by other techniques [1]. We also report additional DTA work.

2. Experimental procedure

The preparation of the sphene and zircon gels from acidic, neutral, or alkaline aqueous media has been described previously [1]. The starting liquids for the sphene gels were aqueous calcium nitrate solution, tetraethyl orthotitanate dissolved in isopropyl alcohol, and a colloidal aqueous dispersion of silica. These liquids were mixed, and the pH was controlled by addition of nitric acid or ammonia solutions. The resultant mixtures were dried and then calcined at 600° C to remove organics and nitrates. Aqueous zirconyl nitrate solution and the silica dispersion were used to make the zircon-based material, the pH being adjusted where necessary with ammonia solution. These mixtures were also dried and calcined in air at 600° C.

^{29}Si MAS NMR spectra were obtained on Bruker WH-400 and AC-200 multinuclear Fourier Transform NMR spectrometers equipped with 9.4 and 4.7 T superconducting magnets, respectively, using home-built magic angle spinning probes [9] and Delrin rotors. Spectra were obtained on the WH-400 instrument at a frequency of 79.46 MHz using 30° (3.7 μsec) pulses, typically with 8192 data points and a spectral width of 25 000 Hz, and Fourier transformed with 50 Hz of line broadening. Spectra were obtained on the AC-200 instrument at a frequency of 39.76 MHz using 15° (4.4 μsec) pulses, with 8192 data points and a spectral width of 16 000 Hz, and Fourier transformed with 25 Hz of line broadening. Typically up to 1000 scans were obtained, with a 5 sec relaxation delay between scans, but larger numbers of scans were helpful with some amorphous samples, especially on the AC-200 instrument. Longer relaxation delays, e.g. 300 sec between scans, were observed to affect relative peak areas in some cases, as discussed in a later section. The samples were spun at approximately 3300 Hz at an angle of 54.7° to the magnetic field. Chemical

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§*Present address*: Australian Nuclear Science and Technology Organization, Menai, New South Wales 2234, Australia.

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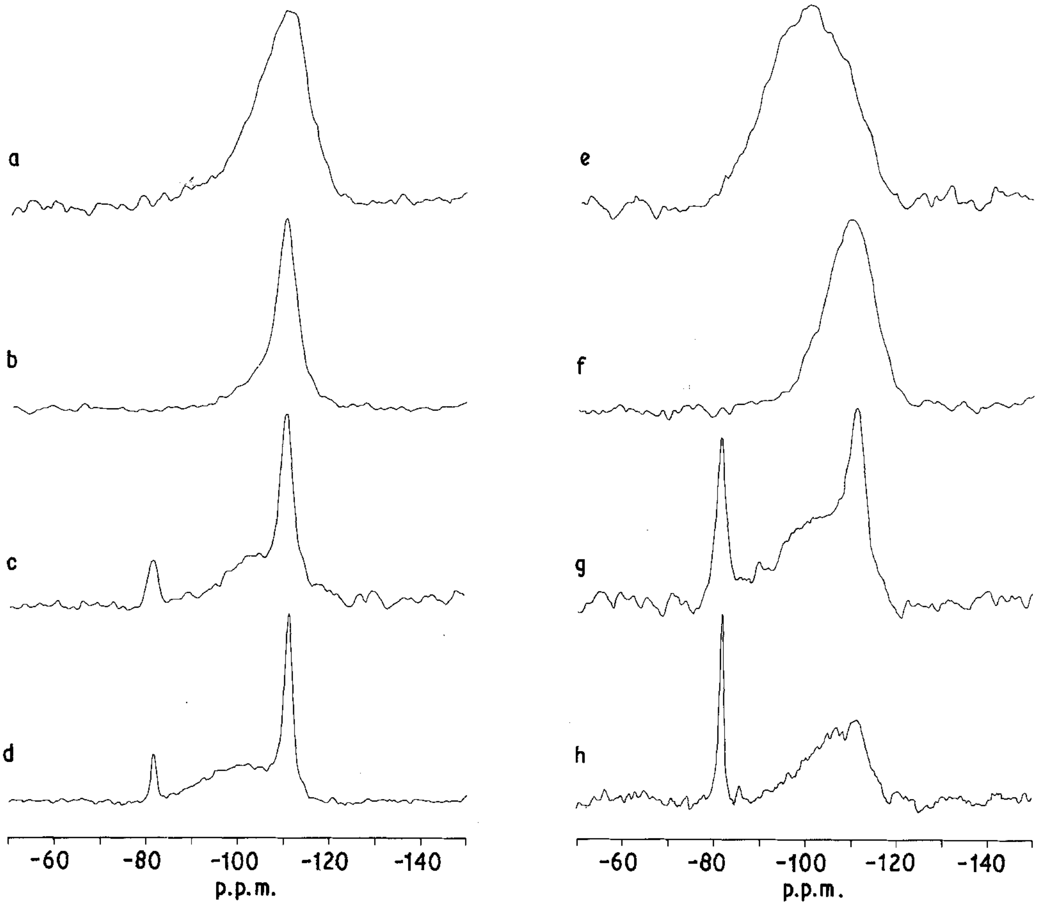

Figure 1 39.76 MHz ^{29}Si MAS NMR spectra of calcined zircon gels, prepared from a neutral (ph ~ 6) aqueous medium (a–d), and from an alkaline (pH ~ 9) aqueous medium (e–h), after various degrees of heating. Heating conditions were: a and e, 1 h at 800° C; b and f, plus 1 h at 1000° C; c and g, plus 1 h at 1300° C; d and h, plus 1 h at 1500° C.

shifts of sharp peaks were reproducible to ± 0.1 p.p.m., and are reported in p.p.m. to low field of tetramethylsilane. Many peaks had spinning sidebands of low to moderate intensity.

A Stanton-Redcroft STA-781 model instrument was employed for the DTA work. α-alumina was the reference material and samples weighing 60 to 90 mg were used. For a given substance, the sample mass was kept constant at the different heating rates. Since the DTA signal is essentially proportional to heating rate, a compromise had to be reached for the appropriate sample mass, between signal observability at low heating rates and undue perturbation of the temperature profile, due to exothermic sample behaviour, at high heating rates. The actual heating rates were 0.5 to 50° C min^{-1}. DTA results at a single heating rate have been published previously [1, 10]. To analyse the DTA curves, the modified Kissinger equation, given by

$$\ln(\alpha/T_p^2) = -E/RT_p$$

was used, where α is the heating rate, E the activation energy, T_p the temperature of the exothermic crystallization peak, and R the gas constant [11].

3. Results and discussion

3.1. Zircon gels

Calcined zircon gels made from acid (pH ~ 1) and neutral (pH ~ 6) solutions gave similar NMR spectra, consisting of a single broad peak at about − 111 p.p.m., which is similar to the value of − 112 p.p.m. observed in vitreous silica [12]. This is consistent with the previous X-ray observation of poorly crystallized ZrO_2 in such samples [1]. In these materials of $ZrSiO_4$ stoichiometry, the presence of ZrO_2 requires the presence of SiO_2, which must be amorphous to be consistent with the absence of any sharp X-ray reflections due to silicon-bearing material.

However the single broad NMR peak obtained from the X-ray amorphous material made from the alkaline (pH ~ 9) starting solution was centred at − 100 p.p.m., significantly different from the position of the amorphous SiO_2 peak. The difference suggests that the calcined gel structure has Si–O$^-$ terminal oxygens, or possibly that Zr–O–Si linkages are formed.

Fig. 1 shows ^{29}Si MAS NMR spectra of the neutral and alkaline calcined zircon gels after varying degrees of further heating to induce crystallization. Heating any of these calcined gels for 1 h at 800° C had virtually no effect on the NMR spectra, as expected from previous XRD results [1], and therefore the top spectra of Fig. 1 (heated at 800° C; Figs 1a and e) are also representative of the calcined gels themselves. Since the gels prepared from acid and neutral solutions gave similar NMR spectra throughout the heating sequence, spectra of the neutral gels are shown in Fig. 1 as representative of both.

Heating for 1 h at 1000° C sharpened the peak at − 111 p.p.m. for the acid and neutral preparations (compare Figs 1a and b), and this is attributed to a decrease in the range of bond angles and bond distances for the silicon sites ([12] and references therein). In this temperature range we would expect incipient cristobalite formation as the material rearranges and becomes less disordered. However the peak is still too broad to arise from well crystallized material. Cristobalite would give a sharper NMR peak (−108.5 p.p.m. [13]; −109.9 p.p.m. [4]), and cristobalite was not evident from XRD [1].

After heating for 1 h at 1000° C, the peak in the spectrum of the sample made from the alkaline starting mixture moved from −100 to −110 p.p.m. (compare Figs 1e and f; also note the similarity of Figs 1a and f). The peak was considerably broader than that observed from the acid and neutral preparations after the same time of heating at 1000° C (Fig. 1b), consistent with the presence of amorphous silica with a much wider range of bond angles and bond distances than in the corresponding materials prepared from acid and neutral starting mixtures. The lack of crystalline silicon-containing material is consistent with XRD work showing that tetragonal or cubic ZrO_2, but not crystalline SiO_2 or $ZrSiO_4$, forms in this material after this heat-treatment [1]. The results also suggest that any Zr–O–Si linkages in the calcined gel cannot be strong, since otherwise the material would not separate so readily into its constituent oxides on heating to 1000° C. In this context, Wies *et al.* [14] were unable to find NMR evidenced of Zr–O–Si bonding in the early stages of polymerization of a SiO_2–TiO_2–ZrO_2 gel formed by the alkoxide route.

Heating the samples at 1300° C for 1 h caused further sharpening of the peak near −111 p.p.m., due to increased crystallization of cristobalite as evidenced from XRD of the acid and neutral mixtures, and a peak at −81.5 p.p.m. also appeared which is assigned to crystalline zircon [15]. The proportion of zircon was considerably larger in the samples made from the alkaline starting media, as expected from XRD [1]. A broad low-intensity resonance centred at about −103 p.p.m. also became visible following heating at 1300° C, in the spectra of all samples regardless of pH of the starting materials. This apparently arises from residual amorphous material containing an appreciable proportion of terminal Si–O bonds. This material was not detected in previous XRD work, and deserves further study.

Heating at 1500° C for 1 h produced further increases in the intensities of the peaks from the crystalline species. However the broad peak centered at −103 p.p.m. remained, even with the material derived from alkaline starting media. From related XRD work on the crystallization of alkaline $ZrSiO_4$ based gels [16], crystallization would be expected to be substantially complete after heating at 1500° C, but of course admixtures of amorphous material would not be observed by conventional XRD techniques.

However our standard conditions of spectra acquisition (5 sec delay between pulses) overestimate the amount of amorphous material present in these samples. Spin-lattice relaxation times [17] must be shorter in the amorphous than in the crystalline material, since allowing longer delays between pulses (from 0.4 sec to at least 300 sec) gives a trend of diminishing relative peak intensity of the amorphous component. Spectra obtained at sufficiently long delays (300 sec to 2 h) between pulses show that the amorphous material is actually a very minor component. A single-scan experiment, after a relaxation delay of 2 h, on the alkaline zircon gel that had been heated to 1500° C, gave a large zircon peak but the higher-field signals were barely detectable. Shorter spin-lattice relaxation times in the amorphous component are consistent with a greater degree of atomic motion and/or the presence of traces of paramagnetic impurities, and allow the possibility of selective NMR study of this component, via rapid pulsing and saturation of the major-component signals [18]. This technique has potential for investigating the presence and composition of small amounts of siliceous glassy material which could have deleterious effects on the properties of otherwise-fully-crystalline ceramics.

DTA measurements on the calcined gels prepared from acid and neutral solutions yielded virtually no observable endo- or exothermic peaks attributable to

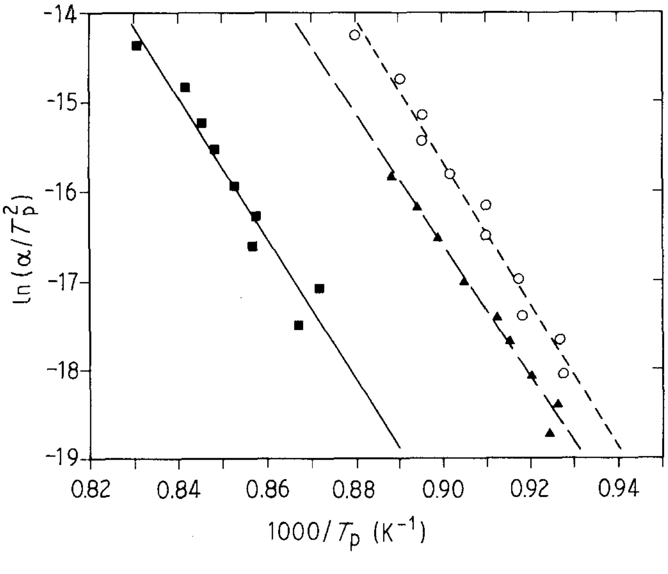

Figure 2 Kissinger plots of DTA results for: alkaline zircon gel (■); acidic sphene gel (▲); and vitreous sphene (○).

TABLE I DTA peak temperatures as function of heating rate for alkaline zircon gel, acidic sphene gel, and vitreous sphene*

Heating rate ($K sec^{-1}$)	$ZrSiO_4$ gel	$CaTiSiO_5$ gel	$CaTiSiO_5$ vitreous
0.008		1082	
0.012		1080	
0.017		1087	
0.025		1093	
0.033	1153	1096	1089
0.050	1147	1105	1090
0.083	1167	1112	1099
0.117	1166	1118	1099
0.167	1173	1125	1109
0.250	1179		1117
0.333	1183		1117
0.500	1188		1123
0.833	1204		1136

*Peak temperatures, in K, are considered accurate to within ± 3 K.

zircon crystallization, and this is no doubt due to the very sluggish and complex crystallization path deduced previously [1]. However, well defined exothermic peaks were observed from the preparation made with alkaline media, and yield an activation energy of 330 ± 30 kJ mol^{-1}. The results as a function of heating rate are presented in Table I and a plot of ln (α/T_p^2) against $10^3/T_p$ appears in Fig. 2. The correlation coefficient of the linear regression line is 0.98. No significant curvature of the line joining the experimental points was observed. This suggests constancy of the number of nucleation sites for the initiation of crystallization, as indicated in a recent discussion [19] of the applicability of the Kissinger equation to the crystallization of fine powders. Unfortunately there have been no previous determinations of the activation energy of crystallization of radiation-amorphized zircon with which to compare the value of 330 ± 30 kJ mol^{-1} derived from the gradient of the Kissinger plot, and formation of vitreous zircon by quenching a melt has not been reported.

3.2. Sphene gels

In contrast to the results on the calcined zircon gels, XRD did not show much difference in crystallization behaviour of sphene gels made from starting solutions of different pH values in the range of 1 to 9 [1]. NMR spectra of calcined sphene gels all showed a broad peak near −111 p.p.m., assigned to amorphous silica. The lower-field absorption differed greatly in intensity depending on the initial pH (Fig. 3). This absorption was not precisely centred at −79.1 or −80.8 p.p.m., the values appropriate to crystalline and vitreous sphene respectively [8], but for the acid and alkaline samples the intensity was concentrated in the −65 to −90 p.p.m. range (Figs 3a and c), consistent with its arising from isolated SiO_4 tetrahedra [4, 5].

Crystallization of some sphene, as expected from XRD results [1], was evidenced by the appearance of a fairly sharp NMR peak near −79 p.p.m. after heating the calcined gels for 1 h at 800° C (Figs 4a and d). Some sharpening of the peak at −111 p.p.m. was also evident, as with the zircon gels described above, and this might be attributed to an increase in local ordering in this non-crystalline phase, together with the formation of the small amount of cristobalite which was detected by XRD [1]. Additional peaks appear at −83.5, −88.6, and −95.8 p.p.m. in the spectrum of the neutral sphene gel only, after heating at 800° C (Fig. 4a), and merit further study.

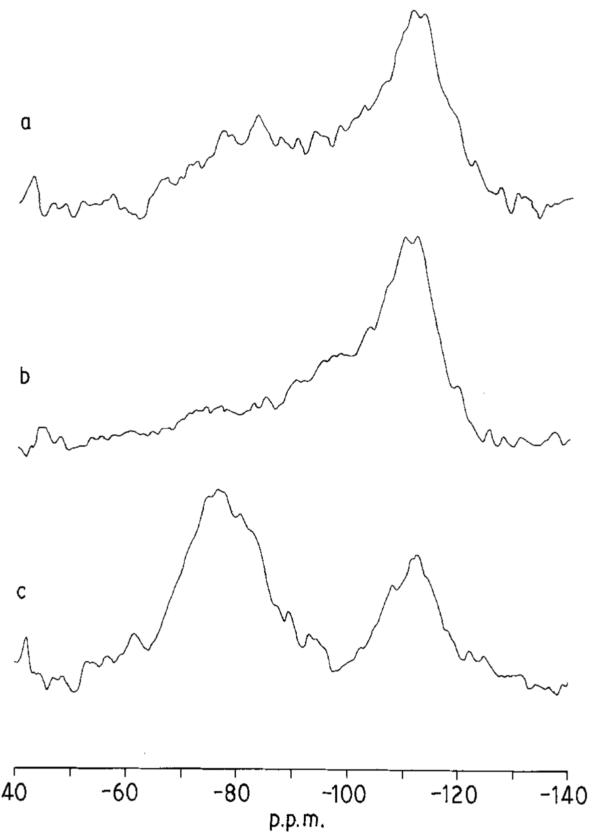

Figure 3 79.46 MHz ^{29}Si MAS NMR spectra of calcined sphene gels, prepared from aqueous solution under the following conditions: a, acid; b, neutral; c, alkaline.

Heating to 1000° C sharpened the peaks at −79.1 p.p.m. and −111 p.p.m., consistent with further crystallization of sphene and cristobalite (Figs 4b and e). Only two of the three intermediate-chemical-shift peaks of the neutral sphene gel, prominent after heating to 800° C, were still detectable after heating at 1000° C, and these had greatly diminished in intensity (Fig. 4b). After heating at 1300° C for 1 h, virtually the only NMR feature was the sharp sphene peak at −79.1 p.p.m. (Figs 4c and f). Crystallization was expected to be essentially complete at 1300° C, both from previous results [1] and from the proximity of this temperature to the melting point of sphene (1382° C). However a small amount of amorphous material remains after heating at 1300° C in the neutral-sphene-gel sample. This is shown by the very broad, weak absorption between −85 and −115 p.p.m., which is more evident in the expanded-vertical-scale spectrum included in Fig. 4c.

Consistent with the similarities of the XRD results for the preparations formed from starting solutions of different pH values, NMR spectra of the acid and basic sphene gels after heating were generally quite similar, except that the cristobalite resonance was barely detectable in the acid sphene gel sample after heating at 1000° C. However NMR spectra of the neutral sphene gel do reveal a major difference. The intriguing intermediate-chemical-shift peaks observed

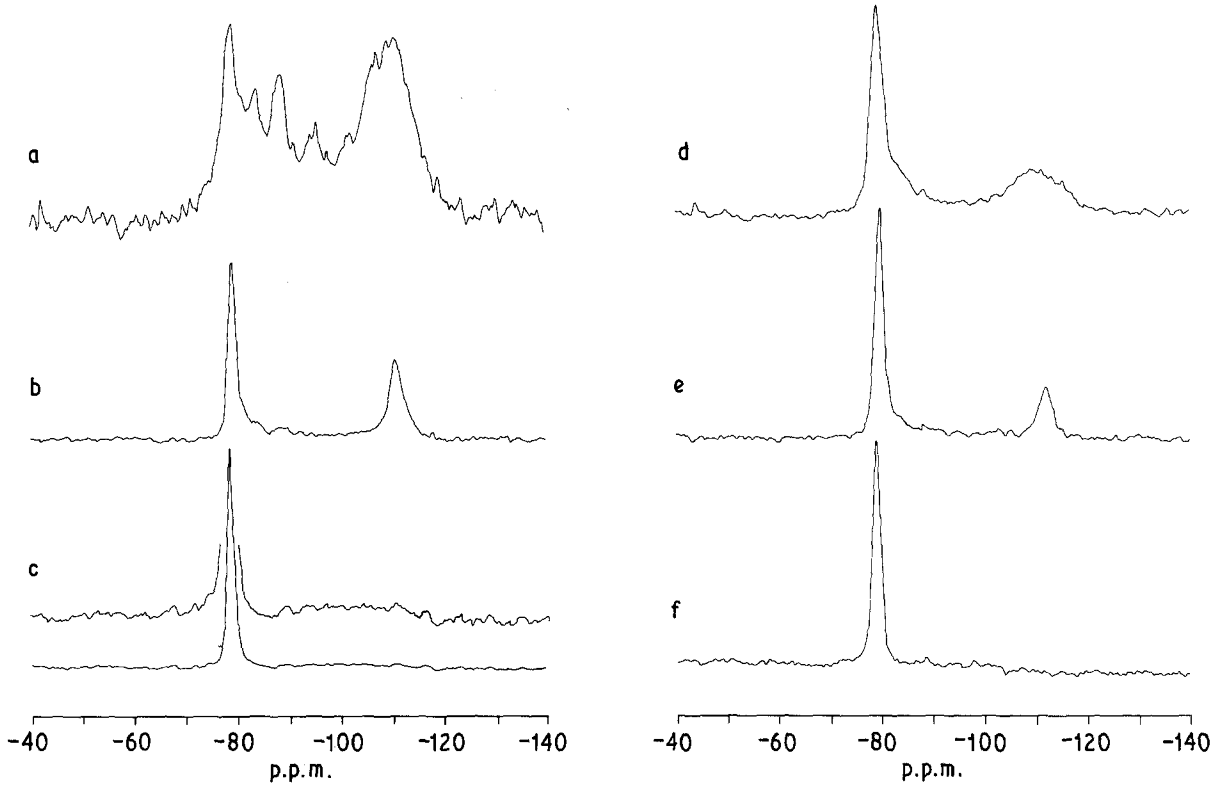

Figure 4 39.76 MHz ^{29}Si MAS NMR spectra of calcined sphene gels, prepared from a neutral aqueous medium (a–c) and from an alkaline aqueous medium (d–f), after various degrees of heating. Heating conditions were: a and d, 1 h at 800° C; b and e, plus 1 h at 1000° C; c and f, plus 1 h at 1300° C.

in the neutral sphene gels after heating at 800° C suggest that a different crystallization path may be followed, in which intermediate species are longer-lived when neither acid nor base catalysis of crystallization can occur.

DTA results as a function of heating rate were obtained on the calcined sphene gel made from the acid starting mixture and peak temperatures are given in Table I. For comparison, equivalent results on vitreous sphene are also given. As for the calcined zircon gel, no systematic curvatures were observed in the Kissinger plots for the calcined sphene gel and for vitreous sphene (Fig. 2). The correlation coefficients of the linear regression lines were 0.99 in both cases. The activation energies of crystallization for the calcined gel and the vitreous material were found to be 315 ± 30 and 335 ± 30 kJ mol^{-1} respectively, i.e., the same within experimental error. No results on radiation-amorphized sphene are available.

4. Conclusions

^{29}Si MAS NMR has provided a convenient method of monitoring local silicon environments in gels having sphene and zircon stoichiometries, and their changes on heating. The results depend on the pH of the starting solutions used in gel synthesis, and confirm the fundamental structural differences between zircon gels made from acid and alkaline media. Activation energies for crystallization of about 300 kJ mol^{-1} were deduced from Kissinger plots obtained by differential thermal analysis of selected sphene and zircon gels.

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