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Thermodynamic analysis of chemical vapour deposition from methoxysilanes

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Thermodynamic equilibrium calculations for the systems *n*-methoxysilane, $SiH_{4-n}(OCH_3)_n$, $n = 1$–4, were performed using the STANJAN computer code. The required enthalpy and entropy data for the methoxysilanes were estimated using the MOPAC computer program for semi-empirical molecular orbital calculations. The calculated solid-phase compositions were not sensitive to ± 10% changes in the *n*-methoxysilane enthalpy and entropy values. For $n = 2$, 3 or 4, the equilibrium solids were comprised of SiO_2 and C. The purest SiO_2 was predicted for 2-MEOS at atmospheric pressure, low temperature, and an excess of hydrogen. For all *n*-methoxysilanes, the solid carbon content increased rapidly at moderate temperatures but did not continue to increase at the highest temperatures.

1. Introduction

There is continued interest in chemical vapour deposition (CVD) of SiO_2 with appropriate electrical and mechanical properties for integrated circuit technology via more accessible reaction conditions. Current methods include low-temperature deposition through oxidation of silane [1] or dichlorosilane [2]. Thermal decomposition of tetraethoxysilane, $Si(C_2H_5O)_4$, at temperatures near 700 °C and low pressures has produced SiO_2 films with desirable properties [3]. Diacetoxyditertiarybutoxysilane has also yielded high-quality SiO_2 films via chemical vapour deposition (CVD) [3]. Other researchers have studied the preparation of silicon oxycarbide glasses, which promise enhanced mechanical and thermal properties. Synthesis routes for these glasses have included pyrolysis of silicone polymers [4] and sol/gel processing of alkyl-substituted alkoxysilanes [5]. Coatings of these glasses may be obtainable through CVD technology.

In this work, equilibrium calculations were performed for the *n*-methoxysilanes, $SiH_{4-n}(OCH_3)_n$ with $n = 1$–4, as possible new CVD source gases. CVD using *n*-methoxysilanes offers possible routes to SiO_2 or solids with various Si/O/C content. Although chemical vapour depositions are often not equilibrium reactions because of mass transfer and kinetic limitations, the equilibrium calculations are valuable in guiding experimental investigations. Equilibrium studies give some indication of the range of experimental parameters which may yield the desired products. Equilibrium calculations identify limitations on the amount of deposit formed and can be used to infer which species might be important in the rate-limiting mechanism of the deposition process.

2. Method of calculation

The computer code used in this work was version 3 of STANJAN [6]. This interactive PC program applies the method of element potentials for chemical equilibrium analysis of single- or multi-phase systems. The method of element potentials has the advantage of requiring fewer variables than equilibrium calculation methods based on minimization of Gibbs' free energy. The variables in the element potential method are those representing the potentials of each element type and the total number of moles in each phase. In comparison, Gibbs' energy minimization methods must include, as variables, the mole fraction of every reagent species and possible product species. Another advantage of the element potential method is the program's robustness in handling species with very small mole fractions. Additionally, it is impossible to generate negative mole fractions, which can occur and must be corrected for in the implementation of certain mole fraction search methods. Version 3 of STANJAN assumes that the vapour forms an ideal gas and the condensed phases are ideal solutions. A discussion of the element potential algorithm, as implemented in the STANJAN code, is available in the Version 3 Manual.

The required thermodynamic data were values of enthalpy and entropy as a function of temperature for each reagent and possible product species. The required data for the *n*-methoxysilanes was estimated [7] using the MOPAC code [8] with Pitzer–Gwinn corrections [9]. MOPAC is a semiempirical molecular orbital program which can provide, among other parameters, estimates of molecular enthalpy, entropy and heat capacity. The MOPAC calculations were performed using the PM3 Hamiltonian with rotational contributions purposely excluded. The rotational contributions were later added back into the thermodynamic quantities using moments of inertia and barriers to rotation available from the literature [10] and as estimated from the MOPAC-calculated geometries for the various rotors within the molecule. The resultant enthalpy, *H*, and entropy, *S*, values for

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TABLE I Comparison of thermodynamic parameters, calculated using MOPAC, with available literature values

Species	ΔH_f° (298 kcal mol^{-1})	Source	S° (298 cal mol^{-1})	Source
1-MEOS	− 62.58	MOPAC	67.59	MOPAC
2-MEOS	− 142.18	MOPAC	83.63	MOPAC
3-MEOS	− 220.71	MOPAC	96.22	MOPAC
	− 189 ± 3	[16]		
4-MEOS	− 324.73	MOPAC	139.2	MOPAC
	− 293 ± 3	[14]		
	− 281.8	[17]		

TABLE II Sources of thermodynamic data used in the equilibrium calculations

Species	Reference
H_2	[11]
H_2O	[11]
O_2	[11]
CO	[11]
CO_2	[11]
CH_4	[11]
C_2H_6	[11]
CH_3OH	[12]
CH_3OCH_3	[15]
$SiH_3(OCH_3)$	MOPAC
$SiH_2(OCH_3)_2$	MOPAC
$SiH(OCH_3)_3$	MOPAC
$Si(OCH_3)_4$	MOPAC
C(s)	[11]
Si(s)	[11]
α-SiC(s)	[11]
β-SiC(s)	[11]
SiO_2, quartz	[11]
SiO_2, low cristobalite	[11]
SiO_2, high cristobalite	[11]

the *n*-methoxysilanes are shown as a function of temperature and compared to available literature values in Table I. Thermodynamic data for all other species were obtained from the JANAF [11] and the TRC Thermodynamic Tables [12]. The species included in the calculations are listed in Table II. Preliminary results showed that SiH, SiH_4, and C_2H_6 were not formed over a wide range of conditions, so these species were eliminated from subsequent calculations.

Equilibrium products were determined for the *n*-methoxysilane reagents as a function of temperature and pressure, for various H_2:*n*-methoxysilane ratios. The temperature was varied from 400–1400 K and the H_2:*n*-methoxysilane ratio spanned the values of 0.1:1 to 100:1. Most calculations were performed using 0.2 or 1.0 atm total pressure, to cover likely conditions for depositing wear-resistant coatings.

Results from equilibrium calculations have often been presented in a format termed a "CVD phase diagram" [13]. This format displays the predicted solid phases as a function of two independent variables, typically temperature and composition. The solid composition varies throughout a multiple-component phase region, yet these variations are not indicated. In this work, the mole fractions of the solid species were intentionally presented because the solid composition is of interest for the preparation of Si–O–C solids. Using this representation, a graph of the solid-phase composition must be generated for each overall system stoichiometry. In presentation and discussion of these results, the calculated α-SiC and β-SiC compositions were summed together and called SiC. Similarly, the three silicon dioxide species used in the equilibrium calculations were treated as a single SiO_2 entity.

As indicated earlier, all calculations were performed with thermodynamic data for the *n*-methoxysilanes generated using MOPAC. Because the accuracy of these values was unknown, the sensitivity of the equilibrium results to the *n*-methoxysilane thermodynamic values was tested. The enthalpy and entropy values of the *n*-methoxysilanes were varied and the change in the solid-phase composition was determined.

3. Results and discussion

Fig. 1a–d show the composition of the solid phase as a function of temperature for a H_2:*n*-methoxysilane ratio of 25:1 and a pressure of 0.2 atm. The graphs for 2-, 3-, and 4-MEOS indicate that at low temperatures, nearly pure SiO_2 was the thermodynamically preferred product. As the temperature increased, the solid phase contained more carbon, and eventually carbon became the predominant solid species. Virtually no silicon nor SiC were formed. The results for 1-MEOS were characteristically different, because of the low oxygen to silicon ratio in the precursor molecule. The equilibrium solid formed from 1-MEOS was a 50/50 mixture of SiC and SiO_2 at low temperatures. As the temperature increased, more carbon was again incorporated into the solid.

The equilibrium strongly favoured the formation of solid silicon-containing species. Over the entire range of conditions studied, the total concentration of silicon-containing species in the gas phase did not exceed 1×10^{-6} mol out of 1.0 mol of available silicon.

The sensitivity of the calculated solid-phase composition to the estimated thermodynamic data for the *n*-methoxysilanes was addressed. The calculations were repeated using modified thermodynamic data for the *n*-methoxysilanes to assess the effect on the equilibrium composition. For these calculations, the data for all species but *n*-methoxysilanes remained unchanged. The enthalpy and/or the entropy values for *n*-MEOS were altered by ± 10%. This corresponded to varying the ΔH_f° by 6, 14, 22 and 32 kcal mol respectively, for 1-MEOS through 4-MEOS. The amount of this enthalpy variation was much greater than the best accuracy of determination of ΔH_f° for the

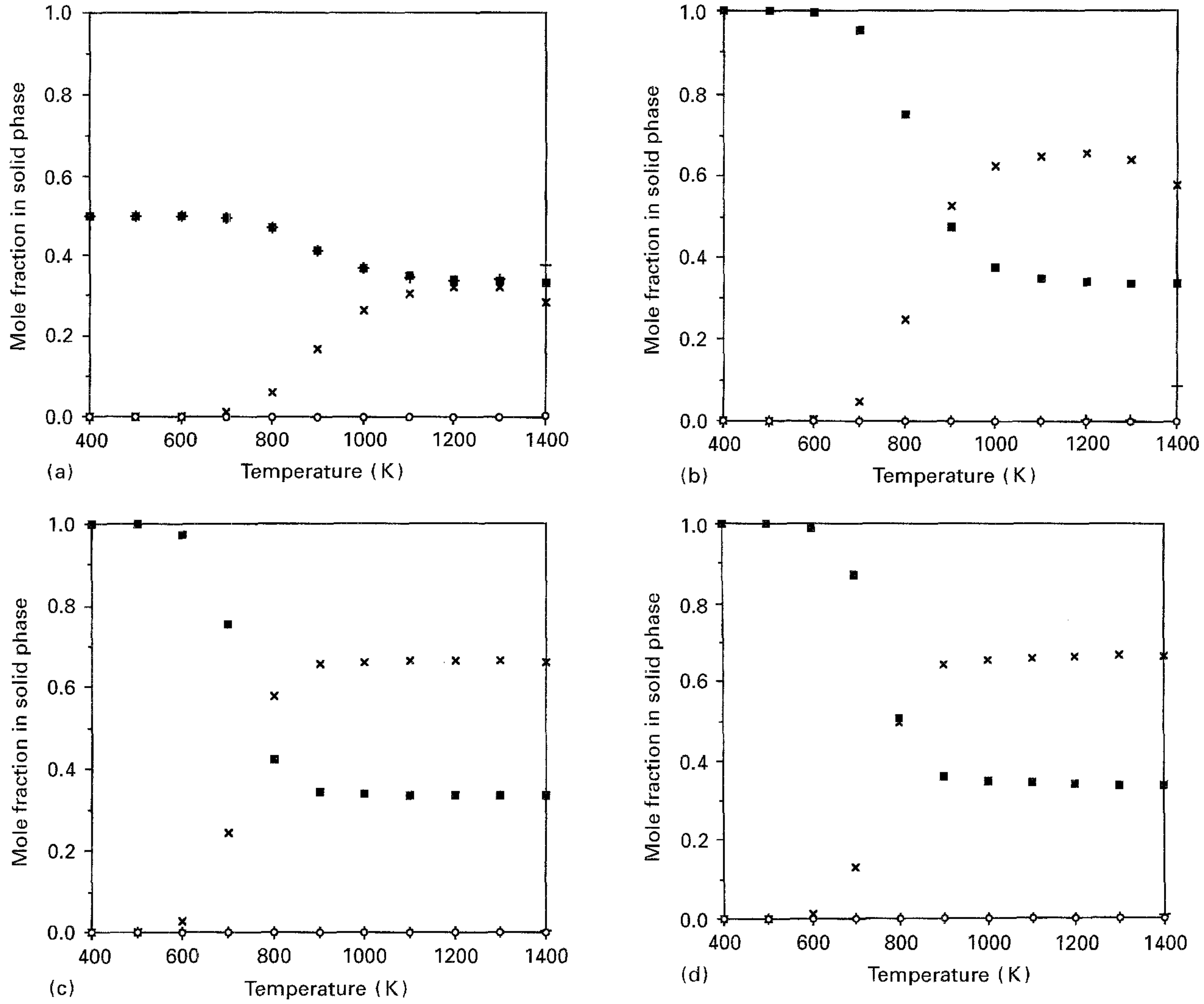

Figure 1 Solid-phase equilibrium composition at 0.2 atm and an H_2:*n*-MEOS ratio of 25:1. (a) 1-MEOS, (b) 2-MEOS, (c) 3-MEOS, (d) 4-MEOS. (■) SiO_2, (×) carbon, (+) SiC, (○) silicon.

TABLE III Thermodynamic values derived using MOPAC for *n*-methoxysilanes

	1-MEOS		2-MEOS		3-MEOS		4-MEOS	
$I(K)$	$H(T)$ (kcal mol^{-1})	$S(T)$ (cal mol^{-1})	$H(T)$ (kcal mol^{-1})	$S(T)$ (cal mol^{-1})	$H(T)$ (kcal mol^{-1})	$S(T)$ (cal mol^{-1})	$H(T)$ (kcal mol^{-1})	$S(T)$ (cal mol^{-1})
400	− 60.4	73.7	− 138.8	93.2	− 216.4	108.3	− 300.7	122.2
500	− 57.9	79.2	− 135.0	101.8	− 211.4	119.3	− 294.5	136.0
600	− 55.2	84.3	− 130.6	109.7	− 205.9	129.4	− 287.6	148.6
700	− 52.2	89.0	− 126.0	116.9	− 199.8	138.7	− 280.2	160.0
800	− 48.9	93.3	− 121.0	123.5	− 193.4	147.2	− 272.3	170.6
900	− 45.4	97.4	− 115.8	129.7	− 186.7	155.1	− 263.9	180.4
1000	− 41.8	101.2	− 110.5	135.3	− 179.7	162.5	− 255.3	189.5
1100	− 38.1	104.8	− 105.0	140.5	− 172.5	169.4	− 246.4	198.0
1200	− 34.2	108.1	− 99.4	145.4	− 165.1	175.9	− 237.2	206.0
1300	− 30.2	111.3	− 93.7	149.9	− 157.4	182.0	− 227.8	213.6
1400	− 26.1	114.3	− 88.0	154.2	− 149.6	187.7	− 218.1	220.7

alkoxysilanes, reported to be within 1 kcal mol^{-1} [14]. The ± 10% variation in enthalpy and entropy yielded equilibrium solid compositions identical to those determined using the original data. This sensitivity analysis revealed that minor adjustments in the thermodynamic data did not drastically alter the predicted equilibria.

A 50% increase in the enthalpies of *n*-MEOS did not change the equilibrium solid composition calculated for any conditions. The insensitivity of the results to the changed thermodynamic data was associated with the nearly complete conversion of *n*-MEOS. Using the original thermodynamic data, the equilibrium concentrations of the *n*-methoxysilanes were already below the reported threshold used by some researchers [15]. Making *H* more positive and *S* more negative for the *n*-MEOS molecules further reduced their concentrations in the equilibrium mixture. However, the observed changes in the *n*-MEOS gas composition were too insignificant to alter the solid-phase composition.

A 50% reduction in the methoxysilane enthalpies had no effect on the equilibrium solid-phase composition for 1-MEOS and 2-MEOS reagents under most conditions. The greatest observed change in the solid mole fractions was the order of 10^{-7} at 0.2 atm and 400 K. The 3-MEOS and 4-MEOS equilibria were more sensitive to a 50% reduction in *n*-methoxysilane

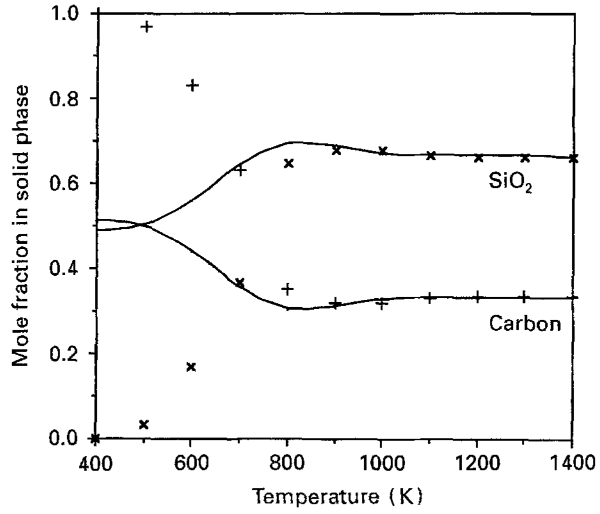

Figure 2 SiO_2 and carbon content of the equilibrium solid phase for an H_2:3-MEOS ratio of 0.1:1 at 0.2 atm pressure, (———) using the originally calculated H values, (+, ×) using values lowered by 50%.

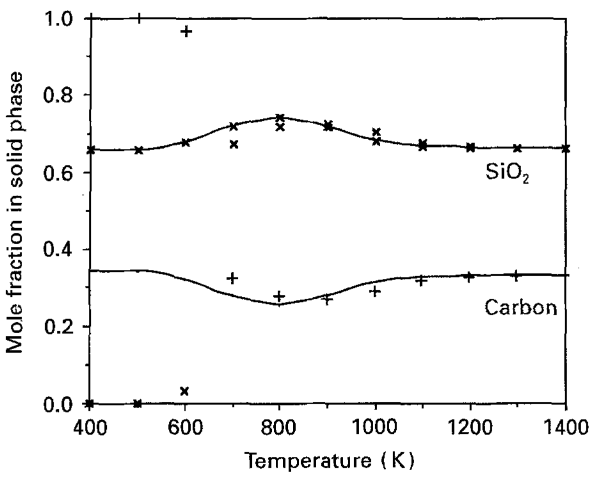

Figure 3 SiO_2 and carbon content of the equilibrium solid phase for an H_2:4-MEOS ratio of 0.1:1 at 0.2 atm pressure, (———) using the originally calculated H values, (+, ×) using values lowered by 50%.

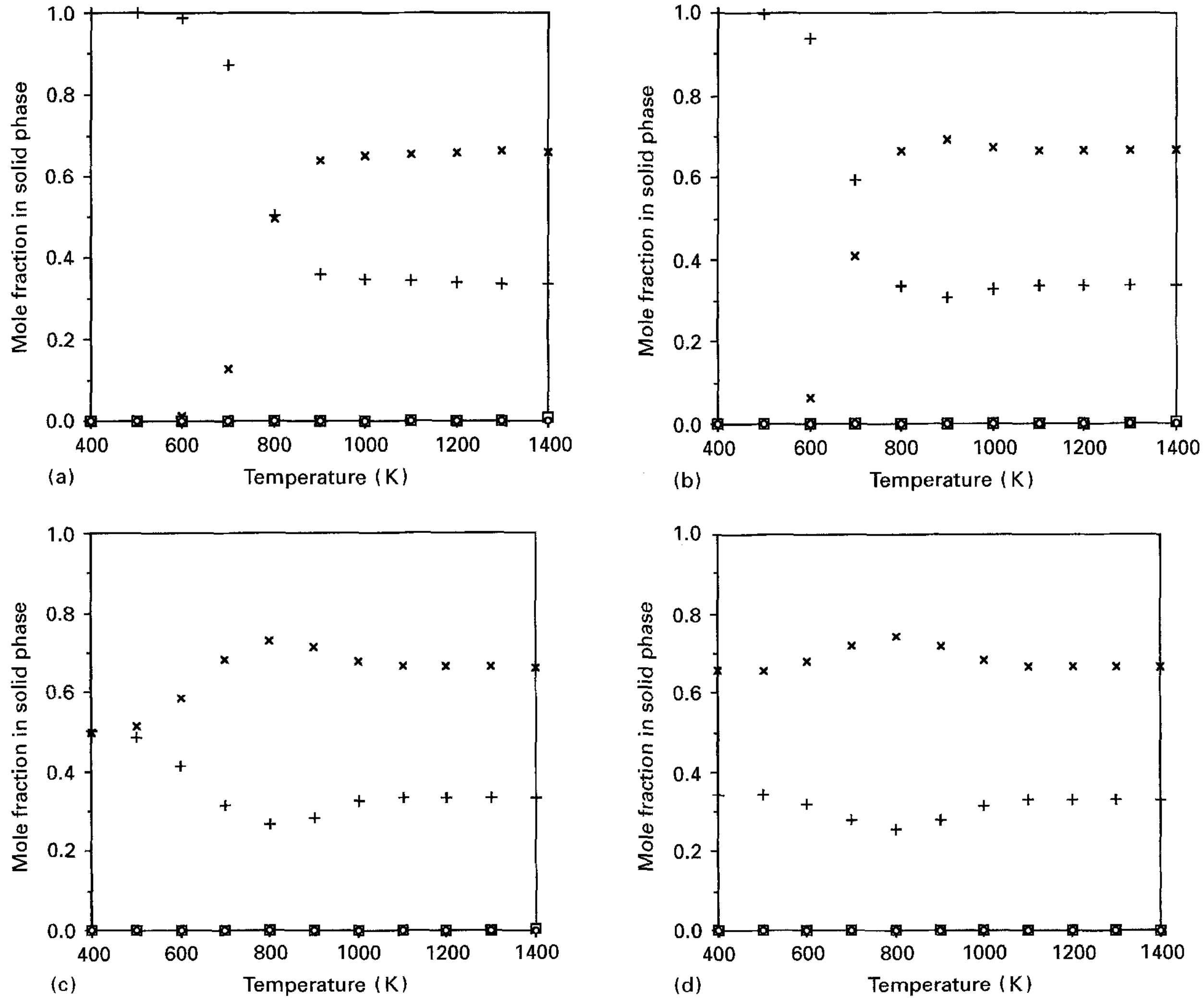

Figure 4 Effect of the reagent ratio on the equilibrium solid-phase composition for 4-MEOS at 0.2 atm. H_2:4-MEOS ratios of (a) 25:1, (b) 10:1, (c) 2:1, (d) 0.1:1. (+) SiO_2, (×) carbon, (□) SiC, (O) Si.

enthalpy. Systems with low H_2:n-MEOS reagent ratios and low temperatures had the largest changes such as those indicated in Figs 2 and 3. The prediction of pure SiO_2 solid phase was extended to higher temperatures than for the original thermodynamic data. The high-temperature results were unchanged.

The effect of changing the H_2:4-MEOS reagent ratio is shown in Fig. 4. The temperature at which significant amounts of solid carbon formed decreased for systems with less hydrogen. For a H_2:4-MEOS ratio of 0.1:1, carbon was the predominant solid species even at the lowest temperature. For low H_2:4-MEOS ratios, more than half of the available carbon formed solid. The maxima in the carbon content, observed for H_2:4-MEOS ratios up to 10:1, can be explained by changes in the gas-phase composition. As the temperature increased, more carbon was incorporated into the solid, with the majority of the remaining carbon forming CH_4. However, as the temperature increased further, more CO was formed at the expense of both CH_4 and solid carbon. Higher hydrogen contents yielded more CH_4 at a given temperature. With a 25:1 H_2:4-MEOS ratio, less than half of the available carbon formed solid and the amount of solid carbon never decreased at higher temperatures.

The low-temperature equilibrium solids for 2-MEOS and 3-MEOS reagents at low hydrogen contents were not comprised of predominantly carbon. This was because of the lower C/Si ratio for these species compared to 4-MEOS. Calculations for 1-MEOS, with the lowest C/Si, never yielded significant amounts of carbon.

The temperature at which carbon comprised 50 mol % of the solid phase was mapped out as a function of the H_2:n-MEOS ratio. Fig. 5 shows the temperature at which the solid phase changed from predominantly SiO_2 to predominantly carbon. 1-MEOS is not shown because it yielded a solid phase that was a mixture of SiO_2 and SiC. The transition temperature decreased for a given reagent as the hydrogen content decreased. The transition temperature was also lower for reagents containing more carbon. A higher total pressure favours the formation of carbon-containing gas species and shifts the transition temperature to higher values.

The equilibrium calculations indicate the possibility of forming nearly pure SiO_2 at low temperatures. The temperatures below which the solid contains less than 0.1 mol % carbon in SiO_2 are shown in Fig. 6 for various conditions. The temperature decreased for

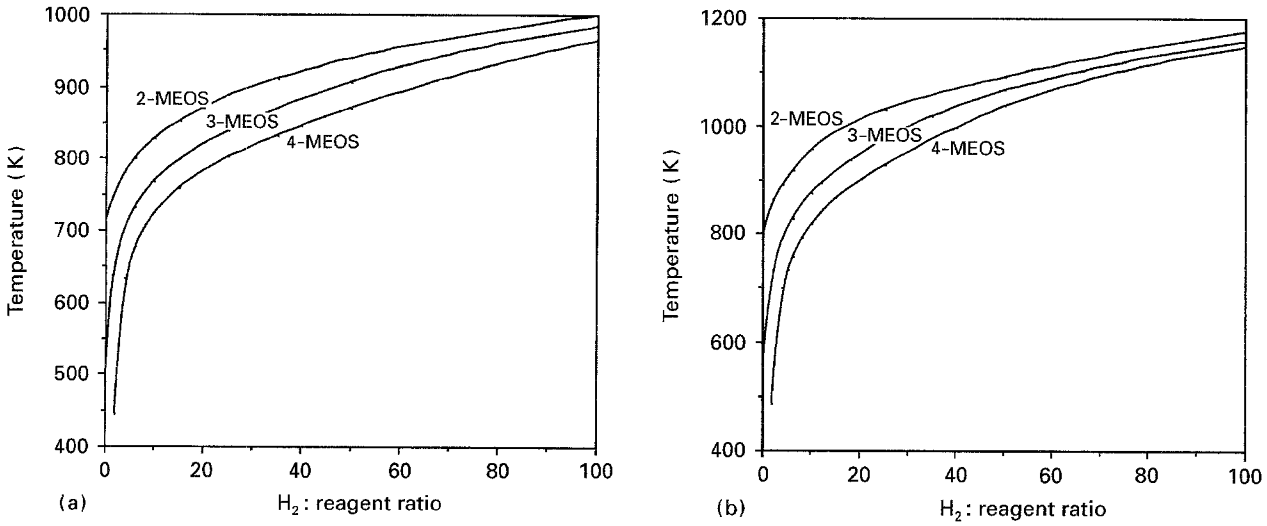

Figure 5 The temperature at which the equilibrium solid phase was predominantly carbon for various reagents: (a) 0.2 atm, (b) 1.0 atm.

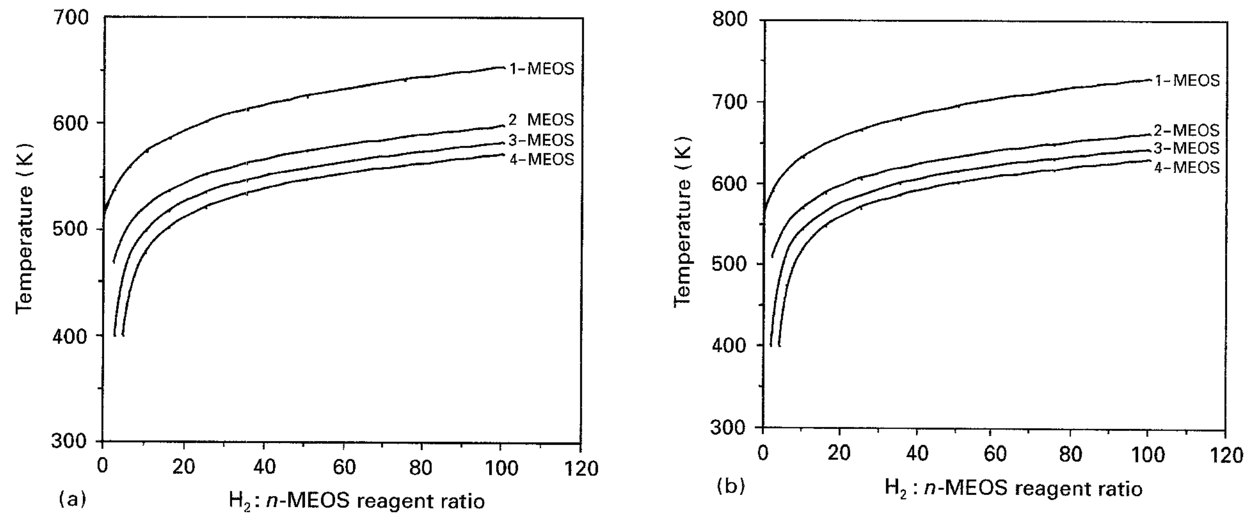

Figure 6 The temperature at which the equilibrium solid contained more than 0.1 mol % carbon: (a) 0.2 atm, (b) 1.0 atm.

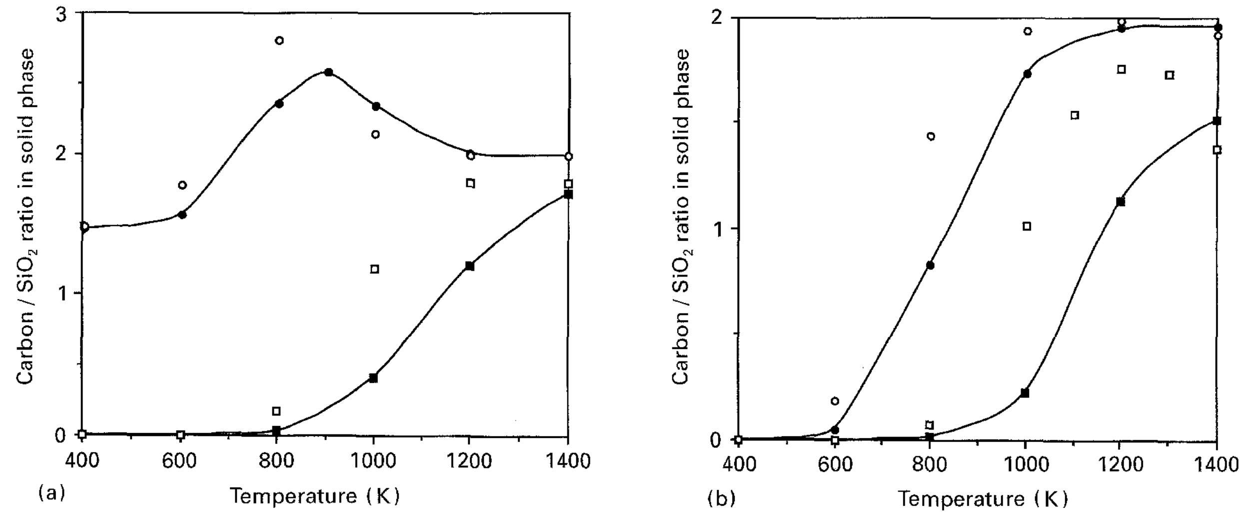

Figure 7 The temperature at which the carbon content of the equilibrium solid reached 0.1 mol %. (a) 4-MEOS; (b) 2-MEOS. (■) 1 atm, 100:1; (●) 1 atm, 1:1; (□) 0.2 atm, 100:1; (○) 0.2 atm, 1:1.

a given reagent as the hydrogen content was reduced. The temperature for producing nearly pure SiO_2 was also reduced for a lower total pressure. This corresponds to the same pressure-dependent behaviour observed for the formation of a majority carbon in the solid phase.

The effect of pressure is shown more clearly via plots of the C/SiO_2 ratio illustrated in Fig. 7. For 4-MEOS, the results for a given reagent ratio are shifted to lower C/SiO_2 ratios at the higher pressure and lower temperatures. The higher pressure favours the formation of solid carbon over that of carbon-containing gaseous species. A large excess of hydrogen favours the formation of CH_4 and yields less solid carbon. The differences diminish at high temperatures. For 2-MEOS, the lower pressure and low hydrogen content again favours the formation of solid carbon. The 2-MEOS retains more pressure and composition dependence at high temperatures.

4. Conclusions

The equilibrium calculations indicate that *n*-methoxysilanes are possible source gas species for CVD of pure SiO_2 or mixtures of SiO_2 and carbon. Although the thermodynamic data for the *n*-methoxysilanes was generated using a semiempirical method, the equilibrium results were not sensitive to small changes in these data.

With the exception of 1-MEOS, the equilibrium solids were comprised of SiO_2 and carbon. The formation of pure SiO_2 was predicted at low temperatures, yet may not be the experimentally observed product due to kinetic limitations at these temperatures. The formation of pure SiO_2 was enhanced by reaction at atmospheric pressure rather than reduced pressure, and the use of excess hydrogen. 2-MEOS yielded pure SiO_2 at the highest temperature, which implies it may be the best candidate for producing SiO_2. Solid Si–O–C mixtures were predicted over a wide range of conditions, with a correspondingly wide range of compositions. The equilibrium solid compositions for 3-MEOS and 4-MEOS at elevated temperatures did not vary with temperature.

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