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Measurement and Prediction of H_2O Outgassing Kinetics from Silica-Filled Polydimethylsiloxane TR55 and S5370

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ABSTRACT

The isoconversional technique was employed for the measurement and prediction of H_2O outgassing kinetics from silica-filled polydimethylsiloxane TR55 and S5370 in a vacuum or dry environment. Isoconversional analysis indicates that the energy barrier for H_2O release from TR55 and S5370 is an increasing function of the fractional H_2O release. This can be interpreted as the release of H_2O from physisorbed water and then chemisorbed water with decreasing OH density from the surfaces of the embedded silica particles. Model-independent predictions of H_2O outgassing based on the measured kinetics follow the trend of actual isothermal outgassing at elevated temperatures, and suggest gradual outgassing in dry storage over many decades at low temperatures for both TR55 and S5370.

INTRODUCTION

Silica-filled polydimethylsiloxane (PDMS) composite systems, generally known as silicones, can be synthesized to have broad ranges of chemical and mechanical properties suitable for varying applications [1]. This great versatility is due, in part, to the presence of silica fillers which significantly alter the mechanical properties of PDMS. Unfortunately, silica surfaces are well known to have a high affinity for water adsorption [2-4]. Absorbed water may play an important role in the bonding between SiO_2 particles and the silicone matrix. The outgassing of water may change the nature of the silica/polymer bonding, affecting the mechanical behavior of the materials. A decrease in the segmental mobility of the polymer chains has been reported for long-term storage of certain types of PDMS in desiccating atmospheres [5]. The H_2O outgassing may also present a compatibility issue in sealed systems containing these types of silicones over a long period of time at room

or slightly elevated temperatures. Understanding of the mechanisms of water interactions and the H_2O outgassing kinetics in PDMS is, therefore, important for the prediction of the aging in a variety of PDMS systems. In particular, TR55 and S5370 are chosen for this study because of their broad range of commercial applications (most notably in the aviation and food processing industries). TR55 is composed of 70 wt. % polysiloxane gum formulation and 30 wt. % fumed silica filler pretreated with a silating agent. S5370 is composed of 15% diatomaceous silica filler, 60% high molecular weight polysiloxanediol, 12% low molecular weight polysiloxanediol, 6% polymethylhydrogensiloxane, 5% diphenylmethylsilanol, and 2% tetrapropoxysilane. In this report, the isoconversional method of analysis was employed in conjunction with temperature programmed reaction (TPR) experiments to extract H_2O outgassing kinetics from TR55 and S5370. Moisture outgassing prediction models were then constructed for these silicones in a dry/vacuum environment at different elevated temperatures. These outgassing prediction models will be shown to follow the trend of isothermal outgassing data. Implications of the models on H_2O outgassing from TR55 and S5370 in dry storage over many decades at room or slightly higher temperatures and its effect on the mechanical properties of these silicones will be explored. The accuracy and limitation of the isoconversional analysis in predicting moisture outgassing from silica-filled PDMS family will also be discussed.

EXPERIMENTAL SETUP AND ANALYSIS METHOD

For a typical TPR experiment, a thin slice of silicone (sub-millimeter thick) was enclosed in a 1-cm^2 platinum foil envelope to assure uniform heating. The side of the envelope facing the mass spectrometer was thoroughly perforated. The loaded foil was then

attached to a sample holder by way of mechanical clamps and transferred into an ultrahigh vacuum (UHV) sample chamber with a base pressure of 10^{-6} Pa through a differentially pumped load lock. In the sample chamber, the sample holder sat on a rotatable XYZ manipulator. The sample temperature was measured using a type K thermocouple inserted between the Pt envelope front surface and one of the clamps holding the envelope. Heating of the sample was done by passing current through a flat spiral tungsten coil located 2 mm behind the sample. The sample chamber was connected through a 6 mm diameter orifice with a separately pumped detector chamber equipped with a quadrupole mass spectrometer. The base pressure in the detector chamber was usually a decade better than that in the sample chamber. During the TPR experiment, the sample was positioned 2 mm away from the orifice and faced the detector chamber. This arrangement guaranteed that only gases originating from the portion of the sample facing the 6 mm orifice contributed to the signals detected by the quadrupole mass spectrometer.

After the TPR spectra were obtained, the kinetics of the reactions were extracted by analyzing the TPR spectra of similarly prepared samples at different heating rates in accordance with the isoconversional method of thermal analysis as described below.

The rate equation for a solid-state reaction can be approximated by [6]:

$$\frac{d\alpha}{dt} = k.f(\alpha) = \upsilon.e^{-\frac{E}{RT}}.f(\alpha) \qquad (1)$$

where t is time; α is the reacted fraction (0 to 1); k is the rate constant; υ is the pre-exponential factor which includes many constants describing the initial state of the sample such as three dimensional shape factors of initial particles, molecular mass, density, stoichiometry, active surface factors, number of lattice imperfections, and so forth; E is the activation energy for the rate controlling process; R is the gas molar constant, T is

temperature in Kelvin; and $f(\alpha)$ is an analytical function determined by the rate-limiting reaction mechanism.

With a heating rate of $\beta = dT / dt$:

$$\frac{d\alpha}{dT} = \left[\frac{\upsilon}{\beta} \cdot f(\alpha)\right] \cdot e^{-\frac{E}{RT}} \tag{2}$$

Taking the natural logarithm on both sides of equation (1) yields

$$\ln\left(\frac{d\alpha}{dt}\right) = -\frac{E}{RT} + \ln\{\upsilon f(\alpha)\} \tag{3}$$

A plot of $ln(d\alpha/dt)$ vs. T^{-1} at some α value for a set of β values has the slope $-E/R$ [7]. A plot of E vs. α is thus obtained by repeating the above procedure at other chosen α values between 0 and 1. This kinetic extraction procedure was first proposed by Friedman [6-7]. Note that both E and $\{vf(\alpha)\}$ can be obtained from the Friedman method based on equation (3).

The time prediction, t_α, for a specific conversion α to be reached at the isothermal temperature T_o can be obtained from the rate equation (1) as following:

$$t_\alpha = \int_0^{t_\alpha} dt = \int_0^{\alpha} \frac{d\alpha}{\{\upsilon f(\alpha)\} e^{-\frac{E}{RT_o}}} \tag{4}$$

To scale up the results from the above kinetic prediction (which derives from experiments on small samples) for comparison with actual isothermal outgassing experiments involving large samples, the total weight of the silicone has to be taken into account according to the simple formula:

Total outgassing = outgassing per unit weight × total weight of the silicone sample (5)

RESULTS AND DISCUSSIONS

Fig. 1(a) shows a typical H_2O TPR spectrum of as-received TR55, at a heating rate of 0.15 K/s, after 4 hours of vacuum pumping. This H_2O desorption spectrum looks complex and very broad, clearly indicating that the H_2O desorption kinetics in TR55 cannot be adequately described by a single activation energy process. Upon integration of the mass 18 signal in Fig. 1(a) with respect to time and calibration of the mass spectrometer's response, a plot of the wt. % of moisture released from TR55 as a function of temperature was obtained and is presented in Fig. 1(b). The total moisture content in TR55 was measured to be on the order of 0.23 wt. % after 4 hours of vacuum pumping. Fig. 2(a) shows mass 18 TPR spectra of three similar TR55 samples at heating rates of 0.15 K/s, 0.025 K/s and 0.004 K/s. A plot of E versus α established by the isoconversional technique using the TPR spectra in Fig. 2(a) is presented in fig. 2(b). It is seen that the energy barrier for H_2O outgassing from TR55 is an increasing function of the fractional H_2O release. Certainly, most of the physisorbed water (water molecules that are hydrogen bonded to each other or to the silanol group), which has a desorption activation energy barrier less than 63 kJ/mol, had been pumped off prior to the start of the TPR experiments and was not recorded in the TPR spectra reported here [2-4]. The increase in the value of E with α can be interpreted as the release of H_2O via the condensation of OH groups from the surfaces of the embedded silica particles according to the equation:

$$SiOH + SiOH + heat \rightarrow Si_2O + H_2O(g) \qquad (6)$$

As the chemical reaction (6) goes on, OH bonds have to diffuse from farther and farther distances before they can combine to give off H_2O, causing the activation energy barrier, E, to increase with increasing fractional H_2O release as seen in fig. 2(b). A cartoon depicting the different ways H_2O can be desorbed from within a silicone sample is presented in fig. 3 to

illustrate this point. Note that above 550K, some of the moisture released may be due to the decomposition of the silicone.

Similar experiments performed on S5370 yield a value of about 0.15 wt% for the total moisture released by TPR after 1 hour of vacuum pumping. The mass 18 TPR spectra of three similar S5370 samples at heating rates of 0.1 K/s, 0.01 K/s and 0.002 K/s are presented in fig. 4(a). A plot of E versus α for the H_2O outgassing from S5370 obtained from the isoconversional methodology is presented in fig. 4(b). It is seen from fig. 2(b) and fig. 4(b) that only 20% of the moisture released from TPR of TR55 has a desorption activation energy barrier less than 126 kJ/mol while the corresponding number for S5370 is 80%. This is because most of the moisture released from TPR of TR55 takes place at higher temperatures while the majority of H_2O released from TPR of S5370 comes out at lower temperatures. This difference in the outgassing kinetics between TR55 and S5370 suggests that the OH population is much denser on the surfaces of the diatomaceous silica fillers used in S5370 than on the surfaces of the fumed silica fillers used in TR55. Yet, the weight percentage of moisture recorded by TPR from TR55 is higher than that from S5370, suggesting a higher total silica surface area for the former one. The kinetic predictions of H_2O outgassing [based on equation (4)] from TR55 and S5370 at 295K in a dry environment are presented in figs. 5(a) and (b). It is seen from fig. 5 that much of the moisture outgassing from TR55 and S5370 occurs during the first few years of dry storage followed by much slower outgassing rates over the next many decades. The slow moisture outgassing from TR55 and S5370 in a dry environment even at room temperature as presented in fig. 5 also suggests a gradual stiffening of the silicones with time, since a correlation between desiccation and a decrease in the segmental mobility of the polymer chains of certain types of PDMS has been established

[5]. It is interesting to note that the H_2O outgassing problem is much worse in the case of S5370 than in the case of TR55 at 295K despite the fact that the total moisture potential is higher in TR55 than in S5370. This seemingly contradictory behavior can be easily understood by recognizing that most of the moisture released from TPR of TR55 takes place at higher temperatures (higher energy barrier) while the majority of H_2O released from TPR of S5370 comes out at lower temperatures (lower energy barrier).

In order to test the accuracy of kinetic measurements and predictions based on the isoconversional analysis of TPR outgassing spectra, a set of long-term (i.e. > 300 days) isothermal outgassing experiments of TR55 were undertaken. The TR55 samples used in the long-term isothermal outgassing experiments had a weight of 37.9g, and were pumped for a few hours in a high vacuum environment to get rid of physisorbed water. The comparisons between isoconversional kinetic predictions and isothermal long-term H_2O outgassing from TR55 at 348.7K and 315.5K are presented in fig. 6(a) and (b), respectively. In fig. 6, the dashed and solid lines represent kinetic predictions and isothermal outgassing data, respectively. The light shaded areas are 35% error bands around the prediction lines. It is seen that: (1) the shapes of the kinetic prediction lines resemble that of the isothermal outgassing data and (2) the agreement between the prediction models and isothermal experiments is excellent at 348.7K but degrades to around 35% level of accuracy at 315.5K. Given the unavoidable slight differences in preparation conditions and sample variations between TPR experiments (performed at Lawrence Livermore National Laboratory) and long term isothermal experiments (performed at BWXT Y12), the prediction models do follow the trend of actual isothermal outgassing. This report confirms that the isoconversional technique is a valuable thermal analysis tool in accelerated outgassing studies. In accelerated

outgassing studies, the kinetics obtained from short-time scale and high temperature outgassing experiments can be used to predict the trend of the materials at lower temperatures over extended periods of time. The main advantages of the isoconversional technique are its ease of use (model-independent) and its abilities to predict outgassing trend at any temperature within or a little bit below the temperature range studied from a set of short-time scale experiments at different heating rates. However, the accuracy of the H_2O outgassing kinetic predictions from silica-filled PDMS by the isoconversional technique is observed to reduce from an excellent agreement at a moderate temperature of 349K to, probably, an "order of magnitude" prediction at room temperature. The lower accuracies associated with extrapolated predictions at lower temperatures are attributed to the much lower signal to noise ratios of the outgassing species recorded by the mass spectrometer during TPR experiments at low temperatures. In addition, there is a possibility that some of the moisture producing reaction pathways captured in the TPR spectra at very high temperatures (such as the decomposition of the silicone matrix itself above 550K) may not necessarily happen at all at much lower temperatures. The end result is a somewhat over-predicted amount of moisture outgassing from silica-filled silicones at the lowest temperature end of the TPR spectra. More accurate outgassing predictions usually require exact mechanistic model fitting of the TPR spectra, a task which is very difficult if at all possible for TPR spectra that cover a very broad temperature range and involve multiple reaction pathways such as those described in this report. In such difficult situations, the isoconversional technique serves as a valuable tool to predict the trend of the outgassing process under study as long as the operator is aware of the potential weaknesses of the technique as described above.

SUMMARY

The technique of isoconversional thermal analysis in conjunction with linear heating technique has been employed in the kinetic extraction and prediction of H_2O outgassing from TR55 and S5370. The energy barriers for H_2O release from TR55 and S5370 increase with increasing fractional H_2O release. This can be interpreted as the release of H_2O from physisorbed water and then chemisorbed water with decreasing OH density from the surfaces of the embedded silica particles. As the temperature rises above 550 K, some of the recorded H_2O signal may be attributed to the decomposition of the silicones. Model-independent predictions of H_2O outgassing based on the measured kinetics agree do follow the trend of isothermal outgassing and suggest that much of the moisture outgassing from TR55 and S5370 occurs during the first few years of dry storage followed by much slower outgassing rates in the following decades. Within the context of accelerated aging studies, when the outgassing TPR spectra are very broad and involve mutiple reaction pathways such as in the case of H_2O outgassing from silica-filled PDMS, the isoconversional technique serves as a valuable tool to predict fairly accurately the outgassing trend at moderate temperatures (around 349K) and to set upper limits for long-term outgassing at room temperature.

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FIGURE CAPTIONS:

Fig. 1: (a) A typical H_2O TPR spectrum of as-received TR55 at a heating rate of 0.15 K/s after 4 hours of vacuum pumping; (b) Wt% of moisture released from TR55.

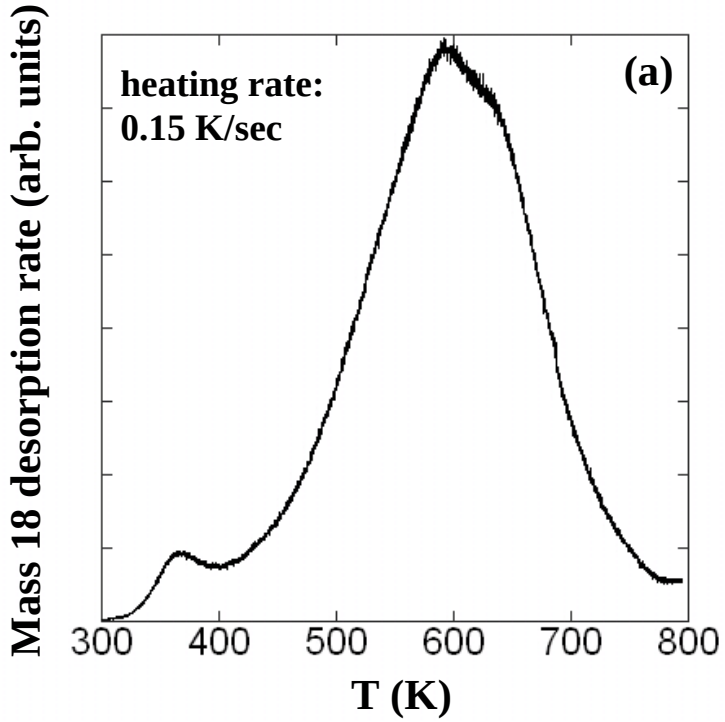
Fig. 2: (a) Mass 18 TPR spectra of three similar TR55 samples at different heating rates; (b) E vs. α for the moisture outgassing process from TR55.

Fig. 3: A cartoon depicting the different ways H_2O can be desorbed from within a silicone sample.

Fig. 4: (a) Mass 18 TPR spectra of three similar S5370 samples at different heating rates; (b) E vs. α for the moisture outgassing process from S5370.

Fig. 5: The kinetic predictions of moisture outgassing from TR55 (a) and S5370 (b) at 295K.

Fig. 6: Comparison between moisture outgassing kinetic predictions and long term isothermal outgassing data at 348.7K (a) and 315.5K (b).


heating rate:
0.15 K/sec
(a)
Mass 18 desorption rate (arb. units)
300
400
500
600
700
800
T (K)

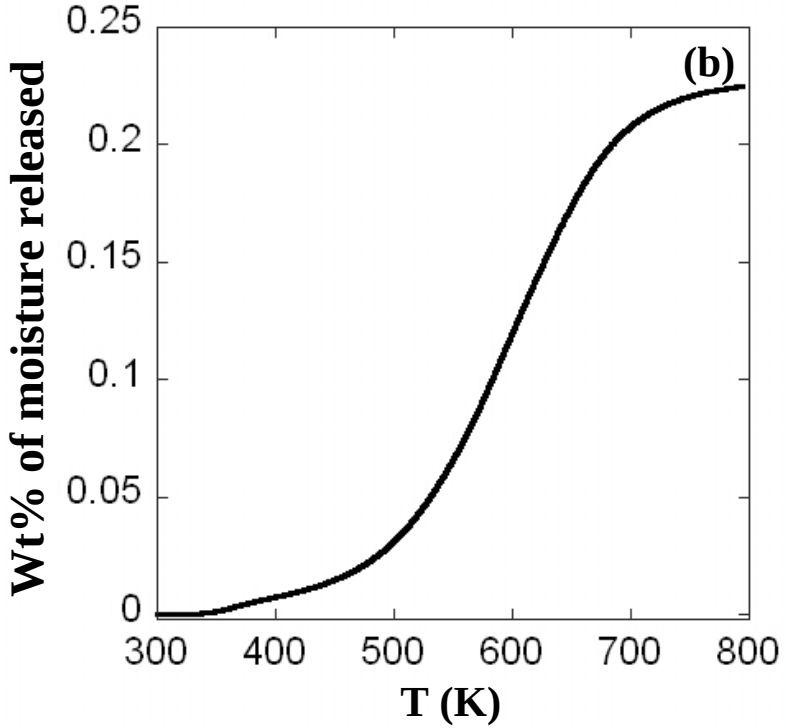

(b)
Wt% of moisture released
0.25
0.2
0.15
0.1
0.05
0
300
400
500
600
700
800
T (K)

Fig. 1

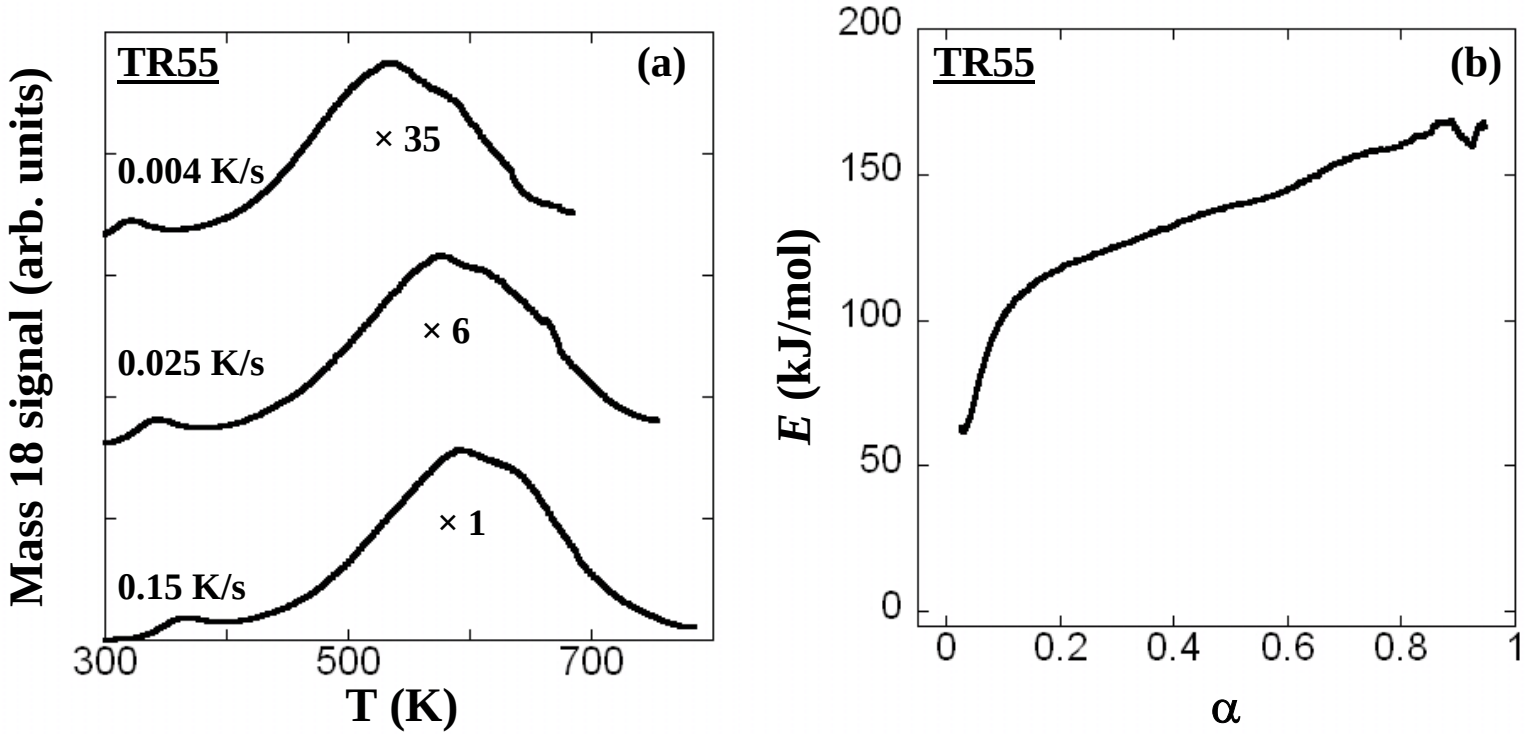

TR55
(a)
× 35
0.004 K/s
× 6
0.025 K/s
× 1
0.15 K/s
Mass 18 signal (arb. units)
300
500
700
T (K)
TR55
(b)
200
150
100
50
0
E (kJ/mol)
0
0.2
0.4
0.6
0.8
1
α

Fig. 2

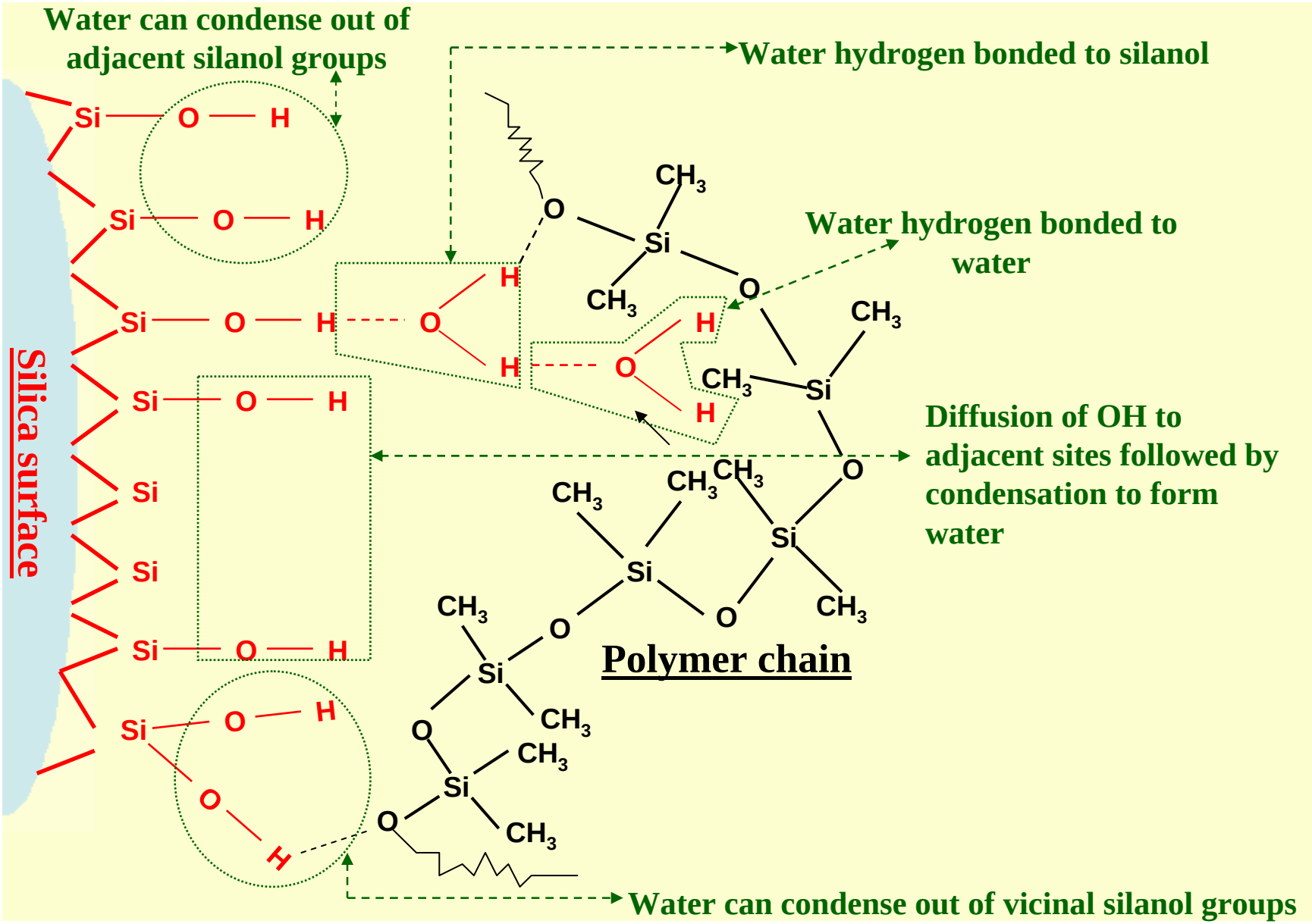

Water can condense out of adjacent silanol groups
Water hydrogen bonded to silanol
Water hydrogen bonded to water
Diffusion of OH to adjacent sites followed by condensation to form water
Silica surface
Polymer chain
Water can condense out of vicinal silanol groups

Fig. 3

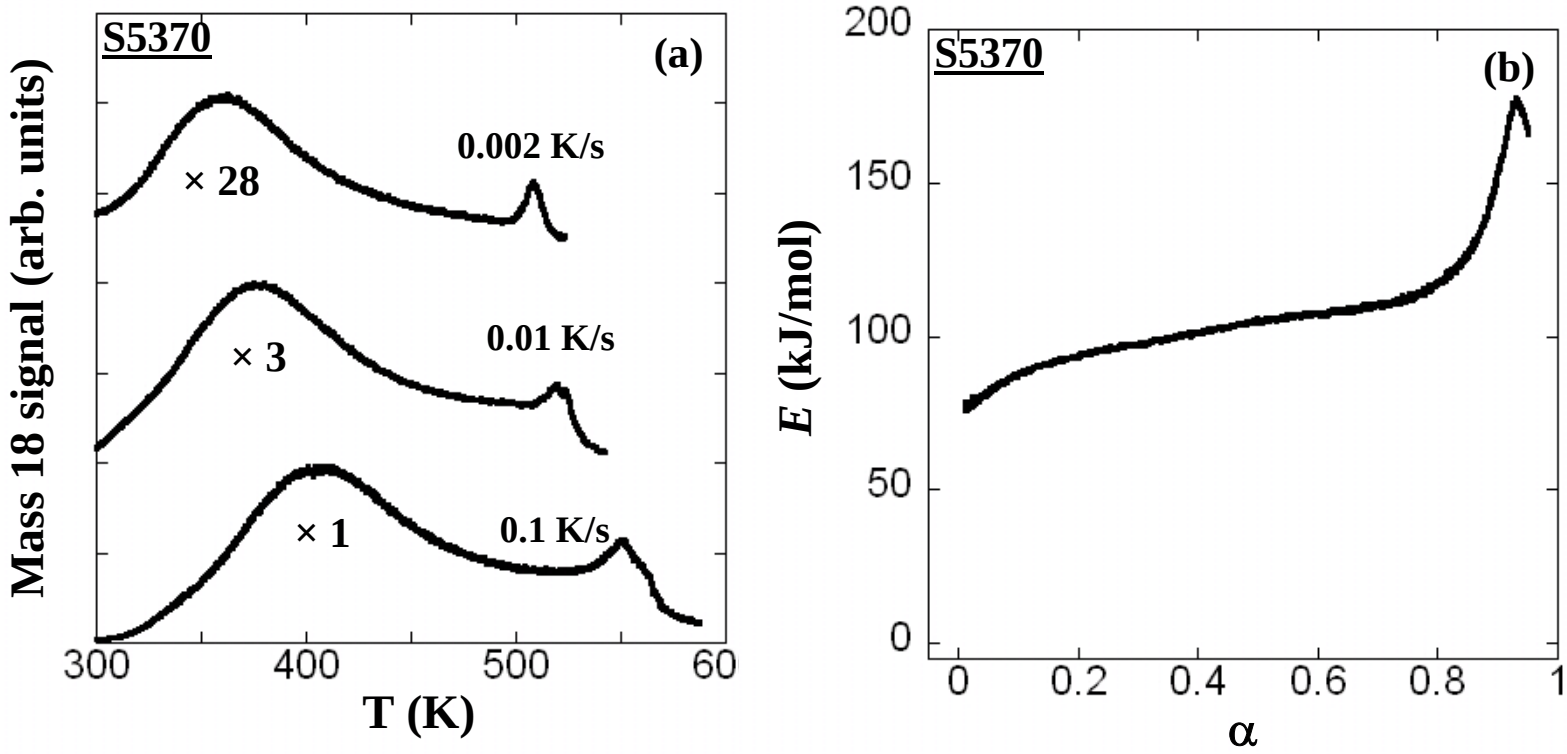

S5370
(a)
0.002 K/s
× 28
0.01 K/s
× 3
0.1 K/s
× 1
Mass 18 signal (arb. units)
300
400
500
60
T (K)
S5370
(b)
200
150
100
50
0
E (kJ/mol)
0
0.2
0.4
0.6
0.8
1
α

Fig. 4

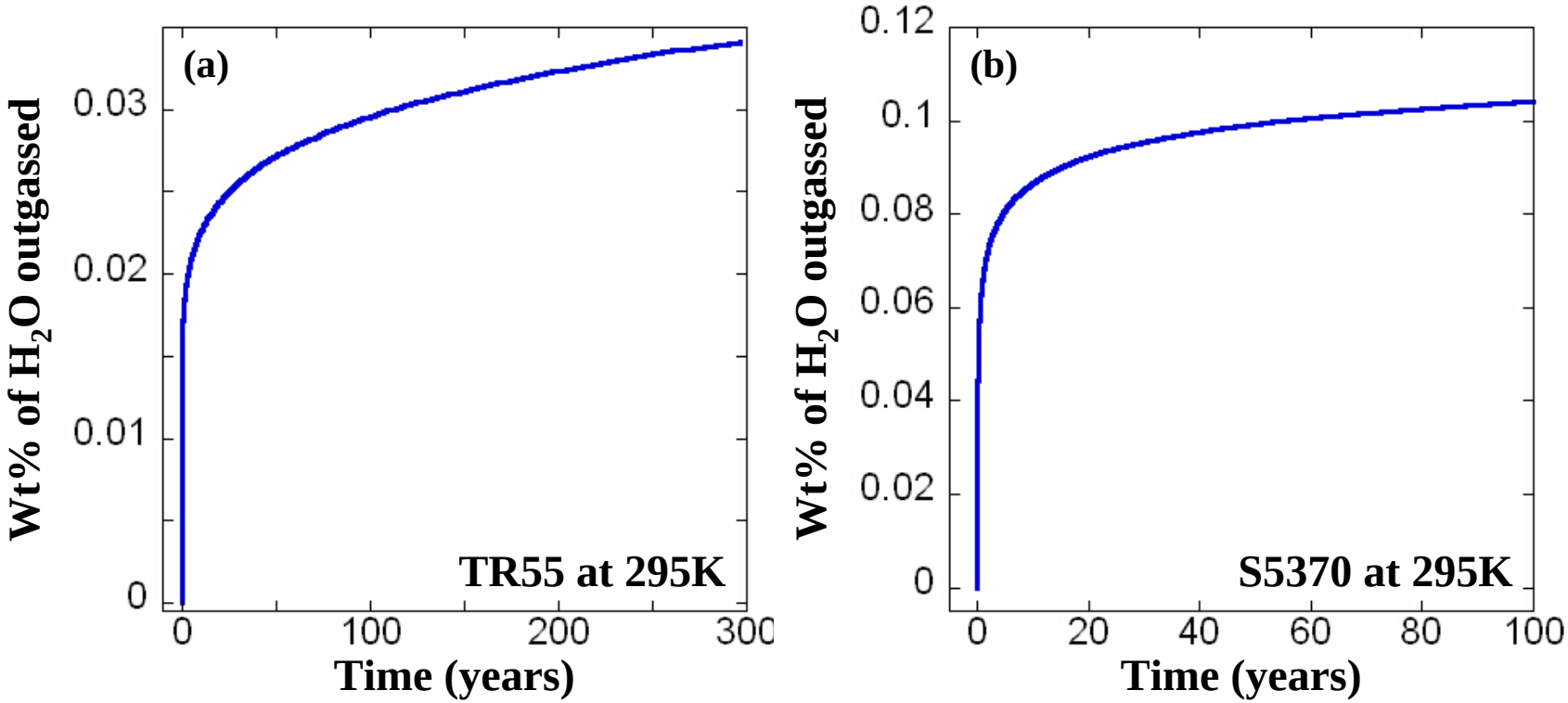

(a)
Wt% of H_2O outgassed
0.03
0.02
0.01
0
0
100
200
300
Time (years)
TR55 at 295K
(b)
Wt% of H_2O outgassed
0.12
0.1
0.08
0.06
0.04
0.02
0
0
20
40
60
80
100
Time (years)
S5370 at 295K

Fig. 5

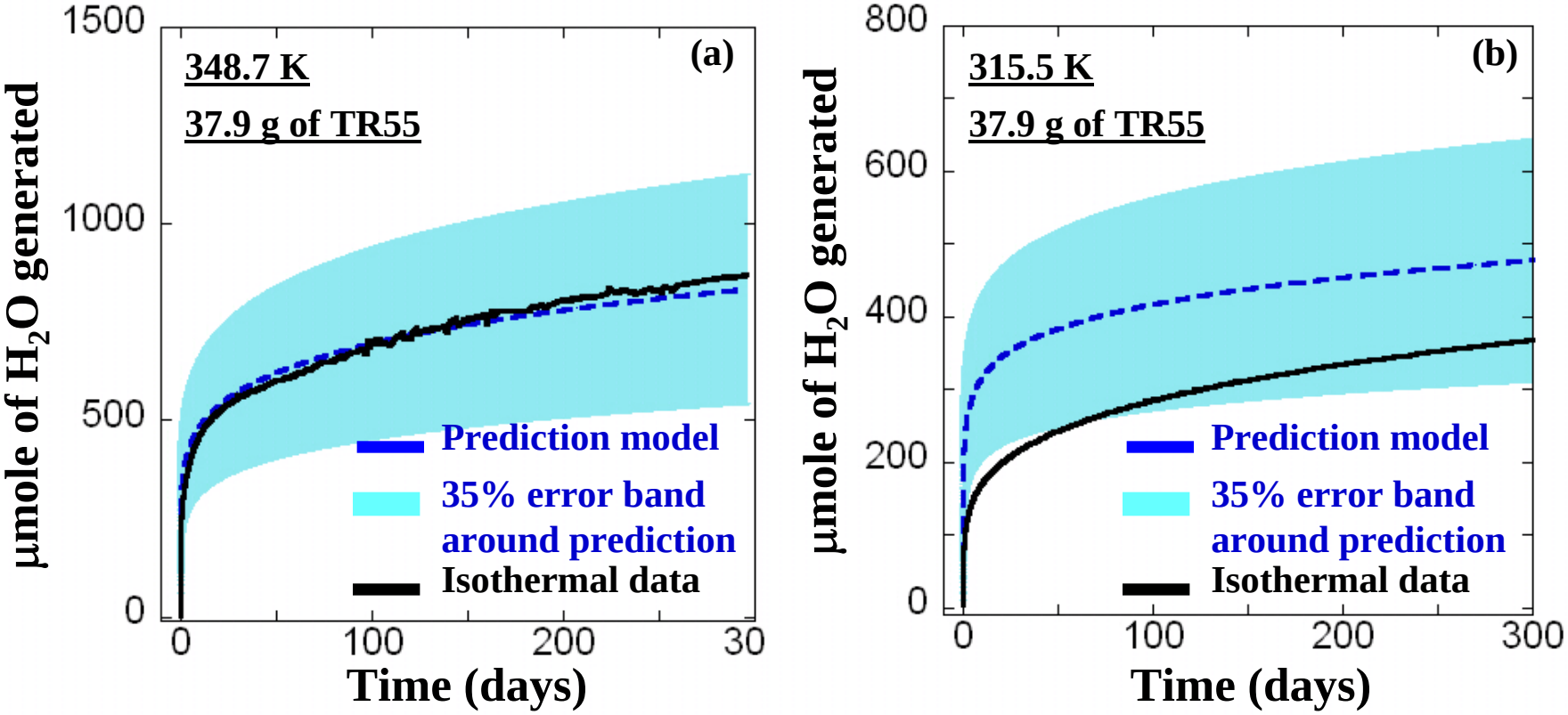

(a)
348.7 K
37.9 g of TR55
µmole of H2O generated
Time (days)
Prediction model
35% error band around prediction
Isothermal data
(b)
315.5 K
37.9 g of TR55
µmole of H2O generated
Time (days)
Prediction model
35% error band around prediction
Isothermal data

Fig. 6