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TiO_2 Permselective Membranes

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TiO_2 Permselective Membranes

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Abstract

Hydrogen permselective membranes were synthesized by chemical vapor deposition of TiO_2 or SiO_2 layers within the pores of Vycor tubes used as supports. The reaction mechanism and kinetics of TiO_2 or SiO_2 formation were investigated in terms of the heterogeneous reactions between gaseous $TiCl_4$ or $SiCl_4$ with hydroxyl groups in the solid and between gaseous H_2O and chloride groups in the solid. The growth of the oxide layers can be characterized as a polymerization proceeding by alternating reactions of the gaseous reactants with groups on the solid surface. In addition, condensation reactions occur between surface chloride groups and nearby hydroxyl groups or two neighboring hydroxyl groups, that contribute to the overall mechanism of the oxide layer formation. For the case of TiO_2 deposition, chlorination of the surface hydroxyl groups seems to be the rate-limiting step in the growth of the deposit layer.

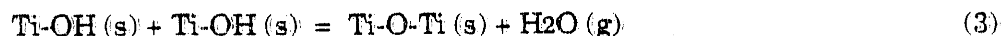
Introduction

Hydrogen permselective membranes synthesized by the chemical vapor deposition of various oxide films were introduced in our recent paper [1]. The membranes consist of a thin layer of SiO_2, TiO_2, Al_2O_3, or B_2O_3 supported on a porous Vycor tube. We have been interested in the reaction mechanism and kinetics of the formation of the oxide deposit inside the porous Vycor substrate, which play a crucial role in the location, geometry, and chemical structure of the

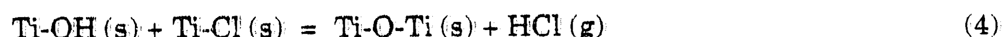
deposit layer. In the recent paper [1] we have qualitatively discussed the general features of the reaction mechanism involving heterogeneous reactions between gaseous $TiCl_4$ and surface hydroxyl groups and between gaseous H_2O and chloride groups in the solid:

$$\text{Si-OH (s)} + \text{TiCl}_4\text{ (g)} = \text{Si-O-TiCl}_3\text{ (s)} + \text{HCl (g)} \quad (1)$$

$$\text{Ti-Cl (s)} + \text{H}_2\text{O (g)} = \text{Ti-OH (s)} + \text{HCl (g)} \quad (2)$$



$$\text{Ti-OH (s)} + \text{Ti-OH (s)} = \text{Ti-O-Ti (s)} + \text{H}_2\text{O (g)} \quad (3)$$



$$\text{Ti-OH (s)} + \text{Ti-Cl (s)} = \text{Ti-O-Ti (s)} + \text{HCl (g)} \quad (4)$$

The above reaction steps, (1) - (4) constitute a polymerization mechanism with final product TiO_2. A similar mechanism applies to the formation of SiO_2 layers from $SiCl_4$ and H_2O. We have further investigated the above reaction mechanism experimentally by isolating each step and studying the kinetics separately. In this report we present some recent kinetic experiments on the above reactions.

Experimental

Membrane synthesis and permeation measurement were described in our recent paper[1]. Membrane formation by both one- sided and opposing reactants geometry was investigated. The resulting membranes were characterized by SEM and electron microprobe line scan analysis. Selected samples were examined by TEM.

Kinetic measurements were conducted by a DuPont 951 TGA system interfaced to a microcomputer. A sample of powdered Vycor glass approximately 20 mg and 100 - 200 μm particle size range was placed as a thin layer on a quartz pan inside the quartz housing, and subjected to flowing reactant gases. The weight of the sample was measured continuously.

Before each reaction sequence the Vycor sample was pretreated by heating in

N_2 flow of 150-200 cm3/min at 450°C or 600°C for 3-4 hours to stabilize the number of surface OH groups. The sample was then brought to the reaction temperature and subjected to a flow of a 5% $TiCl_4$ - N_2 (or 10% $SiCl_4$ - N_2) stream to measure the rate of the chlorination reaction. The chlorination continued until the weight leveled off. Subsequently hydrolysis was conducted on the same sample by introducing a stream of 5% H_2O - N_2. Between the chlorination and the hydrolysis steps, a purge stream of 150-200 cm3/min N_2 continued for 0.5 hour to remove all traces of gaseous reactants and products from the TGA. The cycle of chlorination and hydrolysis with intermediate N_2 purge was repeated 2 or 3 times.

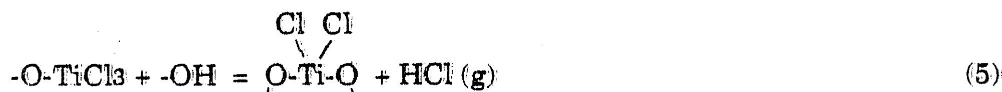
Results and discussion

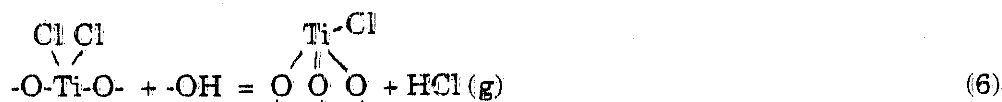
Figure 1 shows a TGA trace for two complete cycles of reaction of $TiCl_4$ and H_2O with a Vycor sample. Figure 2 shows a TGA trace of the analogous reactions with $SiCl_4$ and H_2O. In both cases the chlorination is initially rapid but levels off gradually. During the purge period after chlorination, the weight slowly decreased. Subsequent hydrolysis resulted in weight decrease due to the replacement of -Cl groups by -OH groups. The general features of the second cycle of the reactions are similar to those of the first one.

Table 1 summarizes the reaction time and weight change for chlorination, purge, and hydrolysis at various reaction temperatures. Various samples were pretreated at different temperatures to study the effect of the initial -OH concentration on the surface. In general the samples pretreated at higher temperature resulted in lower total weight increase during the chlorination. This verifies that the chlorination step largely if not wholly involves the reaction between $TiCl_4$ and silanol groups, -OH, to produce -O-$TiCl_3$ groups and gaseous HCl. The total uptake of -$TiCl_3$ clearly depends upon the concentration of the initial surface -OH groups which is determined by the thermal pretreatment.

The weight decrease during the purge period can be interpreted as due to

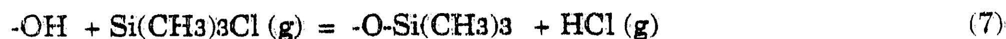
consecutive reactions of titanium chloride groups already attached to the surface with neighboring surface -OH groups:





which is consistent with our experimental observation that when the purge was prolonged, the weight loss during the subsequent hydrolysis declined. This decline suggests the loss of surface chloride groups available for hydrolysis during the N_2 purge. It appears that the chlorination reaction is relatively fast but does not saturate all surface -OH groups. When one of two nearby -OH groups reacts according to (1), further reaction of gaseous $TiCl_4$ with the neighboring unreacted -OH group becomes very slow because of steric hinderance, competing with reactions (5) and (6).

In order to confirm this interpretation, an experiment was carried out using $Si(CH_3)_3Cl$ instead of $SiCl_4$. The reaction of $Si(CH_3)_3Cl$ with Vycor surface can be written as



whereupon there is no opportunity for subsequent reactions like (5) and (6). In this experiment, chlorination was slower, the final weight gain was much higher and there was no weight change during the purge period. This result, shown in Figure 3, clearly indicates that weight loss during purge with $SiCl_4$ or $TiCl_4$ reaction is due to reactions (5) and (6) rather than any desorption of chemisorbed silicon or titanium chlorides.

The rate of reactions (5) and (6) depends on the concentration of the surface -OH groups and the already attached chloride groups. This is clearly shown in Table 1 when we compare two samples pretreated at different temperature. The weight decrease during the purge after the first chlorination is higher for the sample pretreated at the lower temperature.

Concerning the hydrolysis step, the decrease in weight is due to the replacement of -Cl groups with -OH groups and to the condensation reactions of two -OH groups into a siloxane, -O-, bridge (3). The results from two cycles of reactions listed in Table 1 verify the contribution of both reactions to the weight loss. While the weight increase for the second and third chlorination is less than that for the first, the weight decrease for the second and third hydrolysis periods is not much less and in some cases is greater than that for the first one. This may be explained by taking into account the location and accessibility of the reactive groups in the deposit layer. During the first chlorination all silanol groups are on the surface and hence are accessible to the bulky $TiCl_4$ or $SiCl_4$. In subsequent chlorinations the silanol groups at the top, or surface layer, are accessible but the groups buried in subsurface layers are increasingly inaccessible, With the area of the top layer decreasing with the deposition of additional layers, the number of $-TiCl_3$ or $-SiCl_3$ groups attached decreases. By contrast, during the hydrolysis period, the small water molecule can penetrate and hydrolyze chloride groups in subsurface layers as well as in the top layer. Similarly, the condensation of silanol groups can occur with little obstruction throughout the deposit. The extent of both of these reactions can increase with the number of deposit layers, although this increase is expected to taper off after the second or third layers.

Conclusion

The mechanism and kinetics of TiO_2 and SiO_2 formation was investigated in terms of alternating steps of heterogeneous reactions of $TiCl_4$ and H_2O on the Vycor surface. In addition to the chlorination of surface hydroxyl groups and the

subsequent hydrolysis of attached chloride groups, the consecutive reactions of the surface chloride groups and nearby hydroxyl groups contribute to the mechanism of the oxide layer formation. The consecutive reactions are relatively slow, thus the number of Si or Ti atoms attached in each additional reaction cycle depends on several factors, such as the concentration of initial -OH groups, the concentration of $TiCl_4$ (or $SiCl_4$) in the gas phase, and the temperature. For the case of TiO_2 deposition, chlorination of the surface hydroxyl groups seems to be the rate-limiting step in the growth of the deposit layer. The kinetics of deposit growth depend strongly on the initial concentration of -OH groups on the Vycor surface.

Table 1. Weight change, and time taken by chlorination (C), purge subsequent to chlorination (P), and hydrolysis (H) reactions in first, second, and third cycles. Sample V600 indicates Vycor sample pretreated at 600°C; sample S600 indicates Silica gel sample pretreated at 600°C. The time reported for chlorination is that of the initial rapid rate period.

			1st Cycle						2nd Cycle						3rd Cycle					
			C		P		H		C		P		H		C		P		H	
Sample	Reactant	Reaction Temp (°C)	Δm (%)	t (min)	$-\Delta m$ (%)	t (min)	$-\Delta m$ (%)	t (min)	Δm (%)	t (min)	$-\Delta m$ (%)	t (min)	$-\Delta m$ (%)	t (min)	Δm (%)	t (min)	$-\Delta m$ (%)	t (min)	$-\Delta m$ (%)	t (min)
V600	$SiCl_4$	600	5.19	1.5	1.31	22	1.20	1	5.29	2	1.47	20	1.09	1						
V450	$SiCl_4$	450	7.15	10	0.28	10	2.75	3	5.33	10	0.22	10	3.02	3						
S600	$SiCl_4$	600	8.33	<1	1.78	25	2.06	1.5	9.00	<1	1.7	20	2.39	1						
V450	$TiCl_4$	450	6.49	17	1.18	20	0.51	3	5.51	12	1.03	20	1.08	4	5.25	10	0.51	12	1.28	3
V600	$TiCl_4$	450	5.04	10	1.02	20	0.74	5	4.70	10	0.68	20	1.08	5						
V600	$TiCl_4$	600	4.76	10	0.70	15	1.08	2	4.05	5	0.54	7.5	1.03	3						
V600	$TiCl_4$	200	6.52	18	0.87	22	1.88	2	5.41	22	1.35	30	1.21	8	3.86	25	0.24	5		
V200	$TiCl_4$	200	10.62	45	1.55	32	2.20	10												

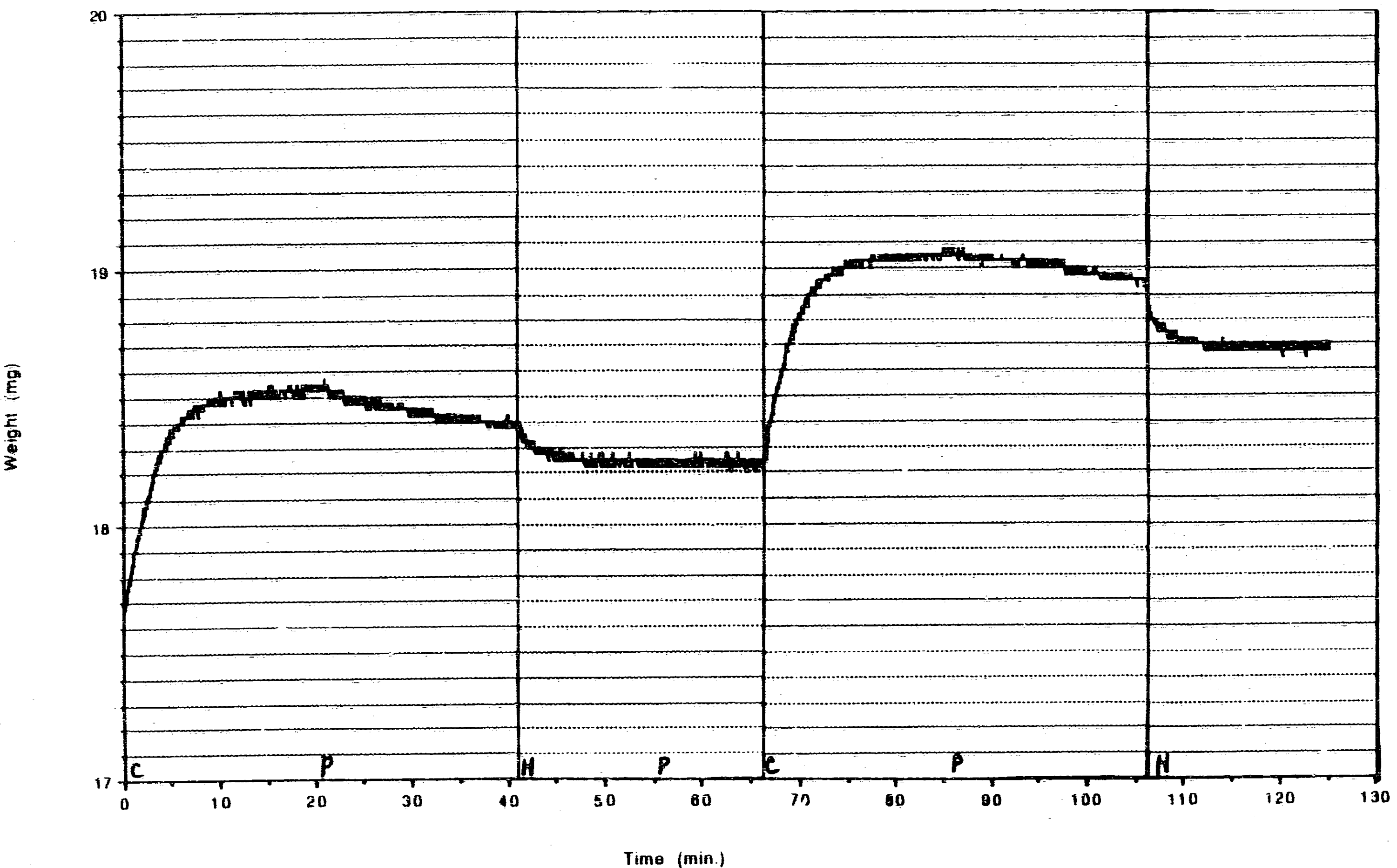


Figure 1. Weight of Vycor sample pretreated at 600°C during the two cycles of reaction with 5% $TiCl_4$-N_2 at 450°C, subsequent purge with N_2, and hydrolysis at the same temperature. Point P indicates the termination of $TiCl_4$ flow and beginning of purge period. Point H signifies the start of hydrolysis.

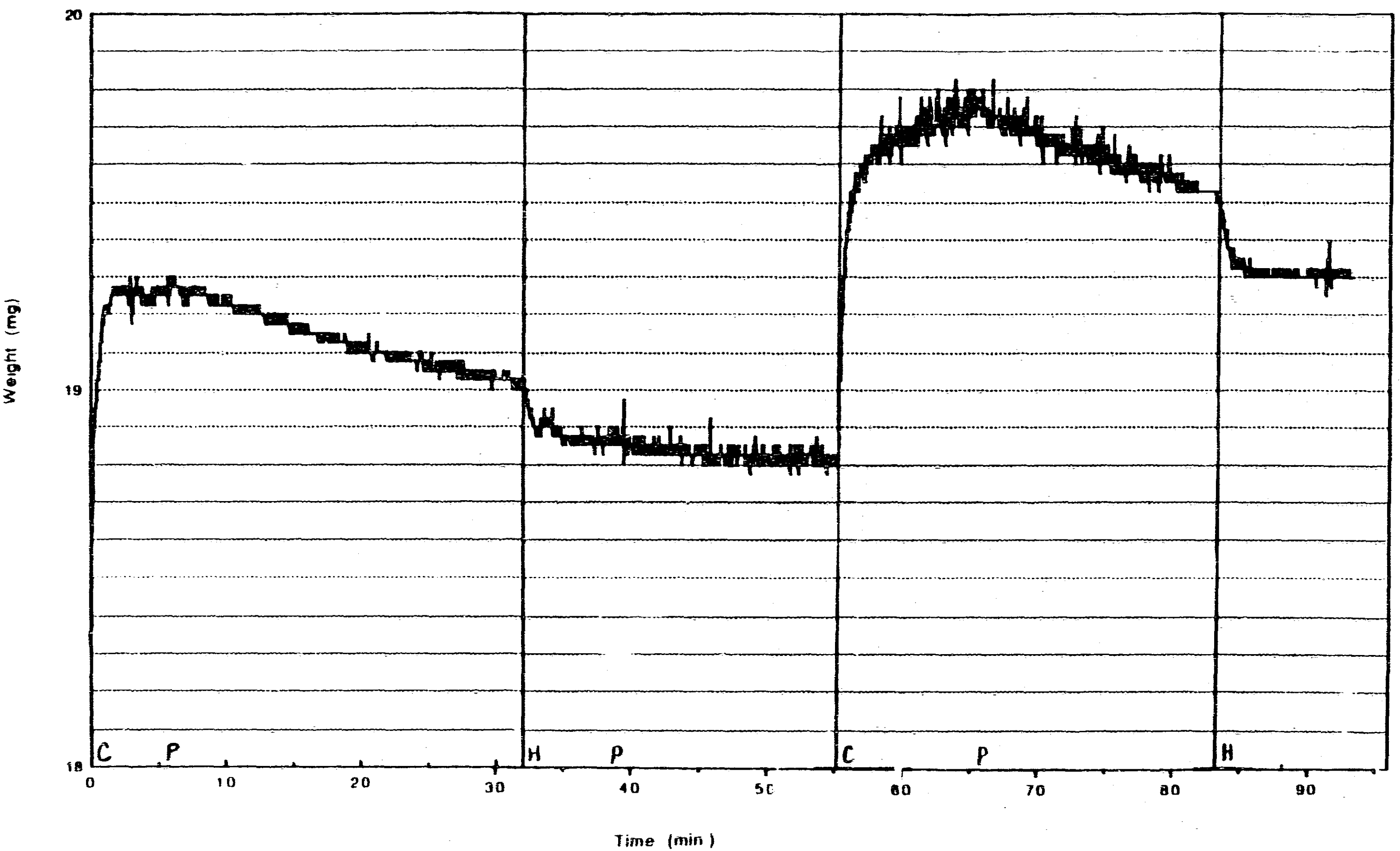


Figure 2. Weight of Vycor sample pretreated at 600°C during the two cycles of reaction with 10% $SiCl_4$-N_2 at 600°C and subsequent purge with N_2, and hydrolysis at the same temperature. Point P indicates the termination of $SiCl_4$ flow and beginning of purge period. Point H signifies the start of hydrolysis.

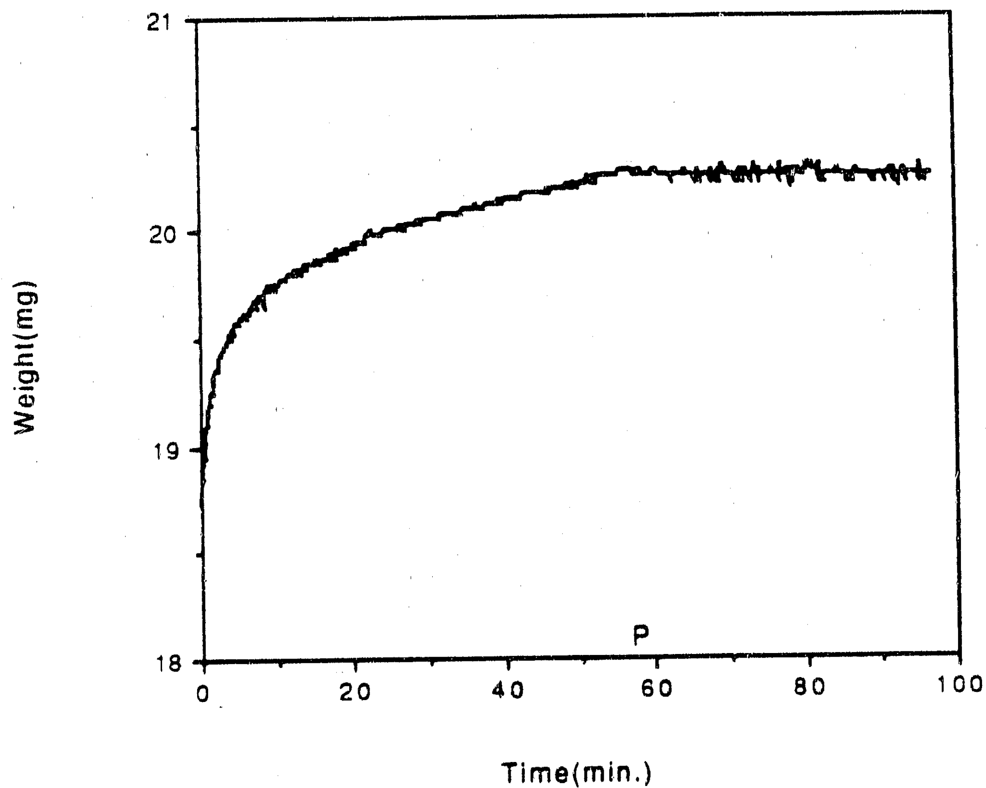


Figure 3. TGA trace of Vycor sample pretreated at 600°C during first reaction with 5% $Si(CH_3)_3Cl$-N_2 at 600°C and subsequent purge with N_2 at the same temperature. Point P indicates the termination of $Si(CH_3)_3Cl$ flow and beginning of purge period.

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