Catalyzed and Promoted Direct Reaction of Ethyl Chloride with Silicon Using Stirred-Bed Reactor

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Abstract:

In this paper a stirred-bed performed of the copper catalyzed synthesis of ethylchlorosilanes from silicon and ethyl chloride was described. A Si-catalyst mixture prepared by reaction of CuCl and Si was employed. The compositions of products were mainly ethyltrichlorosilane, diethyldichlorosilane, and ethyldichlorosilane and mainly depended on the extent of Cu in the mixture and the reaction temperature. A promoting effect on the extent of adsorption was observed on the addition of certain additives. The kinetic data revealed the direct depended of the reaction rate on C_2H_5Cl pressure.

Keywords: Direct synthesis, high vacuum, methylchlorosilanes

Introduction:

The silicones industry got its start in the late 1930(1) and became viable after Rochow(1940) discovery of the direct process which reacts elemental silicon with methyl chloride to produce methylchlorosilanes(2,3). The copper catalyzed reaction of C2H5Cl with Si gave fair yields of the corresponding ethylchlorosilanes(ECS)(4).In the most successful applications(5),the reaction leads mainly to diethyldichlorosilane (DEDCS), ethyldichlorosilane (EDCS), and ethyltrichlorosilane(ETCS) and the value varying widely with the reaction condition.The reaction may be implicated in the promoting both the cracking of EtCl and the initially formed(ECS) .Process conditions for the optimum yields of DEDCS are closely parallel to those for dimethyldichlorosilane (6).However ,it appears that(EDCS)and not (DEDCS) is the major objective of the commercial operation in the USSR. Selectivity to this monomer is increased to about 50wt.% of the product by feeding 10-30Vol.% HCl or H_2along with EtCl at reaction temperatures of 350-380 °C and adding CaS_2 and antimony or bismuth promoters to the contact mass(7-9).

Although many details studies have been made on the reaction of CH_3Cl with Si, very little is know about the reaction of EtCl with Si and the literature regarding this reaction is even smaller. The present work was therefore undertaken in order to understand the reaction and the composition of products that may be formed. We have selected CuCl as catalyst and stirred-bed reactor on which the reaction have been investigated.

Experimental

1- Apparatus: The vacuum system consisted of a number of specialized parts, involving vacuum apparatus, reactor, mass spectrometer, and temperature controller unit. These parts are connected as indicated in schematic diagram in fig.(1).

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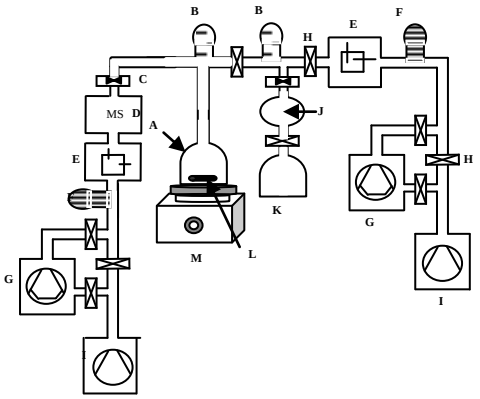


Fig.(1) A Block Diagram of The Stirred System A= Stirred-Bed Reactor, B= Perini Gauge, C=Needle Valve, D= Mass Spectrometer, E= Trap, F= Penning Gauge, G=Diffusion Pump, H= Valve, I = Rotary Pump, J= Bulb, K= EtCl Cylinder, L= Magnetic Bar,M = Magnetic Stirrer

The analysis of gas composition is performed by a Qudruvac (Q200) mass spectrometer partial pressure gauge, obtained from Lybold-Heraus. The method adopted in the work for quantitative analysis is the solution of linear simultaneous equation method (10). The measurement of specific surface was made using micromeritic, model ASAP- 2400.

2- Catalyst and promoters: Copper was used as catalyst, which was mixed by chemical precipitation through the reduction of freshly prepared CuCl with Si to the extent of 5, 10, 15 wt. % of the total composition. The promoters used with the catalyst were fine powder of Al,Zn,$ZnCl_2$ and $CaCl_2$ and their certain combinations (Zn + Al) and (Al,$ZnCl_2$,$CaCl_2$).

3- Procedure: The mixture of silicon powder (99.99 purity) and freshly prepared CuCl was transferred into the reactor and dried under vacuum of (10-4 torr) for at least (10 hr) at 180°C .The reaction system was disconnected from other parts of the system and heated to 350°C . The mixture then becomes ready for use after (2-2.5hr) at such temperature .The reactor that contained 5.0g of mixture was opened to the pumps and when a vacuum of (10-5torr) was attained in the system; the reactor was then cooled to the temperature at which the experimental started. The gas section was supplied with doses of C_2H_5Cl which were allowed to react with the mixture. The pressure variation is measured simultaneously during the reaction period until a relatively steady state value was obtained and the products formed were analyzed continuously.

Results and Discussion

1- The interaction of C_2H_5Cl : The adsorption on Si powder occurred at room temperature up to 350°C , analysis of the gas phase indicate the presence of EtCl only and no further reaction occurred at temp.≥400°C , some C_2H_4,C_2H_6 and H2 appeared in the gas phase , suggesting that EtCl dissociated at these temperatures . There is no adsorption on copper powder below 200°C, but EtCl readily decomposed above this temperature forming C_2H_4 , C_2H_6 , and H_2 , but no chlorine gas was detected in the gas phase . On Si- Cu mixtures , the adsorption was started at 180°C and at 400°C reached values of 30.221 , 32.019 , and 36.547 mm3\ g on 5% , 10% , and 15% copper mixtures respectively , and ECS have been detected in the gas phase . Table (1) shows the percentage of each of the ECS and C_2H_4 formed in the product mixture at 200 , 250 , and 300 °C .

Table (1) The composition (%) of the gas phase products in the reaction of EtCl with Si-CuCl powder in a Stirred-Bed reactor. EtCl was not considered as a constituent of the gas phase.

% CuCl	Temp. °C	Products Composition (%)			
		Ethylene	ETCS	DEDCS	EDCS
5 %	200	17.5	82.5	0	0
	250	46	50	4	0
	300	56	11	0	33
10 %	200	9.0	32	47	13
	250	20	45	35	0
	300	1	89	10	0
15 %	200	6	59	9	26
	250	6	81	1	12
	300	3	90	0.5	6.5

The results obtained on table (1) reveal the following:-

1- ETCS was the main product relative to other ECS.

2-The percentage of DEDCS in the products was highest (47%) on 10% Si-Cu mixture at 200°C .

2- Effect of additives: - The reaction was carried out using a mixture of 10% Si-Cu containing 1.0% of the additives. The results obtained indicate that the adsorption increased on all catalysts containing additives as compared with the adsorption on mixture in absence of any additive. This means that such additives behaved as promoters and enhanced the extent of adsorption and subsequent C_2H_5Cl dissociation. The adsorption was also accompanied by the evolution of ECS and the results obtained presented in table (2).

Table (2) The composition (%) of the gas phase products throughout the reaction of EtCl with 10 % Si-CuCl powder in a Stirred-Bed reactor. EtCl was not considered as a constiteunt of the gas phase.

Additive	*Temp.°C*	*Products Composition (%)*				
		Ethylene	*ETCS*	*DEDCS*	*EDCS*	*TECS*
Zero	200	44	33	6	17	0
	250	28	55	5	12	0
	300	5	89	2	4	0
Al	200	32	55	13	0	0
	250	6	75	10	9	0
	300	5	87	7	1	0
$CaCl_2$	200	43	33	6	18	0
	250	32	49	5	14	0
	300	7	81	3	9	0
Zn	200	13	27	42	18	0
	250	12	18	63	7	0
	300	2	33	38	28	0
$ZnCl_2$	200	9	26	43	21	0
	250	12	16	56	16	0
	300	5	40	44	11	0
Zn+Al	200	2	5	70	23	0
	250	5	10	60	25	0
	300	4	19	55	22	0
$ZnCl_2$+$CaCl_2$+Al	200	3	13	48	36	0
	250	2	10	56	32	0
	300	5	12	51	32	0

The results of table (2) obtained indicate the following:-

1- Al alone does not affect selectivity but acts as a good co promoter when added with Zn to the Si-catalyst.

2- $CaCl_2$ had no effect on the catalyst, however it acted as a co promoter with $ZnCl_2$ and Al to increase the selectivity for EDCS and DEDCS.

3- The selectivity is indicated by the DEDCS\ ETCS ratio which is presented in table (3).

Table (3) The selectivity for the synthesis in Stirred-Bed reactor at 250 °C for the reaction of ethyl chloride with 10 % Si-CuCl catalyst.

Sample	*DEDCS / ETCS*
Si-CuCl	0.088
Al	0.133
Zn	10.16
MgO	0.53
$ZnCl_2$	3.5
$CalC_2$	0.102
Al + Zn	6
Al + $ZnCl_2$ +$CaCl_2$	5.6

3- Kinetics of Adsorption:-Kinetics of the reaction have been investigated over a wide range of pressures and temperatures .The variation of the rate of C_2H_5Cl adsorption at a given temperature with C_2H_5Cl pressure was determined by measuring the rate r_1 of C_2H_5Cl adsorption at an initial pressure p_1; the pressure was then rapidly changed to different constant value p_2 at the same surface coverage(θ) and the new rate r_2 recorded. These rates are assumed to depend on p^n , consequently the pressure dependence (n) may be evaluated from the relation: $r_1 \backslash r_2 = (p_1 \backslash p_2)^n$. The rate of reaction was found directly depended on the C_2H_5Cl pressure giving rise to an apparent reaction order of unity with respect to C_2H_5Cl reactant(table4).

Table (4) Influence of EtCl pressure on the reaction rate of EtCl with Si-catalyst.

Si-catalyst	*Reaction condition*		*Reaction rate/ torr.s^{-1} x 10^4*	*Order with respect to EtCl*
	Temp. / ºC	*Pressure/torr*		
5 % Si-CuCl Powder	200	0.4 - 0.57	0.66 - 1.02	1.1
		0.58 - 0.75	1.02 – 1.41	1.05
	250	0.38 - 0.59	3.2 – 4.44	1.0
		0.58 - 0.78	4.44 – 6.7	1.1
	300	0.38 - 0.60	6.7 – 10.9	1.1
		0.60 - 0.79	10.9 – 14.54	0.99
10 % Si-CuCl Powder	200	0.38 - 0.57	1.1 - 1.7	1.1
		0.57 - 0.76	1.7 - 2.36	1.1
	250	0.38 - 0.58	4.9 - 7.4	0.98
		0.58 - 0.77	7.4 - 10.1	1.1
	300	0.37 - 0.59	10.4 - 18.2	1.2
		0.59 - 0.79	18.2 - 24.23	0.98
15 % Si-CuCl Powder	200	0.40 - 0.60	0.58 – 1.0	1.1
		0.60 - 0.76	1.0 – 1.4	0.99
	250	0.40 - 0.60	3.0 – 4.2	0.98
		0.60 - 0.76	4.2 – 6.3	1.05
	300	0.40 - 0.60	6.3 – 10.2	1.1
		0.60 - 0.76	10.2 – 14.01	1.0

The activation energies (Ea) of the C2H5Cl adsorption were determined by comparing the rates of C2H5Cl adsorption at two different temperatures, but virtually the same gas pressure and value of θ (table5).

Table (5) Influence of Temperature on The Reaction Rate of EtCl on Si-CuCl mixture.

Si-catalyst	*Reaction condition*		*Reaction rate torr.s^{-1} x 10^4*	*E_a/kJ.mol^{-1}*	*E_a/kJ.mol^{-1}*
	Pressure/torr	*Temp. / ºC*			
5 % Si-CuCl Powder	0.4	200 - 250	0.66 - 1.02	59.2	47.2
		250 - 300	1.02 – 1.41	35.2	
	0.58	200 - 250	3.2 – 4.44	61	52.5
		250 - 300	4.44 – 6.7	44	
	0.78	200 - 250	6.7 – 10.9	60.1	51..15
		250 - 300	10.9 – 14.54	42.2	
10 % Si-CuCl Powder	0.38	200 - 250	1.1 – 4.9	61.4	49.4
		250 - 300	4.9 – 10.4	37.5	
	0.58	200 - 250	1.7 – 7.4	60.5	52.6
		250 - 300	7.4 – 18.2	44.8	
	0.76	200 - 250	2.36 – 10.1	59.8	51.6
		250 - 300	10.1 – 24.23	43.6	
15 % Si-CuCl Powder	0.4	200 - 250	0.58 – 1.0	56.2	46
		250 - 300	1.0 – 1.4	36.2	
	0.60	200 - 250	3.0 – 4.2	59	50.5
		250 - 300	4.2 – 6.3	42	
	0. 76	200 - 250	6.3 – 10.2	60	50.6
		250 - 300	10.2 – 14.01	41.2	

The value of the pre-exponential factor (A) were derived from the rate equation using appropriate values of Ea and the rate of adsorption . The values of (A) were thereafter used to calculate the values of the entropy of activation ($\Delta S\neq$) using the relation ship : $A = (kT / h) Cg\ Cs \exp(\Delta S\neq/R)$, where Cg and Cs are the concentration of C2H5Cl per unit volume(cm3) and of surface sites per unit area (cm2) respectively(11,12) . The ($\Delta S\neq$) and other kinetic data , which were determined for the interaction of EtCl with Si-Cu catalyst , are indicated in table (6).

Table (6) Activation Energy (Ea), Pre-exponential Factor (A), and The Entropy of Activation ($\Delta S\neq$) For The interaction of EtCl with Si-CuCl catalyst.

Si – catalyst	**Temp./ ºC**	**Reaction rate/molecules Cm^2.S^{-1}**	**Average Ea/ kJ.mol.$^{-1}$**	**A/ molecules Cm^2.S^{-1}**	**-$\Delta S^{\neq}$ J.mol.$^{-1}$.K^{-1}**
5% Si-CuCl Powder	200	2.15 × 10^9	50.3	2.8 × 10^{16}	509.1
	250	8.1 × 10^9			
	300	7.5 × 10^{13}			
10% Si-CuCl Powder	200	4.4 × 109	51.2	2.97 × 1016	508.5
	250	1.96 × 1010			
	300	4.16 × 1014			
15% Si-CuCl Powder	200	1.01 × 109	49.0	1.45 × 1016	502.1
	250	7.88 × 109			
	300	7.6 × 1013			

The resulting kinetic data revealed the following:

1- The rate of C2H5Cl adsorption depended directly on the pressure of C2H5Cl as indicated from the values of pressure dependence (n) .

2-The Ea of adsorption on each mixture was constant and did not depend on the extent of adsorption (θ) , but depended on the type of Si-catalyst mixture.

3- The reactivity of the mixture for interaction with C2H5Cl may fit in such a sequence:

15% > 10 > 5%

Conclusions

The conclusions that can be drawn from the foregoing results and discussions may be formulated as in the following:

1-The adsorption of C2H5Cl on Si powder at temperatures ≤ 350°C was mainly molecular but at temperatures greater than 350°C the adsorption was accompanied by the liberation of the decomposition products of C2H5Cl such as C2H4,C2H6, and H2.

2- The composition of product formation as well as the reaction rate depended to a great extent on the amount of copper in the Si-catalyst mixture.

3- Introduction of certain additives into 10% Si-catalyst mixture caused a promotion of the reaction and the selectivity at 300°C for DEDCS formation increased by the addition of these additives.

4- The kinetic investigation of the reaction indicated that the reaction rate directly

depended on C2H5Cl pressure giving rise to an apparent reaction order of unity with respect to C2H5Cl reactant. The rate also depended on temperature in accordance with Arrhenius equation.

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التفاعل المباشر المحفز والمرقى لكلوريد الاثيل مع السليكون باستخدام مفاعل الفرشة الثابتة

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الخلاصة:

يتناول هذا البحث دراسة التفاعل المباشر بين غاز كلوريد الاثيل ومسحوق السليكون لتحضير مركبات اثيل كلوروسيلان (Ethylchlorosilanes) باستخدام مفاعل من نوع الفرشةالمتحركة (Stirred – Bed Reactor). حضر مخلوط العامل المساعد مع السليكون بتفاعل مسحوق السليكون مع مسحوق كلوريد النحاس (I) . كانت نواتج التفاعل بصورة عامة مركبات سليكونية اشتملت على Ethyltrichlorosilane و Diethyldichlorosilane و Ethyldichlorosilane وان نسب هذه المركبات اعتمدت بصورة مباشرة على نسبة النحاس في مخلوط التفاعل وعلى درجة حرارة التفاعل . تمت دراسة تأثير إضافة بعض العناصر أو المركبات إلى مخلوط العامل المساعد مع السليكون على امتزاز غاز كلوريد الاثيل . وجرى كذلك دراسة حركيات التفاعل ضمن مدى من الضغوط ودرجات الحرارة وتم اختبار اعتمادية سرعة التفاعل على كل من الضغط ودرجة الحرارة . ودلت النتائج المستحصلة أن سرعة تفاعل غاز كلوريد الاثيل كانت تعتمد اعتمادا مباشرا على ضغطه الجزئي في الطور الغازي وان مرتبة التفاعل (n) بالنسبة إلى غاز كلوريد الاثيل بلغت الواحد الصحيح في جميع الأحوال .