Production of Organosilane by The Direct Reaction of Silicon with Methyl Chloride

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Abstract

The aim of this work is to study the production of organosilane by the catalytic reaction of Methyl chloride (CH_3Cl) with silicon (Si) and using copper (Cu) as catalyst in a fluidized bed reactor. Gas chromatographic (GC) technique was used on-line for analysis of the reacted gas.

The experimental work was carried out using columns with dimensions 5 cm internal diameter and 50 cm height stainless steel used as a fluidized bed reactor. Gas distributor was fitted at the bottom of column with 25 holes of 0.1cm hole diameter.

The reaction started with experiments at different bed temperatures (200-400) ^{o}C and the catalyst used is only copper (Cu) in two different percent (10 % and 15 % of the silicon) in order to anticipate the optimum temperature and catalyst value required for the best conversion of organosilane, these two variables were kept constant for the remaining experiments.

Experiments were performed to reflect the effect of each of these variables: particle diameter, bed height and reacted gas velocity on the organosilane production. It was found that organosilane conversion was the highest at 350 ^{o}C and 15% copper. The gas velocity at a value little more than minimum fluidization velocity is gave better conversion than low velocity that gave fixed bed or high velocity and that gave turbulent fluidization, higher level of contact mass, and finally higher particle diameter this gives homogenous fluidization concerning the reacted gas velocity.

Keywords: Organosilane, direct reaction of silicone with methyl chloride.

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إنتاج السلين العضوي بالتفاعل المباشر بين السليكون والمثيل كلورايد

الخلاصة

يهدف هذا البحث لدراسة انتاج مركبات السليكون العضوية من خلال تفاعل غاز كلوريد المثيل مع السليكون و بوجود النحاس كعامل مساعد في مفاعل الطبقة المتميعة , استعمل الغازكروموتوجرافي لتحليل كمية الغاز المتفاعل مباشرة بعد خروجها من المفاعل .

اقيمت التجارب في عمود ستينلس ستيل بقطر ٥ سم وارتفاع ٥٠ سم كمفاعل الطبقة المتميعة ووضع موزع الغاز في قاعدة عمود المفاعل حيث احتوت على ٢٥ ثقب قطر الواحدة ١ ملم من الداخل , بدئ التفاعل بتجارب عند درجات حرارة مختلفة تتراوح بين ٢٠٠ الى ٤٠٠ م^o مع اضافة النحاس كعامل مساعد بنسبتين مختلفتين ١٠ و ١٥ % وذلك لايجاد افضل ظروف للتفاعل من خلال اعطائنا افضل نسبة تحول للاوركانوسلين(organosilane) والتي تتمثل بدرجة الحرارة ونسبة العامل المساعد وابقيت ثابتة لبقية التجارب.

انجزت مجموعة من التجارب لدراسة تاثير عدة متغيرات منها : قطر جسيمات السليكون ، ارتفاع السليكون داخل المفاعل (وزن السليكون) و سرعة غار المثيل كلورايد الداخل على نسبة تحول الاوركانوسلين. وجد ان افضل نسبة تحول للاوركانوسلين هي عند درجة حرارة ٣٥٠ م^o و ١٥ % من العامل المساعد , وان سرعة الغاز التي هي اعلى بقليل من اقل سرعة للتميع افضل من السرع الواطئة التي تتمثل بالطبقة الثابتة او السرع العالية التي تعمل دوامات . وتزداد نسبة التحول بزيادة ارتفاع السليكون في عمود التفاعل وكذلك بزيادة قطر الجسيمات (ضمن حدود البحث) لكن مع الاخد بنظر الاعتبار سرعة الغاز الداخل.

Introduction

The discovery of the 'Direct Synthesis' or 'Direct Process' for organochlorosilanes by Rochow and Muller is generally referred to as the Rochow process, as shown in equation (1), promptly led to the first practical large scale production of organosilanes and silicone polymers.

$$Si + CH_3Cl \xrightarrow[\substack{Cu\ (0.5 - 5\ \%) \\ Zn\ (100 - 5000\ ppm) \\ Sn\ (5 - 100\ ppm) \\ Al\ (500\text{-}4000ppm)}]{280 - 350\ ^{o}C} (CH_3)_2SiCl_2\ (\ Di\ ,\ 70 - 90\ \%) \quad .....(1)$$

CH_3SiCl_3 (Tri , 4 -12 %)

$(CH_3)_3SiCl$ (Mono, 1 - 5 %)

CH_3HSiCl_2 (MH, 0.5 - 5 %)

$(CH_3)_2HSiCl$ (M_2H, 0.1 - 0.5 %)

The primary commercial use for methylchlorosilanes involves their conversion to a broad range of silicone polymers by the processes of hydrolysis, condensation and equilibration, as shown in eq.(2)

$(CH_3)_2SiCl_2 + H_2O$ (excess) $\longrightarrow$ $[(CH_3)_2SiO]_n$ n = 3,4,5… …(2)

Process conditions can be selected to give primarily cyclic or linear products. Polymethylsilicons or siloxanes compris three commercially important classes of polymers: fluids, elastomers and resins. These polymers, along with organofunctional and other silane monomers, have found their way into virtually every industrial product and application. As a result, some thousands of individual products are marketed by the major silicones manufacturers to a very broad spectrum of industrial consumers (Lewis and Rethwish, 1993).

Distillation columns and their ancillary equipment probably account for about half of the capital cost of a direct synthesis plant. The product mixture to be separated and refined consists of many closely boiling compounds, some of which form azeotropic mixtures. Moreover, the refined products have stringent purity requirements related to their end-use. For example, dimethyldichlorosilane must contain less than 0.05wt%. methyltrichlorosilane to satisfy premium grade elastomer specifications. The principal monomers, methyldichlorosilane,trimethylchlorosilane, methyltrichlorosilane and dimethyldichlorosilane, are isolated by continuous fractionation in multiple columns. Batch distillation may be used for the recovery of dimethylmonochlorosilane (70 ^oC) and tetramethylsilane (66 ^oC) and for the azeotropic separation of trimethylchlorosilane from tetrachlorosilane, (Lewis and Rethwish, 1993).

Because of the difficulties in separation of the organosilanes products, (Lewis and Rethwish, 1993), this research is taking the whole product $[(CH_3)_2SiCl_2$, CH_3SiCl_3, $(CH_3)_3SiCl$, CH_3HSiCl_2, $(CH_3)_2HSiCl]$as the yield of organosilane. The aim of this research is to find the best temperature for the reaction which gives highest conversion of Organosilane for two different catalyst weight percent (10 % and 15 %) , the effect of each of the hydrodynamic variables was studied : weight of the contact mass[Wt] , reacted gas velocity CH_3Cl (U) , particle diameter (dp) . These variables mentioned above have not been studied before in most of the papers (Floquet et al., 1994, Lewis et al., 2002, and Weber et al., 1989), instead most of the papers are concerned with the promoters added to the contact mass (General Electric Company 1964, Ward et al., 2001, Lewin 2001, Aramata et al., 2001, and Lewis and Ward 2002) to increase the selectivity for one of the products.

Sun et al. (1997) studied the direct process for synthesizing methylchlorosilanes from methylchloride plus silicon in the presence of catalytic amounts of copper (Cu_3Si), the coadsorption of methyl radicals and Cl_2 led to selective formation of dimethyldichlorosilane. Adsorption of methyl groups alone produced trimethylsilane from two different active sites with very different kinetices, adsorption of chlorine alone produced $SiCl_4$.

Experimental Procedure

A stainless steel column with (5cm) inner diameter and (50cm) height was used as shown in Fig. (1), an electrical heater rod with (1.5m) was turned around the column, the outlet from the reactor column was connected to a cyclone to collect the fine particle to be recycled to bed, then it would go to a filter to collect any particle that cyclone did not catch before entering the gas chromatograpy (GC**)**, Three J-type temperature thermocouples were used to detect temperature in three sites and one K-type was connected to the controller to control the temperature in the reactor. The thermocouples were calibrated with voltmeter (mv), Two temperature readers were used, one J-type, connected to selector to read the temperature at gas inlet, inside the reactor, and gas outlet, the second was K-type, it read and controlled the temperature, the controller was connected to contactor and then to the heater, it read the temperature inside the reactor and controlled it. Gas chromatography (GC) was used to analyze the reacted gas and the product, on-line directly. The GC name is ‘Gaw-Mac Spectra’ by Gaw-Mac Internment Co.LTD. Ireland with integration type ‘varion 4290’, U.S.A.The setting for the GC was:

DC = 130mA, DT = 330 ^{o}C, Column teperature = 210 ^{o}C, ATGC = 1.0, ATintig = 16, Flow of H_2 = 40ml/min, Column diameter 1/8 * 2m long, 5% OV1 on Chromosorb W, mesh 60 ~ 80.

The run began with preparing an amount of pulverized silicon with Cu catalyst (10 % and 15 % of silicon) and pouring it inside the column from the top. Rochow and Patnode, (1945), found that the efficient utilization of methyl chloride is enhanced as the proportion of the metallic catalyst, specifically copper, is increased up to about 10 percent, the rate of conversion of the methyl chloride to methyl silicon chlorides falls off as the silicon is used up, but it falls off much more rapidly when contact masses of low copper content (e.g., from 1 to 5%) are used.

Rochow (1945), effected a reaction between the silicon and the hydrocarbon halide while the latter was in vapor state, and, more particularly, while the said components were intimately associated with a metallic catalyst (e.g. copper) for the reaction, for instance, the silicon may be in the form of an alloy thereof with copper or other metal that has a catalytic effect upon the reaction between silicon and hydrocarbon halide. Set the controller on the reaction temperature (350 ^{o}C), the heater began to work slowly because it was connected to voltage variant (which was set on 60%) so the temperature rose slowly, to avoid any deflection in temperature so the temperature of the reactor did not rise more than ±5 ^{o}C after reaching the set point (350 ^{o}C).

Methylchloride(CH_3Cl) flows to the pre-heater and then to the reactor, the tube that carrying the product goies directly to the GC for analysis.

Every 15 min the product was injected into the GC (online) to be analyzed. The same procedure was followed with different velocities, height of bed, and particle diameter.

According to the following chemical reaction:

$$Si+2CH_3Cl \longrightarrow (CH_3)_2SiCl_2 + \text{other product}$$

or

$$A + 2B \longrightarrow C$$

The conversion of the organosiliane can be calculated by the following equations:

$$X = 1 - \frac{F_B}{F_{Bo}} \quad ....(3)$$

Where:

F_B = molar flow rate of CH_3Cl leaved (unreacted) the reactor.

F_{Bo} = molar flow rate of CH_3Cl was fed to the reactor.

X = moles of CH_3Cl reacted dividing by the moles of CH_3Cl fed.

F_B/F_{Bo}= percent left (unreacted) of CH_3Cl = GC reader

Result and Discussion

Ten Figures are made to show the behavior of the reaction, the experiments done on two different amounts of catalysts (10 % and 15 %), for each amount of catalyst the effects of four variables are explored (temperature, reacted gas velocity, Particle diameter and weight of the contact mass), three experiment were done on each variables.

.For fixed amounts of contact mass (150 gm), gas velocity (2.1 cm/s) and particle diameter (100 μm). In Fig. (2) the conversion of organosilane is plotted against time for different reaction temperatures with 10 % Cu catalyst, the temperature of 350 ^oC shows the best production of organosilane with time.

This temperature was selected to be constant for the remaining experiments, the increase in organosilane conversion is due to increase in formation the (η-phase) (Cu_3Si) with time which is responsible for formation of organosilane (Wessel, T.J., et.al 1996), but at more higher temperature (400 ^oC) there is more deflection and decrease in the production of organosilane because at this temperature. The catalyst decay is due to formation of coke.

Wessel and Rethwish (1996), showed that the deactivation was correlated with the presence of coke. Their TGA analysis result in the suggestion that cokes formed over layer on the surface there by blocking sites which are active for silicon gasification.

Lewin (2001), proposed a method of controlling a process for the manufacture of alkylhalosilanes which comprises contacting an alkylhalide with metallurgical grade silicon, at a temperature of 250 ^oC in a 350 ^oC in the presence of tin or tin compounds, and copper or copper compounds it is characterized in that you add to the silicon containing contact mass amounts by weight based on the silicon and calculated as elemental metal of 0.2 to 10 wt% of copper or copper compounds and 5 to 200 parts per million of tin or a tin compound as co-catalyst and in that there is also added to said contact mass, in addition to the amount of phosphorus normally present in metallurgical grade silicon, an amount based on the silicon present and calculated as elemental phosphorus, of 25 to 931 part per million (ppm) of phosphorus promoter selected from the group consisting of elemental phosphorus and metal phosphides.

Aramata et al. (2002), prepared organohalosilanes by reacting metallic silicon with a halogenated hydrocarbon in the presence of copper or a copper compound catalyst and an activated aluminum, aluminum alloy or aluminum carbide promoter. The reaction is carried out at a temperature of 250–400 ^oC. in a stirred tank reactor or a fluidized bed reactor. The inventived process shortens the time required for activation in the Rochow reaction and increases the selectivity for desirable diorganodihalosilanes.

De Cooker et al. (1975) investigated the synthesis of methylchlorosilanes with silicon-hydrogen bond, based on the reaction of silicon and methylchloride with copper as a catalyst at a temperature of 332 ^oC and pressure of 1 atmosphere.

For a contact mass and catalyst (150 gm, 10 %), particle diameter (100 μm) and a temperature (350 ^oC), Figure (3) shows the conversion vis time for different gas velocities (for variable gas velocity (1.4, 2.1, 2.8 cm/s). Fig. (3) shows the decrease in organosilane conversion with increase in the reacted gas velocity, the increase in gas velocity shortens the contact time between reacted gas and the contact mass which means less time for reaction. These curves for 1.4, 2.1 and 2.8 cm/s, present fixed bed, fluidized bed (little above minimum fluidization velocity) over high fluidization velocity respectively, there is a little advantage in the fluidized bed curve (little above minimum fluidization velocity) than the fixed bed were the surface area exposed to reacted gas is higher and the mixing is more efficient but it can be seen that for higher velocity 2.8 cm/s (turbulent fluidization) the conversion of organosilane decreases for many reasons, less contact time and more losses for smaller particle size.

Fig. (4), shows the effect of different weight of contact mass (height of the bed) where the conversion of organosilane increases as the height of the bed increases , more height of the bed means more contact time for the reacted gas to contact the solid (Si) .

Fig. (5), shows comparison between variable particle diameter for silicon, there is a big increase in conversion of organosilane with increase in particle diameter for the two curves (54 and 100μ) because the velocity used for this reaction is the fluidization velocity (little above minimum fluidization velocity of the 100μ), so the 100μ gives better mixing and less losses of particle than the lower size 54μ, where the conversion begins to decrease after awhile in spite of the higher surface area because of the losses in particles, but the comparison between the two curve (100 and 150μ) shows less increase in conversion of organosilane , they are more close to each other, at the 150μ curve, the fluidization is more stable (approximates the minimum fluidization velocity) where it gives more homogenous mixing.

The same set of experiments were done on the other weight percent of catalyst (15%), the same result is predicted but with higher production in organsilane for all the variables other than the 10 % of catalyst as shown in Fig.(6, 7, 8, 9, and 10). The comparison between the two amouns of the catalyst is shown Fig. (11, 12, and 13) for the three variables for the optimum temperature 350 °C where it is obvious that the conversion for the 15 % catalyst is more than the 10 %, as the copper represents the sole of the reaction where without it the reaction does not carry on, it is responsible for production of the η- phase , the increase of copper in the contact mass mean more production of η- phase with time resulting of poduction more organosilane.

Conclusions

The study was done to predict the optimized circumstances for the direct reaction of methyl chlo with silicon and copper as catalyst the reaction started with experiments at different bed temperature in (200-400)°C and catalyst Cu was percent (10 % and 15 %) in order to anticipate the optimum temperature and catalyst value required for the best organosilane productions. Experiments were performed to reflect the effect of each of these variables: particle diameter, bed height and reacted gas velocity on the organosilane productions. It is found that organosilane production is the highest at 350°C and 15 % catalyst ,Gas velocity little more than minimum fluidization velocity gives better yield than low velocity that give fixed bed or high velocity that gives turbulent fluidization, higher level of contact mass, and finally higher particle diameter that give homogenous fluidization concerning the reacted gas velocity. these variables are very important for design the fluidized bed reactor in which it gives a clear view for the design and pilot plant building of these important materials that used in different applications in the industry.

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Notation

d_p = particle diameter, μm
F_B = molar flow rate of CH_3Cl leaved (unreacted) the reactor, mole/s
F_{Bo} = molar flow rate of CH_3Cl fed to the reactor, mole/s
T = temperature, °C
u = reacted gas velocity, cm/s
Wt = weight of bed, gm
X = conversion = moles of CH_3Cl reacted dividing by the moles of CH_3Cl fed

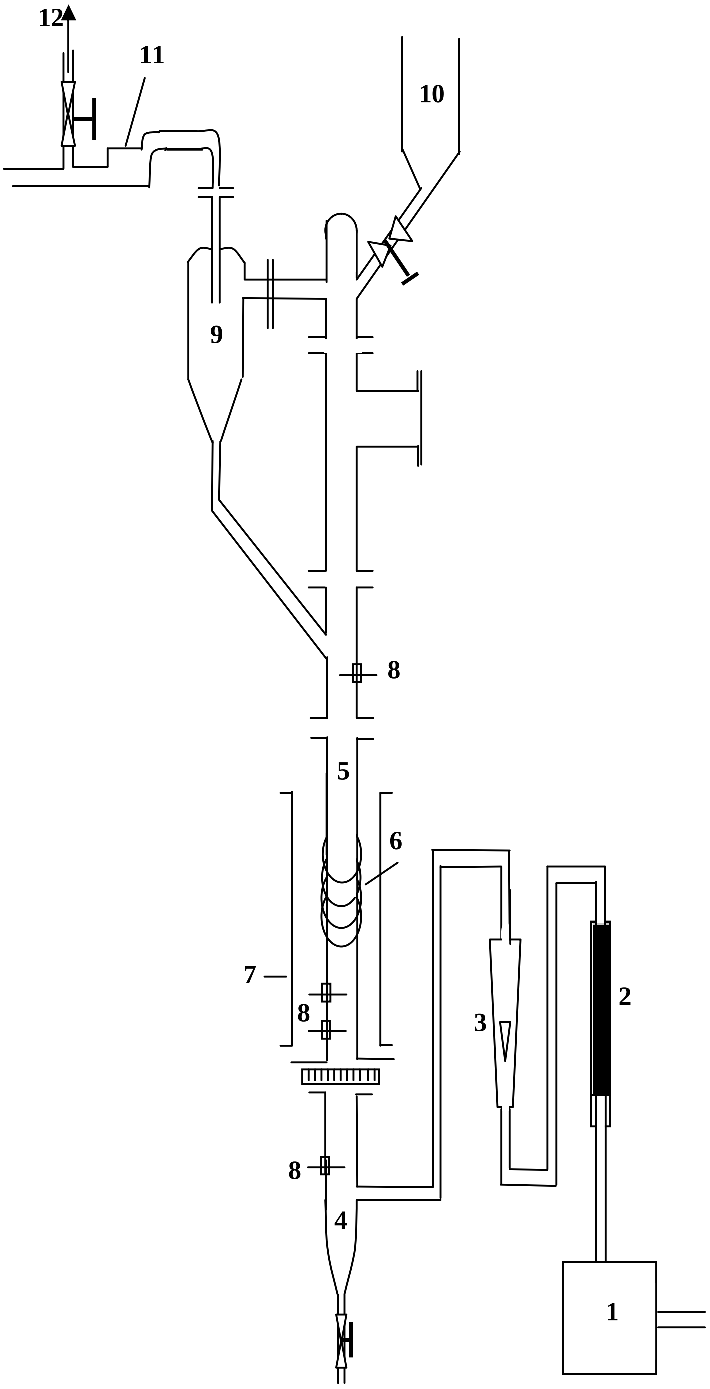
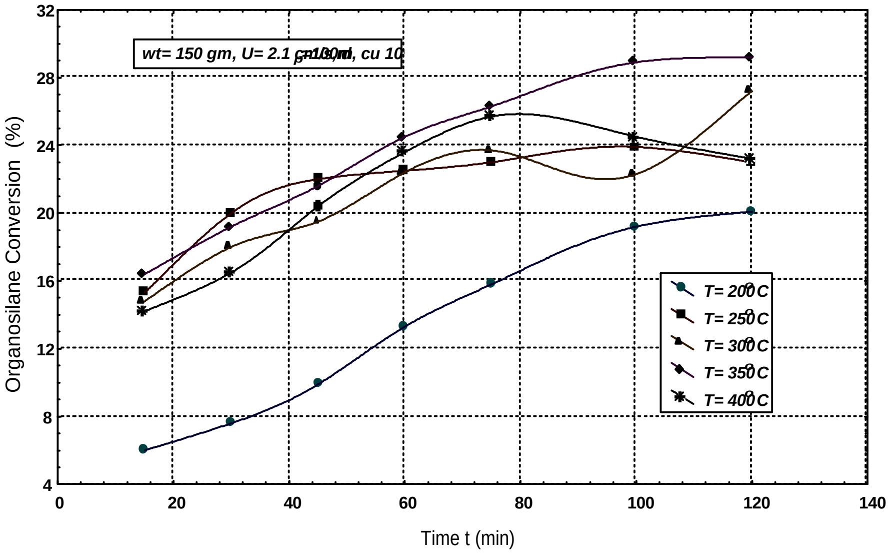
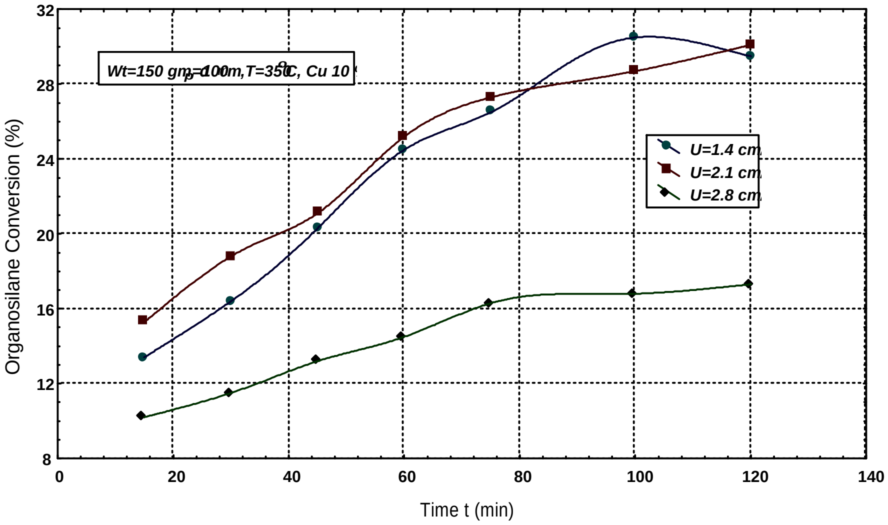


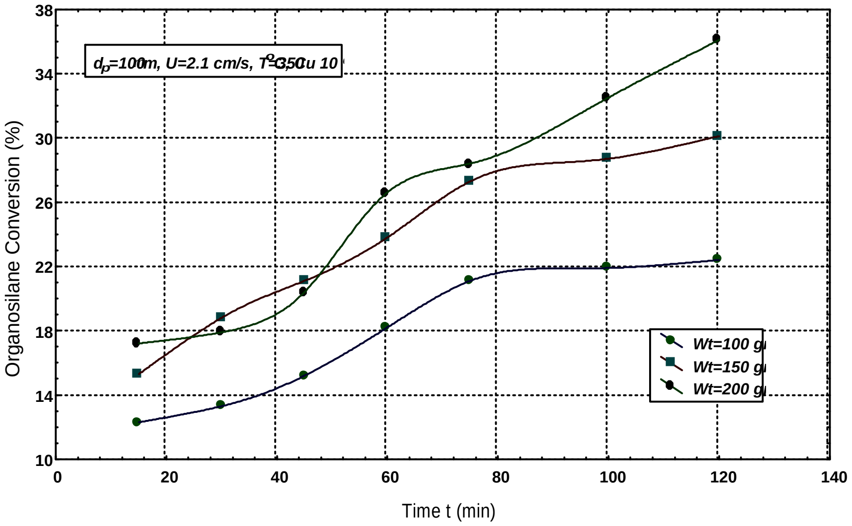
Fig. (1): Reactor system: (1) Preheater (furnace): (2) silica gel column: (3) flow meter: (4) stainless steel cone under distributor: (5) stainless steel column: (6) electrical heater: (7) jaket (aluminum) cover with fiber glass:(8) sensors: (9) cyclone:(10) stainless steel storage: (11) filter: (12) line goes to GC.



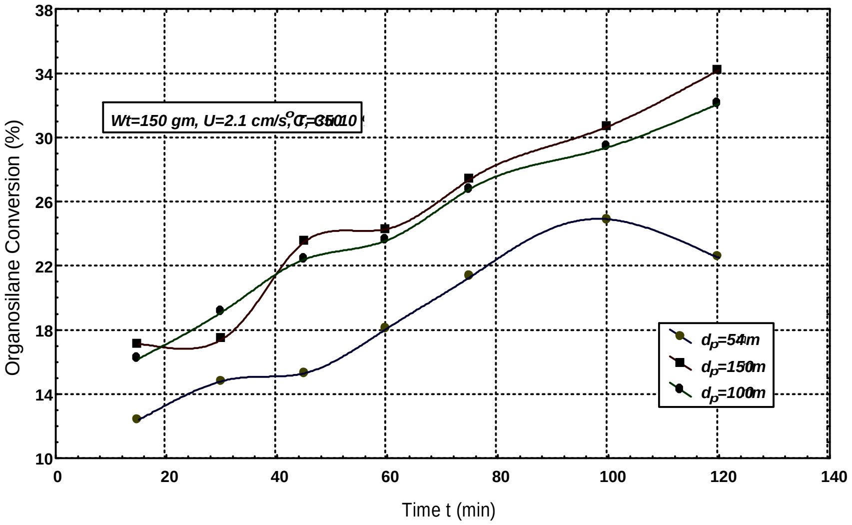
Figure(2): Organosilane conversion % vs. time, for different temperature



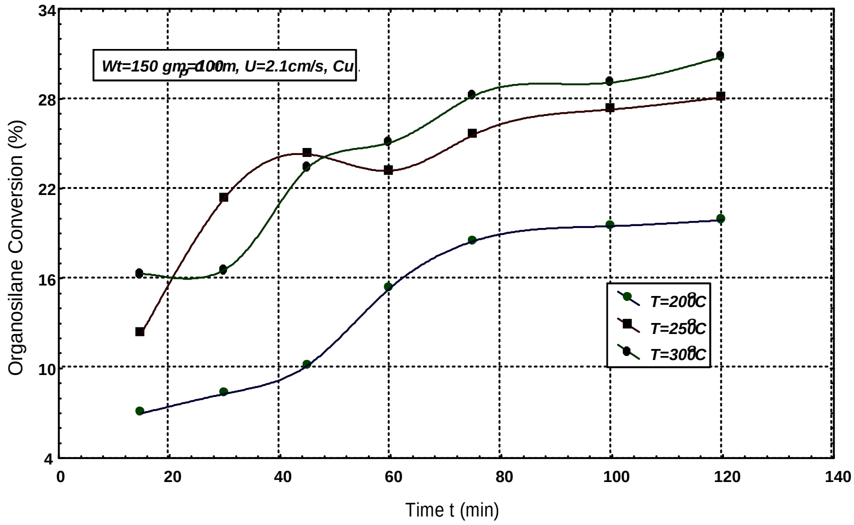
Figure(3): Organosilane conv. % vs. time, for different reacted gas veloc



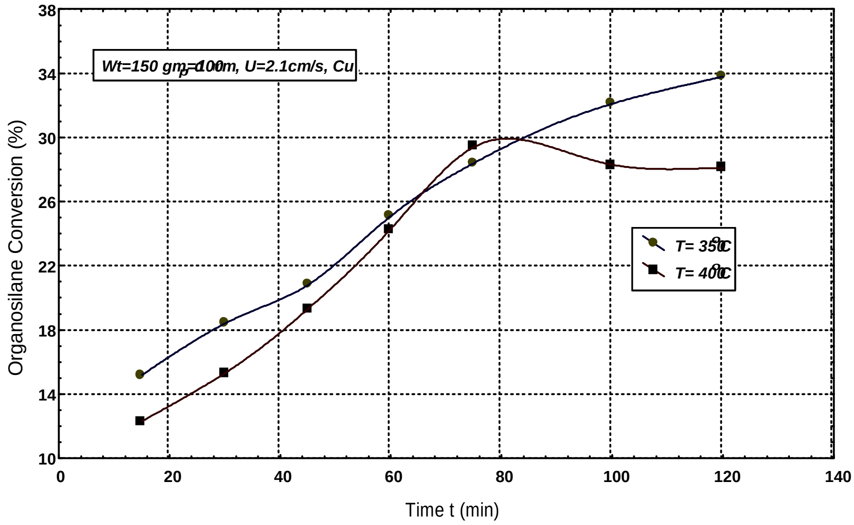
Figure(4): Organosilane conv. % vs time, for different weight of bed.



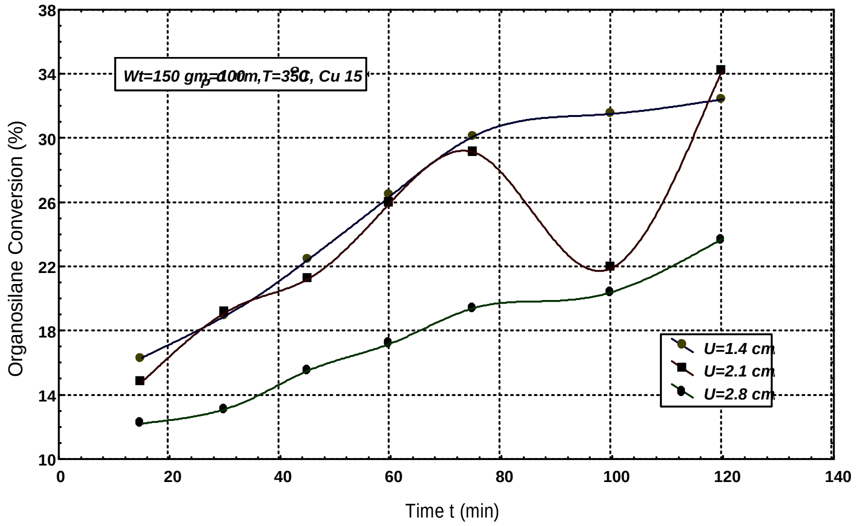
Figure(5): Organosilane conv. % vs time, for different particle diamet



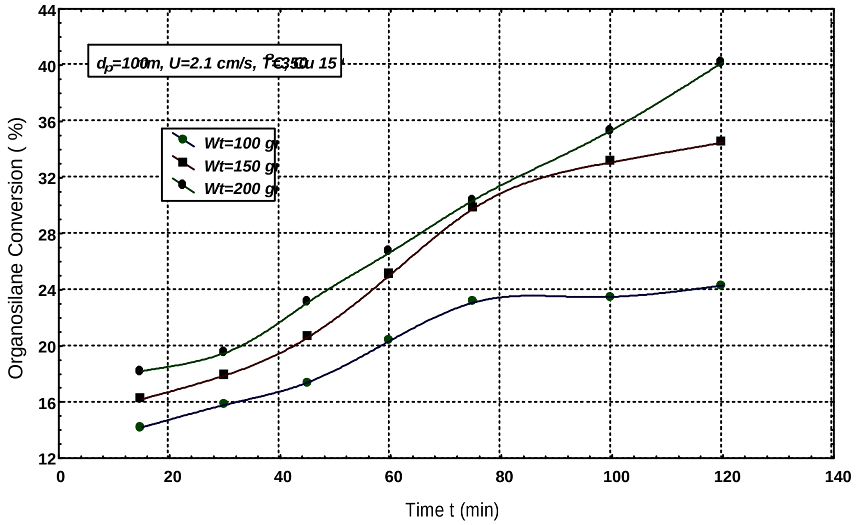
Figure(6): Organosilane conv. % vs. time, for different temperature.



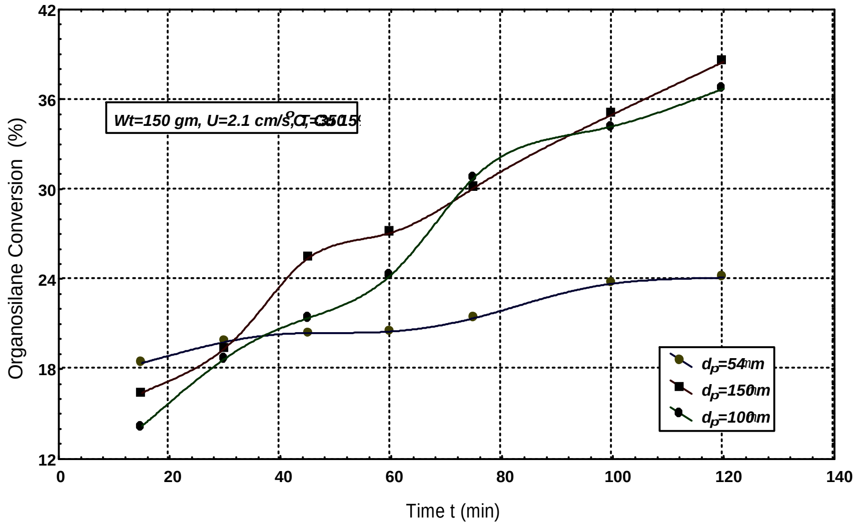
Figure(7): Organosilane conv. % vs. time, for different temerature.



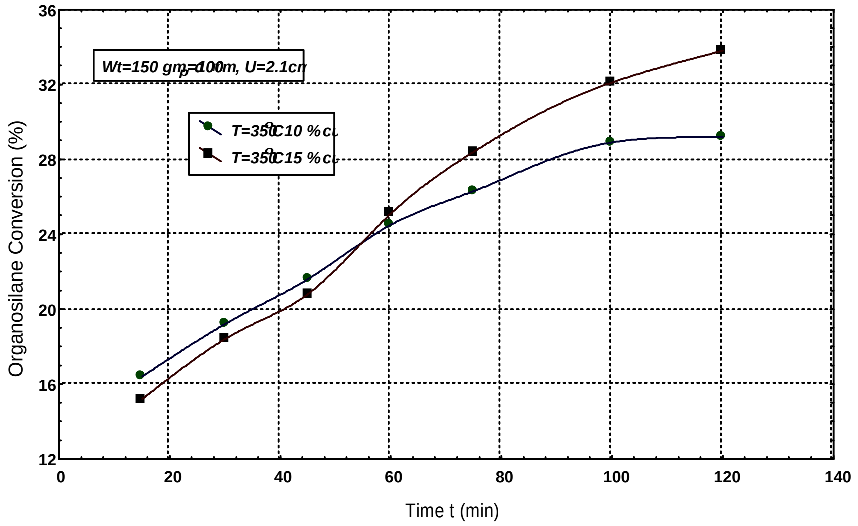
Figure(8): Organosilane conv. % vs. time, for different reacted gas vel



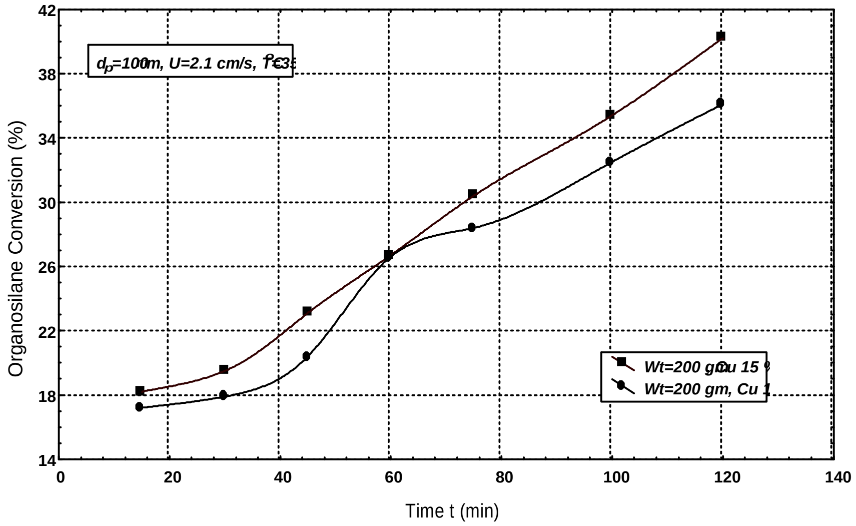
Figure(9): Organosilane conv. % vs time, for different weight of bed.



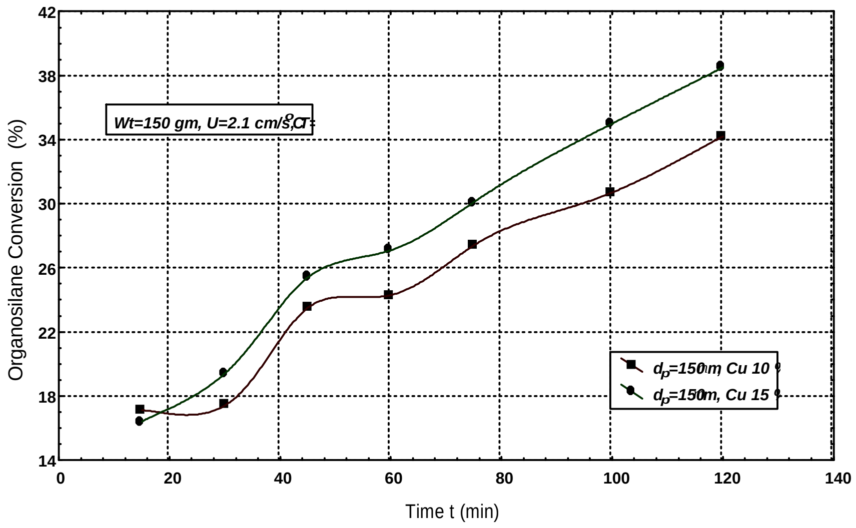
Figure(10): Organosilane conv. % vs time, for different particle diame



Figure(11): Organosilane conv. % vs. time for different catalyst (cu %



Figure(12): Organosilane conv. % vs time, for different catalyst (cu %



Figure(13): Organosilane conv. % vs time, for different catalyst (cu %