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TPD STUDY FOR DIRECT SYNTHESIS OF METHYLCHLOROSILANES

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Abstract—Temperature programmed desorption (TPD) was performed to obtain information about the role of silicon, catalyst (copper), and promoters (zinc and tin), and to characterize the active sites for the formation of silanes. Use of infrared spectroscopy allowed rapid analysis of the gas-phase product composition. During TPD where methyl chloride was used as an adsorbate, methyl chloride (MeCl), hydrogen chloride (HCl), methane (CH_4) and silanes were produced from contact masses. Although dimethyldichlorosilane (DMDC), methyltrichlorosilane (MTCS), methyltrichlorosilane (MTCS), trimethylchlorosilane (TMCS) and dimethylchlorosilane (DMCS) were produced during the direct reaction, tetrachlorosilane (QCS), trichlorosilane (TCS), methyltrichlorosilane (MTCS), and methyldichlorosilane (MDCS) were the major silanes observed during the TPD. Zinc promotion to silicon-copper contact mass (CuSi mass) increased the production of TCS, while tin promotion decreased the production of silanes having H atom, and increased the production of MTCS. Copromotion of 0.5 wt% zinc and 0.2 wt% tin increased the MTCS production further; however, the copromotion of zinc (0.5 wt%) and tin containing a small amount of tin (0.01 wt%) produced QCS as a major silane product. The silicon sites having two or three surface species such as CH_3, Cl and H were proposed as the active sites responsible for the formation of silanes, and the silicon sites of $=SiCl_2$ and $=Si(CH_3)Cl$ were the most abundant under the steady state condition.

Key words: *Direct Synthesis, Methylchlorosilanes, Promoters, TPD*

INTRODUCTION

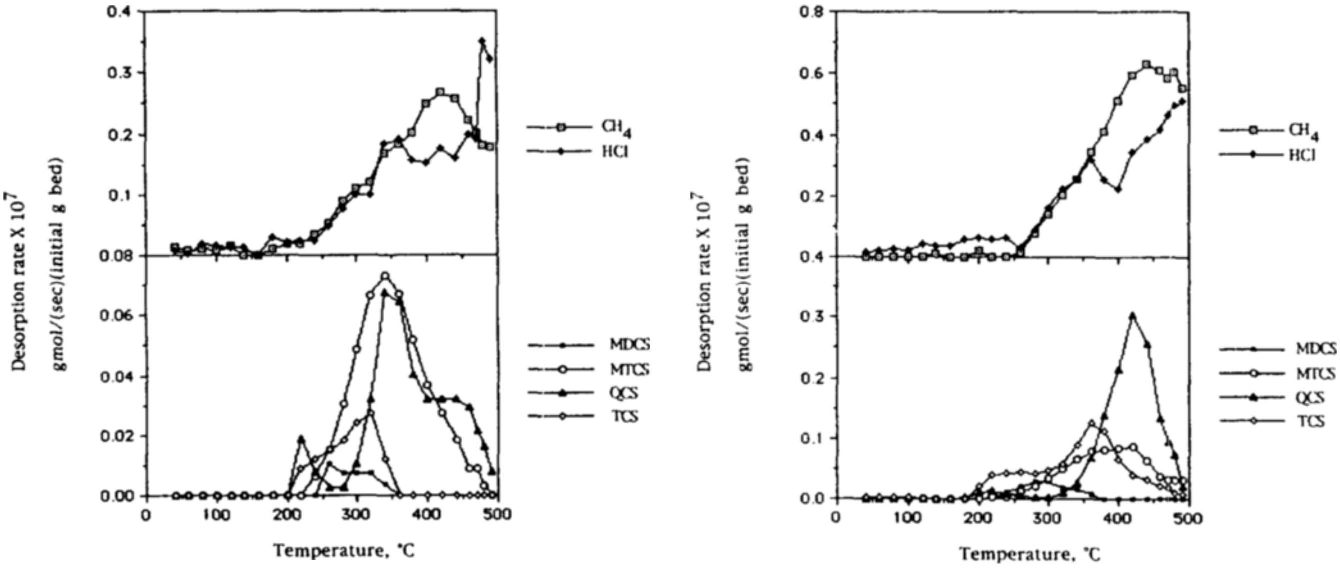
The copper-catalyzed direct synthesis reaction became a common method of synthesizing monomeric organosilicon compounds [Rochow, 1948; Voorhoeve, 1967; Ward and Carrol, 1982; Frank et al., 1985a; Banhdzer et al., 1986; Frank and Falconer, 1985; Ward et al., 1986]. However, little is known about the active surface structure and the role of copper and promoters. The active structure appears to be copper-silicide [Gorte and Schmidt, 1975] although the exact stoichiometry of this alloy is unclear. Copper appears to weaken the silicon-silicon bond, isolating the silicon atom from the bulk silicon phase, so that the activated silicon atom can react with methyl chloride to form methylchlorosilanes [Kim, 1990]. Promoters are frequently added to increase activity and selectivity. It was recently proposed by Ward et al. that a copper-silicon contact mass promoted with 0.5 wt% zinc and 200 ppm tin was several times as active as an unpromoted mass, while also giving increased selectivity for DMDC and stability [Ward et al., 1986; Kim, 1990]. Kim and Rethwisch [1992] proposed that it was attributed to a synergistic effect between zinc and tin, and the synergistic effect was suggested to be due to the ability of zinc to increase adsorption of methyl chloride and the role of tin to increase the surface mobility of Cl and H [Kim, 1990; Kim and Rethwisch, 1992].

Application of TPD to the direct reaction is intended to determine what kind of desorbing species including silanes are produced from the surface of contact mass, how surface species (CH_3, H, and Cl) are attached to the surface, and how the catalyst and the addition of promoters influence the MeCl chemisorption and desorption properties. The desorption temperature and the amount for each product during TPD were carefully measured and compared for various contact masses. Specifically, the product distribution during the desorption was compared to those obtained during the reaction process. Hence, the objectives are to obtain additional information about the interaction of silicon and surface metal (Cu, Zn, and Sn) and to characterize the active catalytic structure and active sites for the formation of silanes.

EXPERIMENTAL

The sample composition and the preparation procedures of contact masses used for the experiments of TPD were described in the report by Kim and Rethwisch [1992]. Sample names were derived from their compositions. For example, CuZnSnSi(5/0.5/0.01) is a sample containing 5 wt% Cu, 0.5 wt% Zn, 0.01 wt% Sn, and the balance (94.5 wt%) Si. An asterisk added to a sample name indicates that the sample was prepared by the impregnation method. High purity silicon (Union Carbide, 80-100 mesh, 99.99% pure) and reagents (>99.99% pure) were used to minimize the uncertainty due to the impurities. The continuous fixed bed reactor system with the temperature programmer was used for TPD experiment. A Mattson Polaris infrared spectrophotometer was used to analyze the desorbed gases as a function of heating temperature [Friedrich et al., 1989].

For these studies, ca. 2 g of freshly prepared contact mass was activated by heating it under inert gas at 310℃ for 3 h. The sample was then cooled to room temperature and evacuated, and the flow of methyl chloride, which was used as an adsorbate, was initiated. Two exposure conditions were used for MeCl preadsorption; (1) 310℃ for 30 min to determine the surface species under initial reaction conditions and (2) 310℃ for 5 h to determine the surface species under steady state reaction conditions. Following preadsorption of MeCl, the reactor system was evacuated for about 30 sec at room temperature to remove gas phase methyl



(a) (b)

Fig. 1. TPD spectrum of CuSi (5/95) for MeCl adsorbed at 310°C (a) for 30 min (b) for 5 h. Flowing gas was a mixture of H_2 and N_2 at 3 ml/min and heating rate was kept to be 12 K/min.

chloride. A carrier gas flow rate of 3-5 cc/min was controlled for the best analysis with FTIR. Linear temperature ramps for the heating of the reactor (typically 10-12 K/min) were provided with a programmable temperature controller. Infrared spectra of the desorbing species were taken every minute and the corresponding temperature was also measured. Helium, or a mixture of hydrogen and nitrogen, was used as the carrier gas for flushing desorbed species during TPD experiments. However, the same qualitative results were observed for either carrier gas, though more total desorption was observed for the H_2/N_2 (5/95) mixture [Kim, 1990], which was reported by Kim. Therefore, the H_2/N_2 was used to see the effect of promoters.

RESULTS

In both cases when MeCl was adsorbed at 310°C for 30 min and for 5 h on the contact masses, silanes in addition to MeCl, CH_4 and HCl were observed. QCS, TCS, MTCS and MDCS were the only silane products observed regardless of the type of contact masses, though DMDC was the major reaction product during the direct reaction [Rochow, 1948; Voorhoeve, 1967; Ward and Carrol, 1982; Frank et al., 1985a; Banholzer et al., 1986; Frank and Falconer, 1985; Ward et al., 1986; Kim, 1990; Kim and Rethwisch, 1992]. Indeed, the distribution of desorbed products during TPD was completely different from that obtained during reaction.

Methyl chloride desorbed from the surfaces over a broad range of temperatures, and was largely independent of the contact masses and the adsorption conditions. When MeCl was adsorbed at 310°C for 30 min, methane (CH_4) and HCl desorbed from the CuSi mass in about equal amounts [Fig. 1(a)]. Both began desorbing at ca. 250°C and continued to desorb up to 500°C. Methane had a peak in desorption rate at about 400°C, while HCl roughly increased in desorption rate over the entire range. Silanes were also produced above 250°C; however, the total amount of silanes produced during TPD was significantly less than CH_4 and HCl. The primary silane product was MTCS which had a desorption peak at ca. 340°C. Slightly less QCS was produced and a peak was observed at 340°C with a large shoulder at 440°C. TCS had a peak at 325°C with a shoulder at 225°C. Significantly less MDCS was produced and it occurred as a broad band from 250-350°C. Addition of zinc to the contact mass (CuZnSi*) had little effect on CH_4 and HCl though the total amount of HCl was increased relative to CH_4 (Fig. 2). There was a significant increase in the amount of silanes produced relative to the CuSi. The largest change was observed for TCS which increased to become the dominant silane, peaking at 330°C. QCS which had 3 peaks for the CuSi, had only one peak at 410°C for the CuZnSi*. A wide peak at ca. 360°C was observed for MTCS, while MDCS had a small band from 250-400°C. Promotion with tin (CuSnSi*) increased the CH_4 formation, but significantly decreased the formation of hydro-

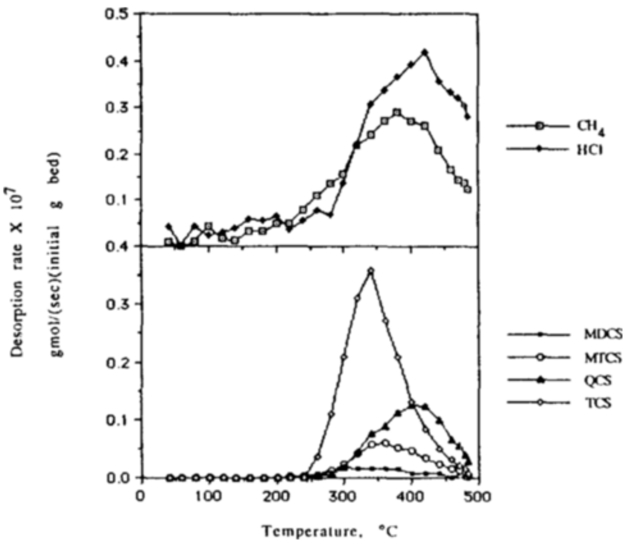


Fig. 2. TPD spectrum of CuZnSi* (5/0.5) for MeCl adsorbed at 310 °C for 30 min. Flowing gas was a mixture of H_2 and N_2 at 3 ml/min and heating rate was kept to be 12 K/min.

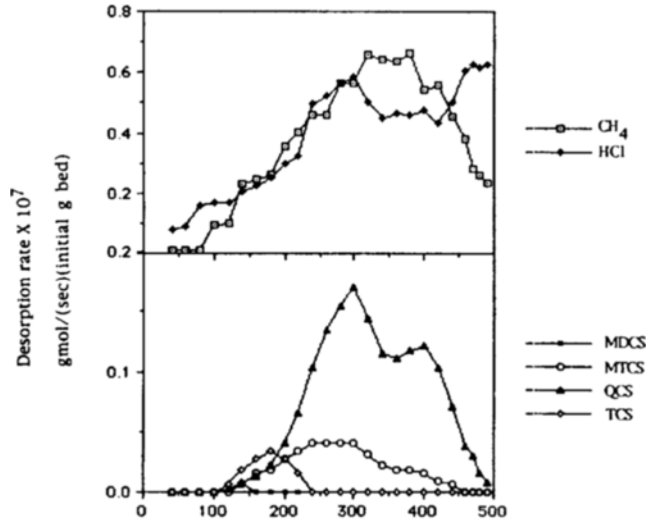


Fig. 3. TPD spectrum of CuZnSnSi (5/0.5/0.01) for MeCl adsorbed at 310°C for 30 min. Flowing gas was a mixture of H_2 and N_2 at 3 ml/min and heating rate was kept to be 12 K/min.

gen-containing silanes (MDCS and TCS). MTCS was the dominant silane with a peak at 350℃, while QCS peaked at 410℃ and had a long tail extending to 150℃. A small amount of TCS was produced at 220℃ and little MDCS was observed. The desorption products for the CuZnSnSi* containing 0.2 wt% tin were similar to those for the CuSnSi*. However, more HCl was produced for the CuZnSnSi*. In the silanes, the peak for MTCS was broader (relative to the CuSnSi*) peaking at ca. 340℃, QCS peaked at 430℃ with a tail to 210℃. Small amounts of TCS and MDCS were observed. On the other hand, the CuZnSnSi containing a small amount of tin (0.01 wt% tin) produced mainly QCS, different to the CuZnSnSi* containing 0.2 wt% tin (Fig. 3). Almost the same amounts of CH_4 and HCl were also desorbed. The peak of QCS desorption was observed at 340℃ with a large shoulder at 440℃. MTCS was also produced with peaks at 340 and 440℃, and the peak of TCS appeared at 240℃. However, little MDCS was observed.

Methyl chloride is adsorbed at reaction temperature for 5 h to determine changes in the surface species under steady state reaction conditions. However, the same species (MeCl, CH_4, HCl, QCS, TCS, MTCS and MDCS) were also observed from all types of contact masses. Analysis of this data indicated large differences between the TPD results from the steady-state and the inherently non-steady state reactions. The amounts of CH_4 and HCl were doubled, while the silane production was increased by a factor of 5 for the CuSi sample after extended reaction [Fig. 1(b)]. In addition, QCS became the dominant silane. Short reaction time gave a QCS peak at 340℃ with a shoulder at 440℃. After 5 h of reaction, the peak at 340℃ had gone and the shoulder had grown to become a peak at 420℃. The MTCS peak was essentially unchanged in magnitude, with a shift in peak temperature from 340℃ to 420℃. There was a significant increase in TCS production with wings extending from 200-500℃. For the CuZnSi* sample the production of silane and nonsilane species was roughly doubled with desorption of TCS (the dominant silane) beginning at 200℃, nonsilanes at 250℃, and the remaining silanes at ca. 300℃. The 5 h reaction caused a larger increase in the amount of QCS compared to the CuZnSi* under initial reaction condition. The tin promoted sample (CuSnSi*) doubled CH_4 and MTCS production after 5 h reaction, while showing a significant increase in QCS production relative to initial reaction. Similar results were obtained for the copromotion with both 0.5 wt% zinc and 0.2 wt% tin (CuZnSnSi*). However, in the case of CuZnSnSi containing a small amount of tin, QCS was still a dominant silane species with peak at 420℃. MTCS was also desorbed mainly at 420℃, and the peak of TCS moved to 340℃.

DISCUSSION

Although the peaks in the TPD spectra and the product distributions as well as the total desorbed amount of each desorbed product were affected by the type of contact mass and by the adsorption conditions of MeCl, the same group of desorbed products were always produced. The desorption products and their distribution during TPD were different than those obtained during reaction. The major products during reaction were DMDC, MTCS, MDCS, DMCS, TMCS and CH_4, while the major products during TPD were QCS, TCS, MTCS, MDCS, CH_4 and HCl. This suggests that the products obtained during TPD were formed by the reaction of surface species (CH_3, Cl and H). And we propose the surface species as CH_3, Cl and H which are chemisorbed or bound to the surface elements. In other words, the products observed during reactions such as DMDC are not strongly sorbed and desorbed as they are produced.

The production of CH_4 and HCl during TPD suggests the existence of surface CH_3, Cl and H species. Moreover, the formation of silanes during TPD suggests the existence of active silicon sites, which are the surface silicon atoms having Si-Cl and Si-CH_3 bonds (or Si-H bond). In this study, desorption temperatures of each product observed during TPD were correlated with the sites where surface species are attached and with the structures of active silicon sites. Surface reaction is expected to occur by surface diffusion of surface species (CH_3, Cl and H). Mobility of each surface species is affected by the compositions of surface elements and their structure on contact masses. However, it is generally expected to increase in order $CH_3 \ll Cl < H$. Hence, surface reactions will usually occur between sites where CH_3 is attached and diffusing Cl and H.

Silicon powder produced HCl and CH_4 during TPD, suggesting that MeCl does dissociatively adsorb on the silicon surface as Si-Cl and Si-CH_3. The cracking of surface CH_3 can provide the formation of ≡SiH site on the surface. On the copper-silicon pair, MeCl is proposed in many papers to adsorb as Cu-Cl and Si-CH_3 [Kim, 1990; Voorhoeve and Vlugter, 1965; Fikhtengol'ts and Klebansky, 1957]. When promoter(s) is added, we can think the dissociative adsorption of MeCl on the pairs of Si-promoter and Cu-promoter. In these cases, Pauling electronegativity [Pauling, 1960] values suggest that proposed surface sites (≡SiCH_3, CuCH_3 and SnCH_3) may exist for CH_3 group, while ≡SiCl, CuCl, SnCl and ZnCl sites may exist for Cl. Chlorine adsorbed on copper, tin, or zinc may transfer to silicon to form Si-Cl bond due to the high mobility of surface Cl. Hydrogen resulting from the cracking of CH_3 has high mobility, and hence it can be attached to all surface elements to provide ≡SiH, CuH, ZnH and SnH sites.

Two or more surface species may be attached to one surface element, especially to silicon. Hence, the structure of the sites

Table 1. Total desorbe amount of each product using H_2/N_2 as a carrier gas

Methyl chloride was adsorbed at 310℃ for 30 min. Valuex×10^5 is in gmol/g bed

Contact mass	CH_4	HCl	QCS	TCS	MTCS	MDCS	Total silanes
CuSi (5/95)	51.1	57.9	7.6	1.4	7.5	0.4	16.9
CuZnSi* (5/0.5)	53.1	94.3	17.5	29.3	7.1	2.1	56.0
CuSnSi* (5/0.3)	63.4	49.7	4.1	0.2	5.6	0.2	10.1
CuZnSnSi* (5/0.5/0.2)	60.9	76.3	7.2	0.9	12.6	0.8	21.5
CuZnSnSi (5/0.5/0.01)	135.1	173.2	27.7	1.1	5.4	0.0	34.2
Si	14.3	134.9	-	-	-	-	-
ZnSi* (3/97)	29.8	135.1	-	-	-	-	-
SnSi* (3/97)	81.9	79.8	35.0	9.3	7.8	0.1	52.2
ZnSnSi* (3/1/96)	76.2	118.5	40.7	1.0	5.8	0.5	48.0

Table 2. Total desorbed amount of each product using H_2/N_2 as a carrier gas

Methyl chloride was adsorbed at 310℃ for 5 h. Valuex×10^5 is in gmol/g bed

Contact mass	CH_4	HCl	QCS	TCS	MTCS	MDCS	Total silanes
CuSi (5/95)	111.8	89.2	30.5	14.7	12.6	1.6	59.4
CuZnSi* (5/0.5)	159.9	126.2	67.0	80.9	13.9	5.2	167.0
CuSnSi* (5/0.3)	238.0	91.5	36.3	2.9	16.7	1.2	57.3
CuZnSnSi* (5/0.5/0.2)	239.5	78.4	32.2	3.1	16.0	1.5	52.8
CuZnSnSi (5/0.5/0.01)	201.7	824.4	118.7	2.7	12.1	2.1	135.6
Si	22.1	183.7	-	-	-	-	-
ZnSi* (3/97)	51.9	358.6	24.9	2.6	-	-	27.5
SnSi* (3/97)	98.2	146.6	57.3	13.0	6.7	0.1	77.1
ZnSnSi* (3/1/96)	233.7	251.7	121.8	16.7	9.5	-	148.0

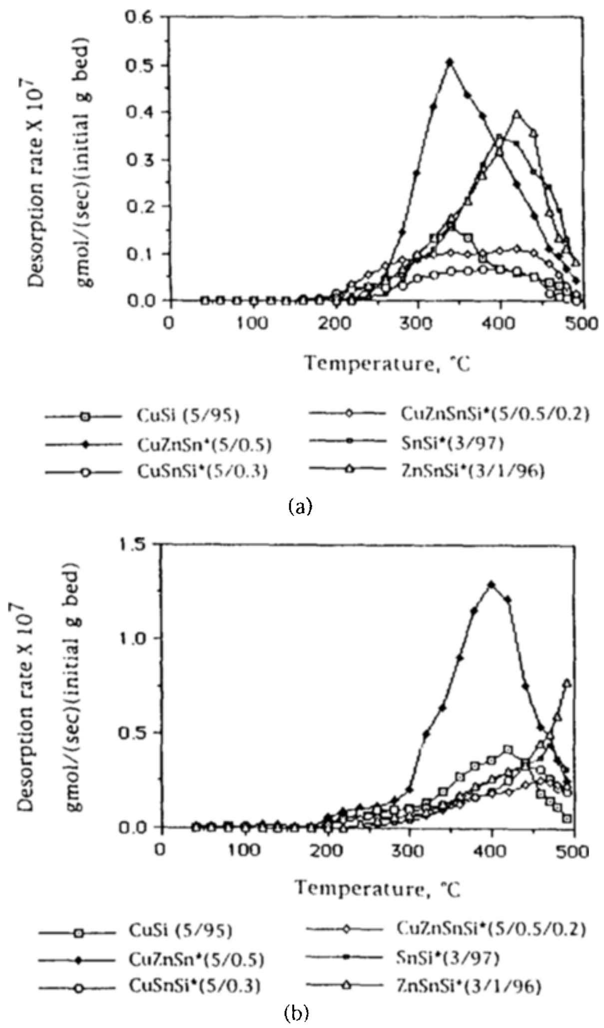


Fig. 4. Total number of silane products observed during TPD for MeCl adsorption at 310°C (a) for 30 min (b) for 5 h.

proposed above may be more complex under reaction conditions. Therefore, it is difficult to assign the peaks of each product to specific surface sites. However, surface silicon, having two or three surface species, may produce silanes rather than CH_4 or HCl. In this sense, the peaks of CH_4 and HCl desorption were basically correlated with the sites in which surface elements (Cu, Zn, Sn and Si) contain one surface species (CH_3 and Cl), while the peaks for silane desorption were correlated with the number (two or three) of attached surface species in active silicon sites, although the desorption peaks of each product are a little dependent on the existence, the structure, and the distribution of surface metals, and by the adsorption conditions.

CH_4 is formed on the surface CH_3 site with diffused H. Silicon powder produced CH_4 in the temperature range of 380-460℃ under both MeCl adsorption conditions. These peaks can be proposed to result from $\equiv$Si-CH_3 sites. Since all contact masses also produced a major CH_4 peak in the temperature range from 400-460℃ for both adsorption conditions, this also results from the $\equiv$Si-CH_3 sites. Copper and tin also act as sites for CH_3 when zinc exists by showing CH_4 desorption at 340 and 360℃, respectively. Desorption peaks for HCl were observed at several different temperature positions. Silicon powder produced HCl desorption peaks mainly at 440-480℃ for both adsorptions (Table 1, 2). Hence, the HCl desorption peaks at 440-480℃ are tentatively assigned to chlorine bound to silicon atoms ($\equiv$Si-Cl site). Almost all contact masses produced HCl at 440-500℃ and so the HCl was considered to desorb from $\equiv$Si-Cl site. This $\equiv$Si-Cl site on the contact masses is expected to be formed by surface diffusion of chlorine after dissociative adsorption of MeCl. Little HCl desorption from SnCl or CuCl sites was also observed from SnSi* and ZnSnSi* or CuSi and CuZnSnSi by producing HCl at 300-340 or 360℃, respectively. Hence, the proposed configurations for MeCl adsorption on various contact masses were supported.

The silanes produced during TPD were proposed to be formed by the reaction between silicon sites containing two or three surface species (CH_3, Cl and H) and diffusing surface Cl and H. In this case, since the total amount of silane products represents the number of active silicon sites on the surface, total desorbed silanes versus temperature were calculated and are shown in Fig. 4. The contact masses where MeCl adsorbed at 310℃ for 30 min apparently produced silanes in two different temperature regions i.e., below and above 380℃ [Fig. 4(a)]. The silanes, which are formed by surface reaction with silicon atoms having three adsorbates (-SiA_3 site), are expected to desorb at a lower temperature than those on silicon atoms having two adsorbates ($=$SiA_2 site), where A represents surface species such as CH_3, Cl or H. Therefore, the temperature region of 280-380℃ is assigned to -SiA_3 site, while the range of 380-500℃ is assigned to the $=$SiA_2

Table 3. Total desorbed amount of H, Cl and CH$_3$ during TPD. H$_2$/N$_2$ gas was used as a carrier gas
Methyl chloride was adsorbed at 310℃ for 30 min. Value$\times 10^5$ is in gmol/g bed

Contact mass	in total products			in silane products			% in silane products		
	H	CH$_3$	Cl	H	CH$_3$	Cl	H	CH$_3$	Cl
CuSi (5/95)	110.9	59.1	116.1	1.8	7.9	57.9	7.2	7.2	85.6
CuZnSn* (5/0.5)	178.8	62.3	277.6	31.4	9.2	183.4	4.3	3.1	92.6
CuSnSi* (5/0.3)	113.4	69.1	83.7	0.4	5.8	34.2	0.0	5.6	94.4
CuZnSnSi* (5/0.5/0.2)	138.9	74.3	147.2	1.7	13.4	70.9	0.2	2.8	97.0
CuZnSnSi (5/0.5/0.01)	309.4	140.6	303.7	1.1	5.4	130.3	0.8	3.9	95.2
Si	149.2	14.3	134.9	-	-	-	-	-	-
ZnSi* (3/97)	164.8	29.8	135.1	-	-	-	-	-	-
SnSi* (3/97)	171.2	89.9	271.4	9.4	7.9	191.5	0.9	3.1	96.0
ZnSnSi* (3/1/96)	196.2	82.5	302.7	1.5	6.3	184.2	0.0	3.8	96.2

site. After a long reaction time [Fig. 4(b)] most silane desorbed above 380℃, regardless of the type of contact mass. Hence, the $=\mathrm{SiA_2}$ site is considered to be the silicon site responsible for the formation of the majority of silanes during the steady state reaction. Moreover, because all silanes observed during TPD have two or more Cl atoms, at least one of two adsorbates in the silicon site of $=\mathrm{SiA_2}$ must be Cl. The other adsorbate could be Cl, CH$_3$ or H. But, since silanes having two H atoms were never produced during the direct reaction, the $=\mathrm{SiHCl}$ is unlikely. Therefore, the most abundant active silicon sites are proposed to be $=\mathrm{SiCl_2}$ and $=\mathrm{Si(CH_3)Cl}$. Similarly, $-\mathrm{SiCl_3}$ and $-\mathrm{Si(CH_3)Cl_2}$ could be the most abundant silicon sites, if the silicon sites of $-\mathrm{SiA_3}$ are considered as the active site for the formation of silanes. Hence, the formation of silanes can be considered by correlating the desorption peak of each silane with given surface reaction.

QCS was desorbed at 360 and 400-500℃ regardless of the type of contact mass, and so these are assigned to the surface reaction of silicon sites $-\mathrm{SiCl_3}$ and $=\mathrm{SiCl_2}$ with diffused Cl, respectively. Variation of desorption temperature is also due to the surface condition as described above. TCS may also be formed on $-\mathrm{SiCl_3}$ or $=\mathrm{SiCl_2}$ sites with diffused H or H and Cl, respectively, since all contact masses produced TCS in the temperature range of 300 to 380C and above 380℃. The same active sites ($-\mathrm{SiCl_3}$ and $=\mathrm{SiCl_2}$) were considered for production of both QCS and TCS. However, TCS for each site desorbs at a lower temperature than QCS. This may be caused by a difference in surface mobility, since the mobility of surface H is expected to be higher than that of surface Cl. Possible explanations of MTCS formation during TPD are the reaction of $-\mathrm{Si(CH_3)Cl_2}$ site and surface Cl, or the reaction of $=\mathrm{Si(CH_3)Cl}$ site and surface Cl, and those are assigned to the MTCS desorption at 340-360℃ and above 400℃. In the case of MDCS desorption, the peak at 300℃ may result from the reaction between $-\mathrm{Si(CH_3)Cl_2}$ and surface H, while the peak at 380℃ may result from the reaction between $=\mathrm{Si(CH_3)Cl}$ and surface H and Cl. The same silicon sites [$-\mathrm{Si(CH_3)Cl_2}$ and $=\mathrm{Si(CH_3)Cl}$] were again considered for the formation of both MTCS and MDCS, and the slightly lower desorption temperature of MDCS compared to MTCS from each silicon site is also due to high mobility of H, as discussed above for QCS and TCS.

The effects of catalyst and promoters during TPD are discussed in terms of the total desorbed amount of each product, the total desorbed amount of CH$_3$, Cl and H, and the distribution of CH$_3$, Cl and H in silane products. The residue of surface species remaining on the surface was not included in the comparison. The amount of total desorbed H atom is considered as H resulting from CH$_3$ cracking ; but it may include H supplied from the H$_2$/N$_2$ carrier gas. However, because the same effects of catalyst and promoters were obtained from using helium as a carrier gas [Kim, 1990], H from the carrier gas was ignored in calculation.

As the reaction time increased, the total desorbed amount of each product increased regardless of the type of contact masses was increased. Since the total desorbed amount of surface Cl also increased, the total amount of active silicon sites responsible for the formation of silanes appeared to increase significantly. This suggests that the reactive surface area of the contact masses increased, and this is consistent with the result of the surface study using SEM by Frank et al. [1985a, b].

The CuSi mass produced almost equal amounts of CH$_4$ and HCl, and almost equal amounts of QCS and MTCS. Zinc promotion of CuSi (CuZnSi*) increased the total desorption of CH$_3$ and Cl and the production of all silanes which supports the ability of zinc to increase the adsorption of MeCl. The TCS production was increased significantly, although the CuZnSi* did not produce TCS during reaction with MeCl. Zinc promotion increased surface Cl more than CH$_3$. This is consistent with the proposed role of zinc to act as a chlorine reservoir and to increase coking of surface CH$_3$ [Kim, 1990; Kim and Rethwisch, 1992]. An increase in the proportion of Cl in silane products and decreases in the proportions of CH$_3$ and H were also observed (Table 3). The decrease in the proportion of CH$_3$ in silane products is also consistent with zinc increasing the coking of surface CH$_3$ groups. However, the decrease in the proportion of H is explained by high mobility of surface H, resulting in more production of HCl.

For the CuSnSi* contact mass during TPD an increase in MTCS production and a decrease in the production of MDCS and TCS were observed. Since tin promotion also increased MTCS production during reaction, this is consistent with the result that tin increases the formation of silanes by surface reaction even during reaction with MeCl. Tin promotion also increased the proportion of Cl in silane products, but decreased the fraction of CH$_3$. The proportion of H in silane products decreased significantly. These are also due to tin increasing the mobility of surface H resulting in more production of non-silane products. Decrease in the proportion of H desorbed as silanes also support this explanation.

The overall activities of both copromotions were the highest during reaction [Ward et al., 1986; Kim, 1990; Kim and Rethwisch, 1992]; however, the total number of silanes desorbed from CuZnSnSi* was less than CuZnSi*, while that from CuZnSnSi was almost as large as CuZnSi* and showed the highest with CuZnSi*. Hence, no relationship between the total silane desorbed (total number of active sites) and the overall reaction activity was obtained. The activity is considered to be related not only to the number of silicon sites, but also to the adsorption rate of MeCl, to the mobility of surface Cl and H, and to the surface reaction between the active silicon site and the diffused Cl and H. Copromotion with 0.5 wt% zinc and 0.2 wt% tin (CuZnSnSi*) showed a similar trend to that of the CuSnSi* for the distribution of silane products, but produced more MTCS. The proportion of Cl in silane products also increased. However, the CH_3 proportion in silane products was less than in CuSi, CuZnSi* and CuSnSi*, while the H fraction from the CuZnSnSi* was higher than the CuSnSi*, but less than the CuSi and CuZnSi*. However, the copromotion of 0.5 wt% zinc and 0.01 wt% tin (CuZnSnSi) increased the production of QCS. Total desorption of CH_3, Cl and H were also increased. It also increased the proportion of Cl in silane products but less than CuZnSnSi*. The proportion of CH_3 and H were a little higher than those of CuZnSnSi*. Therefore, the effect of copromotion was also explained by the ability of zinc to increase MeCl adsorption and to act as a Cl sink, and by the role of tin to increase surface mobility.

CONCLUSIONS

The product distribution during TPD was completely different from that during reaction. The only silanes observed during the TPD were QCS, TCS, MTCS and MDCS, although DMDC, MTCS, MDCS, TMCS and DMCS were produced during the direct reaction with MeCl. A variety of surface sites were suggested and supported by comparing the desorption peaks of CH_4 and HCl. The silicon sites having two or three surface species were considered as the actives sites responsible for the formation of silanes. The silicon sites of $=SiCl_2$ and $=Si(CH_3)Cl$ were the most abundant under steady state conditions. QCS and TCS were expected to be formed on the silicon sites of $=SiCl_2$ and $-SiCl_3$, while MTCS and MDCS on the silicon sites of $=Si(CH_3)Cl$ and $-Si(CH_3)Cl_2$, by the surface reaction with diffused Cl and H.

Zinc promotion to CuSi mass increased the production of TCS, while tin promotion increase the MTCS production. Tin promotion decreased the production of silanes having H atoms. Copromotion of 0.5 wt% zinc and 0.2 wt% tin increased the MTCS production further. However, the copromotion of zinc and tin containing a small amount of tin (0.01 wt%) produced QCS as a major silane product. The effects of promoters were explained by the proposed roles of zinc to increase the MeCl adsorption and to act as a chlorine sink, and by the role of tin to increase the mobility of the surface Cl and H, and to increase silane formation by surface diffusion.

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