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Deactivation of CuSi and CuZnSnSi Due to Coke Formation during the Direct Synthesis of Methylchlorosilanes

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Coke formation and the subsequent deactivation of silicon samples prepared using CuCl (CuSi) and CuCl copromoted with zinc and tin (CuZnSnSi) were studied during the direct reaction of silicon with methyl chloride to form methylchlorosilanes. Two types of coke, designated α and β, were identified when samples were subjected to post reaction analysis using temperature-programmed-oxidation and thermogravimetric analysis (TGA). Deactivation was correlated with the presence of β-coke. TGA results suggest that β-coke forms an overlayer on the surface, thereby blocking sites that are active for silicon gasification. The main effect of copromotion by zinc and tin was to decrease the amount of coke deposited; however, copromoted samples experienced more extensive deactivation than CuSi because coke that is formed is more likely to block active sites and result in deactivation. Incorporation of hydrogen into the feed stream suppressed coke formation and increased the stability of the samples for the direct reaction.

INTRODUCTION

Modern economic production of methylchlorosilanes is carried out by the copper catalyzed reaction of methyl chloride (MeCl) with silicon, i.e., the direct reaction,

$$\mathrm{MeCl(g)} + \mathrm{Si(s)} \xrightarrow{\mathrm{Cu}} \mathrm{(Me)}_x\mathrm{H}_y\mathrm{SiCl}_z\mathrm{(g)} \qquad [1]$$

where $x + y + z = 4$. Dimethyldichlorosilane (DMDC), Me_2SiCl_2, is the desired product since it has the greatest number of large-volume commercial applications. The most important of these is its use as a starting material in the production of silicon-based polymers, including silicone rubber. Thus, the direct reaction is carried out industrially to maximize the selectivity for DMDC.

Side reactions during the direct reaction lead to the formation of carbonaceous residue, or coke, on the surface of the copper-silicon particles (1). This can cause a reduction in the overall DMDC production rate by blocking surface sites that are active for silane formation. Indeed, Voorhoeve *et al.* (2) and Frank *et al.* (3) reported that above 623 K curvature is present in the Arrhenius plot for the direct reaction due to the deactivating effect of excessive carbon deposition at these temperatures. Because of the deleterious effects associated with coke formation, and due to accumulation of impurities, it is necessary to continually remove spent silicon particles from industrial fluidized bed reactors and replace them with fresh stock to maintain a constant methyl chloride conversion (4).

In spite of the significance of coke formation and the subsequent deactivation during the direct reaction, these processes have not received much attention and are not well understood. The present study examines coke deposition and its effect on the rate of formation of DMDC with CuSi and CuZnSnSi (zinc and tin are present as promoters) samples with particular attention being paid to the latter. Copromotion of CuSi with zinc and tin dramatically increases the activity and the selectivity of the system (5–10). However, we are aware of no reported studies which consider its deactivation behavior.

EXPERIMENTAL METHODS

Samples were prepared using high purity polycrystalline silicon (Advanced Materials Inc., 80 × 100 mesh, 0.09 m^2/g, 99.99% purity) which was acid treated to reduce the level of metallic impurities and remove the native oxide layer which passivates the surface. The copper catalyst and zinc and tin promoters were incorporated using a ball-milling technique described elsewhere (7, 10). Briefly, cuprous chloride (CuCl) (AESAR, 99.999%) and the metal promoters, zinc (AESAR, 99.99%) and tin (AESAR, 99.9999%), when used, were ball-milled in hexane for 24 h and then vacuum dried. The resulting powder was then combined with the acid treated silicon and slurried in hexane, which was subsequently removed under vacuum at 90°C. The composition of the unpromoted material (CuSi) corresponded to 10 wt% Cu and 90 wt% Si while that of the promoted material (CuZnSnSi) corresponded to 10 wt% Cu, 1 wt% Zn, 0.02 wt% Sn, and the balance (88.98 wt%) silicon. Chlorine was neglected in these calculations because the majority of the chlorine is driven off during activation of the samples (11).

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Reaction kinetics and temperature programmed oxidation (TPO) studies were carried out using a continuous-flow, fixed-bed reactor system operating at atmospheric pressure (100 kPa). Approximately 1 g of sample was loaded into a 0.64 cm (0.25 in) OD × 0.46 cm (0.180 in) ID stainless steel reactor tube. The samples were then activated at 380°C for 3 h under a 10 standard cubic centimeter per minute (sccm) stream of helium (Air Products, 99.998%). Following activation, the samples were cooled to the desired reaction temperature and a flow of 5 sccm each of He and methyl chloride (MeCl) (Matheson, 99.9%) was initiated. Both the He carrier gas and the MeCl reactant were purified by flowing through Oxy-Trap (to remove traces of oxygen) and 4 Å molecular sieves (to remove water) before entering the reactor. In some experiments, 2.5 sccm each of hydrogen and helium were used along with 5 sccm of MeCl. The gas flow rates employed ensured that external diffusion limitations were not present (6) and provided for MeCl conversions below 10%; therefore, the reactor was modeled as differential.

The composition of the reactor effluent was determined by on-line Fourier transform infrared (FTIR) spectroscopy. Transfer lines between the reactor and IR gas cell (0.32 cm (0.125 in) OD × 0.14 cm (0.055 in) ID 316 stainless steel tubing) were maintained between 400 and 415 K to prevent condensation of products. The IR gas cell was maintained at 373 K to minimize deposition on the KBr windows and provide a uniform temperature for analysis. Spectra were collected at 4 cm^{-1} resolution and were quantified using a least-squares method (9, 12).

Following the reaction kinetic studies, some samples underwent TPO analysis to characterize the carbon deposited on their surface. After reaction, the sample was cooled to approximately 313 K in a stream of He. Helium flow was terminated and the sample was heated linearly with time (10 K/min) to between 675 and 725 K under a stream of 10 sccm oxygen. At sufficiently high temperatures, the deposited carbon was oxidized and removed as CO_2 and H_2O. The TPO effluent was analyzed approximately every 45 s by infrared spectroscopy so that plots of the rates of CO_2 and H_2O production versus temperature were obtained. Two coke peaks, designated α- and β-coke, were observed. The individual contributions of α- and β-coke combustion to the TPO profiles and the hydrogen-to-carbon (H/C) ratio for each peak were determined by regressing the CO_2 and H_2O production profiles, assuming a linear combination of the profiles for α- and β-coke. For a single crystal a Gaussian desorption profile is expected; however, on a powder sample, readsorption phenomena distort this shape. Therefore, the terms were allowed to take on both Gaussian and Lorentzian character.

Samples were also examined using thermogravimetric analysis (TGA) and Auger electron spectroscopy. In each case, the sample was cooled to room temperature after reaction and removed from the reactor. For TGA analysis, approximately 50 mg of sample was placed in a DuPont model 2950 Thermogravimetric Analyzer and heated linearly at 10 K/min from room temperature to 825 K. During the thermal treatment, the furnace was purged with a stream (100 cc/min) of pure oxygen. The sample temperature and weight (±0.10 μg) were recorded approximately once per second. A PHI model 3067 scanning Auger microprobe was used for Auger electron spectroscopy (AES). Post reaction samples were prepared for AES analysis by pressing them into indium foil to hold the powder and to reduce charging during analysis. A beam energy of 5 keV and a beam current of 20 nA were used to collect the Auger data.

RESULTS

The rate of DMDC production as a function of time for reaction of 50 kPa MeCl (and 50 kPa He) with CuZnSnSi at various temperatures is given in Fig. 1. At lower temperatures, 513 and 533 K, the reaction rate remained essentially constant (±5%) over the course of the experiment. For reaction temperatures $\geq$563 K, however, an initial period of steady-state reactivity was observed which was followed by a period of decreasing DMDC production. The decline in activity was the largest immediately after the steady-state period and became more gradual at longer reaction times. Deactivation was more severe at higher temperatures so that for reaction times greater than approximately 240 min, the rate at 583 K was actually less than that at 563 K. The reaction rate over CuSi (not shown) was essentially constant with time at 583 K; however, deactivation was observed at temperatures $\geq$613 K. The steady-state rate of DMDC production at 563 K for CuZnSnSi was more than 50 times greater than that for CuSi.

Product selectivities vs times on stream for CuZnSnSi reacted at 583 K in 50 kPa MeCl are summarized in Fig. 2.

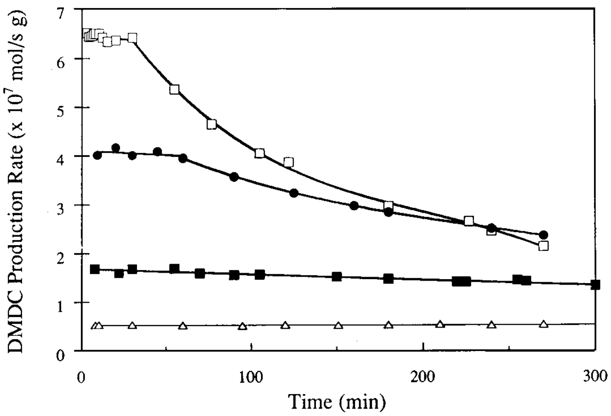

FIG. 1. Rate of DMDC production for CuZnSnSi in 50 kPa MeCl and 50 kPa He at various reaction temperatures: (-□-) 583 K, (-●-) 563 K, (-■-) 533 K, and (-△-) 513 K.

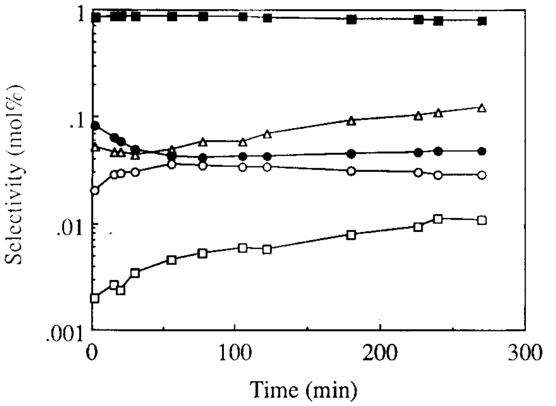

FIG. 2. Product selectivity during reaction of 50 kPa MeCl and 50 kPa He with CuZnSnSi: (-■-) DMDC, (-△-) methane, (-●-) MTCS, (-○-) TMCS, and (-□-) DMCS.

The selectivity for DMDC was initially ca. 87 mol% which was an order of magnitude greater than that of any other silane product. In contrast, DMDC accounted for only 27 mol% of the products formed on CuSi at the same reaction conditions. The observed effect of zinc and tin copromotion, to enhance the formation of DMDC, is consistent with results reported by other investigators (5–10). As the reaction progressed the selectivity for DMDC decreased slightly, reaching a minimum value of 79 mol% when the reaction was terminated (270 min). Similarly, trimethylchlorosilane (TMCS), Me_3SiCl, exhibited decreasing selectivity with reaction time after reaching a maximum at 55 min. The selectivity for methyltrichlorosilane (MTCS), $MeSiCl_3$, decreased over the first 75 min of reaction and then remained essentially constant. The most dramatic changes were observed for methane, the only non-silane product, and methyldichlorosilane (MDCS), $MeSiHCl_2$. The selectivity for methane more than doubled after 270 min compared to its initial value while that for DMCS increased 5.5 fold during the course of the reaction.

Figure 3 shows the TPO (CO_2) profiles for CuZnSnSi after reaction with 50 kPa MeCl for 270 min at various reaction temperatures. After low temperature reaction, 498 and 523 K, the profiles are similar and consist of a single peak, denoted as the α-coke, centered at ca. 530 K. In contrast, the TPO profiles of samples reacted at 563 and 583 K exhibited two distinct peaks. The α peak was present, but at increased intensity relative to that observed for CuZnSnSi reacted at $T \leq 523$ K. The second peak (β-coke) was centered at ca. 615 K. The TPO (H_2O) profiles gave essentially the same results observed for CO_2 except that the peaks were somewhat broader. The broadening of the peaks probably resulted from the stronger surface adsorption of H_2O relative to CO_2.

The amount of desorbed carbon and the hydrogen to carbon (H/C) ratio and the peak desorption temperature for α- and β-coke are summarized in Table 1. The amount of desorbed C was ca. 10 mmol/g sample. For comparison, a monolayer on these samples would be ca. 1 μmol/g. The H/C ratios for α- and β-coke were essentially constant at 1.4 and 0.6, respectively, independent of temperature. This suggests that the β-coke is more aromatic in nature than α-coke.

The amount of α-coke on CuZnSnSi increased 72% when the reaction temperature was increased from 498 to 583 K. Although no β-coke was observed after reaction at 498 or 523 K, the β peak was more than twice as large as the α peak after reaction at 563 K ($C_C(\beta)/C_C(\alpha) = 2.4$). The amount of β-coke was 43% greater after reaction at 583 K than after reaction at 563 K and the ($C_C(\beta)/C_C(\alpha)$) ratio increased slightly to 2.5. This suggests that higher reaction temperatures enhanced the formation of α-coke and induced the formation of β-coke.

The results for TPO on CuSi as well as those for the starting materials (Si and CuCl) are also summarized in Table 1. Carbon deposition was more extensive over CuSi than over CuZnSnSi at similar conditions. As shown in Table 1, the total carbon content on CuSi was 42% greater than that on CuZnSnSi due mainly to the more than twofold increase in $C_C(\alpha)$. Coke formation on CuCl and pure Si was also examined after 270 min reaction in 50 kPa MeCl at 583 K. In both cases, the only products observed during reaction with MeCl were CH_4 and HCl. As shown in Table 1, α- and β-coke were observed on CuCl and CuSi; however, no coke was detected with Si. The H/C ratios for the α- and β-coke on CuCl were essentially the same as those for the CuZnSnSi sample.

Carbon deposition on CuSi and CuZnSnSi was also characterized by TGA. The samples were reacted with 50 kPa

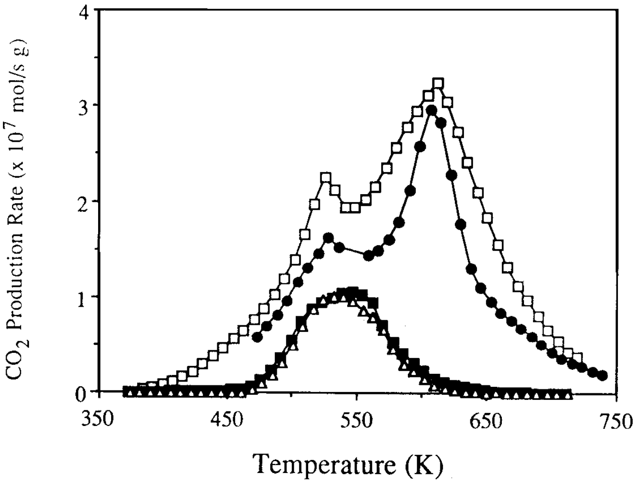

FIG. 3. Temperature-programmed-oxidation (TPO) profiles of CuZnSnSi after 270 min reaction in 50 kPa MeCl and 50 kPa He at: (-□-) 583 K, (-●-) 563 K, (-■-) 533 K, and (-△-) 513 K (heating rate 10 K/min).

TABLE 1

Amount and H/C Ratio of α- and β-Coke on Contact Masses after 270 Min of Direct Reaction at Various Reaction Temperatures[a]

Sample	Reaction temp. (K)	α coke peak				β coke peak					Total carbon (g/g)
		$T_{\max}(\alpha)$ (K)	$C_C(\alpha)$ (mmol/g)	$C_H(\alpha)$ (mmol/g)	$\frac{C_H(\alpha)}{C_C(\alpha)}$	$T_{\max}(\beta)$ (K)	$C_C(\beta)$ (mmol/g)	$C_H(\beta)$ (mmol/g)	$\frac{C_H(\beta)}{C_C(\beta)}$	$\frac{C_C(\beta)}{C_C(\alpha)}$	
CuZnSnSi	498	532	4.91	6.88	1.40	—	—	—	—	0.00	0.059
CuZnSnSi	523	543	5.67	7.42	1.31	—	—	—	—	0.00	0.068
CuZnSnSi	563	524	6.11	8.70	1.48	608	14.9	9.86	0.66	2.44	0.252
CuZnSnSi	583	525	8.50	11.20	1.31	611	21.4	12.5	0.58	2.52	0.359
CuZnSnSi-H_2	583[b]	523	1.14	2.10	1.84	609	16.7	10.5	0.62	1.45	0.214
CuSi	583	523	20.6	26.4	1.28	604	22.0	15.9	0.72	1.06	0.512
CuCl	583	515	1.75	2.52	1.44	609	4.83	2.50	0.52	2.71	0.079
Si	583	—				—				—	0.000

[a] Reaction carried out in 380 Torr MeCl and 380 Torr He. Values are given normalized per gram of reaction mass.

[b] 190 Torr H_2 in feed.

MeCl at 583 K for 270 min prior to TGA analysis. Quantitative analysis by TGA was not possible because the baseline for sample weight was constantly increasing due to oxidation of silicon, and to a lesser extent, oxidation of copper and promoters. For all samples peaks were observed in the differential weight loss spectrum at ca. 543 and 633 K. These are consistent with the α- and β-coke peaks, respectively, observed in TPO. For the CuZnSnSi sample a sharp increase in sample weight was observed immediately following β-coke combustion (ca. 630 K). No such increase in sample weight was observed for the CuSi sample reacted at 583 K. However, the TGA spectrum of CuSi after reaction at 613 K for 270 min with 50 kPa MeCl had more intense α- and β-peaks than the CuSi sample reacted at 583 K, and a sharp increase in sample weight, similar to that for CuZnSnSi, was observed at ca. 653 K.

Addition of 25 kPa H_2 to the feed stream during reaction of 50 kPa MeCl at 583 K reduced the amount of carbon deposited on CuZnSi as shown in Table 1. C_C(Total) was decreased by 40% relative to CuZnSnSi at the same reaction conditions in the absence of hydrogen. The formation of α-coke was particularly inhibited with $C_C(\alpha)$ being reduced from 0.10 wt% C to 0.014 wt% C while a smaller reduction in β-coke was observed ($C_C(\beta)$ decreased by 22%). Addition of H_2 to the feed had little effect on the rate of DMDC production, but it decreased the rate of deactivation. For example, after 270 min on stream, the rate of DMDC production, was approximately two times greater for the sample which had H_2 in the feed. However, hydrogen addition also caused a 10-fold increase in the steady-state rate of formation of methyldichlorosilane (MDCS) (a hydrogen containing silane) and a 6-fold increase in methane production.

Auger electron spectroscopy was used to study representative samples of CuSi reacted in varying MeCl pressures for 200 min at 548 and 613 K and CuZnSnSi samples reacted in 50 kPa of MeCl at 513 and 573 K. These results could not be effectively quantified due to surface charging which distorted the low energy (76 eV) Si signal. However, the results qualitatively agree with those of TPO. For CuZnSnSi reacted at 513 K, negligible carbon signal was observed. Increasing the temperature to 573 K leads to deposition of carbon with a graphitic peak shape. For CuSi, significant carbon deposits were observed at both 548 and 613 K though the signal was more intense at 613 K. Again the peak shapes suggest graphitic carbon.

DISCUSSION

A sharp oxidative weight gain was observed in TGA after removal of β-coke. We propose that this weight gain was caused by the exposure of readily oxidized, active sites following the oxidative removal of a coke overlayer. No such weight increase was observed after the combustion of α-coke, consistent with the observation that formation of α-coke did not reduce the direct reaction rate. It is generally accepted that the active sites for DMDC formation (direct reaction) contain surface silicon atoms alloyed with copper (4, 13–15). Silicon oxidation is greatly enhanced in this alloyed state (16). Thus, exposure of these sites to oxygen by removal of β-coke is expected to lead to rapid oxidation. This sharp increase in sample weight following β-coke removal was observed only for CuZnSnSi and CuSi samples which had experienced a decline in DMDC activity during reaction with MeCl. Therefore, we propose that β-coke can block the sites active for DMDC formation. For CuSi reacted at 583 K the activity remained essentially constant though significant β-coke formation was observed. However, unlike the above samples, there was no significant increase in sample weight observed in TGA following β-coke removal, i.e., the β-coke did not block active sites even though the amount of coke deposited at 583 K was greater over CuSi than over CuZnSnSi (Table 1). This indicates that the presence of β-coke alone is not a sufficient condition for deactivation; rather, deactivation occurs only when β-coke is deposited on silicon sites which are active for silane formation.

Why does blockage of active sites by β-coke appear to occur more readily over CuZnSnSi than over CuSi even though more β-coke (and more total coke) is formed on the latter? This apparent anomaly may be explained by the amount of bulk metallic copper in the unpromoted (CuSi) sample compared to the promoted (CuZnSnSi) sample. Anderson and McConkey (17) observed significant coking for metallic copper exposed to methyl chloride even at temperatures as low as 473 K. In the present study, α- and β-coke formed on the CuCl sample, but did not form on pure Si during the direct reaction with 50 kPa MeCl for 270 min at 583 K (Table 1). Furthermore, Frank and Falconer indicated that on a low surface area Cu_3Si bulk alloy sample, only small amounts (ca. 18 at% by Auger spectroscopy) of carbidic carbon are deposited after 60 min in 75 kPa MeCl at 613 K (3). These results suggest that coke formation occurs more rapidly over bulk copper than over silicon or Cu_3Si. Thus, coke formation is proposed to occur primarily in regions with bulk metallic copper present.

Gasper-Galvin *et al.* (7) proposed that a key role of Zn and Sn as promoters is to increase the dispersion of copper on the silicon surface. Indeed, the Cu/Si ratio for the Auger electron spectra of CuZnSnSi samples was more than twice as intense as for CuSi samples. In addition, Andrianov *et al.* (18) reported that zinc increased the rate of formation of copper silicide, η-Cu_3Si, the active phase for the direct synthesis. Thus, on promoted samples (CuZnSnSi) copper is present primarily as a highly disperse copper silicide phase, while unpromoted samples (CuSi) would have lower dispersion of copper resulting in more pure metallic copper sites (bulk copper). We propose that this higher concentration of bulk copper sites is responsible for the greater coking observed over CuSi.

The greater dispersion of copper in the promoted sample is consistent with the observation that coke caused a decrease in activity for CuZnSnSi while no corresponding decrease was seen for CuSi. Bulk metallic copper particles are not active for the direct synthesis reaction; however, CuCl produced both α- and β-coke, suggesting that the bulk copper sites on CuSi can also produce both α- and β-coke. Coke formed at these bulk copper sites would not decrease the catalytic activity. Coke formed at active sites, though formed more slowly, would block those sites leading to the observed decrease in direct synthesis activity. Indeed, Frank and Falconer reported the formation of coke overlayers on Cu_3Si samples during the direct synthesis reaction (3).

Chlorine may have also influenced coking in this system. Indeed, chlorine content has a significant impact on coking in Pt-Al_2O_3 reforming catalysts (19, 20). Increasing the chlorine content was reported to decrease the amount of coke formed over metallic sites; however, the formation of coke over oxidic sites was increased because Cl increased the acidity of the support. We have previously demonstrated that the addition of Zn as a promoter increased the amount of chlorine retained by a sample (11). If a similar retardation of coking by chlorine over metals is active in this system we would expect to see a reduction in coking over the zinc containing samples. Indeed, at similar conditions less coke formation occurs over CuZnSnSi than over CuSi. Thus, the increased chlorine content may be in part responsible for the reduced coking observed over CuZnSnSi.

Two coke peaks (α- and β-coke) were observed in TPO and TGA studies. We have demonstrated that α-coke has a H/C ratio of ca. 1.4 while β-coke has a ratio of ca. 0.6. Also, α-coke is removed at a lower temperature. How do α- and β-coke differ? One possibility is that α-coke acts as a precursor, losing additional hydrogen to form β-coke and hydrogenated products such as methane and DMCS. A second possibility is that there is only one type of coke and that the two peaks correspond to different combustion sites for coke perhaps catalyzed by different metals. Another possibility is that α- and β-coke are produced independently in parallel reactions, potentially on different sites. For example, over Pt-Al_2O_3 reforming catalysts, separate TPO peaks are observed for coke forming on acidic (oxide) sites and those forming on metallic sites (19, 20). Each of these possibilities is discussed briefly below.

The use of α-coke as a precursor for β-coke can be represented schematically as follows:

$$\text{MeCl} \rightarrow \alpha\text{-coke} + a\text{H}^* \rightarrow \beta\text{-coke} + b\text{H}^* \quad [2]$$

where H^* indicates a surface hydrogen species. The addition of hydrogen to the reaction stream would shift the equilibrium to the left, suppressing coke formation. Indeed, the total amount of carbon deposited was reduced by a factor of 2 (Table 1) when H_2 was added to the reaction gas over CuZnSnSi at 583 K. However, the amount of α-coke decreased by 86% compared to only a 22% reduction for β-coke. If α-coke is a precursor for β-coke an 86% reduction in α-coke should have lead to a comparable or larger decrease in the amount of β-coke formed. A simple reaction kinetics model based on Eq. [2] indicates that there is no set of rate parameters which reproduces the observed effect of H_2. This strongly suggests that β-coke was not formed by the dehydrogenation of α-coke.

As noted above, the presence of two coke peaks could also result from the catalytic combustion of coke at different types of surface sites. However, the catalyzed oxidation of coke at different sites does not explain the observed difference in H/C ratio for the two coke peaks. Post TPO analysis indicated that essentially all of the coke was removed from the samples. Given the amount of coke removed, there is no source or sink term for the hydrogen. Thus, while different sites could catalyze the formation or removal of coke, this would be unlikely to result in different H/C ratios if only one type of coke were present.

The above discussion suggests that α- and β-coke are distinct species which are formed on one or more types of sites. Measurement of coke deposition over CuCl alone (with no silicon or promoters present) indicated both α- and β-coke were present, and essentially no coke was formed over an uncatalyzed silicon sample (see Table 1). Thus, it appears unlikely that Si, Zn, or Sn are required for coke formation. Both metallic copper sites and copper chloride sites are expected over the CuCl sample, suggesting that these two types of sites could be responsible; however, there is insufficient information to say specifically which sites are responsible for α- and β-coke formation.

CONCLUSIONS

Two types of coke (α and β) are formed during the direct reaction which were identified using temperature-programmed oxidation (TPO). These can be differentiated in terms of their chemical composition (α-coke possessed a higher H/C ratio) and their activation energies (β-coke formation was enhanced to a greater extent at higher reaction temperatures). The formation of α-coke did not effect activity for the direct reaction. On the other hand, deactivation of CuZnSnSi was correlated with the presence of β-coke. It is proposed that β-coke forms an overlayer on surface reaction sites which render them inactive. The amount of coke deposited on the surface of CuSi during the direct reaction was greater than that deposited on CuZnSnSi. However, the promoted sample experienced more extensive deactivation. This was attributed to zinc's ability to increase the dispersion of copper on the surface leading to fewer metallic copper particles on the CuZnSnSi samples. This results in less coke deposition; however, if coke is formed on CuZnSnSi, it is more likely to be located at active sites, resulting in deactivation. Deactivation was reduced by incorporating hydrogen into the reactor feed. This is related to its ability to inhibit coke formation.

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