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# Methyl Spillover on Silica-Supported Copper Catalysts from the Dissociative Adsorption of Methyl Halides

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**Transmission infrared spectroscopy has been used to investigate the chemistry of methyl halides adsorbed on silica-supported copper catalysts. The infrared data show that after dissociative adsorption of $CH_3I$ on the copper particles at 298 K, methyl groups are present on the copper surface and the silica support. Methyl groups adsorbed on the copper particles are characterized by an infrared absorption band near 2920 $cm^{-1}$. Other bands in spectrum are characteristic of $SiOCH_3$ groups. The IR data suggest that methyl groups migrate or "spillover" onto the silica support where they react with surface hydroxyl groups to form $SiOCH_3$. Spillover of methyl groups is observed for the dissociative adsorption of $CH_3Br$ and $CH_3Cl$ on $Cu/SiO_2$ as well, although higher temperatures are required to activate the C−Br and C−Cl bonds. Possible mechanisms for methyl spillover are proposed.**

## INTRODUCTION

In recent years, there have been many studies of hydrocarbon fragments adsorbed on single-crystal metal surfaces under ultrahigh vacuum conditions (1–3). Hydrocarbon fragments are formed from the dissociation of alkyl halide precursors through either thermal or photochemical reaction pathways. For example, adsorbed methyl groups can be formed through the thermal or photochemical dissociation of methyl iodide, methyl bromide, or methyl chloride.

$$CH_3X\ (a) \xrightarrow[\text{metal surface}]{h\nu \text{ or } \Delta} CH_3\ (a) + X\ (a) \qquad [1]$$

These studies of $CH_3$ and other hydrocarbon fragments have led to a greater understanding of the reaction chemistry and bonding of alkyl fragments on metal surfaces (1–3).

Gaining insight into heterogeneous catalysis through ultrahigh vacuum studies on single-crystal metal surfaces is a primary goal of surface science. The assumption is that ultrahigh vacuum/single crystal surface studies can provide useful models for reactions that occur at high pressures and on surfaces of more complex structure and composition, as is the case for real catalysts. One difference between single-crystal metal surfaces and supported metal catalysts is the presence of the support and the role the support has on the chemistry. The migration of atoms or molecular fragments onto the support is but one of several possibilities that has no analogy in single-crystal metal surface chemistry. Therefore, reaction mechanisms and reaction products could be quite different for a supported metal catalyst compared to an unsupported atomically flat single crystal surface.

Spillover of atomic species such as hydrogen has been examined in detail (4–6). There are however, only a few examples of spillover of molecular fragments onto a support (7, 8). An excellent review article by Conner and Falconer discusses the spillover phenomenon for both atoms and molecular fragments as well as proposed mechanisms for spillover and the importance of spillover in heterogeneous catalysis (9).

Here we examine the chemistry of methyl halides, $CH_3X$ and $CD_3X$ where $X =$ Cl, Br, and I, on silica-supported copper catalysts and discuss the bonding and chemistry of fragments formed from their reaction on $Cu/SiO_2$. Transmission infrared spectroscopy is used to probe the surface chemistry of these molecules. Similar to the single-crystal surface chemistry of methyl halides, it is shown that adsorbed methyl groups form from the dissociation of methyl halide precursors on the surface of the copper particles. There are, however, notable differences between the results obtained in ultrahigh vacuum/single-crystal experiments and those obtained on highly dispersed silica-supported copper particles because of the formation of silica-bound products from methyl spillover. The IR data show that the C–$X$ bond dissociates in adsorbed methyl halides and surface bound products form on both the Cu particles and the silica support. In particular, the data show that methyl reacts with surface silanol groups to form $SiOCH_3$.

## EXPERIMENTAL SECTION

The infrared cell used in these experiments is a modified version of a cell designed by Yates and coworkers (10, 11). The cell consists of a $2\frac{3}{4}$-in. stainless steel cube with

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two differentially pumped barium fluoride windows and a sample holder through which thermocouple and power feedthroughs are connected to a tungsten sample grid. The sample holder design is such that the sample may be cooled to near liquid nitrogen temperatures and heated resistively up to 1200 K. The cell is attached to an all stainless-steel vacuum system through a 2-ft stainless-steel bellows hose. The vacuum system is pumped by an 80 liter/s ion pump after being rough pumped with a turbomolecular pump.

Samples are made by spraying a slurry of copper nitrate trihydrate (Strem Chemicals, 99.999%) and silica (Cabosil, M-5, 200 $m^2$ $g^{-1}$) suspended in acetone and water onto a photoetched tungsten grid (Buckbee-Mears). In some cases copper(II) acetate monohydrate (Aldrich, 99.99%) was used as a precursor for the copper particles. Unless otherwise noted, the samples were made using copper nitrate. A template is used to mask half of the tungsten grid, allowing one side to be coated with $Cu/SiO_2$ and the other with $SiO_2$. Typically, 25–30 mg are deposited on each side. Metal loadings on the order of 15% are used in most of these experiments although metal loadings of 2, 5, 10, and 12% were used where specified.

After preparation, the sample is loaded into the infrared cell, wrapped in heating tape and baked out overnight at 473 K. After bakeout the vacuum system reaches a base pressure $<1 \times 10^{-8}$ Torr. The sample is then reduced by introducing 400 Torr of hydrogen (Air Products, research grade) into the infrared cell for 15 min followed by evacuation for the same length of time. The reduction is continued by introducing hydrogen for 30, 60, and then 120 min and evacuating after each reduction period for 15 min. The sample is then oxidized in 100 Torr of oxygen (Air Products, 99.6%) for 10 min to remove hydrocarbon impurities from the copper surface and reduced again for 30 min as done previously. This oxidation/reduction step is repeated once more if necessary to remove residual organics before cooling to room temperature.

The infrared cell is then placed on a linear translator inside the FT–IR spectrometer sample compartment. The linear translator allows the sample to be moved such that the $Cu/SiO_2$ or the $SiO_2$ half of the sample is in the infrared beam path for data collection. This method allows the reaction chemistry of both the oxide-supported catalyst and the oxide support alone to be examined under identical reaction conditions. Infrared spectra shown represent the average of 1000 scans at an instrument resolution of 4 $cm^{-1}$. The spectra reported here have all been referenced to a background spectrum of either the $Cu/SiO_2$ or $SiO_2$, prior to reaction, whichever is appropriate. Some spectra have been baseline corrected to remove a sloping background.

$CH_3I$ (Aldrich, 99.5%), $CD_3I$ (Cambridge Isotopes, 99.5%), $CH_3OH$ (EM science, 99.8%), $CD_3OH$ (Cambridge Isotopes, 99.5%) were purified using several freeze–pump–thaw cycles before use. $CH_3Br$ (Matheson, 99.5%), $CH_3Cl$ (Matheson, 99.5%), $CD_3Br$ (Cambridge Isotopes, 99%), and $CD_3Cl$ (Cambridge Isotopes, 98%) were all used directly without further purification.

## RESULTS

### 1. *Characterization of* $Cu/SiO_2$

Cu particle size distributions were determined using scanning transmission electron microscopy (TEM). Electron micrographs were obtained with a Hitachi H-600 electron microscope operated at an acceleration voltage of 100 kV. For a 15% Cu sample, the Cu particles ranged in diameter from 1.8 to 5.5 nm. The average particle diameter was estimated to be near 3.9 nm. The copper surface area is approximately 13% of the total catalyst area.

$Cu/SiO_2$ samples were characterized with infrared spectroscopy using both the frequency of the infrared absorption band of adsorbed CO on the copper surface and the reaction chemistry of CO with the surface by monitoring adsorbed and gas-phase species. At 298 K, 10 Torr of CO was introduced into the infrared cell and spectra were collected for both $Cu/SiO_2$ and $SiO_2$ samples. Since CO does not adsorb to any extent on $SiO_2$ at room temperature, the spectrum recorded of the $SiO_2$ side of the sample is essentially that of the gas-phase. The gas-phase spectrum of CO was then subtracted from the $Cu/SiO_2$ spectrum to produce a difference spectrum of CO adsorbed on the copper particle surface. The infrared band associated with adsorbed CO on these samples appears in the range of 2137 to 2147 $cm^{-1}$. Upon evacuation for 5 min, the integrated area of the CO adsorption band decreases by 95% from its original intensity and shifts slightly to lower frequency. After evacuation for approximately 20 min, the band disappears completely from the spectrum. There is however a band near 2020 $cm^{-1}$ which is observed after the adsorption of CO which is more robust under vacuum than the 2147 $cm^{-1}$ band. This 2020 $cm^{-1}$ feature is observed in most, but not all cases and its significance is unknown. Importantly, there is no evidence in the infrared spectrum for the formation of any carbonate species on the copper particles or for the formation of gas-phase $CO_2$.

There is some discrepancy in the literature concerning the assignment of the vibrational bands for CO adsorbed on oxide-supported copper particles. For the most part, literature assignments of bands above 2120 $cm^{-1}$ are attributed to CO adsorbed on copper oxide (12, 13). However, several studies have shown that CO adsorbed on copper particles with atomically rough surfaces can also give rise to bands with frequencies above 2120 $cm^{-1}$ (13–15). Using a combination of techniques, DeJong and Geus (14) and Van der Grift *et al.* (15) have shown that samples which were fully reduced but of a rough surface morphology gave IR absorption band frequencies above 2120 $cm^{-1}$ for adsorbed CO and did not give an IR absorption band frequency near

2100 cm$^{-1}$ as had been previously assigned to fully reduced copper. In addition to an IR band frequency above 2120 cm$^{-1}$, oxidized copper particles produce two other species upon reaction with CO, gas phase $CO_2$ and surface carbonates. Neither of these species are detected in this study. Therefore, by taking into consideration the frequency of the absorption band for adsorbed CO, the fact that these bands disappear upon evacuation and the lack of formation of gas-phase $CO_2$ and surface carbonate, the CO adsorption data indicate that the sample processing procedure described above produces reduced Cu particles with an atomically rough surface.

### 2. *Adsorption of $CH_3I$ and $CD_3I$ on $Cu/SiO_2$ at 298 K*

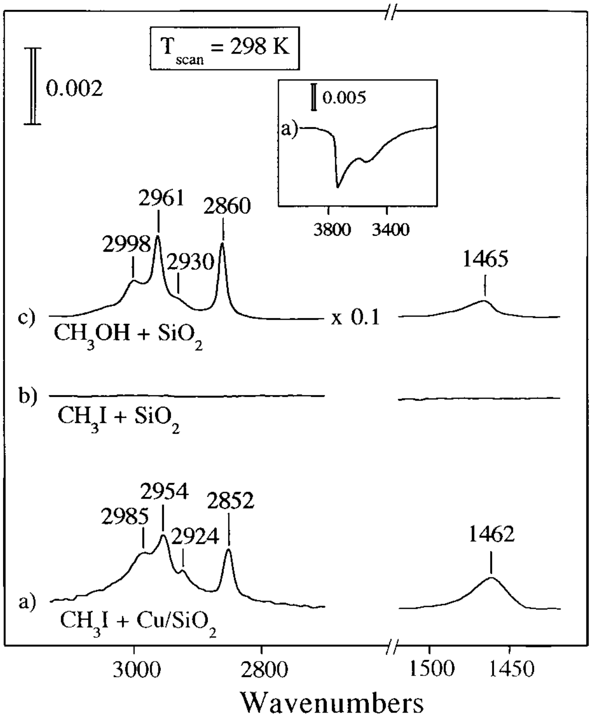

**FIG. 1.** (a) Infrared spectrum recorded after reaction of 15.0 Torr of $CH_3I$ with $Cu/SiO_2$ for 70 min at room temperature. (b) Infrared spectrum recorded after reaction of 15.0 Torr of $CH_3I$ with $SiO_2$ for 70 min at room temperature. (c) Infrared spectrum recorded of $SiOCH_3$ formed from reaction of $CH_3OH$ with $SiO_2$. Prior to recording spectrum c, the sample was heated to 523 K under vacuum to remove any physisorbed $CH_3OH$ and cooled back down to room temperature. The inset shows the hydroxyl group region associated with spectrum a, i.e., after reaction of $CH_3I$ with $Cu/SiO_2$. All spectra were recorded at a temperature of 298 K and a pressure of $1 \times 10^{-6}$ Torr.

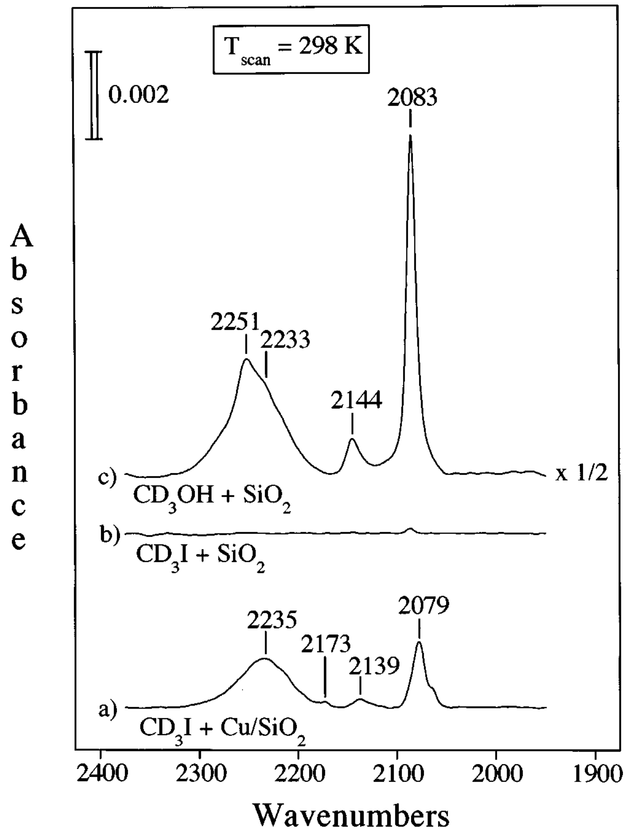

**FIG. 2.** (a) Infrared spectrum recorded after reaction of 15.0 Torr of $CD_3I$ with $Cu/SiO_2$ for 60 min at room temperature. (b) Infrared spectrum recorded after reaction of 15.0 Torr of $CD_3I$ with $SiO_2$ for 60 min at room temperature. (c) Infrared spectrum recorded of $SiOCD_3$ formed from reaction of $CD_3OH$ with $SiO_2$. Prior to recording spectrum c, the sample was heated to 523 K under vacuum to remove any physisorbed $CD_3OH$ and cooled back down to room temperature. All spectra were recorded at a temperature of 298 K and a pressure of $1 \times 10^{-6}$ Torr.

Fifteen Torr of methyl iodide was introduced into the infrared cell containing both the $Cu/SiO_2$ and the $SiO_2$ samples for 70 min at room temperature and then evacuated. The spectra of both the $Cu/SiO_2$ and $SiO_2$ samples after evacuation are shown in Figs. 1a and 1b, respectively. As the data show, methyl iodide reacts only on the $Cu/SiO_2$ surface since the spectrum shown in Fig. 1b shows no new infrared absorptions after adsorption of methyl iodide on the pure silica half of the sample under identical conditions. The spectrum recorded of the $Cu/SiO_2$ surface after reaction with methyl iodide (Fig. 1a) shows new absorptions in both the C–H stretching and the $CH_3$ deformation regions. Between 2800 and 3000 cm$^{-1}$, there are four bands observed with frequencies near 2985, 2954, 2924, and 2852 cm$^{-1}$ and one band in the deformation region near 1462 cm$^{-1}$. There is also a loss of intensity in the hydroxyl group region as shown in the inset of Fig. 1. The loss of intensity in this region indicates that SiOH groups are being consumed during the adsorption of methyl iodide on $Cu/SiO_2$.

Experiments using $CD_3I$ corroborate the results found for $CH_3I$. Figure 2b shows that, similar to the $CH_3I$ results, there is little reaction with pure silica after reaction of 15 Torr of $CD_3I$ for 60 min. Figure 2a shows the infrared spectrum recorded after reaction of $CD_3I$ with $Cu/SiO_2$ at room temperature for 60 min. Several bands are apparent in the

C–D stretching region. These bands have frequencies near 2235, 2173, 2139, and 2079 $cm^{-1}$.

As discussed in a preliminary report of this work, many of the features in the spectra shown in Figs. 1a and 2a are similar to those in the spectra recorded after reaction of methanol and deuterated methanol with silica, respectively (16). It is known that $CH_3OH$ ($CD_3OH$) can react with silica surfaces through both strained siloxane bridges and hydroxyl groups to form $SiOCH_3$ ($SiOCD_3$) (17). Figure 1c shows the spectrum taken after 15.0 Torr of methanol was allowed to react with a pure silica sample for 15 min and after heating the sample to 523 K to remove physisorbed methanol. This spectrum displays several bands in the C–H stretching region near 2998, 2961, 2930(sh), 2860 $cm^{-1}$ and one in the $CH_3$ deformation region near 1465 $cm^{-1}$. $SiOCD_3$ was formed from $CD_3OH$ adsorption on a silica sample. The infrared bands observed in the C–D stretching region are near 2251, 2233, 2144, and 2083 $cm^{-1}$ (see Fig. 2c). The calculated isotopic shift between these two surface bound fragments are as follows: 2998/2251 $cm^{-1}$, 1.33; 2962/2232, 1.33; 2930/2144, 1.37; 2861/2083, 1.37. Overall there is fairly good agreement between the frequencies, relative intensities, and isotope shifts for the bands in the $CH_3OH$–$SiO_2$ spectrum and the $CH_3I$–Cu/$SiO_2$ spectrum. The conclusion that can be drawn is that $SiOCH_3$ is present after reaction of $CH_3I$ and Cu/$SiO_2$. As discussed below, there is also evidence from the infrared spectra recorded as a function of temperature that there is another species present on the catalyst which is identified as $CH_3$ groups adsorbed on the Cu particles.

Following the room temperature adsorption of $CH_3I$ on Cu/$SiO_2$ and evacuation, the Cu/$SiO_2$ sample was heated to higher temperatures for 5 min under static conditions (IR cell closed off from pumping system) to observe both gas-phase and surface-bound decomposition products. The sample was cooled down to room temperature after heating to each temperature and a spectrum was then recorded. Figure 3 (left) shows the C–H stretching region of the temperature-dependent infrared spectra for the $CH_3I$–Cu/$SiO_2$ surface species. As the spectra show, by 423 K the band near 2924 $cm^{-1}$ has been removed from the spectrum completely where the other bands are not affected. As will be expanded on in greater detail under Discussion, the band at 2924 $cm^{-1}$ is assigned to methyl groups adsorbed on the Cu particles.

Upon further heating of the Cu/$SiO_2$ sample to 623 K and above, the bands near 2985, 2954, 2852, and 1462 $cm^{-1}$ begin to decrease as gas-phase methane (3016 $cm^{-1}$), CO and $CO_2$ (not shown) are produced. The bands near 2985, 2954, 2852, and 1462 $cm^{-1}$ decrease significantly by 773 K and completely by 873 K (not shown). The right panel of Fig. 3 displays the temperature dependent data for the $CH_3OH$–$SiO_2$ experiment. The bands in this spectrum start to decrease significantly between 623 and 723 K and are gone by 973 K. Figure 3 (right) shows that as the $SiOCH_3$ bands disappear there is the growth of a band at 3016 $cm^{-1}$ due to gas-phase methane along with bands due to CO and $CO_2$ which are not shown. It is concluded that the same gas-phase species are produced upon heating to high temperatures for both the $CH_3I$–Cu/$SiO_2$ and $CH_3OH$–$SiO_2$ reaction.

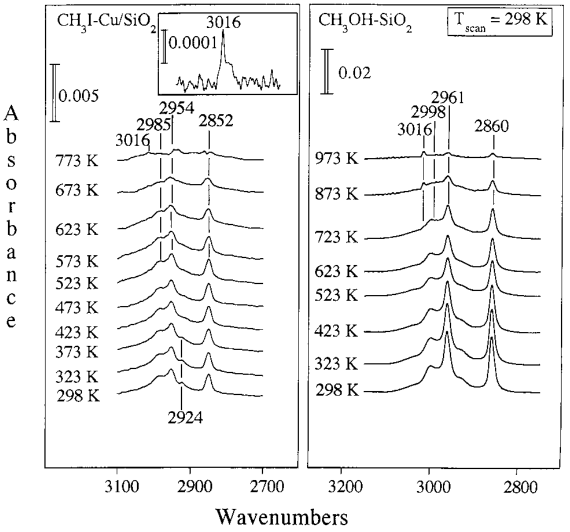

**FIG. 3.** (Left) Temperature-dependent infrared spectra recorded after reaction of $CH_3I$ with Cu/$SiO_2$ at 298 K. The 298 K spectrum is identical to the one shown in Fig. 1a. The valve to the pumping system was closed during heating so that gas-phase products could be detected. A magnification of the region containing an absorption band at 3016 $cm^{-1}$ associated with gas-phase methane in the 773 K spectrum is shown in the inset. (Right) Temperature-dependent infrared spectra recorded after reaction of $CH_3OH$ with $SiO_2$ to form $SiOCH_3$. The 298 K spectrum is identical to the one shown in Fig. 1c.

Similar temperature-dependent data were recorded after reaction of $CD_3I$ with Cu/$SiO_2$. The data show that the band at 2173 $cm^{-1}$ in the spectrum is gone after heating the sample to 473 K. The similarities in the temperature dependence of this band and the 2924 $cm^{-1}$ band in the $CH_3I$–Cu/$SiO_2$ spectrum indicates these two peaks are due to the same species and same mode with an isotope shift of 1.37 upon deuteration.

The adsorption of deuterated methyl iodide at room temperature was also monitored as a function of time. Fifteen Torr of $CD_3I$ was introduced into the IR cell containing Cu/$SiO_2$ for short periods of time followed by evacuation of gaseous $CD_3I$ for 5 min. After each evacuation, a spectrum was recorded and the processes was repeated until the infrared absorption bands had appeared to saturate. Figure 4 shows a plot of the integrated area of the entire C–D stretching region and the integrated area of the 2079 $cm^{-1}$ band versus exposure time. The integrated area levels off after approximately 40 min of reaction.

Two additional types of experiments were carried out with $CH_3I$ and Cu/$SiO_2$. First, the effect of a change in the

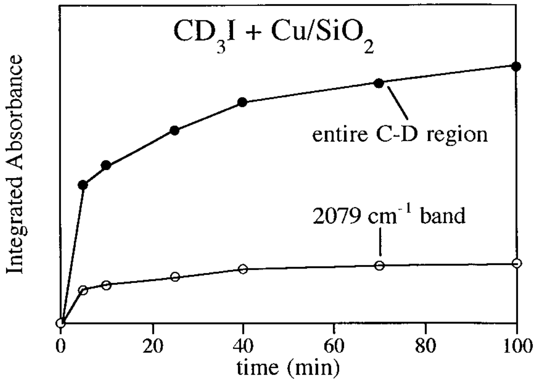

**FIG. 4.** The integrated absorbance of the infrared bands in the spectrum recorded after reaction of $CD_3I$ with $Cu/SiO_2$ is plotted as a function of $CD_3I$ exposure time. 15.0 Torr of $CD_3I$ was introduced into the infrared cell for several minutes prior to evacuation. The IR spectrum was then recorded, after which the bands in the spectrum were integrated. The band at 2079 cm$^{-1}$ (open circles) and the entire CD stretching region (dark circles) were both integrated. A line is drawn through the data points to guide the eye.

precursor copper salt was investigated. Using the same processing method described in the Experimental Section for the copper nitrate salt, the $Cu/SiO_2$ sample produced using the copper(II) acetate monohydrate salt gave the same spectrum shown in Fig. 1a after adsorption of methyl iodide for 1 h at room temperature. Second, in another set of experiments copper nitrate trihydrate was used as the precursor salt but the metal loading was varied from 4 to 15% by weight. In these experiments, there was a decrease in the intensity of all the bands shown in Fig. 1a after reaction with $CH_3I$ for 1 h as the metal loading decreased. The intensities of the bands in the spectrum are quite weak, just above noise level ($5 \times 10^{-5}$ absorbance units) for the 4% $Cu/SiO_2$ sample compared to 0.002 a.u. on the 15% $Cu/SiO_2$. These experiments show that the copper particles are activating the dissociative adsorption.

### 3. *Role of OH Groups in the Reaction of $CH_3I$ with $Cu/SiO_2$*

In an attempt to clarify the role of silica OH groups in the reaction of $CH_3I$ with $Cu/SiO_2$, several experiments were done in order to react or partially remove these groups. First, the tendency of alcohols, particularly methanol, to react with silica through the hydroxyl groups and the strained siloxane bridges on the silica surface was exploited in order to render a portion of the SiOH groups on the silica surface inert to reaction with methyl groups. The $Cu/SiO_2$ catalyst was first exposed to $CD_3OH$ to form Si–$OCD_3$ and Cu–$CD_3OH$. The sample was then heated to 573 K under vacuum to remove any adsorbed species from the surface of the copper particles. After cooling to room temperature an infrared spectrum was recorded. This spectrum showed only bands in the region from 2100–2400 cm$^{-1}$ due to the presence of $SiOCD_3$. The sample was then reacted with 15.0 Torr of $CH_3I$ for 1 h. The spectrum of the C–H stretching region after reaction of $CH_3I$ is shown in Fig. 5a. There are two bands observed in the C–H stretching region at 2921 and 2861 cm$^{-1}$. Importantly, the spectrum shows no evidence for other bands in the spectrum near 2985, 2954, and 2852 cm$^{-1}$. These data show that the hydroxyl groups play a crucial role in the spillover process.

Hydroxyl group participation in the reaction of $CH_3I$ with $Cu/SiO_2$ is also confirmed in the following experiment. A $Cu/SiO_2$ sample was prepared as described in the Experimental Section. After which the sample was heated to higher temperatures near 673 K for 24 h under vacuum and cooled to room temperature. Heating to 673 K caused a 24% decrease in the integrated area of the broad band in the hydroxyl group region. The absorption band for adsorbed CO shifted from 2147 cm$^{-1}$, before heating, to 2143 cm$^{-1}$, after heating, which indicates there is not much change in the copper surface morphology. Following this heat treat-

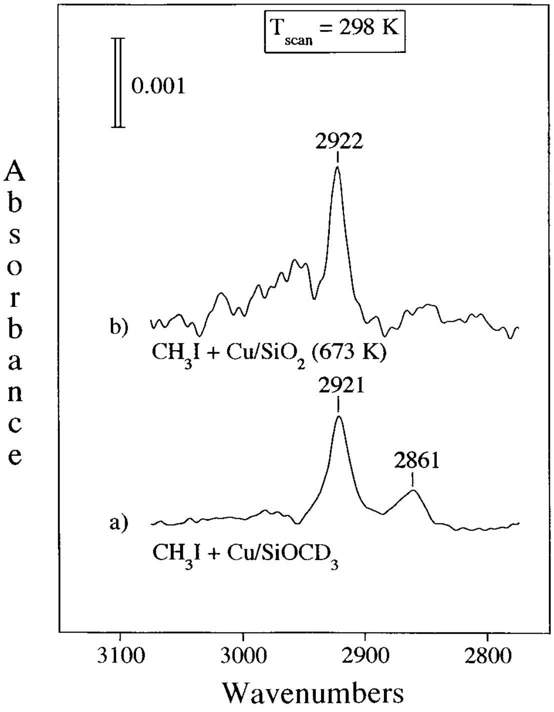

**FIG. 5.** The role of hydroxyl groups in the formation of $SiOCH_3$ from methyl iodide reaction with $Cu/SiO_2$ was investigated. Hydroxyl groups were removed by either reacting silica with $CD_3OH$ to form $SiOCD_3$, or by heating to T = 673 K for several hours, after which it was determined that 24% of the hydroxyl groups were removed. Spectrum a was recorded after reaction of $CH_3I$ with a $Cu/SiO_2$ sample that had been reacted with $CD_3OH$ to form $SiOCD_3$. Two absorption bands at 2921 and 2861 cm$^{-1}$ are present in the spectrum after reaction of $CH_3I$ with this sample. Spectrum b was recorded after reaction of $CH_3I$ with a $Cu/SiO_2$ sample that had been heated to 673 K and cooled back down to 298 K prior to reacting $CH_3I$. There is an absorption band present in the spectrum at 2922 cm$^{-1}$. Importantly, bands due to $SiOCH_3$ are not present in either of these spectra.

ment at 673 K, 15 Torr of methyl iodide was then adsorbed for 1 h at room temperature. After evacuation, only one infrared band was present in the CH stretching region at 2922 cm$^{-1}$ (see Fig. 5b). Again, other bands assigned to $SiOCH_3$ are not present in the spectrum, showing that the hydroxyl groups lost upon heating are an integral part of the formation of $SiOCH_3$.

### *4. Adsorption of $CH_3Br$ and $CH_3Cl$ on $Cu/SiO_2$*

The thermal chemistry of methyl bromide and methyl chloride on $Cu/SiO_2$ has also been investigated. Whereas methyl iodide reacts with $Cu/SiO_2$ at room temperature, methyl bromide and methyl chloride require elevated temperatures before reaction with $Cu/SiO_2$ occurs. Fifteen Torr of methyl bromide or chloride were introduced into the infrared cell and the catalyst was heated to 323 K for 30 min. This procedure was repeated at higher temperatures, increasing in 50 K increments, until $Cu/SiO_2$ reacted with the adsorbate as indicated by new product bands for either gas-phase species or species adsorbed on the surface. For methyl bromide, a reaction temperature of at least 348 K was needed. For methyl chloride, the onset temperature for reaction was near 398 K. The pure silica half of the sample showed no reaction with $CH_3Br$ and $CH_3Cl$ at reaction temperatures of 348 and 398 K, respectively. Once reaction with $Cu/SiO_2$ had occurred, products were built up on the surface by heating the sample in the presence of the methyl halide gas near the onset reaction temperature for several hours. Figures 6b and 6c show the spectra of $Cu/SiO_2$ after reaction with $CH_3Br$ and $CH_3Cl$, respectively. The surface-bound products for both of these reactants, $CH_3Br$ and $CH_3Cl$, exhibit absorption bands near 2993, 2959, 2930(sh), 2857, and 1461 cm$^{-1}$. In fact, the spectra recorded after reaction of all three methyl halides with $Cu/SiO_2$ look quite similar (see Fig. 6).

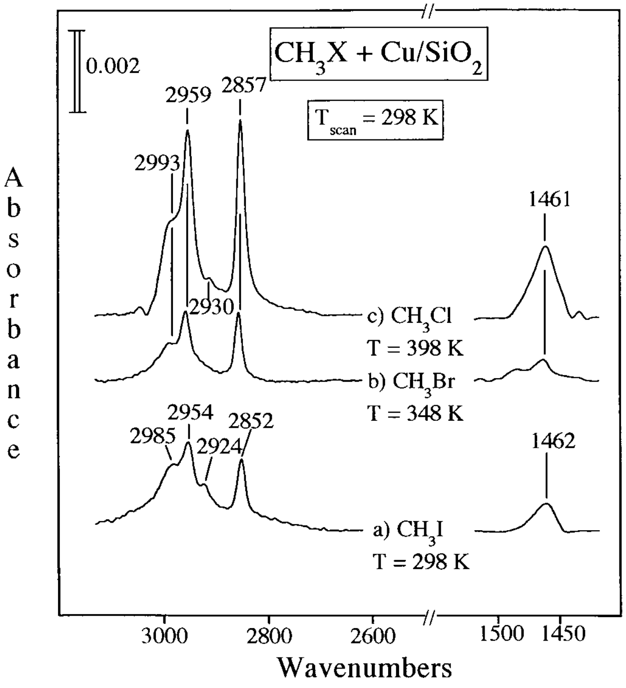

FIG. 6. The infrared spectra recorded at 298 K of $Cu/SiO_2$ after reaction with approximately 15 Torr of $CH_3I$, $CD_3Br$, and $CH_3Cl$ at 298, 348, and 398 K, respectively. The infrared cell was evacuated before each spectrum was collected. The data show that similar spectra are obtained in each case.

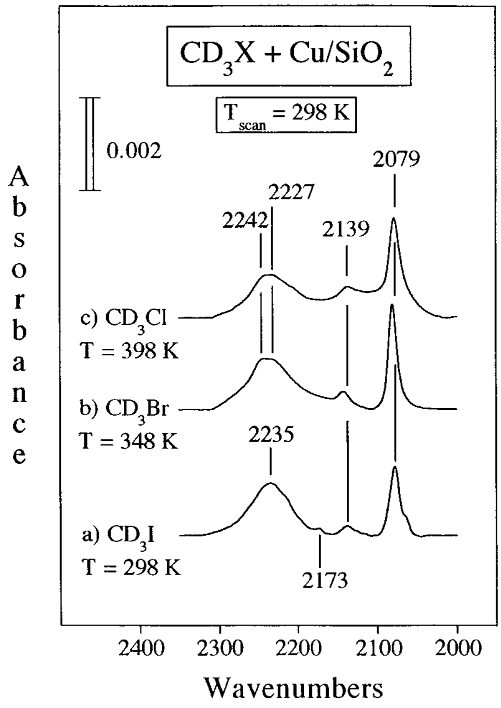

FIG. 7. The infrared spectra recorded at 298 K of $Cu/SiO_2$ after reaction with approximately 15 Torr of $CD_3I$, $CD_3Br$, and $CD_3Cl$ at 298, 348, and 398 K, respectively. The infrared cell was evacuated before each spectrum was collected. The data show that similar spectra are obtained in each case.

The infrared spectra for the products obtained from the deuterated analogs $CD_3Br$ and $CD_3Cl$ after reaction with $Cu/SiO_2$ are shown in Fig. 7, also included in Fig. 7 is the spectrum of $CD_3I$. All of the deuterated methyl halides form species on the surface which have absorption bands in the C–D stretching region near 2242, 2227, 2139, and 2079 cm$^{-1}$. These frequencies represent an isotopic shift of approximately 1.33, 1.33, 1.37, and 1.37 from the bands at 2993, 2959, 2930, and 2857 cm$^{-1}$, respectively, from the perhydro compounds.

## DISCUSSION

### *1. Identification of Adsorbed Species from $CH_3X$ and $CD_3X$ Reaction on $Cu/SiO_2$*

We begin our analysis of the adsorption of $CH_3X$ and $CD_3X$ on $Cu/SiO_2$ by considering the work of Bent and co-workers (3, 18, 19). In their work on single-crystal copper surfaces, it was shown that methyl iodide dissociates on copper surfaces to produce two adsorbed species-methyl groups and iodine atoms. As determined by temperature-programmed desorption experiments, adsorbed methyl groups react and desorb near 450 K to form $CH_4$, $C_2H_6$, $C_2H_4$, and small amounts of propene (3, 18). If we assume that silica-supported copper particles react in a similar manner, we would expect to observe adsorbed methyl groups on the copper surface at 298 K which can then desorb near 450 K upon warming.

The temperature-dependent spectra shown in Fig. 3a show the loss of the band at 2924 $cm^{-1}$ upon warming to 423 K. This temperature is near the reaction temperature for methyl groups adsorbed on single-crystal copper surfaces as discussed above (3, 18, 19). The other bands in the spectrum remain unaffected by heating to 423 K. The band near 2924 $cm^{-1}$ is also similar in frequency to literature values for $CH_3$ groups adsorbed on single crystal copper surfaces (18, 19) (Cu(111), 2835 $cm^{-1}$; Cu(100), 2915, 2760 $cm^{-1}$) and is thus assigned to the symmetric stretch of methyl groups adsorbed on the copper particles. For $CD_3$–Cu this band appears at 2173 $cm^{-1}$ giving an isotope shift of 1.35, the expected isotope shift for a carbon–hydrogen stretching motion. The weaker band near 2861 $cm^{-1}$ seen in the spectrum shown in Fig. 5a may be assigned to methyl groups adsorbed on Cu(111) facets.

The band near 2924 $cm^{-1}$ in the $Cu/SiO_2$ spectrum after reaction with either $CH_3Cl$ or $CH_3Br$ is typically less distinct than it is in the spectrum recorded of $CH_3I$ after reaction with $Cu/SiO_2$. This may be related to a lower coverage of methyl groups adsorbed on the copper particles after reaction with $CH_3Cl$ and $CH_3Br$ because of the higher reaction temperatures needed for the activation of the C–Br and C–Cl bonds. In fact, the 2924 $cm^{-1}$ band assigned to Cu–$CH_3$ does begin to decrease in intensity at temperatures as low as 323 K (see Fig. 3, left). Since the $CH_3Cl$ and $CH_3Br$ react at temperatures above this, some of the methyl groups may desorb/react from the copper surface at the elevated adsorption temperatures.

The second adsorbed species observed in the $CH_3I$–$Cu/SiO_2$ spectrum remains after desorption of the methyl groups from the copper surface and is thermally stable up to temperatures of 623 K. Its thermal stability is more like that of covalently bonded alkyl fragments on the silica support rather than on a metal surface. In addition, the data in the inset of Fig. 1 shows that the silanol (SiOH) groups are being consumed during adsorption of methyl iodide. Other experiments done to remove hydroxyl groups by either reaction with $CD_3OH$ or by preheating to 673 K show that the silica support, and in particular the OH groups, is somehow taking part in the reaction to form this second species on the surface, characterized by infrared absorption bands in the C–H stretching region near 2985, 2954, and 2852 $cm^{-1}$. Similar observations are made for reaction of $CH_3Cl$ and $CH_3Br$ on $Cu/SiO_2$.

As discussed under Results, the $CH_3I$–$Cu/SiO_2$ spectrum shown in Fig. 1a (with the exception of the 2924 $cm^{-1}$ band) and the spectra obtained from the adsorption of $CH_3Br$ and $CH_3Cl$ (Figs. 6b and 6c) on $Cu/SiO_2$ at elevated temperatures all look strikingly similar to the spectrum obtained for $SiOCH_3$ from reaction of methanol with pure silica (Fig. 1c) (20–22). The bands present in the spectra for both $CH_3OH$–$SiO_2$ and $CD_3OH$–$SiO_2$ are similar in both intensity pattern and band frequencies to all of the $CH_3X$–$Cu/SiO_2$ and $CD_3X$–$Cu/SiO_2$ spectra, respectively. The thermal stability and decomposition products of $SiOCH_3$ formed from $CH_3OH$–$SiO_2$ are similar to those for $SiOCH_3$ formed from $CH_3I$–$Cu/SiO_2$. However, higher temperatures are necessary to remove $SiOCH_3$ from the $CH_3OH$–$SiO_2$ sample by about 200 K than from the reaction of methyl iodide on the $Cu/SiO_2$ surface. This may be due to several causes. First, there is a much greater amount, approximately a factor of 20 times more $SiOCH_3$ from the methanol reaction than there is from the $CH_3I$–$Cu/SiO_2$ reaction. Second, the close proximity of the $SiOCH_3$ groups to the copper particles that are absent in the $CH_3OH$–$SiO_2$ experiment, may give rise to a catalytic decomposition of these groups. In fact, it is possible that reverse spillover occurs where the methyl fragments migrate back onto the copper surface at elevated temperatures where they desorb as methane.

From the above discussion, the bands near 2985, 2954, 2852, and 1462 $cm^{-1}$ in the $CH_3X$–$Cu/SiO_2$ spectrum are assigned to $SiOCH_3$. Table 1 shows that vibrational assignments of these bands compared to literature values

**TABLE 1**

**Vibrational Assignment of $SiOCH_3$**

| Mode description[a] | $SiOCH_3$ spillover[b] | $SiOCH_3$ $CH_3OH$–$SiO_2$[c] | $SiOCH_3$ $CH_3OH$–$SiO_2$[d] |
|---|---|---|---|
| CH asymmetric stretch | 2985–2993<br>(2235–2242)[e] | 2998<br>(2251) | 3000<br>(2252) |
| CH asymmetric stretch | 2954–2959<br>(2227–2235) | 2961<br>(2233) | 2958<br>(2231) |
| Overtone or combination band | 2930 (sh)[f]<br>(2139) | 2930(sh)<br>(2144) | 2928(sh)<br>(2145) |
| CH symmetric stretch | 2852–2857<br>(2079) | 2860<br>(2083) | 2858<br>(2081) |
| $CH_3$ deformation | 1461–1462 | 1465 | 1464 |

[a] Assignment taken from Ref. (21).

[b] This work, range of values given from adsorption of $CH_3X$ ($X = Cl$, Br, and I) on $Cu/SiO_2$.

[c] This work, from methanol adsorption on $SiO_2$.

[d] Ref. (22).

[e] $SiOCD_3$ values are given in parentheses.

[f] sh, shoulder.

(21, 22). Because $CH_3I$, $CH_3Br$, and $CH_3Cl$ do not react directly with silica under the conditions used in this study and because the intensity of these bands is dependent on metal loading, it is concluded that the C–X bond in adsorbed $CH_3X$ is activated on the surface of the Cu particles. Subsequently, or concurrently, methyl groups migrate or "spillover" to the silica support where they react with SiOH groups to form $SiOCH_3$ groups.

### 2. *Proposed Mechanisms for Spillover of Methyl*

Spillover of atomic species such as hydrogen and oxygen after dissociative adsorption of the molecular species is a well documented phenomenon. However, the migration or "spillover" of alkyl fragments is not well studied. Spillover is a process which involves the transport of an active species formed on one surface to another which, under the same conditions, does not form the active species (9). The most studied system is that of hydrogen spillover (4–6). For example, dissociative adsorption of $D_2$ on supported rhodium particles results in D atoms formed on the rhodium surface which then spillover onto the alumina support where they react with hydroxyl groups to form Al–OD. The experimental evidence presented here supports a similar spillover mechanism where the methyl groups are formed on the copper surface from the dissociative adsorption of $CH_3X$. The methyl groups then migrate onto the silica support where they react with the silanol groups to form $SiOCH_3$. A pictorial representation of this process is shown in Fig. 8.

The plot of the integrated area of the deuterated absorption bands as a function of time displays a saturation of the spillover product (see Fig. 4). By taking the integrated area of hydroxyl groups on the silica surface before and after adsorption from a number of experiments, we estimate that approximately 5–10% of the total available silanol groups have been consumed when the spillover bands, from $CH_3I$ reaction at room temperature, have been saturated. This shows that the diffusion of methyl groups on the silica surface is limited in range and only occurs in close proximity to the copper particles. We estimate that at saturation, on the order of 25 hydroxyl groups have reacted per copper particle (23).

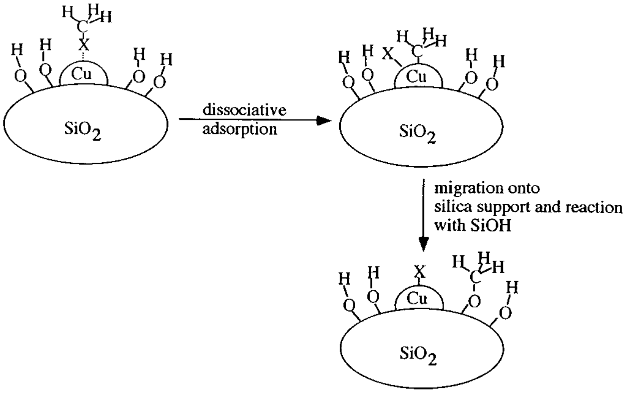

**FIG. 8.** A pictorial representation of methyl spillover on a Cu/$SiO_2$ catalyst from $CH_3X$ dissociation is shown. First, the C–$X$ bond in adsorbed $CH_3X$ is activated on the Cu particles. After C–$X$ bond activation, some of the $CH_3$ groups can spillover onto the silica support where they react with nearby SiOH groups to form $SiOCH_3$.

There are several possible mechanisms for the reaction of methyl groups formed on the copper surface with silanol groups of the silica support. If homolytic bond cleavage is assumed, the enthaply change for these reactions can be estimated from theoretical and experimental bond dissociation energies (BDEs) (24–27).

$$\mathrm{SiOH + Cu{-}CH_3 \rightarrow SiOCH_3 + \tfrac{1}{2}H_2 + Cu} \quad [2]$$

$$\mathrm{SiOH + Cu{-}CH_3 \rightarrow SiOCH_3 + Cu{-}H} \quad [3]$$

$$\mathrm{2SiOH + 2Cu{-}CH_3 \rightarrow SiOCH_3 + H_2O + SiCH_3 + 2Cu} \quad [4]$$

$$\mathrm{2SiOH + Cu{-}CH_3 \rightarrow SiOCH_3 + H_2O + Cu} + {-}^{*}, \quad [5]$$

where — * denotes an activated site.

$$\mathrm{CH_3\cdot + SiOH \rightarrow CH_{4(g)} + SiO\cdot} \quad [6a]$$

$$\mathrm{Cu{-}CH_3 + SiO\cdot \rightarrow Cu + SiOCH_3}. \quad [6b]$$

Reaction [2] is estimated to be slightly endothermic, whereas Reaction [3] is estimated to be thermoneutral. Reaction [4] is exothermic by over 100 kcal/mol. Reaction [5] is analogous to a reaction proposed for hydrogen spillover. Because the nature of the activated site is unknown, we are unable to determine the enthalpy change for Reaction [5]. Reaction [6] is estimated to be highly exothermic. Because model compounds and surface complexes were used for BDEs, the calculated values should only be viewed as rough estimates of the enthaply change. Spillover can be either an endothermic or an exothermic process because entropic factors are also important in these reactions (9).

If the spillover reaction proceeds through Reaction [2] we would expect to observe gaseous $H_2$. Obviously, gaseous $H_2$ cannot be observed with IR spectroscopy. Experiments were performed using a quadrupole mass spectrometer but, unfortunately, the results were found inconclusive in determining if the slight rise in the $H_2$ signal was actually from the spillover reaction or from a rise in the background pressure of $H_2$ in the vacuum chamber. Reactions [3]–[5] may be ruled out based on the fact that there is no evidence in the infrared for the formation of water, Cu–H or Si–$CH_3$. Although the Cu–H stretch, if present, may be too weak for us to detect.

Mechanism [6] is that for a reaction of a methyl radical to form gaseous $CH_4$ and $SiOCH_3$. In a previous paper we had stated that there was no evidence for methane formation after the room-temperature adsorption of methyl iodide (16). We have recently done these same experiments using larger amounts of sample where in fact some gas-phase methane was observed in the infrared spectrum recorded after methyl iodide adsorption at 298 K. These data could be interpreted to confirm the mechanism shown in Reactions [6a] and [6b]. Methyl radicals that are not thermally accommodated with the surface have been observed to evolve during C–I bond dissociation in adsorbed $CH_3I$ on single-crystal copper surfaces (28). Another alternative explanation for the formation of $SiOCH_3$ involves the activation of OH groups that are in close proximity to the copper particles, in which case methyl iodide would react directly with these activated silanol groups. These two possibilities, gas-phase methyl radical reactions and activated OH groups, are not consistent with the results of experiments done on oxidized $Cu/SiO_2$ samples (29). For reaction of $CH_3I$ with oxidized $Cu/SiO_2$, there is no formation of $SiOCH_3$. Methoxy and bidenate formate bonded directly to the copper surface are the two predominant reaction products formed. This suggests that methyl spillover is inhibited by the presence of adsorbed oxygen on the copper surface. Methoxy and bidenate formate are stabilized on the Cu particles, relative to $CH_3$, and do not spillover onto the silica support. All of the data taken together suggest that Reaction [2] is most likely occurring.

## CONCLUSIONS

The results and conclusions of this study are summarized below.

1. $CH_3I$, $CH_3Br$, and $CH_3Cl$ react with $Cu/SiO_2$ to form similar reaction products, one of them being $SiOCH_3$. The other species being $CH_3$ adsorbed on the Cu particles.

2. Reaction of $CH_3I$ (at 298 K), $CH_3Br$ (at 348 K), and $CH_3Cl$ (at 398 K) does not occur directly with silica but occurs only in the presence of copper particles at these temperatures, suggesting that some type of spillover mechanism is operative.

3. The nature of the copper salt precursor (nitrate or acetate) does not appear to be important in these reactions nor does lowering the metal loading (except to decrease the amount of product formed).

4. The copper particle surfaces are of an atomically rough morphology, although the role of morphology in these reactions is not entirely clear.

5. Reaction of $CH_3$ is limited to hydroxyl groups in close proximity to the copper particles. Removal of hydroxyl groups by heating or reaction results in no spillover product formation.

6. As discussed here, different sample pretreatment gives rise to varying amounts of spillover product, $SiOCH_3$. Therefore, due to the variety of processing procedures for oxide-supported copper catalysts, the results of this study suggest that spillover of methyl groups on oxide-supported Cu catalysts may or may not be limited to the preparation and reaction conditions employed in this study.

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