A Comprehensive Study of the Reactions of Methyl Fragments from Methyl Iodide Dissociation on Reduced and Oxidized Silica-Supported Copper Nanoparticles

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Abstract: Transmission infrared spectroscopy and temperature programmed desorption have been used to investigate the chemistry of CH_3I adsorbed on silica-supported copper nanoparticles. The following three factors affect the chemistry of CH_3I on Cu/SiO_2: (i) the oxidation state of the copper, (ii) the hydroxyl group coverage on the silica support, and (iii) the surface roughness of the copper particles. These three factors can be controlled by sample preparation. On reduced-Cu/SiO_2 samples, C−I bond dissociation in adsorbed methyl iodide results in the formation of adsorbed methyl groups on the copper surface. The frequency of the symmetric stretch of adsorbed methyl groups is at 2913 cm^{-1} for copper nanoparticles with atomically smooth surface morphology and at 2924 cm^{-1} for copper nanoparticles with atomically rough surface morphology. In addition to methyl groups adsorbed on the copper nanoparticles, for reduced Cu/SiO_2 samples with Si−OH groups present in close proximity to the copper particles, methyl groups can spill over on to the silica support and react with OH groups to form $SiOCH_3$. The silica hydroxyl coverage also plays a role in methyl reactions on the copper particles as hydroxyl groups provide a source of hydrogen atoms. Methane and ethane are the predominant reaction products for reduced Cu/SiO_2 samples with high hydroxyl group coverage whereas methane, ethane, and ethylene form on samples with low silica hydroxyl group coverage. The copper particle morphology may also play a role in the chemistry of adsorbed methyl groups as there is some evidence for slower methyl reaction kinetics on the copper nanoparticles with rough surface morphology. C−I bond dissociation in adsorbed methyl iodide occurs on oxidized-copper nanoparticles as well. The infrared spectrum taken after adsorption of CH_3I on oxidized-Cu/SiO_2 is consistent with the presence of adsorbed methoxy groups and bidentate formate on the oxidized-copper particles. The chemistry of methyl groups on oxidized-copper particles is similar to that of methanol on oxidized-copper particles. Finally, the use and complexities of characterizing these samples and copper catalysts in general with CO adsorption in conjunction with infrared spectroscopy are discussed.

Introduction

The chemistry of composite systems can be quite complex and often it is not easy to delineate the factors that affect the chemistry of these systems. Oxide-supported metal catalysts are such systems that are not easily understood because both the oxide support and the metal particles can be involved in the chemistry.[1−4] In this study, the surface chemistry of copper nanoparticles supported on silica has been examined. Because copper catalysts are the basis for several modern industrial processes, there is a great deal of interest in them. Methanol synthesis and hydrocarbon coupling reactions are two important examples of copper catalyzed processes which are still not fully understood.[5−12] Several studies have been reported on the

details of the adsorption and decomposition of methanol on model copper catalysts in an attempt to characterize the surface reaction mechanisms which form methanol from CO and H_2.[13−15] Other studies have examined the adsorption of alkyl fragments on single crystal copper surfaces in order to gain insight into Fischer−Tropsch processes and other catalyzed coupling reactions.[16−18]

As is evident in the literature, the results obtained on high surface area copper catalysts vary greatly depending upon sample preparation methods and processing conditions.[19−21] In this study, we will show that the chemistry of Cu/SiO_2 exhibits both similarities and differences compared to single crystal copper surfaces and that sample preparation plays an important role in the surface chemistry of Cu/SiO_2. The following three factors affect the chemistry of the simplest C_1 hydrocarbon fragment, methyl, on Cu/SiO_2 samples: (i) the oxidation state

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of the copper, (ii) the hydroxyl group coverage on the silica support, and (iii) the surface roughness of the copper particles.

Methyl iodide is used as the precursor for the formation of adsorbed methyl groups in this study. In general, it has been previously shown that adsorbed alkyl groups can be produced on single crystal metal surfaces under ultrahigh vacuum conditions[22–24] through the thermal or photochemical dissociation of an alkyl halide precursor (eq 1).

$$RX(a) \rightarrow R(a) + X(a) \qquad (X = Cl, Br, or I) \qquad (1)$$
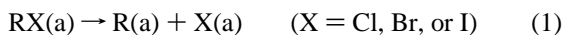
In the past ten years, studies of the surface chemistry of these fragments have led to a better understanding of how alkyl fragments bond and react on clean single crystal metal surfaces.[25] As there is great interest in the selective partial oxidation of alkyl groups through reaction with adsorbed oxygen on metal surfaces,[26–29] there have also been several recent studies on the reactions of alkyl groups and adsorbed oxygen. Bol and Friend have shown that both ethyl and 2-propyl iodide can react with an oxygen covered rhodium surface to selectively afford oxygenated hydrocarbon fragments.[26] Among the several products reported, acetaldehyde from ethyl iodide and acetone from 2-propyl iodide were formed when reacted with surface oxygen. Bol and Friend[27] and separately Solymosi and co-workers[28] have investigated the partial oxidation of CH_2 groups, formed from the dissociative adsorption of diiodomethane to produce formaldehyde on an oxygen covered Rh(111) surface. Zhou et al. have also reported the oxidation of adsorbed methylene to produce formaldehyde on a Pt(111) crystal using chloroiodomethane as a methylene precursor.[29] Despite the large number of studies concerning alkyl fragment adsorption on single crystal metals, and the vast literature on hydrocarbon adsorption on supported metal catalysts, there have been very few which have examined the adsorption of alkyl fragments on supported metal catalysts.[3,4,30–34]

In this study, the adsorption and reaction chemistry of methyl groups, from methyl iodide dissociation, on Cu/SiO_2 samples have been investigated with transmission infrared spectroscopy in conjunction with temperature programmed desorption (TPD). As discussed above, reaction of methyl fragments from methyl iodide dissociation on Cu/SiO_2 is dependent upon the sample preparation conditions employed. Although Cu/SiO_2 catalysts have been known to be difficult to characterize, we will use both the frequency of the IR absorption band of adsorbed CO on the copper particle surface and the products formed from CO adsorption to deduce the surface morphology and oxidation state of the copper particles. TEM measurements are also used to determine particle size. The information obtained from the sample characterization will be used to aid in the interpretation of the subsequent reactivity of Cu/SiO_2 samples prepared under different conditions.

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Experimental Section

The IR experiments described here were performed in an infrared cell which has been described previously.[35,36] The cell consists of a 2.75-in. stainless steel cube with two differentially pumped barium fluoride windows and a sample holder through which thermocouple and power feedthroughs are connected to a tungsten sample grid. The temperature is monitored by spot welding thermocouple wires to the top of the sample grid. The sample holder design is such that the sample may be cooled to near liquid nitrogen temperatures and heated resistively up to 1300 K. The cell is attached to an all stainless steel vacuum chamber through a 2-ft bellows hose. The vacuum system is rough pumped using a turbomolecular pump and then pumped with an 80 L/s ion pump.

Samples are made by spraying a slurry of copper(II) nitrate trihydrate (Strem Chemicals, 99.999%) and silica (Cabosil, M-5, 200 m^2/g) suspended in acetone and water onto a tungsten grid (Buckbee-Mears). A template is used to mask one half of the tungsten grid, allowing one side to be coated with Cu/SiO_2, and the other side is either left blank (for detecting gas-phase species) or coated with pure silica (to monitor the reactions of the silica support without the presence of the metal particles). Metal loadings on the order of 15% by weight are typically used in these experiments. The copper surface area is approximately 13% of the total catalyst surface area.

After the sample is prepared, it is mounted inside of the infrared cell, wrapped in heating tape, and processed using one of three methods. The three different processing procedures will be denoted as reduced-Cu/SiO_2(473 K), reduced-Cu/SiO_2(673 K), and oxidized-Cu/SiO_2 throughout the manuscript. The reduced-Cu/SiO_2(473 K) and reduced-Cu/SiO_2(673 K) are samples that have been reduced under different conditions. The processing for all three samples begins with a 12 h, 473 K bakeout. The copper is then reduced with hydrogen. Hydrogen (Air Products, Research Grade) is introduced into the sample cell in 400-Torr quantities for 15 min followed by a 15-min evacuation. Hydrogen is introduced for increasingly longer periods of time (30, 60, and then 120 min), and each reduction period is followed by a 15-min evacuation. Following this initial reduction, the samples are then oxidized in 100 Torr of oxygen for 10 min followed by evacuation and a 30-min reduction in hydrogen. This oxidation/reduction cycle is repeated if necessary to remove residual organics. Nothing further is done for the reduced-Cu/SiO_2(473 K) sample but preparation of the reduced-Cu/SiO_2(673 K) sample continues from this point. The reduced-Cu/SiO_2(673 K) sample is then resistively heated to 673 K in the presence of 400 Torr of hydrogen for periods of 12 h or longer until the IR frequency of adsorbed CO is near 2100 cm^{-1}. Preparation of oxidized-Cu/SiO_2 samples follow the exact same procedure as for the reduced-Cu/SiO_2(473 K) samples; however, after the last reduction the sample is then oxidized in 5 Torr of oxygen at 473 K for 120 min.

After processing, the IR cell is placed on a linear translator inside the spectrometer sample compartment. Either the Cu/SiO_2 or the SiO_2 (or blank) can be translated into the infrared beam for data acquisition. This design enables us to examine the chemistry of both Cu/SiO_2 and SiO_2 (or gas-phase species) during the course of a particular experiment. A Mattson RS-1 FT-IR spectrometer equipped with a narrow-band MCT detector was used for the infrared measurements. Spectra were recorded by averaging 1000 scans at an instrument resolution of 4 cm^{-1}. Absorbance spectra shown represent single beam spectra referenced to the appropriate single beam spectrum of the Cu/SiO_2 or SiO_2 sample prior to reaction. The transmission range of SiO_2 goes down to approximately 1300 cm^{-1}.

TPD experiments were performed in a high vacuum chamber which consists of a 400 L/s ion pump, sample cell, and quadrupole mass spectrometer (DetecTorr II, UTI Instruments). The temperature was ramped by interfacing a programmable power supply to a PC. A heating rate of 1 K/s was used. A maximum of twelve different masses were monitored simultaneously. The TPD data have been corrected for fragmentation of other species using the cracking fragmentation

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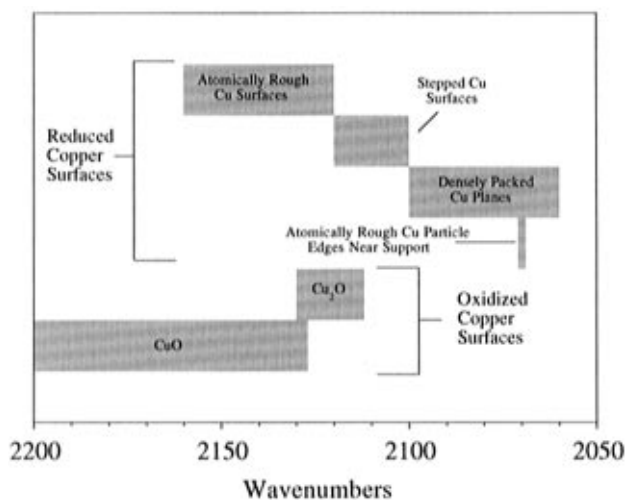
Figure 1. A compilation of the wide range of values reported in the literature for the frequency and assignment of CO adsorbed on various copper surfaces that differ in surface morphology and oxidation state. There is significant overlap in the frequency range for CO adsorbed on reduced and oxidized copper making it difficult to use the frequency of the CO absorption band as the only measure of the oxidation state of the copper surface atoms. See text for further discussion.

patterns given in ref 37. After introduction of high pressures (approximately 15 Torr) of CH_3I in the sample cell, the cell was pumped with a turbomolecular pump for 2 h before opening the valve to the mass spectrometer chamber and acquiring TPD data.

CH_3I (Aldrich Chemical Co.) and CD_3I (Cambridge Isotopes Laboratories) both had a purity of 99.5%. CH_3I and CD_3I were transferred into glass sample bulbs and subjected to several freeze−pump−thaw cycles prior to use. CH_3OH (EM Science, 99.8%) was also transferred into a glass sample bulb and subjected to several freeze−pump−thaw cycles prior to use. CO was obtained from Matheson Gas Products and used as received with a purity of 99.99%.

Results

Catalyst Characterization. The characterization of oxide-supported metal catalysts remains a challenge, especially for oxide-supported copper catalysts. The methods traditionally used by surface scientists are not usually adaptable to these catalysts or the environment in which they are studied. Adsorption of CO is one of the most widely used methods of characterizing the oxidation state of Cu/SiO_2 catalysts because of its ease and adaptability for making in-situ measurements. However, there is a considerable amount of controversy in the literature concerning the assignment of the CO stretch in adsorbed CO on the surface of copper in its three oxidation states: Cu(0)−Cu metal, Cu(I)−Cu_2O, and Cu(II)−CuO.[38−47] In addition to the great variance in values for the CO frequency of CO adsorbed on oxidized and reduced copper, it has also been observed that the frequency of adsorbed CO is highly sensitive to surface structure.[38,39] Figure 1 displays a compilation of band frequencies and assignments from the literature for CO adsorbed on different copper surfaces.[38−47] It is fairly

Figure 2. The infrared spectra of CO adsorbed on (a) reduced-Cu/SiO_2(673 K), (b) reduced-Cu/SiO_2(473 K), and (c) oxidized-Cu/SiO_2 in the presence of an equilibrium pressure of CO (7.8 Torr). Gas-phase contributions have been subtracted from the spectra shown above.

well agreed upon that IR bands between ∼2065 and 2110 cm^{-1} are indicative of CO adsorbed on reduced copper particles.[38−42,46,47] However, the region between 2110 and 2200 cm^{-1} is not as clearly defined. In some cases, bands in the 2115−2130 cm^{-1} region have been assigned to CO adsorbed on Cu_2O/SiO_2 [38,40,42] and bands in the 2125−2200 cm^{-1} region to CO adsorbed on CuO/SiO_2.[39,42−46] In other cases, bands near 2130 cm^{-1} have been assigned to CO adsorbed on atomically rough, reduced-copper particles.[38,39] It has also been suggested that it is not the location of the CO absorption band which is the critical factor, but the stability of the species under vacuum at room temperature and the formation of CO_2 or surface carbonate from reaction with surface oxygen which indicates whether the sample is oxidized or reduced.[39,42]

Here we characterize the three different Cu/SiO_2 catalysts prepared in this study using CO adsorption in conjunction with infrared spectroscopy. Three criteria are considered in characterizing these samples: i) the frequency of the CO absorption band, (ii) the stability of the species under vacuum (on reduced samples CO readily desorbs upon evacuation whereas on oxidized samples it does not),[39] and (iii) whether or not there is formation of CO_2 and/or surface carbonate from CO adsorption. The adsorption of CO was done by introducing CO into the infrared cell at 298 K and a spectrum was taken for both the SiO_2 and Cu/SiO_2 halves of the sample ($P_{equilibrium} = 7.8$ Torr). Since CO does not adsorb to any appreciable extent on SiO_2 under these conditions, the spectrum taken of the SiO_2 sample represents gas-phase CO. The gas-phase spectrum is then subtracted from the Cu/SiO_2 spectrum to yield a difference spectrum which shows the infrared spectrum of CO adsorbed on the surface of the copper particles.

After room temperature adsorption of CO on reduced-Cu/SiO_2(673 K), the sample that is reduced for many hours at 673 K, the IR spectrum exhibits an asymmetric absorption band with a peak near 2100 cm^{-1} and a shoulder near 2074 cm^{-1} (see Figure 2). Upon evacuation this band decreases in intensity

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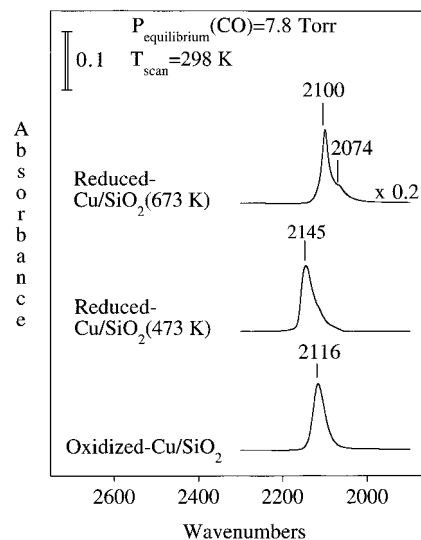
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and after 20 min has lost more than 99% of its intensity. There is an additional band (very weak) observed after evacuation near 2000 cm^{-1}, which we have been unable to assign. The bands near 2100 and 2074 cm^{-1} are clearly assigned in the literature to fully reduced copper surfaces.[38−42,46,47] We therefore conclude that this sample is indeed reduced copper and the surface is of an atomically smooth morphology consisting of Cu(111) and Cu(100) planes.

After room temperature adsorption of CO on reduced-Cu/SiO$_2$(473 K), the infrared spectrum exhibits an asymmetric absorption band near 2145 cm^{-1}. After 5 min under vacuum this band disappears to a negligible intensity (<0.25% of original band). The frequency of this band falls into the frequency range for CO adsorbed on CuO/SiO$_2$ or atomically rough but reduced Cu/SiO$_2$ as discussed above and shown in Figure 1. Because there is no formation of CO$_2$ or surface carbonate and the CO was easily removed upon evacuation of the gas phase, we conclude that the copper is reduced and therefore assign the 2145-cm^{-1} band to CO adsorbed on reduced but atomically rough copper particles.

The absorption band observed in the IR spectrum of CO adsorbed on oxidized-Cu/SiO$_2$ is symmetric with a maximum near 2116 cm^{-1} (Figure 2). Gas-phase carbon dioxide was also observed after introduction of CO into the sample cell. Upon evacuation of the gas phase, the CO absorption band shifted to 2108 cm^{-1} and an additional, weak band became apparent in the spectrum near 1986 cm^{-1}. The integrated area of the CO absorption band decreased by 60% from its original value after evacuation for 5 min and 75% after 60 min. The frequency of the 2116-cm^{-1} band is low for oxidized copper, but it is close to the band observed near 2118 cm^{-1} by Millar, Rochester, and Waugh after the surface oxidation of Cu/SiO$_2$ using N$_2$O to form Cu$_2$O/SiO$_2$.[39] In addition, those samples oxidized with N$_2$O form gaseous CO$_2$ upon reaction with CO and the CO remains present for longer periods of time on the copper surface after evacuation of the gas phase. Therefore, the band at 2116 cm^{-1} is assigned to CO adsorbed on oxidized copper, most probably Cu$_2$O/SiO$_2$.

Transmission electron micrographs were taken of the Cu/SiO$_2$ samples using a Hitachi H-600 electron microscope operating at an acceleration voltage of 100 kV. The particles of these samples were found to have diameters between 2 and 5 nm. For reduced-Cu/SiO$_2$(673 K) samples, the copper particles ranged in size from 3 to 5 nm in diameter. The average diameter, obtained from a sampling of 50 particles, was 3.7 nm. For reduced-Cu/SiO$_2$ (473 K) samples, the copper particles ranged in size from 2 to 5 nm in diameter and the average diameter was 3.4 nm.

In summary, these three samples—reduced-Cu/SiO$_2$(673 K), reduced-Cu/SiO$_2$(473 K), and oxidized-Cu/SiO$_2$—are composed of copper nanoparticles between 2 and 5 nm in diameter. The samples reduced in H$_2$ for long times and at high temperatures, reduced-Cu/SiO$_2$(673 K) samples, consist of Cu nanoparticles that are reduced and have surfaces that are atomically smooth consisting of (111) and (100) planes. Reduced-Cu/SiO$_2$(473 K) samples consist of Cu nanoparticles that are reduced and have surfaces that are atomically rough. Oxidized-Cu/SiO$_2$ samples are oxidized surfaces with a surface stoichiometry of Cu$_2$O; the surface morphology of these samples is unknown.

Room Temperature Adsorption of CH$_3$I on Reduced-Cu/SiO$_2$(673 K), Reduced-Cu/SiO$_2$(473 K), and Oxidized-Cu/SiO$_2$. The infrared spectra shown in Figure 3 were recorded for four different samples—(a) SiO$_2$, (b) reduced-Cu/SiO$_2$(673 K), (c) reduced-Cu/SiO$_2$(473 K), and (d) oxidized-Cu/SiO$_2$—after 15 Torr of CH$_3$I had been introduced into the infrared cell for
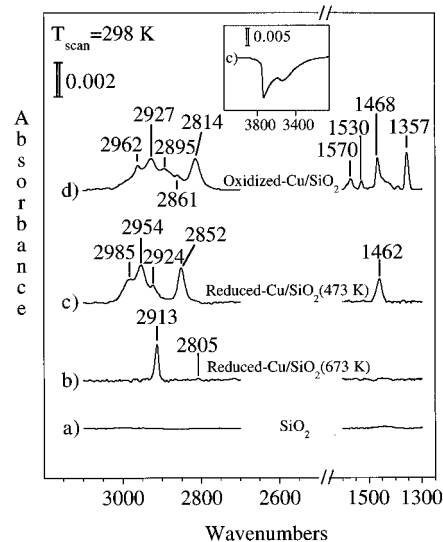
Figure 3. Infrared spectra taken after the adsorption of 15.0 Torr of CH$_3$I for 1 h on (a) SiO$_2$, (b) reduced-Cu/SiO$_2$(673 K), (c) reduced-Cu/SiO$_2$(473 K), and (d) oxidized-Cu/SiO$_2$. The infrared cell was evacuated for 5 min prior to recording each spectrum. The OH stretching region for the spectrum labeled c is shown in the inset. The negative feature shown in the inset indicates there is a decrease in SiOH groups upon adsorption of CH$_3$I on reduced-Cu/SiO$_2$(473 K).

approximately 1 h at room temperature followed by evacuation. It has been previously shown that the surface becomes saturated with surface-bound reaction products after reaction times of approximately 1 h.[3] It is obvious upon initial inspection that each of the three different copper samples exhibits the formation of unique products on the catalyst surface after the room temperature adsorption of methyl iodide. It is also clear that pure silica does not react with CH$_3$I under these conditions as there are no new absorptions after exposure of CH$_3$I to SiO$_2$ (Figure 3a). Therefore, it can be concluded that the adsorption of CH$_3$I on each of the three samples is a result of the presence of the copper particles.

The spectrum taken after methyl iodide adsorption on the reduced-Cu/SiO$_2$(673 K) sample (Figure 3b) is characterized by absorption bands in the C−H stretching region near 2913 and 2805 cm^{-1}. Both the reduced-Cu/SiO$_2$(473 K) (Figure 3c) and the oxidized-Cu/SiO$_2$ (Figure 3d) spectra contain multiple bands in the C−H stretching region, although the frequencies of the bands and the intensity patterns are quite distinct between the two samples. The reduced-Cu/SiO$_2$(473 K) spectrum (Figure 3c) exhibits absorption bands in the region between 2800 and 3000 cm^{-1} near 2985, 2954, 2924, and 2852 cm^{-1} and one in the C−H deformation region near 1462 cm^{-1}. The inset in Figure 3 displays a loss in the OH stretching region for the SiOH groups after reaction with CH$_3$I, indicating consumption of OH groups during adsorption of CH$_3$I onto reduced-Cu/SiO$_2$-(473 K). The oxidized-Cu/SiO$_2$ spectrum (Figure 3d) exhibits infrared bands near 2962, 2927, 2895, 2861, and 2814 cm^{-1} in the C−H stretching region. Several bands are also observed for the oxidized-Cu/SiO$_2$ sample in the region extending from 1300 to 1600 cm^{-1} with frequencies of 1584, 1570, 1530, 1468, 1446, 1428, 1388, and 1357 cm^{-1}. The 1584-, 1446-, 1428-, and 1388-cm^{-1} bands are very weak and are not labeled in Figure 3d. Again, it is clear that different surface species form on each of the Cu/SiO$_2$ samples.
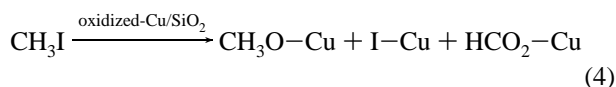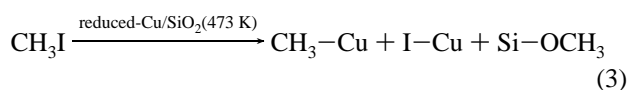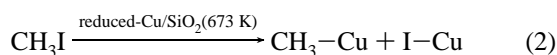
The data presented in the next two sections will show that the following reactions (eqs 2−4) take place upon room temperature adsorption of CH$_3$I on reduced-Cu/SiO$_2$(673 K), reduced-Cu/SiO$_2$(473 K), and oxidized-Cu/SiO$_2$ to yield dif-

Table 1. Vibrational Assignment of Surface Species Formed from Reaction of CH₃I on Silica-Supported Copper

I. Methyl Adsorbed on Copper

mode description[a]	Cu/SiO₂(673 K)[b]	Cu/SiO₂(473 K)[b]	Cu(100)[c]	Cu(111)[d]	Pt(111)[e]
$\nu_s(CH_3)$	2913	2924	2915	2835	2879
$\nu(CH)$	2805		2760		
$\delta_a(CH_3)$			1430		
$\delta_s(CH_3)$			1150	1200	

II. Methyl Adsorbed on Silica-SiOCH₃

mode description[f]	spillover[b]	CH₃OH−SiO₂[g]	CH₃OH−SiO₂[h]
$\nu_a(CH_3)$	2985	2998	3000
$\nu_a(CH_3)$	2954	2961	2958
overtone or combination band	2930 (sh)[i]	2930 (sh)	2928 (sh)
$\nu_s(CH_3)$	2852	2860	2858
$\delta(CH_3)$	1462	1465	1464

III. Methoxide Adsorbed on Copper

mode description[j]	Cu/SiO₂[b]	Cu/SiO₂[k]	Cu/SiO₂[l]	Cu(100)[m]	Cu(110)[n]
$\nu_{as}(CH_3)$	2927	2920	2930	2901	2940
$\nu_{as}(CH_3)$	2895	2880		2861	
$\nu_s(CH_3)$	2814	2824	2821	2787	2840
$\delta(CH_3)$	1468		1443		1460

IV. Formate Adsorbed on Copper

mode description[o]	Cu/SiO₂[b]	Cu/SiO₂[p]	Cu/SiO₂[q]	Cu(110)[r]	sodium formate[s]
combination band $[\nu_{as}(COO) + \delta(CH)]$	2958	2936	2935	2960	2953
$\nu_s(CH)$	2867	2856	2851	2920	2841
combination band $[\nu_s(COO) + \delta(CH)]$	2718[t]				2720
$\nu_{as}(COO)$	1564	1579	1553	1560	1567
$\delta(CH)$	1369				1377
$\nu_s(COO)$	1360	1358	1351	1360	1366

[a] Mode description taken from refs 18 and 48. [b] This work. [c] Reference 18. [d] Reference 48. [e] Reference 49. [f] Mode description taken from ref 52. [g] This work—from methanol adsorption on SiO₂. [h] Reference 51. [i] sh = shoulder. [j] Mode description taken from refs 53 and 54. [k] Reference 13. [l] Reference 14. [m] Reference 53. [n] Reference 54. [o] Mode description taken from ref 55. [p] Reference 56. [q] Reference 11. [r] Reference 54. [s] Reference 57. [t] Only observed at high coverages.

ferent surface-bound products.

$$CH_3I \xrightarrow{\text{reduced-Cu/SiO}_2(673 \text{ K})} CH_3-Cu + I-Cu \quad (2)$$

$$CH_3I \xrightarrow{\text{reduced-Cu/SiO}_2(473 \text{ K})} CH_3-Cu + I-Cu + Si-OCH_3 \quad (3)$$

$$CH_3I \xrightarrow{\text{oxidized-Cu/SiO}_2} CH_3O-Cu + I-Cu + HCO_2-Cu \quad (4)$$

These reactions of CH₃I to form adsorbed methyl groups on reduced copper particles (CH₃−Cu) and the silica support (SiOCH₃) and to form adsorbed oxygenates (CH₃O−Cu and HCO₂−Cu) on oxidized copper particles are discussed in detail below.

Identification of Surface Species on Reduced Cu/SiO₂ Sample. The spectrum recorded after reaction of CH₃I on reduced-Cu/SiO₂(673 K) is simple and consists of two bands with frequencies of 2913 (s) and 2805 (w) cm⁻¹. The simple spectrum suggests there is a single species adsorbed on the surface. The spectrum is not consistent with that of adsorbed methyl iodide which has infrared absorption bands near 3026, 2910, and 1420 cm⁻¹ when adsorbed on a metal surface.[48] The spectrum is more consistent with adsorbed methyl groups formed from the dissociation of the relatively weak C−I bond. The 2913-cm⁻¹ band is close in frequency to the C−H symmetric stretch of adsorbed methyl on Cu(100) (2915 cm⁻¹).[18] On Pt(111), the symmetric C−H stretch in adsorbed methyl has been reported near 2879 cm⁻¹.[49] The assignment of adsorbed methyl groups is given in Table 1. The weaker band at 2805

cm⁻¹ may be due to the symmetric C−H stretch of methyl fragments adsorbed on different sites or to an overtone of the asymmetric deformation mode.[24,49]

The spectrum obtained after reaction of CH₃I on reduced-Cu/SiO₂(473 K) (Figure 3c) is much more complex than the spectrum for reduced-Cu/SiO₂(673 K) (Figure 3b). This spectrum has been assigned previously to two different surface species, Cu−CH₃ and SiOCH₃[3,4] (see Table 1). The band near 2924 cm⁻¹ is assigned to methyl groups adsorbed on the surface of Cu particles with atomically rough morphology and is approximately 10 cm⁻¹ higher in frequency than that for methyl groups adsorbed on atomically smooth copper surfaces (Figure 3b). The remaining bands in the reduced-Cu/SiO₂(473 K) spectrum are assigned to SiOCH₃ groups formed from the reaction of methyl groups, from methyl spillover,[50] with surface hydroxyl groups. It has been previously shown that hydroxyl groups present near the Cu particles can react with methyl groups, from methyl spillover, to form SiOCH₃.[3,4] The identification of SiOCH₃ is made possible by forming this species through the reaction of methanol and silica.[51] The spectrum of SiOCH₃ from reaction of methanol with silica is shown in Figure 4a and the spectrum of reduced-Cu/SiO₂(473 K) after methyl iodide reaction is shown in Figure 4b. There is fairly good agreement between the frequencies and the intensity patterns observed in the two spectra shown in Figure 4 (a and b).

An important experiment that clearly demonstrated the role of silica hydroxyl groups in the chemistry of methyl iodide began with a reduced-Cu/SiO₂(473 K) sample that was then

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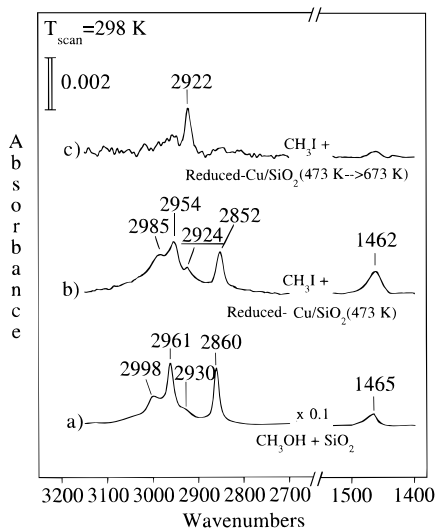
Figure 4. Infrared spectra of (a) SiO_2 after reaction of CH_3OH to form $SiOCH_3$ groups (b) reduced-Cu/SiO_2(473 K) after adsorption of methyl iodide for 1 h and subsequent evacuation. The two spectra labeled a and b are quite similar and indicate that $SiOCH_3$ is formed on reduced-Cu/SiO_2 samples from CH_3I adsorption. One difference between the two spectra is the band near 2924 cm^{-1} which is assigned to CH_3 adsorbed on the copper surface. The assignment of the 2924 cm^{-1} band is confirmed by the spectrum labeled c. The spectrum labeled c was taken following adsorption of CH_3I on a reduced-Cu/SiO_2(473 K) sample that had been heated to 673 K to decrease the coverage of SiOH groups on the support (this sample is denoted as reduced-Cu/SiO_2(473 K→673 K)). The IR data show that $SiOCH_3$ formation is dependent on the silica hydroxyl group coverage. The lone band in the spectrum at 2922 cm^{-1} is due to methyl fragments adsorbed on the copper surface. See text for further details.

heated to 673 K for 1 h under vacuum. This treatment affected the hydroxyl group coverage of the silica support. By integrating the area of the bands in the silica hydroxyl group region before and after heating to 673 K it is estimated that approximately 25% of the Si−OH groups have been removed due to heating. It should be noted that the frequency of adsorbed CO on the copper surface only shifted by 4 cm^{-1} from 2147 cm^{-1} before heating to 2143 cm^{-1} after heat treatment. This small shift in the adsorbed CO frequency demonstrates that the copper surface itself has not changed significantly after the 1 h heating process under vacuum, in contrast to the large change in surface morphology after heating to 673 K for 24 h, as previously discussed. After preparation of the Cu/SiO_2 sample as detailed above (denoted as reduced-Cu/SiO_2(473 K→673 K)), the sample was then exposed to 15.0 Torr of methyl iodide for a period of 1 h. Following evacuation, an infrared spectrum was taken, as shown in Figure 4c. As evidenced by the infrared absorption near 2922 cm^{-1}, only the Cu−CH_3 species is formed on these samples as is observed on reduced-Cu/SiO_2(673 K) samples. The conclusion drawn from these results is that heating to 673 K removes a portion of the SiOH groups but does not significantly change the surface of the copper particles and the adsorption of CH_3I and CH_3 on the Cu particles is the same. However, SiOH groups that play a role in adsorption of CH_3I on reduced-Cu/SiO_2(473 K), most probably those in close proximity to the metal particles, have been removed and do not participate in the reaction.

Identification of Surface Species on Oxidized Cu/SiO_2. Several of the infrared bands observed in the spectrum obtained

after room temperature reaction of CH_3I on an oxidized-Cu/SiO_2 sample (Figure 3d) correlate well with bands observed for methoxide (OCH_3) on copper surfaces, as has been discussed previously.[34] The bands at 2927, 2895, 2814, and 1468 cm^{-1} are assigned to methoxide adsorbed on the copper particles (see Table 1). It is well-known that methoxide can decompose to form surface formate.[13−15] A number of the bands that do not correlate with methoxide in the CH_3I-oxidized Cu/SiO_2 spectrum do match those of adsorbed formate. The bands at 2958, 2867, 2718, 1564, 1369, and 1360 cm^{-1} can be assigned by comparison with literature spectra to bidentate formate adsorbed on the copper particles. (The frequency and intensity pattern of these bands are coverage dependent. The highest coverage spectrum was used for the bidentate formate assignment—see spectrum labeled $T = 473$ K, Figure 9.)[15,55−58] The shoulder at 1584 cm^{-1} is near the 1583-cm^{-1} band observed for unidentate formate adsorbed on an oxidized Cu/SiO_2 catalyst.[59] Although distinct bands in the C−H stretching region for a unidentate formate species (2978 and 2904 cm^{-1}) are not observed, these bands could be easily obscured by the intense absorption bands for adsorbed methoxy and bidentate formate. A possible assignment for the shoulders observed at 1446 and 1428 cm^{-1} is that of the $\delta(CH_3)$ of methoxy groups adsorbed on different surface sites. In summary, the bands in the oxidized-Cu/SiO_2 spectrum have been identified as CH_3O−Cu (2927, 2895, 2814, and 1468 cm^{-1}) and HCOO−Cu (2958, 2867, 2718, 1564, 1369, and 1360 cm^{-1}).[34] The assignments of these bands are given in Table 1. The band at 1530 cm^{-1} does not correlate with any of the above species and is left unassigned.

Temperature-Dependent Infrared and TPD Results for CH_3I on Reduced Cu/SiO_2 Samples. The reaction chemistry of the surface species on reduced Cu/SiO_2 catalysts as a function of temperature was further investigated. Infrared experiments were done by heating the samples in increments of 50 K for 60 s then cooling the sample down to room temperature after which an infrared spectrum was recorded. During these experiments, the infrared cell containing the sample was isolated from the pumping system in order to observe the formation of gas-phase species. Complementary TPD data were collected in separate experiments.

After adsorption of CH_3I on the reduced-Cu/SiO_2(673 K) sample and subsequent evacuation of the gas phase, the sample was warmed to elevated temperatures as described above and then cooled to room temperature before a spectrum was taken. Figure 5 shows the temperature-dependent infrared data for a reduced-Cu/SiO_2(673 K) sample. As the data show, the bands near 2913 and 2805 cm^{-1} begin to decrease in intensity near 423 K and are completely gone by 473 K. Concomitant with the decrease in the 2913- and 2805-cm^{-1} bands is the growth of a band near 3017 cm^{-1}, which is characteristic of gas-phase methane (see inset, Figure 5). This reaction temperature near 423−473 K is also near the temperature where methyl fragments react to form methane, ethane, and ethylene on single crystal copper surfaces.[17,18,24,60]

The TPD data corroborate the infrared results. Figure 6 shows the TPD spectrum after reaction of reduced-Cu/SiO_2(673

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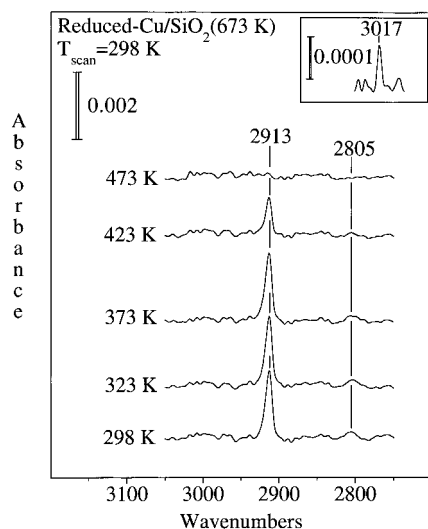
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Figure 5. Infrared spectra taken as a function of temperature after the adsorption of CH_3I on reduced-Cu/SiO₂(673 K). The 298 K spectrum is identical to the one shown in Figure 3b. The sample was then heated to the indicated temperatures and cooled down prior to recording a spectrum. The infrared cell was isolated from the pumping system so that gas-phase products from the desorption/decomposition could be monitored. The inset displays an expanded view of the spectrum labeled 473 K to show the presence of a band near 3017 cm^{-1}, which is assigned to gas-phase methane.
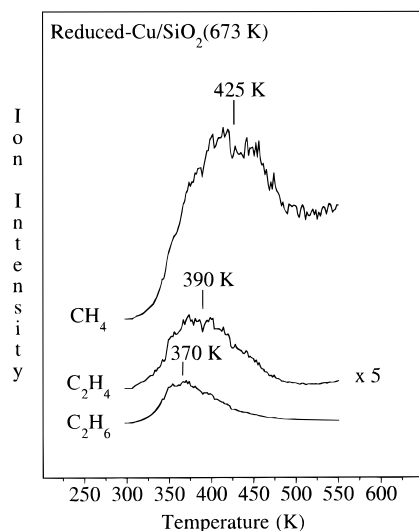
Figure 6. TPD following adsorption of CH_3I on reduced-Cu/SiO₂-(673 K) for 1 h. Three desorption products were detected in TPD: CH_4 (*m/e* 16), C_2H_4 (*m/e* 27), and C_2H_6 (*m/e* 30).

K) with CH_3I. There is a peak near 425 K for CH_4 (*m/e* 16) which is consistent with the temperature-dependent infrared data. In addition to methane, the TPD data show that both ethane (*m/e* 30) and ethylene (*m/e* 27) evolve from the sample near 370 and 390 K, respectively. The TPD data are nearly identical with the results obtained on single crystal copper surfaces.[17,18,24,60] Bent and co-workers have reported the reaction of methyl groups on copper single crystals to form methane, ethane, and ethylene. Methane desorbs with a desorption rate maximum near 450 K on Cu(111)[24] and 470 K on Cu(110)[60] and Cu(100).[18] Ethane desorbs with a desorption rate maximum near 400 K from Cu(110)[60] after adsorption of CH_3I and ethylene formation and desorption occurs near 470 K on Cu-(100).[18] White and co-workers observe similar desorption products from methyl reaction on polycrystalline Cu films.[61]
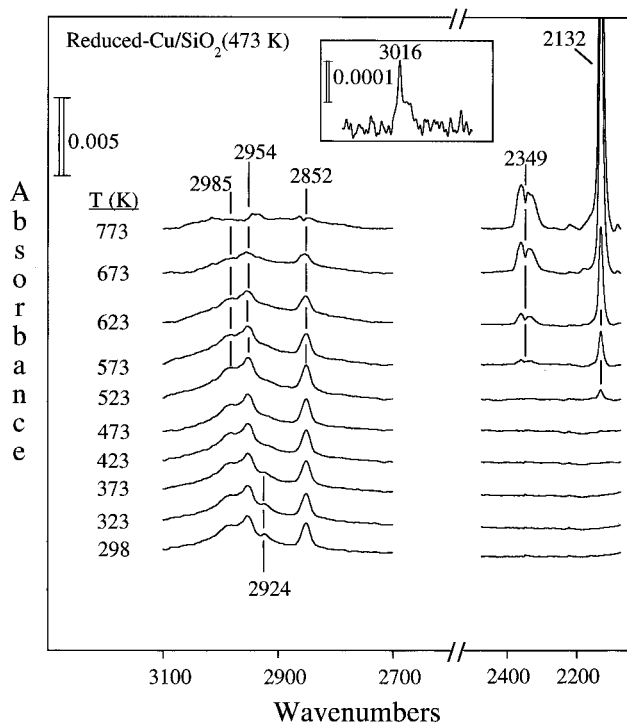

Figure 7. The temperature-dependent infrared spectra recorded after adsorption of CH_3I on reduced-Cu/SiO₂(473 K). The 298 K spectrum is identical to the one shown in Figure 3c. The sample was then heated to the indicated temperatures and cooled down prior to recording a spectrum. The infrared cell is isolated from the pumping system in order to monitor gas-phase products. The inset displays an expanded view of the spectrum labeled 773 K to show the band near 3016 cm^{-1}, which is associated with gas-phase methane.

Reduced-Cu/SiO₂(473 K) samples exhibit more complicated infrared and TPD spectra following methyl iodide adsorption. As discussed above, two surface species have been identified on reduced-Cu/SiO₂(473 K): methyl groups adsorbed on the copper particles and $SiOCH_3$ formed from methyl spillover. These two species differ in thermal stability. Figure 7 displays the temperature-dependent infrared spectra after reaction of CH_3I on reduced-Cu/SiO₂(473 K) at room temperature. As the data show, the band near 2924 cm^{-1} decreases in intensity as the temperature is raised to 423 K concomitant with the growth in a band near 3016 cm^{-1}, attributed to gas-phase methane (expanded spectrum shown in inset). The remaining bands are unaffected. The bands near 2985, 2954, and 2852 cm^{-1} begin to decrease near 573 K and do not fully disappear until 873 K (not shown). Gas-phase CO_2 (2349 cm^{-1}) and CO adsorbed on the copper surface (2132 cm^{-1}) grow in intensity as the temperature is raised above 473 K. These data further support the conclusion that there are two species present on the surface: one that is chemically similar to the species formed on reduced-Cu/SiO₂(673 K), i.e. Cu−CH₃, and one that remains on the surface to higher temperatures, i.e. $SiOCH_3$.

The TPD data corroborate the temperature-dependent infrared data. Figure 8 shows that two sets of TPD peaks are observed, those with desorption rate maxima below 550 K and those above 550 K. A TPD peak is evident at 440 K for methane (*m/e* 16) desorption and another peak is observed at 410 K for ethane (*m/e* 30) desorption. Methane and ethane evolution from reduced-Cu/SiO₂(473 K) have desorption rate maxima that are approximately 20−25 K higher than those observed for the reduced-Cu/SiO₂(673 K) samples. Importantly, there is no TPD

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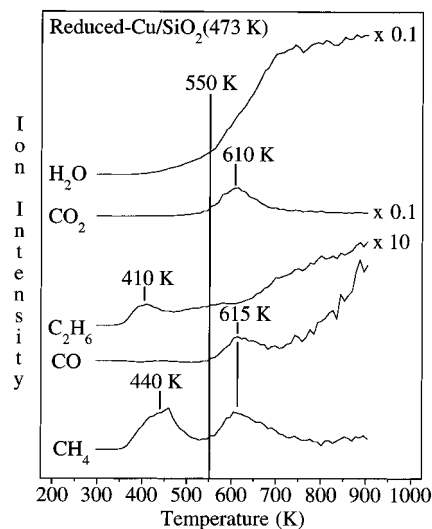
Figure 8. TPD following the adsorption of CH_3I on reduced-Cu/SiO$_2$-(473 K). Desorption peaks were seen in several mass channels including H$_2$O (*m/e* 18), CO$_2$ (*m/e* 44), C$_2$H$_6$ (*m/e* 30), CO (*m/e* 28) and CH$_4$ (*m/e* 16). Desorption peaks below 550 K are due to CH$_3$ reactions on the Cu particles. No desorption peaks were seen for C$_2$H$_4$ (*m/e* 27) (not shown). Desorption peaks above 550 K are due to the decomposition of SiOCH$_3$ groups.

peak for ethylene desorption from the reduced-Cu/SiO$_2$(473 K) sample (not shown) as there was for the reduced-Cu/SiO$_2$(673 K) sample.

TPD peaks evident above 550 K are due to the decomposition of SiOCH$_3$. Desorption of CH$_4$, CO and CO$_2$ occurs near 615 K. Characteristic IR bands for these species are observed in the temperature-dependent infrared spectra (see Figure 7). Water evolution (*m/e* 18) is also observed over a broad temperature range, as the silica support becomes dehydroxylated at higher temperatures.

Temperature-Dependent Infrared and TPD Results for CH$_3$I on Oxidized-Cu/SiO$_2$. After adsorption of methyl iodide on oxidized-Cu/SiO$_2$, a complex infrared spectrum is seen (Figure 3d) which is assigned to two adsorbed oxygenates on the copper surface: methoxide and bidentate formate. The temperature-dependent infrared data (Figure 9) show the formation and desorption of several species which have also been observed in the decomposition reaction of methanol on supported copper catalysts.[13-15] As the sample is heated between 298 and 473 K the bands near 2927, 2895, 2814, and 1468 cm^{-1} decrease in intensity concomitant with the growth of bands near 3538 (not shown), 2958, 2867, 2718, 1564, 1369, and 1360 cm^{-1}. Upon warming to 523 K, these bands decrease sharply as bands near 3608 (not shown), 1663, 1615, and 1429 cm^{-1} develop.

The hydrocarbon bands which grow in intensity between 323 and 473 K are attributed to bidentate formate (CH(O)$_2$) on the copper surface due to both the frequencies of the bands and the fact that they reach maximum intensity and then decrease sharply near temperatures where bidentate formate has been seen to decompose (>425 K) on oxidized Cu/SiO$_2$[13] and Cu(100).[62] The band which develops (along with the bidentate formate bands) at 3538 cm^{-1} is assigned to ν(OH) of Cu$-$OH.[63] The bands which have been attributed to unidentate formate either decrease or become obscured by the intense bidentate formate bands above 373 K.

Heating to 673 K evolved yet another band (not shown) near 1893 cm^{-1}. Also observed is the development and constant
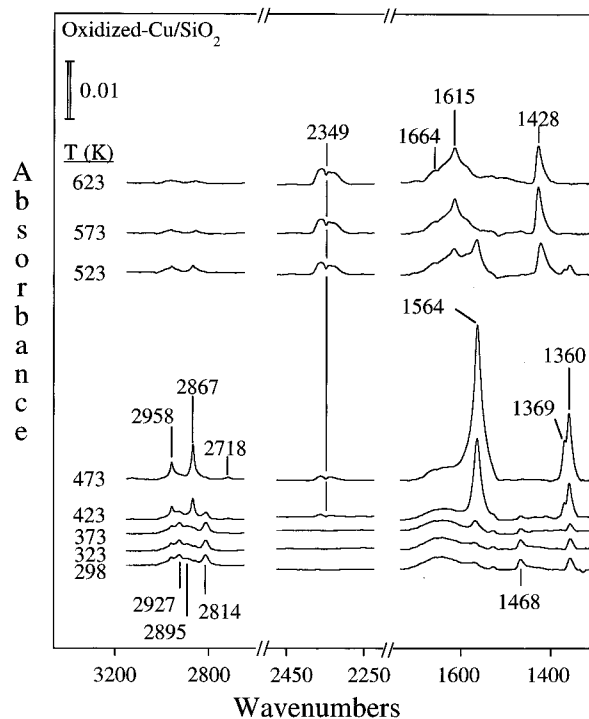
Figure 9. The temperature-dependent infrared spectra recorded after reaction of CH$_3$I on oxidized-Cu/SiO$_2$. The 298 K spectrum is identical to the one shown in Figure 3d. The sample was then heated to the indicated temperatures and cooled down prior to recording a spectrum. As in previous experiments, the infrared cell was isolated from the pumping system in order to observe gas-phase species produced upon heating of the sample.

growth in intensity of a band centered at 2349 cm^{-1} (gas-phase CO$_2$) after heating to 423 K and above. The bands formed at higher temperatures can be attributed to a combination of surface CO$_x$ species which are formed from the decomposition of adsorbed formate. Frequency ranges for adsorbed CO$_x$ species are as follows: bidentate carbonate (CO$_3$),[64] 1590$-$1630 and 1260$-$1270 cm^{-1}; carboxyl (CO$_2$),[65] [a] 1350$-$1420 and 1550$-$1630 cm^{-1}; organic-like carbonate (CO(O)$_2$),[64] 1870$-$1750 and 1250$-$1280 cm^{-1}; and bridged CO,[65b] 1700$-$1900 cm^{-1}. It is most likely that it is a CO$_2$ species which is responsible for the bands at 1625 and 1429 cm^{-1} in the spectrum recorded after heating to 623 K, since it is the initial dehydrogenation product of bidentate formate. Upon further heating, the adsorbed CO$_2$ may disproportionate to yield bridged CO and adsorbed CO$_3$. The 1893-cm^{-1} band cannot be firmly assigned to a specific CO$_x$ species since any other associated bands may be masked by silica absorptions (below 1300 cm^{-1}).

TPD results, presented in Figure 10, provide confirmation of the infrared results and the gas-phase species observed in the IR spectra. Three desorption peaks are evident in the spectrum. H$_2$O (*m/e* 18) and CO$_2$ (*m/e* 44) desorption occur over broad temperature ranges from 400 to 800 K and 500 to 700 K, respectively. Formaldehyde, which was not detected in the IR data, desorbs with a desorption rate maximum of 450 K.[66] Formaldehyde is a product in methanol decomposition on copper surfaces as well.[13]

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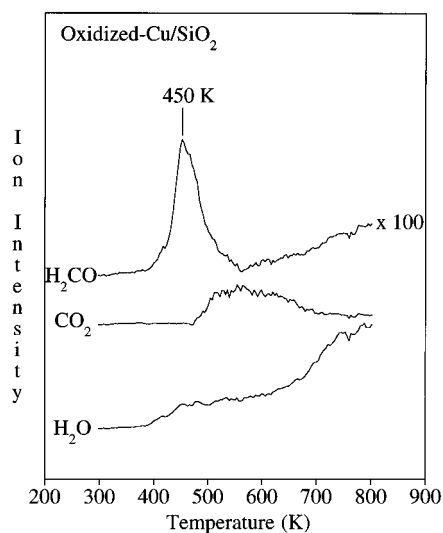(65) Davydov, A. A. *Infrared Spectroscopy of Adsorbed Species on the Surface of Transition Metal Oxides*; Wiley and Sons: Chichester, 1990; (a) p 38, (b) p 118.
(66) Although formaldehyde has the same mass as ethane (*m/e* 30), the observed fragmentation pattern for this peak is only consistent with formaldehyde and not ethane.

Reactions of CH₃ on Si-Supported Cu Nanoparticles

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Figure 10. TPD following adsorption of CH_3I on oxidized-Cu/SiO₂ following adsorption of CH_3I. Desorption peaks were evident for H_2CO (*m/e* 30), CO_2 (*m/e* 44), and H_2O (*m/e* 18).

In addition to the experiments discussed above using copper nitrate as the copper precursor, we have also prepared Cu/SiO₂ samples using copper acetate monohydrate as the copper precursor. These experiments were done to probe the effect of the copper precursor on the chemistry of methyl fragments. Data obtained from the copper nitrate precursor samples are reproduced when methyl iodide is adsorbed onto the Cu/SiO₂ samples made using copper acetate monohydrate, indicating little effect of the copper precursor at least in terms of reaction products formed. Samples with lower copper metal loading were also examined. The reaction products were the same but the band intensities of surface bound species decreased with metal loading (between 15 and 4%).

Discussion

In general, oxide-supported metal particle catalysts are complex and it is often times difficult to determine the important parameters that affect the reactivity of these systems. In this study, we have identified at least three important factors that control the surface chemistry of methyl groups, formed from the dissociative adsorption of methyl iodide, on Cu/SiO₂ samples. These three factors are (i) the oxidation state of the copper particles, (ii) the hydroxyl group coverage on the surface of the silica support, and (iii) the surface roughness of the copper particles. The effects that these three factors have on the chemistry of methyl groups on Cu/SiO₂ are discussed in detail below.

Surface Chemistry of CH₃I on Reduced- and Oxidized-Cu/SiO₂ Samples. Similar to the single crystal surface chemistry of methyl iodide, C–I bond dissociation occurs to give methyl and adsorbed iodine on the copper particle surface of the reduced Cu/SiO₂ samples (Scheme 1). Although we have not detected adsorbed iodine in our experiments, we will assume that, similar to what occurs on single crystal surfaces, the iodine atom strongly bonds to the copper surface. On reduced-Cu/SiO₂(673 K), Cu–CH₃ is the only species formed upon adsorption of CH_3I. This species is characterized by infrared bands near 2913 and 2805 cm⁻¹ (weak). The infrared spectrum of adsorbed methyl groups on reduced-Cu/SiO₂(473 K) samples is characterized by an absorption band near 2924 cm⁻¹ that is assigned to the symmetric C–H stretch of adsorbed methyl groups on atomically rough copper particles.

Scheme 1. Reactions of Methyl Iodide and Methyl Fragments on Cu/SiO₂
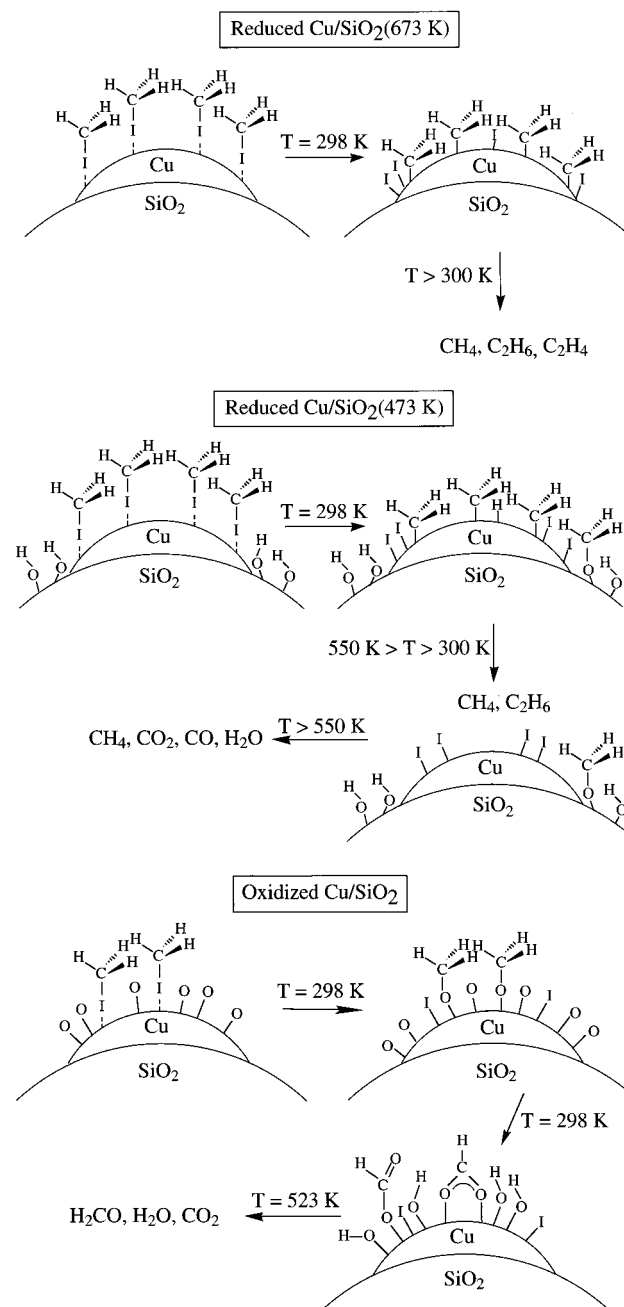
After CH_3I adsorption on reduced-Cu/SiO₂(473 K), methyl groups are present not only on the copper particles but also on the silica support as $SiOCH_3$ groups. The $SiOCH_3$ groups exhibit infrared bands near 2985, 2954, 2852, and 1462 cm⁻¹ (Table 1). Because there is no direct reaction with methyl iodide and the silica surface under the conditions employed in this study, the formation of $SiOCH_3$ is a consequence of C–I bond dissociation on the copper particles, followed by reaction of methyl with the surface hydroxyl groups.

The number of SiOH groups that react with methyl fragments per copper particle on reduced-Cu/SiO₂(473 K) has been calculated from the average particle diameter from TEM measurements, the mass of both copper and silica in the sample, an initial hydroxyl group coverage on the silica of 5 OH groups/ 100 Å², [64] and the percentage of SiOH groups lost after adsorption of methyl iodide. This calculation yields approximately 25 OH groups reacting per copper particle in the sample. Hydrogen atoms produced in the spillover process are

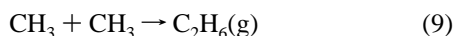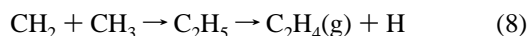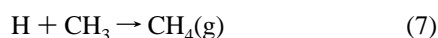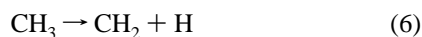available for reaction with methyl groups adsorbed on the Cu particles as discussed in the next section.

There are two possible mechanisms for this reaction. One is a stepwise mechanism (eq 5), similar to that observed for hydrogen spillover, and has been discussed previously.

$$Cu + CH_3I \rightarrow Cu-CH_3 + Cu-I \qquad (5a)$$

$$SiOH + Cu-CH_3 \rightarrow SiOCH_3 + H \qquad (5b)$$

Alternatively, the reaction may be a concerted one occurring at the Cu-silica interface. As the C-I bond dissociates and forms an I−Cu bond, the CH_3 group can simultaneously react with SiOH to form $SiOCH_3$. In contrast to hydrogen spillover, which can occur over macroscopic distances,[50] the CH_3 spillover appears to be limited to OH groups in close proximity to the metal particles. The fact that spillover is limited for CH_3 suggests that the concerted mechanism may be operative in this case.

On oxidized-Cu/SiO_2 samples, the C−I bond in adsorbed CH_3I dissociates as it does on the reduced samples, however, the predominant products that form on the oxidized copper surface are methoxy and bidentate formate (Scheme 1). The infrared spectra of these two surface bound species are assigned by direct comparison to literature spectra (Table 1).

Surface Chemistry of Methyl Groups on Reduced Cu/ SiO_2 Samples and the Role of Silica Hydroxyl Group Coverage. The chemistry of methyl groups adsorbed on the surface of the copper particles as a function of temperature can be discerned from the IR and TPD data. For reduced-Cu/SiO_2-(673 K) samples, identical reaction products are detected in TPD to those produced on a single crystal Cu(110) surface. Therefore, we use the reaction sequence determined for methyl reactions on Cu(110) to explain the results for methyl reactions on reduced-Cu/SiO_2(673 K) samples (eqs 6−9).

$$CH_3 \rightarrow CH_2 + H \qquad (6)$$

$$H + CH_3 \rightarrow CH_4(g) \qquad (7)$$

$$CH_2 + CH_3 \rightarrow C_2H_5 \rightarrow C_2H_4(g) + H \qquad (8)$$

$$CH_3 + CH_3 \rightarrow C_2H_6(g) \qquad (9)$$

Methane can only form if there are available hydrogen atoms for reaction with methyl. It has been shown that the rate determining step in methyl reactions on Cu(110) is α-elimination to yield methylene and hydrogen atoms (eq 6). H atoms then react with methyl groups to yield methane (eq 7). Methylene groups can insert into the Cu−CH_3 bond to give ethyl which rapidly undergoes β-hydride elimination to give ethylene and adsorbed hydrogen atoms (eq 8). At high coverages methyl groups can also couple to evolve ethane (eq 9).

The different product distribution for reduced-Cu/SiO_2(473 K) samples compared to reduced-Cu/SiO_2(673 K) and Cu(110) surfaces suggests that there is another reaction mechanism occurring for methyl groups adsorbed on reduced-Cu/SiO_2(473 K). On reduced-Cu/SiO_2(473 K), there is no evidence for ethylene formation and there is an increase in the amount of methane produced relative to ethane. From the integrated area of the TPD peaks, it was determined that there was nearly an eight-fold increase in the ratio of CH_4:C_2H_6 on reduced-Cu/ SiO_2(473 K) compared to reduced-Cu/SiO_2(673 K) samples.[67] The increased methane production and the absence of ethylene suggest that there is another source of hydrogen besides from α-elimination in adsorbed methyl for the reduced-Cu/SiO_2(473

K) samples. To determine if there is another source of hydrogen atoms, TPD data for deuterated methyl iodide on reduced-Cu/ SiO_2(473 K) were obtained. If CD_3H evolves in TPD, then it is clear there is another source of hydrogen atoms available for the formation of methane. However, if CD_3 groups undergo α-elimination to give CD_2 and D atoms then there should be exclusively CD_4. In experiments with CD_3I on reduced-Cu/ SiO_2(473 K), a significant amount of CD_3H evolution is observed in TPD indicating there is another source of hydrogen atoms available for reaction with CH_3 groups. Hydrogen atoms from SiOH plus methyl reaction (eq 5b) is the most likely source of hydrogen available for reaction with methyl fragments.

The chemistry of CH_3 fragments on reduced samples is summarized in Scheme 1. For reduced-Cu/SiO_2(473 K) samples, the chemistry of $SiOCH_3$ groups from methyl spillover is included in the reaction scheme.

Role of Surface Roughness on the Surface Chemistry of Methyl Groups. As discussed previously, the two reduced Cu/ SiO_2 samples show differences in the copper particle surface morphology. The long reduction at higher temperature (reduced-Cu/SiO_2(673 K)) has an annealing effect on the surface of the copper particles. Similar to adsorbed CO, the frequency of the symmetric stretch in adsorbed methyl is blue-shifted on reduced-Cu/SiO_2(473 K) samples that have particles of rough surface morphology compared to reduced-Cu/SiO_2(673 K). The shift to higher frequency for the rougher surfaces is attributed to adsorption on unsaturated copper atoms.

More subtle differences may also be discerned from the data. The TPD data show different desorption rate maxima on reduced-Cu/SiO_2(673 K) (Figure 6) and reduced-Cu/SiO_2(473 K) (Figure 8). The reduced-Cu/SiO_2(673 K) shows a desorption rate maximum near 370 K for ethane desorption compared to 410 K for ethane desorption from the reduced-Cu/SiO_2(473 K) sample. This difference in the desorption temperature for the two reduced Cu/SiO_2 samples represents a change in the reaction kinetics for methyl fragments adsorbed on copper due to a change in the surface morphology of the copper particles. Diffusion of methyl fragments may be more facile on the smoother copper surfaces.

Surface Chemistry of Methyl Groups on Oxidized-Cu/ SiO_2. The surface-bound products that are formed at room temperature during the adsorption of methyl iodide on the oxidized-Cu/SiO_2 sample can be attributed to the formation and partial dehydrogenation of methoxy groups adsorbed on the copper surface. Scheme 1 depicts the initial formation of methoxy from the dissociative adsorption of the CH_3I and its reaction with adsorbed oxygen. A portion of the methoxy groups dehydrogenate to produce formate and hydroxyl groups adsorbed on the copper surface. Both methoxy and formate are observed at room temperature after adsorption of methyl iodide. Upon warming, the remaining methoxy groups dehydrogenate to increase the concentration of bidentate formate and to form water through the addition of a hydrogen to Cu−OH groups. It is also known from the TPD experiments that formaldehyde is produced in the temperature range where the infrared spectra show methoxy groups dehydrogenating and the bidentate formate coverage increasing. At higher temperatures, above 523 K, bidentate formate undergoes further reaction to produce gaseous CO_2 and adsorbed carbonate. The chemistry of methyl iodide on oxidized-Cu/SiO_2 is identical to that of methanol adsorbed on oxidized-Cu/SiO_2.

(67) The relative yields of methane, ethane, and ethylene were determined by calibrating the mass spectrometer with pure gases and correcting for the different ion-gauge sensitivities. The CH_4:C_2H_6 yield was calculated to be 0.16 for CH_3I reaction on Cu/SiO_2(673 K) and 1.20 for CH_3I reaction on Cu/SiO_2(473 K).

In order to determine if the C−I bond in CH_3I breaks on the adsorbed oxygen to form methoxy or if methyl groups are perhaps formed on vacant copper sites and subsequently react with nearby adsorbed oxygen to form $Cu-OCH_3$, an experiment was done where a fraction of a monolayer of methyl fragments on a reduced-Cu/SiO_2(673 K) sample was prepared. Oxygen was then added in an attempt to observe the formation of methoxy on the copper surface. Even with gentle heating in oxygen (below the desorption temperature of CH_3), the methyl fragments showed no conversion to methoxy. This demonstrates that the methyl fragments, if formed, are not stabilized on the copper surface prior to their reaction with the adsorbed oxygen. This is similar to results observed by Bol and Friend in an analogous experiment on an oxygen pre-covered rhodium surface.[26]

Another important observation is that on the oxidized-Cu/SiO_2 samples, no formation of $SiOCH_3$ is observed. This is significant because it shows that the spillover process is inhibited by the presence of surface oxygen.

Conclusions

The chemistry of methyl groups on Cu/SiO_2 from methyl iodide dissociation has been investigated in this study. It has been shown that the C−I bond in methyl iodide dissociates on Cu/SiO_2 samples at room temperature. The subsequent reaction chemistry of methyl groups on Cu/SiO_2 is dependent on sample preparation. Different sample preparations lead to surfaces with different surface morphology, oxidation state, and hydroxyl group coverage on the silica support. Methyl fragments are formed on the copper particle surface of reduced Cu/SiO_2 samples after the dissociative adsorption of methyl iodide. The frequency of the C−H symmetric stretch is dependent on surface morphology. For smooth surfaces, the frequency is near 2913 cm^{-1} and for rough surfaces the frequency blue shifts to near 2924 cm^{-1}. On samples that are heated to a maximum temperature of 473 K, the hydroxyl group coverage on the silica support is high enough such that some of the methyl fragments migrate to and react with SiOH groups to form $SiOCH_3$ and hydrogen atoms. These hydrogen atoms can then react with methyl groups to form gaseous methane at elevated temperatures. Oxygenated hydrocarbon fragments are formed on the copper particle surface on samples that have been oxidized prior to methyl iodide adsorption. These fragments include methoxy and bidentate formate on the copper surface. In general, characterization of Cu/SiO_2 samples is difficult. The samples characterized in these studies may provide for a better understanding of the reactivity of Cu/SiO_2 catalysts and the results may be applicable to other alkyl fragments from the dissociative adsorption of alkyl halides and other chemical systems, e.g. methanol synthesis.

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