which tend to leave open troughs of exposed nickel atoms.³⁹ Since nickel sites are still available, the benzene can be more strongly bound to the partially oxidized surfaces than the sulfided surfaces, which explains the higher benzene desorption temperature for the oxidized surfaces.

The passivation effect of sulfur and oxygen may be due to simple site-blocking effects where the presence of the coadsorbed adatoms limit the availability of adjacent sites for decomposition. An alternative explanation is that the passivation may result from subtle changes in the π bonding (and possibly π back-bonding) to the surfaces in the presence of surface sulfur or oxygen.

Summary

The major conclusions which emerge from this study are that benzene chemisorption on Ni(110) results in molecular adsorption below 300 K. The adsorbed benzene lies essentially parallel to the surface. Semiempirical molecular orbital calculations indicate that the most likely adsorption site is the atop site at a height of 1.75 Å or a short-bridge site at a height of 1.90 Å. At saturation coverage, 0.2-0.25 ML, a c(4×2) LEED pattern was observed. Decomposition is competitive with molecular desorption above 320 K and, at saturation, decomposition accounts for about 70-80% of the chemisorbed benzene. Carbon-hydrogen bond scission commences at about 320 K, resulting in reaction-limited hydrogen desorption. The formation of a stable partially dissociated fragment such as a phenyl or benzene species near 400 K was based on spectroscopic and isotopic mixing data. This fragment undergoes rehydrogenation to form benzene at 460 K. In addition to this fragment, benzene decomposition also results

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in the formation of a surface carbide. Interestingly, heating the surface to 700 K results in the formation of a subsurface carbon, which is distinguishable from the surface carbide by its carbon 1s core level binding energy and its Auger line shape. The coadsorption of oxygen or sulfur inhibits decomposition and weakens the bonding between benzene and the nickel surface.

Note Added in Proof. Very recent angle-resolved ultraviolet photoelectron spectroscopy (ARUPS) studies by Huber et al.⁴⁰ have shown that at low coverage the benzene molecule is oriented as predicted by the ASED calculations (shown in Figure 2b). Their data did not permit exact identification of the site along the $[1\overline{10}]$ direction but did distinguish the azimuthal orientation, which agreed with our modeling studies. Furthermore, as suggested by the high packing density of benzene on Ni(110) at high coverages, lateral interactions cause a reorientation of the molecules, which was detected by ARUPS.

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Registry No. Ni, 7440-02-0; H₂, 1333-74-0; O₂, 7782-44-7; S, 7704-34-9; benzene, 71-43-2.

Interaction and Catalytic Decomposition of 1,1,1-Trichloroethane on High Surface Area Alumina. An Infrared Spectroscopic Study

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Transmission infrared spectroscopy has been used to study the catalytic decomposition of 1,1,1-trichloroethane, CH₃CCl₃, on high surface area alumina, Al₂O₃, in the temperature range 300-600 K. At 300 K CH₃CCl₃ is reversibly adsorbed on the isolated surface hydroxyl groups of Al₂O₃ via hydrogen bonding. At $T \ge 400$ K an α,β -HCl elimination occurs, forming CH₂=-CCl₂(g). A small amount of surface carboxylate was also formed by means of a minor reaction pathway. It was found that Lewis acid (Al³⁺) surface sites were involved in causing the primary reaction. This was shown by the observation that irreversible adsorption of pyridine on the Al³⁺ sites efficiently quenched the surface reaction. Conversely, surface Al-OH groups are not involved in the CH₃CCl₃ decomposition.

I. Introduction

Contamination of ground water and soil by various chlorinated hydrocarbons is a major environmental concern. The lifetimes in the environment of such compounds and the end decomposition products which are formed are two important factors in environmental control. Thus, studies have focused on the biotic^{1,2} and abiotic^{3,4} transformations, along with incineration,⁵ of compounds such as 1,1,1-trichloroethane. As shown in other studies, the half-life of CH_3CCl_3 may be rather long; for example, the half-life for the hydrolysis of CH_3CCl_3 in ocean water at 25 °C is 1 year.⁶

A desirable method of environmental cleanup could involve the adsorption and/or reaction of undesirable substances on naturally occurring mineral surfaces in the ground such as alumina, Al_2O_3 . Al_2O_3 is a good model material for research purposes because it contains a variety of chemical sites on its surface which can participate in chemical processes. These sites result because Al_2O_3 has a defect spinel structure where Al^{3+} can be in either the octahedral or tetrahedral holes of the oxygen lattice. Various transitional aluminas,⁷ as classified by the ratio of octahedral and

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+{{+ - Associated Hydroxyl Groups -Isolated Hydroxyl Groups

Figure 1. Diagram showing the OH stretching frequency for various types of Al₂O₃ surface sites. The frequency of the isolated Al-OH groups is determined from the coordination of the underlying Al atom(s), according to Knözinger and Ratnasamy.⁸

tetrahedral Al³⁺ coordinated ions and the oxygen lattice packing density,⁸ exist, making surface chemistry on Al₂O₃ a rather complex subject. The surfaces of aluminum oxides are terminated with an oxygen layer, which, according to Pauling's electrostatic valence rule,⁹ is covered with hydroxyl groups to neutralize the surface charge.

There are different classes of chemical sites on the Al₂O₃ surface, and there are differences within each class of site. For example, the hydroxyl groups on the Al₂O₃ surface can be divided into two classes: associated hydroxyl groups are those which are hydrogen-bonded to each other, while isolated hydroxyl groups are non-hydrogen-bonded groups. Within the isolated Al-OH group class, five different kinds of isolated hydroxyl groups have been observed by IR spectroscopy.^{10,11} Knözinger and Ratnasamy⁸ have assigned the differences in O-H frequency to the underlying coordination of Al atoms (hence affecting the electron density around the hydroxyl group). Figure 1 shows these assignments. Heating Al₂O₃ causes Al-OH groups to combine and to desorb as water, exposing Al^{3+} , Lewis acid sites, and O^{2-} surface sites. Such sites can also have varying electron densities as shown in XPS studies performed during dehydroxylation.¹²

The range of different chemical groups that exist on the Al_2O_3 surface can be probed effectively by infrared spectroscopy: Al-OH groups, considered Bronsted acids, can be monitored directly by the O-H stretch; Al^{3+} , Lewis acid sites, and basic O^{2-} sites can be measured indirectly by the adsorption of IR-absorbing probe molecules.¹³⁻¹⁵ The control and measurement of such sites have been recently demonstrated in our laboratories. We observe an approximate linear correlation between the decreasing integrated absorbance of the Al-OH features with the increasing integrated absorbance of physisorbed Al³⁺--CO features at 2195 cm⁻¹. This is observed as Al₂O₃ dehydroxylation occurs in the temperature range from 475 to 1200 K.15

Only a few studies have been published on the interaction between chloroethanes and Al_2O_3 . The most extensive work has been conducted in a series of papers by Mochida and co-workers. Using a series of five chloroethanes, the reactivity order of the chloroethanes on various acidic and basic oxides was determined at 573 K using a pulse technique coupled with a gas chromatograph for product analysis.¹⁶ In all cases, α,β -HCl elimination

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occurred, forming chloroethenes with stereoselectivity determined by the initial chlorine substitution and by the acid-base character of the oxide. Furthermore, these workers postulated that, on Al_2O_3 , the reaction proceeded via a concerted E2 HCl elimination mechanism. They later claimed to confirm an E2 concerted mechanism on Al₂O₃ based on the product distribution from four chloroalkane reactants relative to the product distributions on silica-alumina and potassium hydroxide supported silica gel.¹⁷ A later study investigated the use of steam to regenerate sites for dehydrochlorination¹⁸ of 1,1,2-trichloroethane. By injecting water onto Al₂O₃ in a reactor at 723 K, HCl was liberated from the surface, thus maintaining the dehydrochlorination activity. Tribbeck found that CH₃CCl₃, injected into a gas chromatograph with Al₂O₃ columns, produced 1,1-dichloroethene at temperatures above 353 K.¹⁹ A final study carried out the copyrolysis of chloroethanes and methanol on Al₂O₃.²⁰ CH₃CCl₃ and CH₃OH vapors were passed through a Pyrex glass reactor tube packed with Al_2O_3 pellets. The products of this reaction, analyzed by gas chromatography, were $CH_2 = CCl_2$, CH_3Cl , and H_2O .

One other recent study of interest was the interaction of a chloromethane with Al₂O₃. The reaction of CH₃Cl with the surface hydroxyl groups on Al₂O₃ at $T \ge 380$ K produced CH₃O(a).²¹ This reaction is entirely different from that reported here for CH₃CCl₃.

A first step in understanding how oxide materials can be used in environmental chemistry is understanding the fundamental adsorption/desorption and reaction processes which occur on the surface. Infrared spectroscopy is especially suited for this use because of the ability to distinguish adsorbed species, adsorption geometries, and reaction sites by use of blocking molecules, along with the identification of reaction products. Thus, we have undertaken a study of the interaction of CH_3CCl_3 with Al_2O_3 . We find that it reversibly adsorbs on the surface at 300 K by hydrogen bonding with isolated OH groups. Furthermore, at higher temperatures, we have determined that Al³⁺ sites are needed for the elimination reaction

$$CH_{3}CCl_{3} \xrightarrow{Al_{2}O_{3}} CH_{2} = CCl_{2} + HCl \quad (T \ge 400 \text{ K}) \quad (1)$$

whereas hydroxyl groups are not involved. We also show that a minor reaction channel, involving the formation of surface carboxylates, can be observed.

II. Experimental Section

The infrared cell used in these studies has been described in detail previously.²² It consists of a tungsten grid support held in the middle of a stainless steel cube-shaped cell containing KBr windows. The KBr windows are sealed with differentially pumped Viton O-rings. The support grid containing the Al_2O_3 powder can be electrically heated using an electronic controller,²³ which maintains the grid temperature within ± 1 K, as measured by a thermocouple spot-welded on the top-central region of the grid. The vacuum system used is made of stainless steel and is pumped by a 60 L/s turbomolecular pump and a 30 L/s ion pump, and reaches a base pressure of $P \le 1 \times 10^{-8}$ Torr. The vacuum system also contains a quadrupole mass spectrometer and a MKS Baratron capacitance manometer.

The Al₂O₃ used was Degussa aluminum oxide C (101 m^2/g). The Al₂O₃ was pressed into the holes on half of the tungsten grid support²⁴ (5.2-cm² total exposed grid area) by applying 12000-lb pressure via a hydraulic press. The other half of the grid was left

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Figure 2. Infrared spectra in the ν_{OH} region of Al₂O₃ at 300 K during adsorption of CH₃CCl₃. (a) Spectrum before gas adsorption; (b) adsorption in 4.65 Torr of CH₃CCl₃(g); (c) after evacuation of $CH_3CCl_3(g)$. (b - a) is the difference spectrum of (b) - (a).

empty for IR observation of gas-phase species. The grid was rigidly held between two nickel clamps in the center of the IR cell. After cell assembly, the Al_2O_3 was prepared for studies by outgassing in vacuum at 600 K for 36 h, unless otherwise stated.

The infrared spectrometer used was a purged Perkin-Elmer Model 580B grating spectrometer, coupled with a Model 3500 data station for data storage and manipulation. Infrared spectra, using a spectral resolution of 5.3 cm^{-1} , obtained through the Al₂O₃ deposit, were signal averaged twice, collecting 1 data point/ cm^{-1} . The infrared spectra of gaseous species in the kinetic experiments were acquired by scanning the 825–685-cm⁻¹ region once through the bare tungsten grid with a collection of 2 data points/ cm^{-1} . The spectra were then subtracted from a background spectrum obtained in vacuum and smoothed with a 19-point smoothing function.

The rates of decomposition plots shown here were obtained after calibration of the gas-phase IR intensities of the gases involved as reactants and products. A linear Beer-Lambert plot of moles of gas/cm³ vs intensity of the C-Cl antisymmetric stretch for both CH_3CCl_3 (723 cm⁻¹) and CH_2 = CCl_2 (793 cm⁻¹) was constructed in a blank cell from measured pressures ($P \le 7.54$ Torr) of the gases at 308 K. Since our kinetic measurements were made at a substrate temperature of 550 K, the gas density in the IR cell will decrease due to the increased gas temperature. The measured factors for the temperature-related absorbance decrease are CH_3CCl_3 (0.79 ± 0.08) and CH_2 = CCl_2 (0.90 ± 0.02), and these factors were applied to correct our calibrations made at 308 K.

The 1,1,1-trichloroethane and 1,1-dichloroethene used in these experiments were purchased from Aldrich with 99+% and 99% purity, respectively. The liquids were transferred under nitrogen into glass bulbs after being passed through an alumina column to remove the small amount of stabilizer present. The compounds were then further purified by several freeze-pump-thaw cycles. The pyridine was acquired from Aldrich with 99+% purity, transferred under nitrogen into a glass bulb, and purified with several freeze-pump-thaw cycles. The ethane was used as obtained from Matheson with 99.99% purity. Deuterated ethane (C_2D_6) was purchased from Cambridge Isotope Laboratories in a break-seal glass storage bulb with 98% purity and was used as received.

III. Results and Discussion

A. Reversible Adsorption of CH₃CCl₃ on Al₂O₃. The weak interaction of CH₃CCl₃ on Al₂O₃ at 300 K can be demonstrated by the infrared spectra of the surface OH groups. Figure 2 shows this effect in the O-H stretching region (3800-3200 cm⁻¹) of the



Figure 3. Infrared spectra in selected IR regions showing the depletion of $CH_3CCl_3(g)$ and the formation of $CH_2 = CCl_2(g)$ on Al_2O_3 with changing temperature. The spectra were recorded at the indicated temperatures under an initial CH₃CCl₃ pressure of 10 Torr. The spectra in the 1700-1300-cm⁻¹ region were collected through both the Al₂O₃ and the gaseous species, while spectra in the 1000-650-cm⁻¹ region were collected through the gaseous species only.

IR spectra. Spectrum a shows the Al_2O_3 catalyst before gas adsorption with isolated OH groups appearing as shoulders at \sim 3738 and \sim 3667 cm⁻¹ and the associated, or H-bonded, OH groups appearing as an unresolved set of bands centered at 3540 cm⁻¹. Upon the addition of 4.65 Torr of CH₃CCl₃, the 3738-cm⁻¹ isolated OH band is attenuated, and a slight change of band shape occurs in the associated OH region (spectrum b). The red shift of the isolated OH group at 3738 cm⁻¹ and the increase in absorbance below 3700 cm⁻¹ are indicative that hydrogen bonding of CH₃CCl₃ is occurring,²⁵ as has been demonstrated previously for a variety of reversibly OH-bound adsorbates.^{8,11,26-30} The original associated Al-OH groups below $\sim 3600 \text{ cm}^{-1}$ appear to be unaffected, which is expected if they are initially hydrogenbonded to each other. The changes between the spectra can be better seen in the difference spectrum at the bottom of Figure 2 (spectrum b - spectrum a). The negative feature observed at 3738 cm⁻¹ indicates that these isolated Al-OH groups are the ones affected by CH₃CCl₃ adsorption. The frequency of these bands appears to have shifted into a feature near 3650 cm^{-1} .

The cell was then evacuated at 300 K for 10 min before Figure 2c was obtained. This spectrum is similar to that of the background spectrum, with slight loss of intensity in the associated hydroxyl region, suggesting that CH₃CCl₃ has not irreversibly chemisorbed on, nor reacted with, the isolated Al-OH groups on Al₂O₃. Reactions involving surface Al-OH cause permanent changes in the O-H region of the spectrum.³¹⁻³³ Furthermore,

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TABLE I: Gas-Phase CH₃CCl₃ Vibrational Assignments and Frequencies (in cm⁻¹)

mode	this work ^a	ref 35	ref 36			
 ν _{as} (C-H)	3013	3014	3013			
v.(C-H)	2949	2951	2951			
$\delta_{as}(CH_3)$	1457	1457	1455			
$\delta_{s}(CH_{1})$	1383	1386	1386			
$rock(CH_3)$	1087	1088	1088			
ν.(C-C)	1008	1009	1010			
$\nu_{as}(C-Cl)$	723	724	724			
$\nu_{s}(C-Cl)$		526	526			

^aGas temperature is 300 K.

the absence of any other IR absorbance features in any other region of the IR spectrum of Al₂O₃ after evacuation confirms that CH_3CCl_3 is reversibly adsorbed at 300 K.

B. Decomposition of CH₃CCl₃ over Al₂O₃ at High Temperatures. Since CH₃CCl₃ did not react with Al₂O₃ at 300 K, the effect of increasing the temperature was studied. Figure 3 shows the difference infrared spectra (background subtracted out) in selected IR absorbing regions. The spectra shown in Figure 3 (left panel) are a composite of the spectra of gas-phase species as well as new species produced on the Al₂O₃ surface. These will be separated in Figure 4. Figure 3a shows these absorbances at 300 K for a CH_3CCl_3 pressure of 10 Torr. In the 1700–1300-cm⁻¹ region, two absorbances are seen with peak maxima at 1453 and 1383 cm⁻¹, which have been assigned to the Q band of the antisymmetric CH_3 deformation (reported at 1457 cm⁻¹) and the symmetric CH_3 deformation (reported at 1386 cm⁻¹) of gas-phase CH_3CCl_3 , ³⁴⁻³⁷ Because of the strong oxide absorbance below ~ 1000 cm⁻¹, IR spectra through the Al₂O₃ side of the grid support cannot be obtained in this region. Therefore, the IR beam is focused on the empty grid to obtain gas-phase spectra below 1000 cm⁻¹. Between 1000 and 650 cm⁻¹ a very sharp and intense absorbance feature can be seen at 723 cm⁻¹. (Note that the peak has been multiplied by 1/7 on this absorbance scale.) This feature has been assigned to the antisymmetric C-Cl stretch in CH₃CCl₃ (reported at 724 cm⁻¹). IR features for the C-H symmetric and antisymmetric stretch and CH₃ antisymmetric rock of CH₃CCl₃ are also observed (spectra not shown). Table I lists all IR frequencies observed along with the known gas-phase frequencies and assignments.

When the Al_2O_3 was heated with CH_3CCl_3 in the cell, the infrared spectra began to change when the Al₂O₃ temperature reached ~ 400 K, as can be seen in Figure 3b. The features due to CH₃CCl₃ decrease in intensity, while several new features are These new features become more prominent upon observed. heating to 500 K (Figure 2c), while the CH₃CCl₃ features continue to decrease. The features which develop at 1627, 1613, and 1086 cm⁻¹ (not shown) have been identified as those belonging to 1,1-dichloroethene, CH_2 =CCl₂. These frequencies are similar to those assigned:^{38,39} C=C stretch (R, P bands) at 1622.5 and 1610 cm⁻¹; CH₂ rock at 1086 cm⁻¹. No C-H stretching bands were observed due to the weak intensity of these bands.³⁸ Additional bands at 869 and 793 cm⁻¹ were observed through the empty grid and have also been assigned to $CH_2 = CCl_2(g)$ as the CH_2 wag (reported at 868.6 cm⁻¹) and the antisymmetric CCl_2 stretch (reported at 795.8 cm⁻¹). Several combination bands are also observed at 1578 and 1138 cm⁻¹ (not shown). Table II lists the comparison of frequencies and the assignments for CH2=CCl2. Upon heating to 600 K, the CH₃CCl₃ bands have disappeared, leaving only those bands of CH_2 =CCl₂ and a new band which is evident at 1462 cm⁻¹ in Figure 3d. Furthermore, faint gasrelated bands are observed in the 2900-2700-cm⁻¹ region. These

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TABLE II: Gas-Phase CH2=CCl2 Vibrational Assignments and Frequencies (in cm⁻¹)

mode	this work ^a	ref 38	ref 39	
ν _{as} (C-H)		b	3130 (liquid)	
$\nu_{s}(C-H)$		3045.8	3035 (liquid)	
ν (C=C), R band	1627	1622.5	1620	
ν (C=C), P band	1613	1609.9		
$\delta_{scissor}(CH_2)$		Ь	1391	
$rock(CH_2)$	1086	1086.1	1094	
$wag(CH_2)$	869	868.6	872	
$v_{as}(C-Cl)$	793	795.8	794	

^aAll measurements made at Al₂O₃ temperature of 600 K which causes an unknown increase in average gas temperature. b Weak.



Figure 4. Infrared spectra collected at 600 K of the products of CH₃CCl₃ decomposition on Al_2O_3 . Spectrum a shows the surface + gas phase species, and spectrum b displays the absorption features of the adsorbed species after evacuation.

bands appear to have vibrational-rotational structure.

Figure 4 shows the difference IR spectra of reaction products. Spectrum a displays the bands due to HCl(g) in the 3100-2700-cm⁻¹ region. The agreement with the known vibrationrotation lines of the HCl fundamental absorption band⁴⁰ is within 0.5 cm⁻¹. The 1700-1300-cm⁻¹ region of Figure 4a is identical to that in Figure 3d at 600 K, which contains features due to $CH_2 = CCl_2(g)$ plus a band at 1462 cm⁻¹.

To separate spectral features due to gas products from those due to adsorbed products, IR spectra were obtained through the Al_2O_3 side of the grid after a 30-min evacuation of the IR cell. Two bands due to surface species are observed at 1566 and 1462 cm⁻¹ in Figure 4b. These bands have previously been assigned as the $\nu_a(OCO)$ and $\nu_s(OCO)$ bands of carboxylate species on Al₂O₃ formed from olefin^{41,42} or alcohol decomposition^{43,44} as well as by acetic acid adsorption above 550 K.⁴¹ On the basis of the splitting between these modes, it is possible to determine the adsorption geometry of the carboxylate group on the surface.⁴⁵ In this case $v_a(OCO) - v_s(OCO) = 104 \text{ cm}^{-1}$, which indicates that the carboxylate species is bidentate-bound to the surface; i.e., both oxygens are equivalent. The mode of carbon bonding to a third

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Figure 5. Plot of the rate of CH₃CCl₃ decomposition and CH₂=CCl₂ production at 550 K as measured by IR spectroscopy. The dashed lines indicate the decomposition that occurs in the cell without Al_2O_3 . The Al₂O₃ was dehydroxylated at 600 K for 36 h before reaction.

moiety in the OCO⁻ species is unknown at present.

The HCl bands are no longer present in Figure 4b after evacuation. A spectrum obtained in the hydroxyl region (not shown) shows a small decrease of the isolated Al-OH intensity with a small increase in the associated Al-OH intensity. This may be due to a small amount of HCl adsorbed on the surface⁴⁶ or to the involvement of Al-OH groups in the carboxylate formation.42,44

The infrared spectra obtained during this study indicate that two reaction pathways exist for the decomposition of CH₃CCl₃ over Al_2O_3 . The major reaction pathway is the elimination reaction

$$CH_3CCl_3 \rightarrow CH_2 = CCl_2 + HCl$$
 (2)

which begins at ~ 400 K. Others have indicated that this elimination reaction follows an E2 mechanism.^{16,17} E2 mechanisms are characterized by having a concerted β -hydrogen removal by a base and α -C-X bond breakage and C==C bond formation. The kinetics of reaction in solution for these eliminations is second order-first order each in the base and the reactant-and is dependent on the nature of the leaving group (X substituent).⁴⁷ It is obvious that an α,β -elimination reaction occurs for CH₃CCl₃ on Al₂O₃, and the effect of increasing decomposition rate with oxide basicity has recently been demonstrated.⁴⁸

The minor reaction pathway in this experiment involves breaking all the bonds in CH₃CCl₃ to leave carboxylates on the surface, beginning at 450 K. Further evidence for the complete decomposition of CH₃CCl₃ comes upon visual inspection of the Al_2O_3 after several 600 K decompositions. The Al_2O_3 became light brown in color instead of the usual white color.

C. Kinetics of CH₃CCl₃ Decomposition on Al₂O₃. A study of the rate of decomposition of CH₃CCl₃ was undertaken in an attempt to understand the role of surface sites involved in the reaction mechanism. The rate was monitored via IR measurement of the antisymmetric C-Cl stretch intensity of CH₃CCl₃ (depletion at 723 cm⁻¹) and CH₂=CCl₂ (production at 793 cm⁻¹) through the blank side of the grid support. The CH₃CCl₃ decomposition was carried out at 550 K in order to conveniently monitor the reaction. An initial pressure of 4.65 Torr of CH₃CCl₃(g) was put into the cell with Al₂O₃ at 550 K, and the cell was closed off from the rest of the vacuum system. The behavior of the gaseous species above the Al_2O_3 catalyst is shown in Figure 5. The first point obtained occurs 1 min into the reaction, due to a time gap between filling the cell with gas and beginning an IR scan. As seen by the open symbols in Figure 5, the formation of CH2-CCl2 mirrors the depletion of CH_3CCl_3 . The reaction occurs rapidly, with most



Figure 6. Plot of the decrease in Al₂O₃ activity for sequential CH₃CCl₃ decomposition experiments at 550 K. The concentration of CH₃CCl₃(g) was measured by IR spectroscopy. Experiment 1 was performed after a 36 h, 600 K vacuum treatment. Experiments 2 and 3 were performed after a 12 h evacuation at 550 K of the reaction gases.

of the $CH_3CCl_3(g)$ being depleted in the first 20 min. Blank experiments carried out in the cell without Al₂O₃ are shown by dashed lines. The CH₃CCl₃ decomposition on the hot W grid is slow compared to the rate on Al₂O₃.⁴⁹

The expected 1:1 stoichiometry of CH₃CCl₃ reacting to produce CH_2 =CCl₂ is clearly observed in Figure 5. Overall, we measure that 6.77×10^{-5} mol of CH₃CCl₃ converts to 6.71×10^{-5} mol of $CH_2 = CCl_2$ in this reaction, over an Al_2O_3 deposit (5.8 mg) exposing 0.59 m^2 of surface area. The nearly stoichiometric conversion of CH_3CCl_3 to CH_2 = CCl_2 suggests that the carboxylate formation reaction channel is relatively minor. The extent of reaction compared to the number of available surface sites on Al_2O_3 indicates that a catalytic process is occurring in which site regeneration must occur.

D. Decrease in Al_2O_3 Activity for CH_3CCl_3 Decomposition. The continual performance of the Al₂O₃ catalyst at 550 K was evaluated by running several decomposition reactions over the same catalyst, as shown in Figure 6. The plot displays only the depletion of CH₃CCl₃ for simplicity—the production of CH₂—CCl₂ mirrors the CH₃CCl₃ depletion rates, as was seen in Figure 5. Experiment 1 was carried out over the clean Al_2O_3 catalyst as shown in Figure 5. After a 12-h evacuation at an Al₂O₃ temperature of 550 K, the reaction was repeated (experiment 2). The decomposition of CH_3CCl_3 , shown as experiment 2 in Figure 6, occurs at a slower rate than in experiment 1. After another 12-h evacuation at 550 K, the reaction was carried out again (experiment 3) with the result that the decomposition rate was further retarded.

The reduced performance of the Al₂O₃ catalyst can most likely be explained by blockage of active surface sites. The formation of carboxylate species on the surface may be one example of this. After evacuation in each of the above experiments, infrared spectra obtained through the Al₂O₃ showed an increase of the carboxylate feature intensity. Another possibility could be due to gradual chlorination or carburization of the Al_2O_3 surface, as will be discussed below.

E. Active Al₂O₃ Surface Sites for CH₃CCl₃ Decomposition. As stated in the Introduction, the Al_2O_3 surface contains a variety of chemical sites: both hydrogen-bonded and non-hydrogenbonded Al-OH groups, oxide sites, and Al³⁺ (Lewis acid) sites. The experiments described below have determined which of these

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⁽⁴⁹⁾ The possibility of a gas-phase radical mechanism for CH₃CCl₃ conversion to CH2-CCl2 in these experiments was checked. The radical mechanism is initiated by production of a Cl radical which then attacks C-H bonds to produce HCl(g). An experiment conducted with a mixture of 10 Torr of CD_3CD_3 and 10 Torr of CH_3CCl_3 showed that DCl(g) was not produced, as measured by IR spectroscopy. While these experiments are of low sensitivity, coupled with other experiments to be described, it is clear that the route involving a gas-phase radical mechanism is not significant in this work. For studies of gas-phase pyrolysis, see: Barton, D. H. R.; Onyon, P. F. J. Am. Chem. Soc. 1950, 72, 988. Huybrechts, G.; Hubin, Y.; Van Mele, B. Int. J. Chem. Kinet. 1989, 21, 575.





Figure 7. Effect Al₂O₃ dehydroxylation on CH₃CCl₃ decomposition at 550 K. The plot shows CH₃CCl₃ decomposition and CH₂=CCl₂ formation after two dehydroxylation treatments. The partially dehydroxylated Al₂O₃ experiment was performed after a 600 K vacuum treatment. The highly dehydroxylated Al₂O₃ experiment was performed after a 1000 K vacuum treatment.

sites plays an active role in the reaction.

The first study was the effect of hydroxyl groups on the rate of decomposition. The coverage of Al–OH groups on the Al_2O_3 surface can be controlled^{8,15,50,51} by simply heating the Al_2O_3 to cause Al-OH groups to combine and desorb as water. Figure 7 shows the effect on the CH₃CCl₃ reaction rate for two cases of Al_2O_3 dehydroxylation. The open symbols show the rate after a 600 K Al_2O_3 outgassing, which represents a partially dehydroxylated Al₂O₃ surface. These are the same data points as those in Figure 5. The closed symbols show the rate after a 1000 K dehydroxylation. Such a surface is highly, but not completely, dehydroxylated.¹⁵ The decomposition rate after this pretreatment temperature is much faster than for the 600 K dehydroxylated Al₂O₃. Although the highly dehydroxylated Al₂O₃ leads to a faster rate of decomposition of CH₃CCl₃, the final amount of CH₂=CCl₂ produced is less than that of the partially dehydroxylated Al_2O_3 . Correspondingly, the intensities of the carboxylate features in the IR spectra taken after evacuation are greater for the highly dehydroxylated Al_2O_3 .

Thus, as the concentration of surface Al-OH groups decreases, the rate of CH₃CCl₃ decomposition increases. As previously mentioned, IR spectra obtained in the OH stretching region after reaction and evacuation of the gases at 550 K show only a small increase in the associated Al-OH group intensity and a very small decrease in the isolated Al-OH frequency intensities. These small effects can be attributed to a small amount of HCl adsorption on the surface.⁴⁶ Therefore, the Al-OH surface groups are not involved in the main dehydrochlorination reaction of CH₃CCl₃.

The dehydroxylation procedure described above increases the coverage of Lewis acid sites exposed on the surface since the removal of a H_2O molecule leaves O^{2-} and Al^{3+} sites on the surface. The Lewis acid sites can be indirectly monitored by using IR absorbing probe molecules which coordinate to Al^{3+} sites. Pyridine is a good probe molecule because it is well-known to selectively chemisorb onto Lewis acid sites via the nitrogen lone-pair electrons.^{13,14,52}

We have employed pyridine as a Lewis acid site blocker for the CH₃CCl₃ decomposition reaction to determine whether Al³⁺ sites are involved in this reaction. A 1000 K dehydroxylated Al_2O_3 catalyst was used for these studies in order to eliminate any possibility of Al-OH/pyridine hydrogen bonding and to maximize the rate of CH₃CCl₃ decomposition prior to site blocking. Since pyridine begins to desorb from Al₂O₃ above 475 K,⁵³ the kinetics of CH₃CCl₃ decomposition were measured at 450 K. The open



Figure 8. Inhibition of CH₃CCl₃ decomposition on Al₂O₃ by using preadsorbed pyridine to block Al³⁺ sites. The open symbols indicate the reaction kinetics at 450 K on a clean Al₂O₃ catalyst. The closed symbols indicate the decomposition kinetics on Al₂O₃ containing preadsorbed pyridine. The Al₂O₃ catalyst was initially outgassed in vacuum at 1000

symbols in Figure 8 show the initial rate of CH₃CCl₃ decomposition over Al_2O_3 before pyridine was adsorbed. After a 90-min evacuation of the gaseous products, 4.8 Torr of pyridine gas was expanded into the cell at an Al₂O₃ temperature of 450 K for 30 min. The cell was then evacuated at 450 K for 12 h. IR spectra obtained after evacuation verified that pyridine had indeed adsorbed onto the Al³⁺ sites. The CH₃CCl₃ reaction was then performed in the same manner as before. The closed symbols in Figure 8 show that the CH₃CCl₃ decomposition reaction has been almost completely quenched.

The strong inhibition of CH₃CCl₃ decomposition over a pyridine-covered Al₂O₃ surface demonstrates the importance of the Al^{3+} sites in this reaction. It is likely that a first step in CH_3CCl_3 decomposition involves the abstraction of Cl from the parent molecule by a Al³⁺ site in a concerted fashion with H abstraction. If the abstracted Cl remains bound to Al³⁺, this could eventually lead to the observed deterioration of the catalyst performance. Previous studies of the chlorination of Al₂O₃ surfaces have found that chlorination with CCl₄ occurs from 343 to 800 K.⁵⁴⁻⁵⁶ The mechanism for the chlorination of Al₂O₃ by CCl₄ is the replacement of the lattice O with Cl and the formation of COCl₂ and CO₂. Above 650 K, volatile AlCl₃ species are formed, removing Al from the lattice.^{56,57} Since the reaction temperature in this work is below 650 K, it is unlikely that such species are forming. Also, no IR evidence for the formation of COCl₂ (C=O stretch at 1827 cm⁻¹⁵⁸) or CO₂ was found.

Furthermore, it is interesting to note that recent studies have shown that the dehydrochlorination of CH₃CCl₃ over AlCl₃⁵⁹ or CCl₄- and COCl₂-chlorinated Al₂O₃⁶⁰ occurs at room temperature. AlCl₃ is a strong Lewis acid, while chlorination of Al₂O₃ promotes Lewis acidity.^{54,60} Two hypotheses may explain why our experiments do not show an increase in the rate of CH₃CCl₃ decomposition on used catalysts. The first is that CH₃CCl₃ does not react and replace the surface oxygen. If Cl bonds to Al³⁺ without breaking any Al-O bonds, the Lewis acidity probably does not change very much. Thus, Cl is acting only as a blocking agent on the surface instead of enhancing the acidity. Second, the formation of HCl(g) could be a more favorable process compared

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to Al-O bond breaking. The production of HCl(g), as seen in the IR spectra, would remove Cl from the surface, regenerating most Al³⁺ sites for further reactions without increasing the Lewis acidity of the site. Residual unreactive Cl and possibly adsorbed HCl would eventually block sites active in the decomposition.

As mentioned previously, another reason for the degradation of catalyst performance could be a result of carbon and carboxylate buildup on the surface. Such a process indicates the possible involvement of O^{2-} sites in the reaction. Furthermore, E2 elimination reactions occur with the H abstraction by a base.⁴⁷ Unfortunately, there are no good site-blocking molecules which can be adsorbed on O^{2-} sites at the reaction temperatures to test such a theory.

On the basis of the knowledge that the decomposition of CH_3CCl_3 on Al_2O_3 forms CH_2 =CCl₂ and HCl, that Al^{3+} sites are involved in the reaction, and that H abstraction must occur via a base, it can be surmised that a concerted elimination reaction on Al_2O_3 occurs. In this postulated mechanism, the C-Cl bond of CH_3CCl_3 is attracted to an Al^{3+} site, while the C-H bond of the molecule associates with an O^{2-} site. Further studies are needed to clarify such an hypothesis.

IV. Conclusions

The following results have been obtained for the decomposition of CH_3CCl_3 over Al_2O_3 surfaces in the temperature range 450–600 K.

1. The decomposition reaction

$$CH_{3}CCl_{3} \xrightarrow{\Lambda_{12}O_{3}} CH_{2} = CCl_{2} + HCl_{3}$$

*1 0

is the predominant reaction pathway. Neither CH_3CCl_3 nor CH_2 — CCl_2 is irreversibly adsorbed on the Al_2O_3 surface.

2. A secondary, minor pathway is the formation of carboxylate species on the Al_2O_3 surface.

3. Surface Al-OH groups are not involved in the decomposition reaction.

4. Lewis acid sites, Al^{3+} , are involved in the CH_3CCl_3 decomposition, as found by increasing the concentration of exposed Al^{3+} sites via dehydroxylation or by blocking the sites by preadsorbing pyridine.

5. The CH_2 — CCl_2 formed is relatively unreactive on Al_2O_3 below 550 K.

6. The role of Lewis acid surface sites in the environmental destruction of saturated chloroalkanes may be of importance. However, under aqueous conditions these sites may be deactivated by OH formation.

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Photosensitization of Large-Bandgap Semiconductors. Charge Injection from Triplet Excited Thionine into ZnO Colloids[†]

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The kinetics and mechanism of a diffusion-controlled interfacial charge transfer between excited triplet thionine and ZnO colloids in ethanol have been elucidated with laser flash photolysis. The singlet excited state of thionine, which has a lifetime of 450 ps in ethanol, did not participate in the charge injection process. However, the triplet excited state of thionine was quenched by ZnO colloids. The triplet lifetime (τ_T) decreased from 88 to 15 μ s with increasing ZnO colloid concentration. The maximum charge injection efficiency ($\phi_{TH,2^+}$) which was measured from the yield of dye cation radical was 0.1. The increase in the rate constant for reverse electron transfer (k_r) at high ZnO concentration resulted in a small decrease in charge-transfer efficiency. The dependence of τ_T , $\phi_{TH,2^+}$, and k_r on the concentration of ZnO is described.

Introduction

Photosensitization of a stable, large-bandgap semiconductor has important applications in imaging science and photoelectrochemical conversion of solar energy. This phenomenon often serves the purpose of selectively extending the absorptive range of the semiconductor materials. The principle of a dye sensitization process is illustrated in Figure 1.^{1,2} Control of interfacial charge-transfer processes, viz., charge injection (k_{inj}) and reverse electron transfer (k_r) , is essential in designing efficient photosensitization systems.

One of the intriguing aspects of the photosensitization process is the poor efficiency (often less than 1%) of net charge transfer, although some recent reports have indicated efficiencies of 30-80%.³⁻⁶ Advances have recently been made by employing electrodes with high surface area, e.g., TiO₂ electrodes with fractal surfaces,⁷ and modified sensitizer systems such as antenna-sensitizer molecular devices⁸ or short-bandgap semiconductor colloids.⁹⁻¹² Not only does coupling with a short-bandgap semiconductor extend the photoresponse of the large-bandgap semiconductor, but also the difference in the energy levels of two semiconductor systems improves the efficiency of charge separation.¹²⁻¹⁴ The dye sensitization of a coupled semiconductor

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