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Characterization and Improvements in the Synthesis of the Novel Solid Superacid $AlCl_2(SG)_n$

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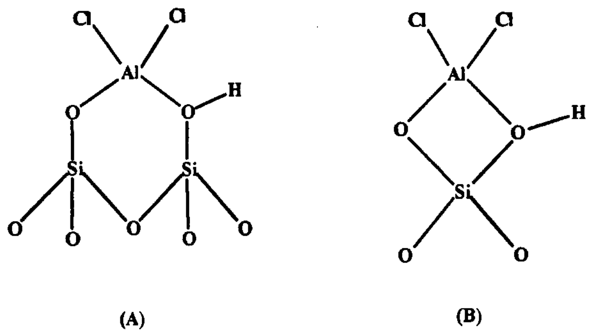
The preparation of the novel solid acid catalyst $AlCl_2(SG)_n$, previously synthesized in CCl_4, has been accomplished with a sealed-tube gas-phase reaction using an extended contact time. Reactivity studies and spectroscopic investigations indicate the similarity in the catalysts prepared via the two different methods. The hydration level of the silica support, prior to use in catalyst synthesis, is examined in this work. Excessively dry silica is deficient in surface silanol (Si–OH) moieties and yields an ineffective catalyst. Exposure of this dry silica to humid air allows sufficient hydration for the preparation of an active catalyst. Calorimetric titration and spectral studies show that the Brönsted acidity of the solid gives rise to its strong acidity.

Introduction

A novel solid acid, denoted as $AlCl_2(SG)_n$, has been reported[1-3] from this laboratory. The material is synthesized by reaction of a slurry of aluminum chloride and silica gel in CCl_4. Characterization by IR and NMR spectroscopy[2] indicates the presence of surface tetrahedral aluminum sites. A simplified model of possible tetrahedral surface sites is illustrated in Figure 1. The unique properties observed for this catalyst arise from the reaction of Al_2Cl_6 with the surface hydroxyl groups on the silica support. A 72-h reflux period is employed for catalyst preparation, in contrast to typical vapor deposition methods,[4-10] which use much shorter contact times. Incomplete reaction of Al_2Cl_6 occurs at short contact times, and catalysts with very short lifetimes result because of desorption of Al_2Cl_6 from the support. The very strong acidity of $AlCl_2(SG)_n$ has been shown by its activity in cracking[2,3] and dehydrohalogenation–hydrodehalogenation reactions[11] under mild conditions where typical zeolite or silica/alumina catalysts are inactive.

The medium employed for the reaction of Al_2Cl_6 with silica gel is critical. Any hydrogen-containing ($CHCl_3$) or -donor (C_6H_6) solvent leads to a much less active solid acid. In a patent issued subsequent to our report,[12,13] it was shown that the gas phase could be used as a reaction medium to prepare a catalyst on alumina that resembled our material. Contacting alumina with sublimed Al_2Cl_6 at high temperatures (550 °C) for an extended period of time (a minimum of 45 min) leads to a material that has reactivity identical to that prepared when $AlCl_3$ reacts with alumina in CCl_4.[1] These preparations employ considerably longer contact times than previously utilized in typical vapor deposition techniques, and as suggested by the CCl_4 studies reported here, these long contact times may be the distinguishing feature which causes these catalysts to possess their unique reactivity. Carbon tetrachloride is an unreactive solvent under these conditions with poor solvating ability. Therefore, its function in the synthesis of $AlCl_2(SG)_n$ could be to provide an inert medium for the reaction of Al_2Cl_6 with the support. If this is the case, it should be possible to prepare $AlCl_2(SG)_n$ with a gas-phase reaction which affords long contact time and uniform contact of Al_2Cl_6 and silica.



(A) (B)

Figure 1. Proposed structures of $AlCl_2(SG)_n$.

Spectroscopic investigations of the solid acids can be used to compare the materials prepared in CCl_4 and the gas phase. The ^{27}Al nuclear magnetic resonance (NMR) of solid[26-30] $AlCl_2(SG)_n$ can be used to compare catalysts made under different reaction conditions. One of the most common methods of examining acid sites on solids utilizes the infrared spectrum of adsorbed pyridine.[14-24] Pyridines bound to Lewis acid sites (including hydrogen-bonded pyridine) exhibit[5] spectral shifts different from that for the pyridinium ion arising from protonation by Brönsted sites.[14] The shift in the frequency of pyridine bound to Lewis sites relative to that of free pyridine gives a qualitative assessment of acid site strengths. This procedure has been used to evaluate

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the acidity of $AlCl_2(SG)_n$ prepared in a series of solvents[2,25] and is found to correlate with the reactivity of the solid in acid cracking reactions.

A "spectroscopic titration" of the catalyst with pyridine would also be an important tool for the characterization of the catalyst surface. Since the pyridinium ion and Lewis-bound pyridine sites have two distinctly different absorbances in the 1400–1700-cm^{-1} region, incremental additions of low concentrations of pyridine can indicate the nature of the most acidic site.

Calorimetry is the most direct method of determining acidity because it yields a value for the enthalpy of interaction which is a direct measure of the bond strength of the solid acid and the donor molecule. The Cal-Ad method has been used previously to determine the surface acidity of a heterogeneous Pd/carbon catalyst[31] and silica.[32] Correlation of enthalpy changes with the spectral changes for various donor concentrations would indicate if there are different types of acid sites and which sites are most reactive. By comparing the results obtained from calorimetric titrations of $AlCl_2(SG)_n$, using pyridine and 2,6-lutidine as basic probe molecules, the contribution to the measured enthalpy from coordination to protonic and aluminum centers can be determined. Steric effects with the latter donor are expected to lead to smaller enthalpies than those for pyridine when sterically hindered, nonprotonic centers are coordinated.

The surface structure of silica consists of hydroxyl (silanol, Si–OH) groups as well as siloxane (Si–O–Si) species. Dehydration of vicinal hydroxyl groups can result in the formation of siloxane bridges. The three-dimensional silica surface contains many different types of silanol environments. Because the dehydration–hydration process is reversible under certain conditions, the content of water in the atmosphere to which the silica is exposed and the temperature at which a sample of silica gel is dried will be factors determining the concentration of surface hydroxyl groups.[33] In addition to silanol groups, species exist in hydrated silica which involve water molecules hydrogen-bonding to surface hydroxyl groups. In the synthesis of $AlCl_2(SG)_n$, reaction of anhydrous Al_2Cl_6 with silanols and water can produce a variety of mixed hydroxo, oxo, and chloro species. Understanding these variables is vital for optimizing solid acid acidity and obtaining reproducibility in catalyst preparation.

Experimental Section

Reagents. The aluminum chloride used to prepare all catalysts and the silica gel support (340 m^2/g) was described in earlier reports.[1-3] Solvent purification was also described earlier. Preparation of the silica support prior to catalyst preparation consists of activation with 1 M HCl, water washing, and drying at 80 °C for 72 h under vacuum (1 mmHg). Following the drying period, adsorption of water at a level of 0.02 g of H_2O/g of dry silica hydrates the support sufficiently for preparation of the active catalyst. This process will be referred to as "conditioning of the silica" and is accomplished by exposure of the dry silica go the atmosphere (approximately 75% humidity) for 24 h. "Hydrated silica" will refer to silica that was washed and not dried at elevated temperature so it has an excessive water content.

Instrumentation. GC analysis for hydrocarbon products was conducted on a Varian Model 940 gas chromatograph equipped with a flame ionization detector and either a $^1/_8$ in. × 8 ft stainless steel Hayesep Q (80–100 mesh) column or a $^1/_8$ in. × 6 ft stainless steel VZ-10 (60–80 mesh) column. FTIR was performed on a Nicolet 5DXB FTIR spectrometer. Magic angle spinning solid-state NMR was performed on a Bruker AM-500 NMR spectrometer on a GE NT-300 superconducting, wide-bore 300-MHz FTNMR spectrometer operating at 7.02 T. $Al(NO_3)_3(aq)$ was the reference for all ^{27}Al NMR studies. UV/vis spectra were obtained using a Perkin-Elmer Lambda 6 UV/vis spectrophotometer.

Reactor. Test reactions utilizing $AlCl_2(SG)_n$ are typically carried out in a batch reactor. The batch reactor consists of a 250-mL Parr pressure bottle with a stainless steel pressure head (consisting of fill/purge valves, pressure gauge, and sample port) and a neoprene stopper gasket.

Catalyst Preparation. The preparation of the supported aluminum chloride catalyst from CCl_4 was carried out as previously reported.[1-3]

Sealed-System Catalyst Preparation. A sealed-system, vapor-phase method for catalyst preparation was devised. A 250-mL Parr pressure bottle was dried to remove traces of water. Silica gel, 2.0 g (prepared as described previously), along with 1.0 g of anhydrous Al_2Cl_6 was sealed in the bottle with a neoprene stopper. The pressure bottle was clamped into the same holder as used for the batch catalytic reactions. The pressure head was not used, but care was taken to use amounts of Al_2Cl_6 that would not exceed 60 psi, the maximum pressure rating for the bottle. The sealed system was placed in an oil bath in the temperature range 175–190 °C to volatilize the Al_2Cl_6. This reaction was allowed to proceed for a minimum of 72 h, after which time the bottle was cooled and the clamps were slowly loosened to carefully break the seal and release the pressure arising from the HCl formed in the reaction. Once the pressure was relieved, the stopper was replaced to protect the catalyst from water. The gray solid obtained appeared homogeneous and was used directly in catalytic experiments.

Infrared Analysis. A sample of $AlCl_2(SG)_n$ was placed in a vacuum desiccator with a pyridine reservoir, and the system was evacuated to generate a pyridine atmosphere inside. The catalyst was kept in the pyridine environment at room temperature for 2–3 h, during which time the color of the catalyst changed to off-white. The catalyst was then removed from the desiccator and placed under vacuum for at least 2 h to remove excess pyridine. This evacuation step was conducted both at room temperature and at elevated temperatures (150 and 300 °C) to remove pyridine bound to different extents by the solid. Infrared spectra were taken as Fluorolube mulls of the catalyst on KBr plates prepared in an inert atmosphere.

The infrared adsorption titration of pyridine was conducted in an inert atmosphere of dry N_2. Injections of pyridine were made into a slurry of 0.10 g of catalyst in 10 mL of CCl_4. After about 5 min of stirring, the catalyst was filtered off and dried. The infrared spectrum was then obtained as a Fluorolube mull. Pyridine loadings ranged from 1.2 to 11 mmol/g.

Calorimetric Titrations. The calorimeter and the procedure to measure enthalpies have been described previously.[32] The cell was loaded with 0.50 g of catalyst and 50 mL of solvent (CCl_4 or cyclohexane) in a dry N_2 atmosphere. The concentrations of pyridine and 2,6-lutidine ranged from 0.2 to 50 mmol/L.

Results and Discussion

Influence of Silica Hydration on the Synthesis of $AlCl_2(SG)_n$. Gel-type silicas are generally prepared by the acid hydrolysis of reactive silicon compounds, such as $SiCl_4$ or $Si(OR)_4$, to obtain polymerized orthosilicic acid, $Si(OH)_4$, which is dehydrated to form the gelatinous solid material. The preparation and structures of the materials produced at various stages of dehydration were recently reviewed by Hench.[33] These gels typically possess some short-range crystalline order but as a whole are amorphous, due to incomplete condensation of silanol functionalities and imperfect ordering during the polymerization process. The surface of this solid consists of Si–O–Si and Si–OH functionalities. Silica gel that has not been heated at elevated temperatures (≥500 °C) contains clusters of hydroxyl functionalities on neighboring silica atoms. Lattice defects exist[34] which consist of neighboring geminal hydroxyl groups (two hydroxyls attached to one silicon atom). Mild heating (to about 100 °C) leads to dehydration and formation of siloxane bridges. The strain on the lattice induced by this reaction is the driving force for the reverse reaction at

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Table 1. Physical Characteristics and Reactivity of $AlCl_2(SG)_n$ Samples Prepared with Silica in Varying Degrees of Hydration

sample[a]	color	$HCl/AlCl_3$	rel cracking activity	details
A	brown	0.7	0.16	C_1–C_3 in large quantity
B	yellow	1.3–1.7	1.0	std R^+ distribn
C	white	2.2	$<10^{-5}$	minimal products obsd

[a] Silica pretreatment: sample A, activate with 1 M HCl and dry at 80 °C for 72 h under vacuum. Sample B: same as for sample A but exposed to atmospheric water for 24 h. Sample C: activate with 1 M HCl and dry at 40 °C for 24 h.

room temperature in the presence of water. If the silica is taken to high temperature, >500 °C, the surface loses more hydroxyl functionalities and the structure becomes more ordered. This reordering at high temperature results in alleviation of the ring strain mentioned above and accounts for the hydrophobicity of silicas which are treated at elevated temperatures.

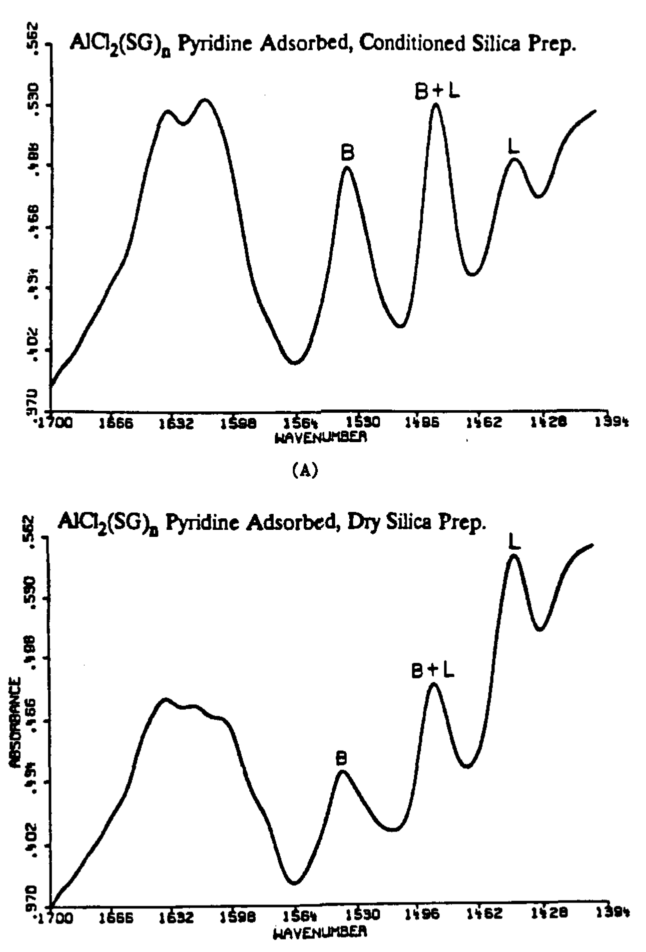
The reaction of Al_2Cl_6 with the silica surface can give rise to a variety of species. Some simple representations are given in Figure 1. Formation of these species corresponds to the evolution of 1 mol of HCl/formula weight of $AlCl_3$ during the synthesis. We have found that conditioned silica gel that evolves from 1 to 1.5 mol of HCl during synthesis leads to an active catalyst. Other aluminum species with less than two bound chlorines must be present and can arise from reaction of Al_2Cl_6 with clusters of SiOH groups on the surface.

The effect of silica hydration on the preparation of $AlCl_2(SG)_n$ is perhaps best illustrated by comparing the activities of catalysts prepared with those of "dry" silica, hydrated silica (excess adsorbed H_2O), and conditioned silica. Table 1 provides a comparison of the activities for the cracking of *n*-hexadecane in a batch system. Silica sample A was activated with 1 M HCl and dried at 80 °C for 72 h, as reported in the literature.[2,3,25] When this silica sample is used directly from the drying oven in the catalyst synthesis procedure, a brown catalyst intermixed with white particles results, indicating less than complete reaction of the Al_2Cl_6 with the silica sample. The reactivity of this catalyst in hexadecane cracking produces isobutane in a small amount with additional C_1–C_3 hydrocarbons. Since Al_2Cl_6 will crack hydrocarbons but deactivate rapidly,[26] the activity seen with this catalyst is not unexpected.

Silica possessing a high adsorbed water content is also unfavorable for $AlCl_2(SG)_n$ preparation. When the acid-washed silica is dried at 40 °C for 24 h, the silica retains a considerable amount of Si–OH groups. The product of the reaction of moist silica and Al_2Cl_6 has a white color, and 2.2 mol of HCl is evolved during synthesis per formula weight of $AlCl_3$ used. At least 10% of the aluminum species do not contain any Al–Cl bonds and are probably six-coordinate aluminum. The solid material prepared from wet silica shows no activity in cracking.

Relatively small variations in the silica hydration produce very different materials upon reaction with Al_2Cl_6. The active version of the catalyst is prepared with dried silica which is allowed to absorb water from humid air for a minimum of 24 h. During this time period, the mass of the silica gel increases by 0.02 g (±0.001 g)/g of dry silica, or 28 mmol of water/g of silica.

Infrared Examination of Adsorbed Pyridine. In order to obtain a qualitative assessment of the different acid sites for $AlCl_2(SG)_n$ prepared with silica at various stages of hydration, the infrared spectrum of adsorbed pyridine can be used. The active catalyst prepared with conditioned silica and the sample prepared with excessively dry silica are degassed under vacuum at 200 °C for 3 h or more, contacted with pyridine vapors for a minimum of 3 h, and degassed a second time at various temperatures to remove excess and weakly bound pyridine. The infrared spectrum is taken (Figure 2) for varying extents of pyridine removal. A band at ~1540 cm^{-1} involves a C–N$^+$–H bending vibration and is used as a fingerprint for the pyridinium ion. A band at 1452 cm^{-1} is assigned to Lewis-bound pyridine, and this includes pyridine that is hydrogen-bonded or bound to aluminum. A third band at 1485 cm^{-1} results from both Lewis and pyridinium species.



$AlCl_2(SG)_n$ Pyridine Adsorbed, Conditioned Silica Prep.

(A)

$AlCl_2(SG)_n$ Pyridine Adsorbed, Dry Silica Prep.

(B)

Figure 2. Infrared spectra of pyridine adsorbed on $AlCl_2(SG)_n$ prepared with (A) conditioned silica and (B) dry silica.

In catalysts made with dry silica and hydrated silica, there are significant amounts of both pyridinium and Lewis adducts on the catalysts. The patterns (Figure 2) for the three peaks are sufficiently different that qualitative judgments can be made as to respective amounts of each acid site type. The pyridinium peak, at 1540 cm^{-1}, for the active catalyst (made with conditioned silica) is more intense than the Lewis/hydrogen-bonding band at 1452 cm^{-1}. This three-band pattern is very reproducible for catalytically active $AlCl_2(SG)_n$. In the case where the catalyst is prepared with dry silica, the pyridinium band is much less intense than the Lewis/hydrogen-bonding peak. The large amount of unreacted Al_2Cl_6 present in the dry silica catalyst sample coordinates pyridine via a Lewis interaction and could contribute to the intensity of the 1452-cm^{-1} peak.

Infrared Titration. Figure 3 illustrates the results of the infrared titration in carbon tetrachloride. Upon addition of 1.2 mmol of pyridine/g of catalyst, the pyridinium ion is the only species present (absorbance at 1540 cm^{-1}). As excess pyridine is added to the catalyst (11 mmol/g), absorbance from another species is observed. This is assigned to a hydrogen-bonded adduct, since coordination to an aluminum center can be ruled out with the results obtained from the calorimetric titrations; vide infra.

Solid-State Magic Angle Spinning NMR. One of the most useful methods for elucidating the coordination number of aluminum is solid-state magic angle spinning nuclear magnetic resonance (abbreviated MAS NMR). The ^{27}Al MAS NMR spectrum (300 MHz) for $AlCl_2(SG)_n$ prepared in CCl_4 with conditioned silica is presented in Figure 4. The peak at 64 ppm

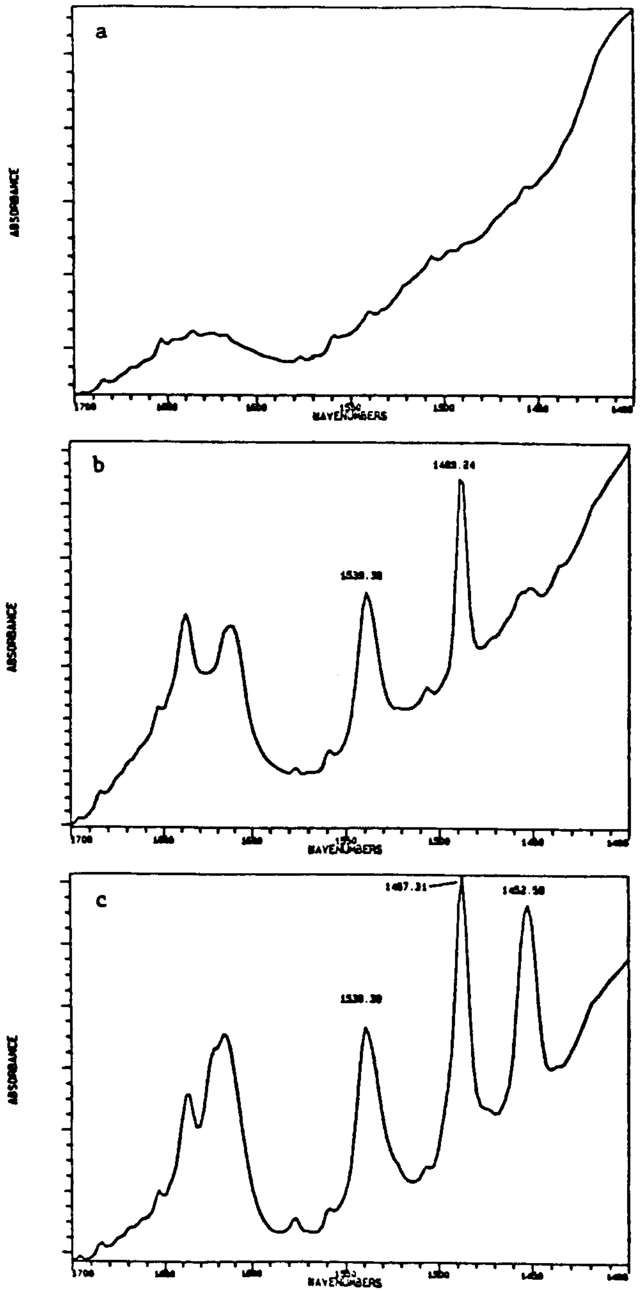


Figure 3. Infrared spectra obtained for titration of active catalyst with (a) no pyridine, (b) 1.23 × 10^{-3} mol/g of pyridine, and (c) 1.13 × 10^{-2} mol/g of pyridine.

is assigned to a Si–O–$AlCl_2$ moiety, which is consistent with the value of 62.8 ppm obtained for aluminum chlorohydrate (Cl/OH = 2.5).[35]

The spectrum for the catalyst prepared with dry silica contains a peak at 0 ppm, indicating the presence of octahedral aluminum. A very prominent feature of this spectrum is a sharp signal at 101 ppm, which coincides with the value of 105 ppm reported for anhydrous Al_2Cl_6.[29] This observation along with the increased intensity for the IR band of Lewis-bound pyridine shows that a substantial amount of Al_2Cl_6 has not reacted with the support. Desorption of 18% of the aluminum chloride from this material occurs at 200 °C under flowing N_2. The catalyst prepared with conditioned silica shows no desorption of Al_2Cl_6 even at 250–275 °C.

The absence of major features in the 40–80 ppm range for the dry silica product is in contrast to the spectrum for the conditioned silica catalyst. This suggests that the strong acid site responsible for catalytic activity in hydrocarbon conversion reactions is the tetrahedral Al species appearing at 65 ppm.

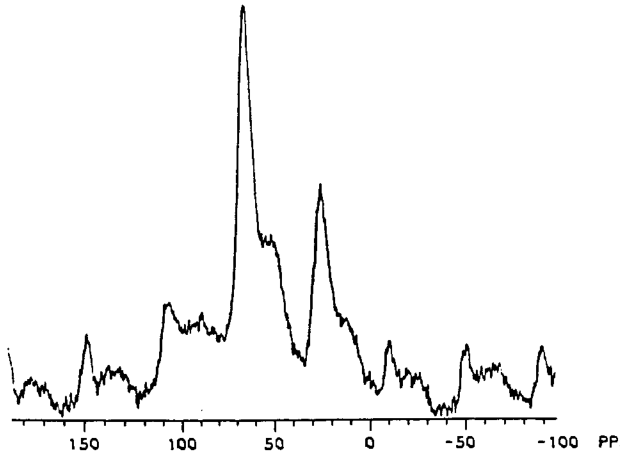


Figure 4. ^{27}Al MAS NMR spectrum of $AlCl_2(SG)_n$.

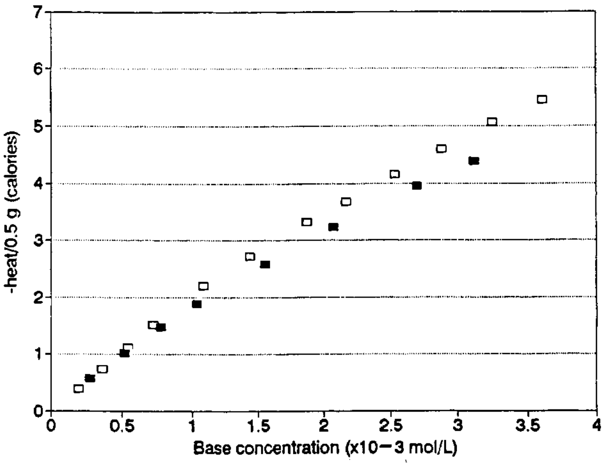


Figure 5. Heats evolved for active catalyst at low concentrations of pyridine (■) and 2,6-Lutidine (□).

Calorimetric Titration. A nonpolar solvent is utilized to elucidate the enthalpy of interaction between $AlCl_2(SG)_n$ catalyst and pyridine. Cyclohexane is the best choice for this, except that the catalyst has been shown to be a good hydrocarbon-cracking and -isomerization catalyst.[3] Carbon tetrachloride is another good solvent, except that it is known to form a complex with strong-electron-donor amines (e.g. pyridine).[35] The results of titrations in both solvents yielded the same heats within experimental error (the value in carbon tetrachloride was corrected by adding 1 kcal mol^{-1} for the heat of complex formation with pyridine). The remaining titrations were done in cyclohexane, since there was no contribution to the heat from isomerization or cracking under the conditions of the calorimetric titration.

To determine the types and strengths of acid sites present on the catalyst surface, a calorimetric titration of the catalyst at low base concentrations was done. Pyridine and 2,6-lutidine were chosen as the probe bases in order to distinguish between protonic and aluminum sites. The inductive effect of the methyl groups on 2,6-lutidine makes it a slightly stronger donor than pyridine. However, the methyl groups can cause steric hindrance with large acceptors, resulting in a weaker interaction. Figure 5 shows the similarity in reactivity between the two bases at low concentration. It is obvious from this experiment that the acid sites on the catalyst are very strong ($\Delta H = -40$ kcal/mol for pyridine). The enthalpy of this interaction is also considerably stronger than the −28 kcal/mol enthalpy of adduct formation between aluminum trimethyl and pyridine and much larger than the −12.6 kcal/mol enthalpy of the interaction of pyridine with silica gel. This titration rules out the possibility of any Lewis acidity other than hydrogen

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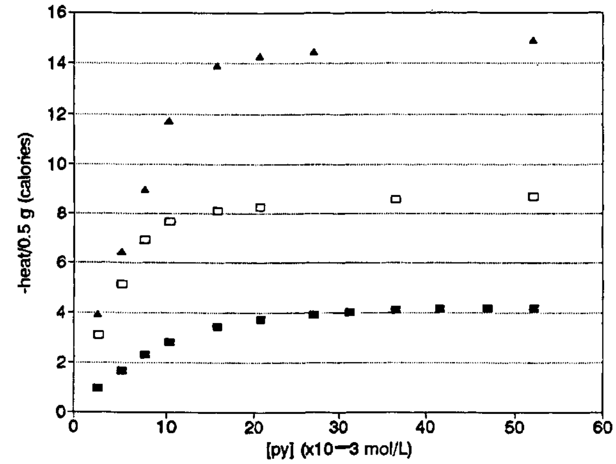

Figure 6. Heats evolved for active catalyst with pyridine over a large concentration range for conditioned silica (■), active catalyst (▲), and deactivated catalyst (□).

bonding, since the enthalpy of adduct formation for 2,6-lutidine is slightly higher than the enthalpy for pyridine adduct formation. Steric constraints are expected with 2,6-lutidine on an aluminum acceptor center and would lead to a reduced enthalpy for this donor compared to pyridine if such centers were involved.

In order to quantify the acid sites present on the catalyst, the Cal-Ad method[31] was attempted. This involves the combination of calorimetric and adsorption titration data. Figure 6 shows the results of the calorimetric titration of the active catalyst over a large pyridine concentration range. Results for catalyst which has been deactivated in a flow reactor by allowing a constant flow of N_2 to pass over it for 24 h at room temperature (this treatment resulted in the loss of HCl and reduced the activity of the catalyst) are also shown. The deactivated catalyst has undergone a loss in the number of acidic sites, resulting in the reduction of the total heat evolved in the titration. A small number of strong sites remain in the deactivated catalyst, as indicated by the heat evolved at low pyridine concentration.

The adsorption titration led to an interesting result. An initial addition of 0.14 mmol of pyridine to 0.5 g of catalyst in 50 mL of cyclohexane was made. The reaction was allowed to come to equilibrium, and the UV/vis spectrum was taken of a sample of the solution above the solid. This spectrum indicated that there was no pyridine in solution but there was a small amount of a new species present at longer wavelength (267 nm). Appearance of this band was accompanied by an increase in base line absorbance at all wavelengths, most likely due to small solid particles in the solvent. At this amount of added pyridine, (nearly 0.3 mmol/g), the IR data for the solid catalyst showed that the pyridinium ion is formed. As successive additions of pyridine were made to the solid in cyclohexane, the absorbance at 267 nm increased. When the amount of pyridine added reached 1.6 mmol/g, free pyridine was found in solution (absorbance at 251 nm). At this and higher pyridine concentrations, the absorbance at 267 nm did not increase.

To identify the species responsible for absorption at 267 nm, small amounts of a cyclohexane solution saturated with HCl were added to a solution of pyridine in cyclohexane. The protonation of pyridine was followed spectroscopically. A species was formed which absorbed at 267 nm, and an increase in base line absorbance at all wavelengths was again observed. From this result, it can be concluded that in the titration of $AlCl_2(SG)_n$, at concentrations between 0.3 and 1.6 mmol/g of pyridine, pyridinium chloride is formed from dehydrohalogenation of the catalyst. The dehydrohalogenation of $AlCl_2(SG)_n$ is also the principal reaction leading to loss of activity when the catalyst is used in cracking. As reported previously,[2,3] addition of HCl to the feed greatly enhances catalyst lifetime for the cracking reactions.

Sealed-System Catalyst Preparation. Preparation of $AlCl_2(SG)_n$ in a vapor-phase reaction using a sealed system was performed to test the proposal that CCl_4 functions as an unreactive medium. Since a key aspect of the CCl_4 synthesis of $AlCl_2(SG)_n$ is the amount of time the catalyst components are allowed to react, the sealed-system reaction was run for a minimum of 72 h.

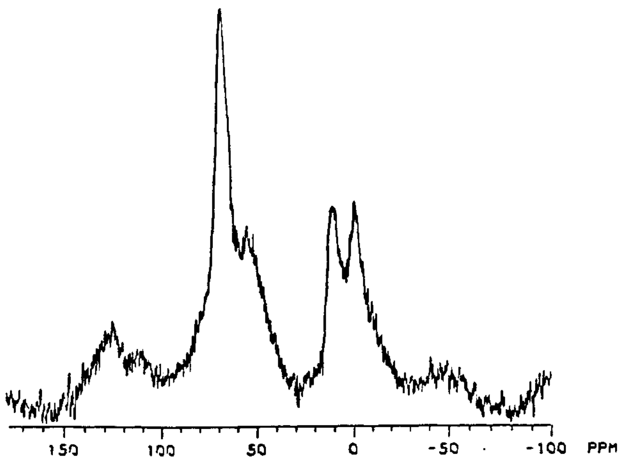

Figure 7. SS MAS NMR spectrum of $AlCl_2(SG)_n$ prepared in a sealed system.

The infrared spectra of pyridine adsorbed on a catalyst made in CCl_4 and the catalyst made in a sealed system over 72 h were compared. The resulting spectrum for the gas-phase preparation is identical to that of the catalyst prepared in CCl_4 (Figure 2A), and implying a similar distribution of acid sites for both samples.

The IR spectrum for pyridine adsorbed on a catalyst prepared in the sealed system with only 18-h reaction time was also recorded. A significantly different pattern was observed, with the Lewis band more intense in relation to the pyridinium peak. This is expected if unreacted Al_2Cl_6 is present in the solid.

The solid-state MAS NMR spectrum for $AlCl_2(SG)_n$ prepared in a sealed system (72 h) is presented in Figure 7 and can be compared to that of the active catalyst prepared in CCl_4 (Figure 4). The signal at 65 ppm attributed to tetrahedral Al sites is very strong for both samples. The spectrum of the gas-phase product contains a peak at 0 ppm which can be assigned to aluminum coordinated to six oxygens. The signal at 20 ppm in Figure 7 is attributed to an octahedral Al site with both chloride and oxygen ligands. This peak is similar to one for the catalyst prepared in CCl_4.

The catalyst prepared by the sealed-system (S/S) method was next compared with the catalyst prepared in CCl_4 in the cracking of *n*-hexadecane. The reactions were carried out in a batch reactor. At 100 °C under 30 psig of hydrogen, 1.0 g of the catalyst prepared by the gas-phase reaction produced 0.22 (±0.02) mol of isobutane/mol of Al sites compared to 0.20 (±0.02) mol of isobutane/mol of Al sites for the $AlCl_2(SG)_n$ prepared in CCl_4. It is apparent that both catalysts give good activity in cracking reactions and are indistinguishable. The same strong acid sites are produced when the catalyst is prepared in carbon tetrachloride or via prolonged contact in the gas phase. We believe that the strong acid sites correspond to the species shown in Figure 1.

Conclusions

An alternative preparation for the novel catalyst $AlCl_2(SG)_n$ is reported, and the effects of silica hydration on catalyst structure and reactivity are determined. A prolonged vapor deposition method, where sublimed Al_2Cl_6 is contacted with silica for an extended period of time (72 h), was found to produce a catalyst similar to the catalyst synthesized in CCl_4. Infrared spectroscopy on adsorbed pyridine showed identical acid site distributions and similar acid strengths for the hydrogen-bonding sites in both preparations. Solid-state NMR experiments revealed the presence of a species with a band at 65 ppm in both the CCl_4-prepared catalyst and the gas-phase catalyst. The presence of this signal in the spectra of all of the strong solid acids capable of low-temperature cracking activity strongly suggests that this species is the active catalytic site.

The preparation of $AlCl_2(SG)_n$ was investigated from the standpoint of silica hydration. The amount of water was found to have a significant influence on the reaction of Al_2Cl_6 with the silica surface. Infrared examination of adsorbed pyridine and solid-state MAS NMR indicated the presence of unreacted Al_2Cl_6 as well as drastically different acid sites on the catalyst prepared with dry silica. Prolonged catalytic activity results only when Al_2Cl_6 is condensed with SiOH groups to form the catalytically active moieties (Figure 1) using properly conditioned silica gel.

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