trum of the solid. During preparation of the KBr pellet, the green solid turned brown and the IR spectrum showed bands of $[Mo_2(CO)_6Cp_2]$ and of $[Pd_2MoBr(CO)_2Cp(dppm)_2]$. When another evaporated sample of the blue-green solution was redissolved in THF, it turned immediately brown. The blue-green Et_2O solution was kept at -20 °C. After 48 h, a yellow-brown solid precipitated (identified as $[Pd_2MoCl(CO)_2Cp(dppm)_2]$) and the supernatant contained $[Mo_2(CO)_6Cp_2]$. When this reaction was carried out in THF instead of Et_2O, it never led to a green solution but instead to a brown solution. However, using a slightly different workup allows isolation of the desired cluster $[Pd_2Mo_2Cp_2(CO)_5(dppm)_2]$.[3c]

Synthesis of $[Pd_2MoCoCp(CO)_6(dppm)_2]$ (13a). A solution of Na$[Co(CO)_4]$ (0.7 mL of a 0.1 M solution in THF) was added to a solution of **11a** (0.086 g, 0.070 mmol) in THF (5 mL). Upon addition, the solution turned from a dark honey color to red violet. The solvent was removed, and the solid was extracted with toluene (15 mL), affording a brown-violet solution. Dark brown crystals of **13a** were obtained by cooling at -20 °C (0.063 g, 0.046 mmol, 66% based on Pd). Anal. Calcd for $C_{61}H_{49}CoMoO_6P_4Pd_2$ (M_r = 1369.7): C, 53.49; H, 3.61. Found: C, 52.91; H, 3.96. ^1H NMR (toluene-d_8): δ 7.66-6.55 (40 H, m, Ph), 4.77 (5 H, s, Cp), 4.21 (2 H, t, ^2J(P-H) = 7.5 Hz, CH_2), 3.57 (2 H, t, ^2J(P-H) = 9.3 Hz, CH_2).

Metal-Exchange Reaction: Conversion of 13a into 3a. A toluene solution of cluster **13a**, prepared as described above from **11a** (0.056 g, 0.045 mmol) and K$[Co(CO)_4]$ (0.019 g, 0.09 mmol), was stirred for 3 days, during which time the color of the mixture changed from the original brown-violet to deep green and an insoluble dark material formed. Filtration through Celite and recrystallization from THF/*n*-hexane afforded a dark green powder of **3a** (0.025 g, 0.019 mmol, 42% yield based on Pd, 84% based on Co).

Synthesis of $[PdPtMoCoCp(CO)_6(dppm)_2]$ (13b). A brown mixture of **11b** (0.133 g, 0.100 mmol) and Na$[Co(CO)_4]$ (1 mL of a 0.1 M solution in THF) in THF (30 mL) was stirred for 1 day, after which time the solvent was removed. Extraction of the solid with toluene (20 mL) afforded a brown-violet solution. Dark brown crystals of **13b** were obtained by cooling at -20 °C (0.1015 g, 0.072 mmol, 72% based on Pt). Anal. Calcd for $C_{61}H_{49}CoMoO_6P_4PdPt$ (M_r = 1458.3): C, 50.24; H, 3.39. Found: C, 50.02; H, 3.64. ^1H NMR (toluene-d_8): δ 7.72-6.61 (40 H, m, Ph), 4.94 (5 H, d, J(P-H) = 1.5 Hz, Cp), 4.61 (2 H, t, ^2J(P-H) = 8.6 Hz, J(Pt-H) = 63 Hz, CH_2), 3.82 (2 H, t, ^2J(P-H) = 10.1 Hz, J(Pt-H) = 38.4 Hz, CH_2).

Synthesis of $[Pd_2WCo(CO)_6Cp(dppm)_2]$ (14). Solid Na$[Co(CO)_4]$ (0.011 g, 0.060 mmol) was added to a suspension of $[Pd_2WCl(CO)_2Cp(dppm)_2]$ (**12**) (0.065 g, 0.049 mmol) in Et_2O (20 mL) at -78 °C. The temperature was raised to ambient, and the color of the reaction mixture turned from yellow-brown to deep red. *n*-Hexane was added, and the resulting solid, which was collected by filtration, was separated from NaCl and excess Na$[Co(CO)_4]$ by dissolution in toluene (50 mL). The resulting violet solution was concentrated to ca. 20 mL, and an equal volume of *n*-hexane was added. This afforded **14** as dark violet microcrystals (0.065 g, 89% based on Pd). Anal. Calcd for $C_{61}H_{49}CoO_6P_4Pd_2W$ (M_r = 1457.54): C, 50.27; H, 3.39. Found: C, 50.41; H, 3.45. ^1H NMR (toluene-d_8): δ 7.28-6.81 (40 H, m, Ph), 5.05 (5 H, s, Cp), 4.59 (2 H, t, ^2J(P-H) = 8.7 Hz, CH_2), 4.13 (2 H, t, ^2J(P-H) = 9.7 Hz, CH_2).

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Preparation, Characterization, and Catalytic Activity of a New Solid Acid Catalyst System

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A series of novel, solid, strong acids have been prepared by the reaction of inorganic oxides with Al_2Cl_6. The objective was to create a solid acid with tetrahedral aluminum centers, which are expected to be stronger Lewis acids than octahedral aluminum centers. Investigations of the acid sites of these solids by the infrared spectroscopy of adsorbed pyridine, calorimetric titrations, and solid-state nuclear magnetic resonance confirm that new strong solid acids have been prepared. The systems exhibit high catalytic activity and selectivity for acid-catalyzed cracking reactions under very mild conditions where present commercial catalysts do not react.

Introduction

Because of the reported advantages of solid acid catalysts, recent research has focused on the preparation and characterization of stronger solid acids.[1-3] These materials exhibit extremely high catalytic activity for reactions such as isomerization, cracking, hydrocracking, dehydration, alkylation, acylation, conversion of methanol to gasoline, etc.[1] Many attempts have been made to use metal halides as homogeneous acid catalysts, and one of the most frequently studied inorganic Lewis acids is aluminum chloride. Aluminum chloride was tested commercially in cracking but was abandoned because of technical difficulties such as corrosion, separation of phases, difficulty in the recovery of the catalyst, and the formation of high molecular weight hydrocarbons.[3,4] As a result, recent research has focused on the anchoring of homogeneous acid catalysts onto inorganic oxides for use as solid acid catalysts.[1-6]

Many patents have been issued for the treatment of inorganic oxides with aluminum chloride.[7-14] The most common method of treating hydroxylated inorganic oxides with aluminum chloride is by vapor deposition.[2,7-13] The vapors of aluminum chloride are passed through the inorganic oxide by using a carrier gas such as helium,[6,8,9,11,13] or aluminum chloride is sublimed from a mixture of the inorganic oxide and aluminum chloride.[10,13] The reaction of aluminum chloride and the inorganic oxide in a solvent has been employed as an alternative to vapor deposition.[7] Past attempts[7] of this reaction have employed solvents other than CCl_4, for example, chloroform ($CHCl_3$), methylene chloride (CH_2Cl_2), ethylene dichloride ($ClCH_2CH_2Cl$), and saturated hydrocarbons. We report that employing CCl_4 with the procedure reported herein

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(1) Tanabe, K. In *Heterogeneous Catalysis*; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1984; Vol. 2, pp 71-94.

(2) Olah, G. A.; Surya Prakash, G. K.; Sommer, J. *Superacids*; Wiley: New York, 1985; p 53.

(3) Pines, H. *The Chemistry of Catalytic Hydrocarbon Conversion*; Academic Press, Inc.: New York/London, 1981; pp 100-122.

(4) Corma, A.; Wojciechowski, B. W. *Catal. Rev.—Sci. Eng.* **1985**, *27*, 29.

(5) Stinson, S. C. *Chem. Eng. News* **1986**, *64* (7), 27.

(6) Melchor, A.; Garbowski, E.; Mathieu, M.-V.; Primet, M. *J. Chem. Soc., Faraday Trans. 1* **1986**, *82*, 1893-1901.

(7) Kelly, J. T.; Sechrist, C. N. U.S. Patent 3 248 343, April 26, 1966.

(8) Olah, G. A.; Messina, G. U.S. Patent 3 993 587, Nov 23, 1976.

(9) Hamner, G. P.; Mattox, W. J. U.S. Patent 3 961 036, June 1, 1976.

(10) Smith, R. M. U.S. Patent No. 2 927 087, March 1, 1960.

(11) Herbstman, S.; Webb, A. N.; Estes, J. H. U.S. Patent 4 066 716, Jan 3, 1978.

(12) Herbstman, S.; Webb, A. N.; Estes, J. H. U.S. Patent 4 113 657, Sept 12, 1978.

(13) Myers, J. W. U.S. Patent 3 449 264, Nov 27, 1961.

(14) Drago, R. S.; Getty, E. E. U.S. Patent 4 719 190, Jan 12, 1988.

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produces a unique very strong acid that does not evolve Al_2Cl_6 when heated. In contrast to the case for CCl_4, preparations with other solvents lead to materials that are poorer catalysts or evolve aluminum chloride from the catalyst surface with time, resulting in only short-term activity.[2,7-13]

Experimental Section

Materials. The supports used for the preparation[14] of the catalysts are silicon dioxide (SiO_2), alumina (Al_2O_3), high-silica zeolite (silicalite), Y-zeolite (LZ-Y82), boron oxide (B_2O_3), titanium dioxide (TiO_2), and magnesium oxide (MgO). All support materials were used as purchased unless otherwise stated. For the silicon dioxide supports the primary material was Davison Grade No. 62 silicon dioxide (donated by W. R. Grace Co.) with a surface area of 340 m^2/g, a pore volume of 1.1 cm^2/g, and a mesh size of 60–200. The three silicon dioxide support materials used for surface area dependence studies were purchased from AESAR. All three supports are 60–325 mesh size with surface areas of 215 m^2/g, 420 m^2/g, and 690 m^2/g and pore volumes of 1.0 cm^3/g, 0.8 cm^3/g, and 0.4 cm^3/g, respectively. The alumina support, acid Brockman activity I (80–120 mesh), had a surface area of 180 m^2/g. A high-silica zeolite, which was donated by Union Carbide, had a surface area of 400 m^2/g and a pore volume of 0.19 cm^3/g. The Y-zeolite was a Linde LZ-Y82 molecular sieve purchased from Alfa Products and is used commercially as a fluid catalytic cracking (FCC) catalyst. The boron oxide was purchased from AESAR and had a mesh size of 60. Bayer AG donated the hydroxylated titanium dioxide (surface area 200 m^2/g), and the magnesium oxide was purchased from Fisher. Aluminum chloride (Al_2Cl_6) was purchased from Alfa Products with a purity of 99.997%.

All solvents were purchased from Fisher Scientific except *n*-dodecane and *n*-hexadecane, which were purchased from Alfa Products. Other reactants used for cracking reactions were activated carbon (Curtin, MCB) and resid (FHC-353 donated by Amoco). Carbon tetrachloride, chloroform, and methylene chloride were dried over phosphorus(V) oxide (Fisher). Benzene was dried by distillation over calcium hydride. Cyclohexane and chloroform (containing ethanol as a stabilizer) were purified by passage through an activated alumina column. Tetrachloroethane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-dodecane, *n*-hexadecane, and cumene were used as purchased. Gold label (99+%) pyridine was purchased from Aldrich and was used without further purification. All solvents were stored over 4-Å molecular sieves (Davison).

The gaseous reactants methane, dimethyl ether, propylene, propane, isobutane, technical grade hydrogen chloride (99.0%), and CP grade carbon monoxide (99.5%) were purchased from Matheson. Hydrogen, helium, argon, and nitrogen were supplied by Airco and Liquid Air. Semiconductor grade hydrogen chloride (99.995%) was purchased from Air Products.

Catalyst Preparation and Catalytic Studies. Our catalyst is prepared[14] by reacting an inorganic oxide with 9.1, 16.7, or 33.3 wt % aluminum chloride (Al_2Cl_6) in refluxing carbon tetrachloride (CCl_4). In a typical preparation, a 250-mL 3-neck round-bottom flask equipped with a reflux condenser and Teflon-coated magnetic stir bar was used. To this is added 10.20 g of silica gel (washed with 1 M HCl and dried under vacuum at 80 °C for 72 h) and 150 mL of carbon tetrachloride (dried over 4-Å sieves). After the system was purged with nitrogen (N_2), 5.10 g of anhydrous aluminum chloride Al_2Cl_6 was added and the mixture was allowed to stir at reflux under a N_2 atmosphere for 5 days in the absence of light.

After approximately 1 h the mixture develops a color that increases in intensity with time over 3 days. The reflux time may vary from 1 to 3 days, and the color of the final product may be bright yellow or dark purple. If the procedure is not followed carefully, or if poor-grade Al_2Cl_6 is employed, tan, black, or white inactive solids result.

The reaction mixture was filtered under a N_2 atmosphere. The filtrate was colorless, and the resulting colored solid product obtained was utilized as the catalyst material for the cracking experiment described below. The catalyst was water sensitive and turned white on exposure to moisture.

The most active catalysts give an EPR signal indicative of a free radical with a *g* value of 2.012. The free radical on the catalyst surface exhibits no activity toward reactions sensitive to the presence of radicals (e.g. free-radical polymerization reactions) and is not believed to play a role in the observed catalytic activity of the catalyst. If the reflux time is too short, the catalyst is less active and has a broad EPR signal at $g = 2.06$. The solvents chloroform, methylene chloride, ethylene dichloride, and benzene were also employed in catalyst preparations. Various preparations of the catalyst give reproducible results with respect to both preparation and activity.

Catalytic studies were conducted in a fixed bed flow reactor system employing ≈1.0 g of catalyst with a system pressure of 10–14 psi. Hydrogen and helium were passed through mineral oil bubblers whereas the HCl was bubbled through sulfuric acid. The gases were allowed to mix and pass through a bubbler that contained a hydrocarbon or a hydrocarbon/carbon tetrachloride mixture. The flow rates of the individual gases were controlled by Teflon needle valves. This gas mixture was then allowed to flow through a catalyst that was supported on a glass frit.

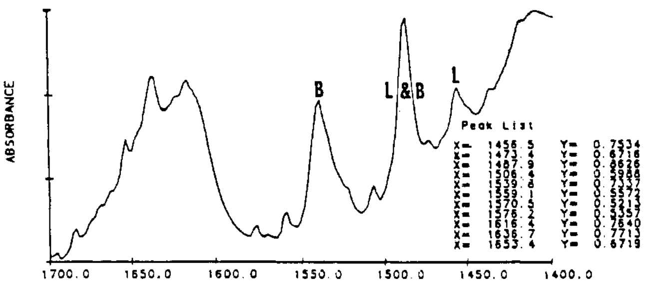

Figure 1. Infrared spectrum of $AlCl_2–SiO_2$ after pyridine adsorption and evacuation at 150 °C.

The catalyst zone was heated by a thermolyne Briskheat flexible electric heat tape controlled by an Omega Engineering, Inc., Model CN 310 digital temperature controller equipped with a J-type thermocouple. Pregas and postgas samples for GC analysis could be obtained through sample ports before and after the catalyst zone. Overall flow rates for the reactor system were monitored by a calibrated bubble flow meter.

This reactor was further modified with a syringe pump to deliver liquid reactants to the catalyst in place of a hydrocarbon or hydrocarbon/carbon tetrachloride bubbler. A preheater zone was added to the system to ensure proper mixing and heating of all reactants before they contacted the catalyst. Typically, only one gas was used as a carrier gas and/or reactant gas. The gas flow rate was regulated by a calibrated rotoflow meter purchased from Gilmont Instruments, Inc.

Instrumentation. All air- and water-sensitive manipulations were performed in a Vacuum Atmospheres Co. Model HE-43-2 inert-atmosphere box or in an Aldrich inert-atmosphere glovebag. All syntheses were conducted under a nitrogen or argon atmosphere and 1 atm of pressure. Routine GC analyses for hydrocarbon products were performed on a Varian Model 940 FID gas chromatograph equipped with a Hewlett-Packard 3390A integrator and a $^1/_8$ in. by 8 ft stainless steel Porapak Q (100–120 mesh) column or a $^1/_8$ in. by 6 ft stainless steel Hayesep Q (80–100 mesh) column. Routine GC analyses for chlorinated hydrocarbons were performed on a Varian Model 3700 TCD gas chromatograph equipped with a Hewlett-Packard 3390A integrator and a $^1/_8$ in. by 8 ft Porapak Q (100–120 mesh) column. GC/FTIR spectroscopy was performed on a Nicolet 5DXB FTIR spectrometer equipped with a Nicolet GC interface and a Hewlett-Packard 5890A gas chromatograph using a 1.5 μm thick DB 130m fused silica capillary column that was 30 m in length. Products were analyzed and confirmed by GCMS.

Gas samples were analyzed on a AEI MS 30 mass spectrometer with a KOITOS DS55 data station. The system was connected to a PYE Unicam 104 gas chromatograph equipped with a $^1/_4$ in. by 5 ft glass Porapak Q (100–120 mesh) column. Solid-state magic angle spinning (MAS) nuclear magnetic resonance spectra were collected on a Nicolet NT-300 (300-MHz) wide-bore superconducting FT-NMR spectrometer. Infrared spectra were obtained as mulls on a Nicolet 5DXB FT-IR spectrometer using KBr plates. All solid–liquid-phase cracking reactions were carried out in 250 or 500-mL Parr pressure bottles equipped with a brass or stainless steel Swagelok pressure head and a neoprene stopper.

Results and Discussion

Characterization of Catalysts with Pyridine Infrared Shifts. An investigation into the nature and strength of the acid sites present on the solid acid catalysts was conducted by using the infrared spectrum of adsorbed pyridine. The procedure was the same as previously described by Parry[15] with the exception that the infrared spectra were obtained from mulls. When pyridine is adsorbed onto the product of the silicon dioxide–aluminum chloride reaction ($AlCl_2–SiO_2$ catalyst) and evacuated (10^{-2} Torr) at 150 °C, bands indicative of both Brønsted and Lewis acid sites are observed (Figure 1). The large band at 1540 cm^{-1} is due to the H–N–C bending mode of the pyridinium ion, which was formed from the protonation of pyridine by Brønsted acid sites. Lewis acid sites are indicated by the presence of a band at 1456 cm^{-1}. Since the IR spectrum is collected after evacuation at 150 °C, hydrogen-bonded pyridine is not present on the surface. The peak at ≈1499

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(15) Parry, E. P. *J. Catal.* **1963**, *2*, 371.

Table I. Infrared Shift Data for Pyridine Adsorbed onto $AlCl_2$–X Catalysts

X[a]	solvent[b]	shift of Lewis band,[c] cm^{-1}	X[a]	solvent[b]	shift of Lewis band,[c] cm^{-1}
SiO_2	CCl_4	18.0	MgO	CCl_4	7.8
Al_2O_3	CCl_4	15.2	SiO_2	$CHCl_3$	9.3
silicalite[d]	CCl_4	18.1	SiO_2	CH_2Cl_2	8.6
B_2O_3	CCl_4	18.1	SiO_2	C_6H_{14}	8.9
TiO_2	CCl_4	14.1	SiO_2	C_6H_6	8.3

[a] Silica used was Davison Grade No. 62 silicon dioxide having a surface area of 340 m^2/g, pore volume of 1.1 cm^2/g, and a mesh size of 60–200. [b] This solvent was used to prepare the catalyst. [c] This shift is measured after pumping at 150 °C on the sample exposed to pyridine. The free pyridine band occurs at 1438.5 cm^{-1}. [d] A high-silica zeolite (Union Carbide) that had a surface area of 400 m^2/g at a pore volume of 0.19 cm^3/g.

cm^{-1} is a band due to a ring bending mode that is present in both Brønsted and Lewis acid bound pyridine and cannot be used to distinguish between the two types of acid sites.[15] These frequencies are consistent with the spectra obtained by Parry[15] and other workers in the area[16] for commercial amorphous silica–aluminas and zeolites. A summary of the infrared shift data for pyridine adsorbed onto the various aluminum chloride treated inorganic oxides ($AlCl_2$–X; X = inorganic support) prepared in this study is presented in Table I.

As seen in Table I, the acid-treated SiO_2, silicalite, and B_2O_3 supports resulted in the largest pyridine shifts for the Lewis acid band. Alumina and titanium dioxide exhibited shifts in an intermediate range, with magnesium oxide resulting in the lowest shift. The pyridine vibration involves the ring bending mode. The inductive effect from the donation of the nitrogen lone pair of the pyridine to a vacant orbital on a Lewis acid increases the $p\pi$–$p\pi$ interaction between the nitrogen and ring carbons, leading to an increase in the bending mode frequency as the strength of the Lewis acid increases.[15] In the case of the aluminum chloride treated inorganic oxides, the Lewis acid strength of the oxochloroaluminum center decreases with the expected basicity[18] of the oxo ligand as estimated from Pauling's electronegativity value[19] for each of the elements in the inorganic oxides: boron, 2.0; silicon, 1.8; aluminum, 1.5; titanium, 1.5; magnesium, 1.2. The low shift for MgO is not unexpected due to the fact that magnesium oxide is a basic[17] support. The small shift is in the range normally expected for hydrogen-bound pyridine, but the band is still present after evacuation at 150 °C and considered to arise from a Lewis acid bound pyridine.

Several silica catalysts were prepared by methods described in the patent literature, using Davison Grade No. 62 silicon dioxide, and the results of the pyridine adsorptions are listed at the bottom of Table I. For each of these, a shift of only 8 or 9 cm^{-1} is observed after evacuation at 150 °C. The strong acid centers are not formed in solvents other than carbon tetrachloride. The other solvents contain reactive hydrogens or are basic molecules that react[20-22] to neutralize the strong acid centers. Solvents that contain carbon–hydrogen bonds or basic solvents like benzene result in catalysts that exhibit lower acidity than those prepared in CCl_4.

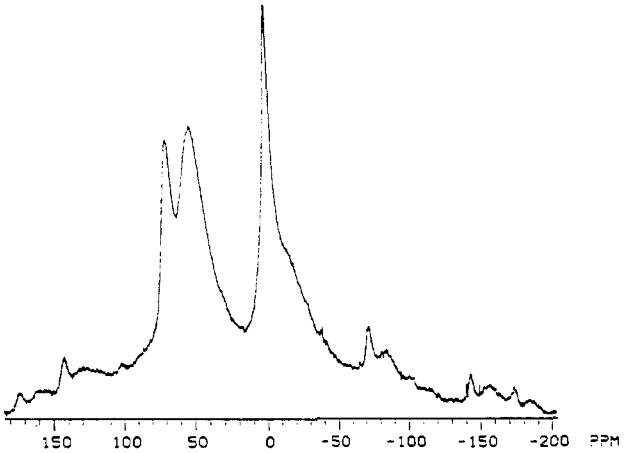
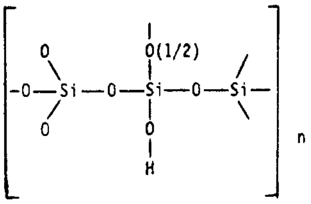


Figure 2. ^{27}Al solid-state NMR spectrum of an active $AlCl_2$–SiO_2 catalyst prepared in the absence of H_2O.

Solid-State MAS NMR Spectra of the Aluminum Chloride Treated Inorganic Oxides. The catalyst prepared by refluxing 2 g of 340 m^2/g SiO_2 and 1 g of Al_2Cl_6 in dry CCl_4 under an N_2 atmosphere yielded the ^{27}Al MAS NMR spectrum shown in Figure 2. The peak at 0 ppm is due to the presence of 6-coordinate aluminum-27, which is formed when the catalyst is exposed to water vapor in the air during the loading the NMR tube. The peaks centered at 55 and 65 ppm are due to 4-coordinate aluminum-27 with composition Si–O–$AlCl_2$. The aluminum becomes 4-coordinate by bonding to oxygen or weakly interacting with hydroxyl on the silica gel surface. This assignment is consistent with the value of 62.8 ppm reported[24] for aluminum chlorohydrate with a ratio of Cl/OH of 2.5. The ^{29}Si MAS contains a peak for framework silicon at −110 ppm and one for silicon bound to aluminum via an oxy bridge at ≈−95 ppm.

These results coupled with the stoichiometry of the catalyst preparation reaction enable us to formulate the structure of the material prepared. The aluminum chloride treated silica gel is normally prepared by using a silica with a surface area of 340 m^2/g and a hydroxyl group concentration of approximately 5 mmol/g.[25,26] A composition of $SiO_2{\cdot}0.15H_2O$ with a repeat unit of



where the hydrogen is arbitrarily located, is roughly ($Si_3O_{5.5}OH$) consistent with this result. The actual material is not a regular polymer of this repeat unit but an average composition of this formula with the hydrogens terminating various length chains to give this average composition. Those silicon atoms attached to four bridging oxygens constitute bulk silica. Since a 2:1 weight ratio of Al_2Cl_6 to silica gel is used, this corresponds to 0.003 75 mol of $AlCl_3$/0.016 mol of silica gel or 3.75 mmol of $AlCl_3$/5 mmol of OH groups. With 1 mol of HCl evolved/mol of $AlCl_3$ used in the preparation, 75% of the OH groups have reacted to produce a material of approximate composition $[SiO_{1.85}(OH)_{0.08}]_{4.3}OAlCl_2$.

If the surface area of the support is doubled, a corresponding doubling in the concentration of available hydroxyl groups occurs. On average, there would be more reactive hydroxyl groups per

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(16) Vedrine, J. C.; Auroux, A.; Bolis, V.; Dejaifve, P.; Naccache, C.; Weirzchowski, P.; Derovane, E. G.; Nagy, J. B.; Gilson, J.; Van Hooff, J. H. C.; Van Den Berg, J. P.; Wolthoizen, J. *J. Catal.* **1979**, *59*, 248–262.

(17) Hair, M. L. *Infrared Spectroscopy in Surface Chemistry*; Marcel Dekker, Inc.: New York, 1967; p 132.

(18) Galchenko, G. L.; Lavut, E. G.; Lavut, E. A.; Vidavsky, L. M. *Boron and Refractory Borides*; Matovich, V. I., Ed.; Springer-Verlag: New York, 1977; pp 331–350.

(19) Purcell, K. F.; Kotz, J. C. *Inorganic Chemistry*; W. B. Saunders Co.: Philadelphia, PA, 1977; pp 54–60.

(20) Thomas, C. A. *Anhydrous Aluminum Chloride in Organic Chemistry*; Noyes, W. A., Ed.; ACS Monograph 87; Reinhold Publishing Co.: New York, 1941.

(21) Kaim, W. *Acc. Chem. Res.* **1985**, *18*, 163–166.

(22) Olah, G. A. In *Friedel-Crafts and Related Reactions*; Olah, G. A., Ed.; Interscience Publishers: New York, 1963; Vol. 1.

(23) Chaing, C. D.; Chu, C. T. W.; Miale, J. N.; Bridger, R. F.; Calvert, R. B. *J. Am. Chem. Soc.* **1984**, *106*, 8143.

(24) Pinnavaia, T. J. In *Heterogeneous Catalysis*; Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1984; Vol. 2, p 142.

(25) Weiss, K. D. Ph.D. Dissertation, University of Florida, Gainesville, FL, 1986.

(26) Burwell, R. L., Jr. *CHEMTECH* **1974**, 370.

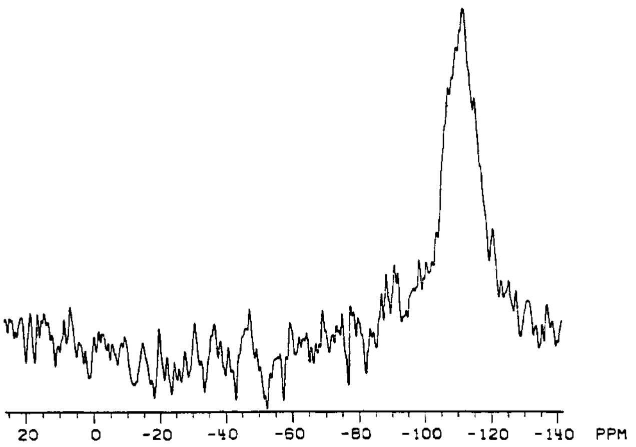

Figure 3. ^{29}Si solid-state NMR spectrum of an $AlCl_2$–SiO_2 catalyst prepared with 100 wt % of aluminum chloride.

unit of $AlCl_3$ employed and on average more species with two Al–Cl bonds hydrolyzed would exist on the silica surface. The resulting ^{27}Al MAS NMR spectrum should then show a significant increase in the number of bands for the $(SiO)_2AlCl$ chloroaluminum species.

When a high-surface-area silica gel is treated with aluminum chloride, several types of tetrahedral aluminum centers are formed. For the high-surface-area silica gel three distinct peaks are detected at 70, 52, and 23 ppm. The peak at 70 ppm is assigned to a Si–O–$AlCl_2$ species that was observed for the 340 m^2/g silica gel. The peak at 52 ppm is most likely due to a tetrahedral hydroxychloroaluminum [Si–O–AlCl(OH)] center, and the peak at 23 ppm is probably due to a 6-coordinate hydroxymonochloroaluminum species.

The ^{29}Si MAS NMR spectrum of the 690 m^2/g silica gel reacted with aluminum chloride in CCl_4 shows at least two distinct peaks centered at −88 and −105 ppm in contrast to what is observed for SiO_2, where only one peak was observed at 105–110 ppm. The peak at −105 ppm is due to the formation of one Si–O–Al bond per silicon atom on the silica surface, and the peak at −88 ppm is due to the formation of two Si–O–Al bonds to one silicon center on the silica surface. These results are consistent with literature values given for amorphous silica–aluminas, aluminosilicates, and zeolites.[27,28] The peaks at −88 and −105 ppm are good evidence for the incorporation of aluminum into the silica and support the fact that the aluminum chloride has actually been chemically bonded to the solid support.

When the 690 m^2/g catalysts discussed previously are used in a catalytic cracking reaction, vide infra, low activities are observed. This may be due to more extensive reaction of aluminum chloride and a decreased amount of the more acidic dichloroaluminum centers on the catalyst surface.

The ^{27}Al MAS NMR spectrum of a sample prepared by reacting 1 g of SiO_2 (340 m^2/g) with 1 g of Al_2Cl_6 (50 wt %) has a large peak at 105 ppm, which is due to aluminum chloride in agreement with the shifts reported in the literature for solution ^{27}Al NMR spectra of Al_2Cl_6 and $AlCl_4^-$.[29] Peaks in the ^{27}Al MAS NMR spectrum are also observed at 38 and 0 ppm, which are due to the hydroxychloroaluminum species discussed earlier. The ^{29}Si MAS NMR spectrum of the same catalyst (Figure 3) exhibits only one peak due to the framework silicon dioxide,[27] indicating that most of the aluminum chloride is on the support surface as Al_2Cl_6.

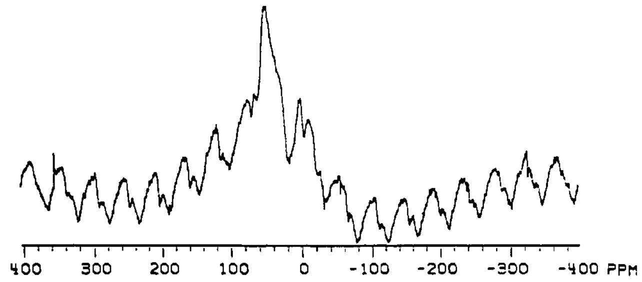

Figure 4. ^{27}Al solid-state NMR spectrum of an $AlCl_2$–SiO_2 catalyst after reaction with *n*-pentane.

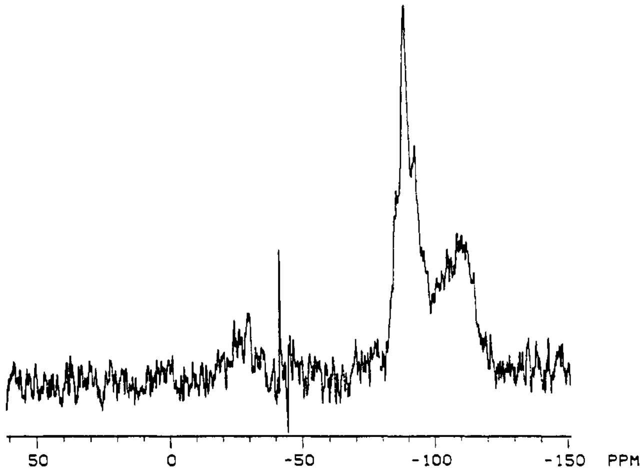

Figure 5. ^{29}Si solid-state NMR spectrum of an $AlCl_2$–SiO_2 catalyst after reaction with *n*-pentane.

In Figures 4 and 5 the ^{27}Al and ^{29}Si MAS NMR spectra of a catalyst after use in a catalytic cracking reaction are shown. In the ^{27}Al MAS NMR spectrum, 6-coordinate and 4-coordinate aluminum centers are present with the 4-coordinate aluminum center peak at ≈70 ppm indicating the presence of an Si–O–$AlCl_2$ species. The oscillation in the ^{27}Al MAS NMR base line is due to paramagnetic material (coke) that deposits on the catalyst surface during catalysis. The ^{29}Si MAS NMR spectrum displays peaks for framework silicon dioxide (−110 ppm) plus the silicon atoms associated with the Si–O–$AlCl_2$– centers (−90 ppm). Thus, under catalytic conditions, the tetrahedral chloroaluminum centers remain stable.

A calorimetric titration was performed on the catalyst prepared by refluxing SiO_2 and Al_2Cl_6 in dry CCl_4 under a nitrogen atmosphere. The purpose of the titrations was to measure the enthalpy of binding of pyridine to the acid sites present on the catalyst surface. The procedure was the same as previously described in the literature.[30–36]

Results form the titrations indicated that the enthalpy of binding for the first 13.6% of the surface acid sites ranged from 48.2 to 17.1 kcal/mol. The results indicate a distribution of acidities with an average enthalpy of binding measured as 36.0 kcal/mol. The stronger sites are titrated first, and the enthalpy for these sites indicates very strong acid centers.

From the ^{27}Al and ^{29}Si MAS NMR data, it has been determined that the catalyst prepared by reaction of an inorganic oxide with aluminum chloride results in a solid material that has tetrahedral chloroaluminum centers. The IR data for adsorbed pyridine indicates both Brønsted and Lewis acid sites are present,

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(27) Thomas, J. M.; Klinowski, J. In *Advances in Catalysis*; Eley, D. D.; Pines, H.; Weisz, P. B., Eds.; Academic Press, Inc.: Orlando, FL, 1985; Vol. 33, p 199.

(28) Maciel, G. E. In *Heterogeneous Catalysis*; Vol. 2, Shapiro, B. L., Ed.; Texas A&M University Press: College Station, TX, 1984; Vol. 2, p 349.

(29) Akitt, J. W. *Annual Reports on NMR Spectroscopy*; Academic: New York, 1975; Vol. 5A, p 466.

(30) Bilgrien, C. J. Ph.D. Dissertation, University of Florida, Gainesville, FL, 1986.

(31) Lim, Y. Y.; Drago, R. S.; Babich, M. W.; Wong, N.; Doan, P. E. *J. Am. Chem. Soc.* **1987**, *109*, 169–174.

(32) Courtwright, R. L.; Drago, R. S.; Nusz, J. A.; Nozari, M. S. *Inorg. Chem.* **1973**, *12*, 2809.

(33) Jacobs, P. A. *Chemical Industries*; Delannay, F., Ed.; Marcel Dekker, Inc.: New York, 1984; Vol. 15, p 367.

(34) Primet, M.; Ben Taarit, Y. *J. Phys. Chem.* **1977**, *81* (13), 1317–1324.

(35) Hatch, L. F.; Matar, S. *From Hydrocarbons to Petrochemicals*; Gulf Publishing Co.: Houston, TX, 1981; pp 15–32.

(36) McVicker, G. B.; Kramer, G. M.; Ziemiak, J. J. *J. Catal.* **1983**, *83*, 286–300.

and the frequency shifts for the Lewis acid bound pyridine indicate a strong acid center. The reactivity of these new solid strong acids was probed by using them in various hydrocarbon conversion reactions.

Catalytic Cracking Activity of the Solid Acids. We decided to study these new acids in the area of catalytic cracking[3,4,35] in both gas–solid flow reactors and liquid–solid batch reactors. The first reaction conducted was the cracking of *n*-pentane with an $AlCl_2$ silica gel catalyst prepared in CCl_4. Samples of the effluent gas from the reaction of *n*-pentane, HCl, and hydrogen in a 2.5:4:1 ratio by volume with a flow rate of 1 mL/17 s at 175 °C were taken and analyzed by GC. Products were trapped at −78 °C with a dry ice–acetone bath, and samples were taken by using a gastight syringe. At this flow rate the ratio of methane, isobutane, *n*-butane, and isopentane to *n*-pentane is low and corresponds to less than 15% conversion. If the flow rate is slowed down by a factor of 2 so that the residence time of the reactants on the catalyst is doubled, a marked increase to 75% percent conversion is observed with >90% of the products being C_4. The ratio isobutane to *n*-butane is 100 to 1. During the time the catalytic reactor was operated an initial increase in activity during the first hour was observed, followed by a decrease of up to 3 orders in magnitude over the next 8 h. The catalyst then stabilizes with its activity decreasing very slowly with time. After 24 h of *n*-pentane cracking, the catalyst is essentially deactivated. The product distribution for this catalyst is similar to those of other cracking catalysts that are reported in the literature, but our activity is much higher at this temperature, vide infra.[3,4] The initial activity is attributed to a few very acidic sites that rapidly deactivate from coke formation. The remaining less acidic sites exhibit a lower activity for cracking and a lower rate of coke formation, producing activity that remains more constant with time. When the cracking of pentane is carried out in the liquid phase at 100 °C, a 10000 to 1 ratio of isobutane to *n*-butane is produced.

The activation energy for the cracking of *n*-pentane (36.6 kcal mol^{-1}) is high, favoring the formation of coke.[3,4] As the hydrocarbon chain length increases, the activation energy decreases[4] up to octane and levels off at $\approx$25 kcal mol^{-1} for higher hydrocarbons. As the rate of reaction increases, the amount of coke formation decreases. The reaction of *n*-heptane (29.4 kcal mol^{-1}), HCl, and hydrogen in a 1:4:0.1 ratio by volume was conducted at 175 °C in a fixed bed flow reactor. The major products of this reaction are propane, isobutane, and *n*-butane, with minor amounts of *n*-pentane, isopentane, ethane, and methane and trace quantities of 2-methylhexane being produced. In this reaction, the catalyst activity increases for 10 h and still shows considerable activity after 90 h. The longer time required to reach optimum production of products from *n*-heptane most likely results from the lower vapor pressure of *n*-heptane compared to *n*-pentane, which results in a lower volume ratio or the hydrocarbon in the feed stream. The formation of coke is initiated by adsorption of a hydrocarbon molecule onto the catalyst surface followed by rapid formations of a highly unsaturated hydrocarbon with a low H:C ratio that can no longer desorb from the catalyst surface.[4] Eventually, a polymeric film covers the surface, blocking the active centers and deactivating the catalyst.[3] In our reactions the recovered catalysts are black in appearance, and by means of FTIR spectroscopy the black material was attributed to the formation of coke.

If the reactions of various hydrocarbons are conducted with carbon tetrachloride in place of hydrogen chloride, the same catalyst selectivity is observed but a greater stability and a longer lifetime results. The CCl_4 probably regenerates the strong active sites that are deactivated by hydrocarbon cracking. When carbon tetrachloride is used, hydrogen chloride and chloroform are detected in the product stream. The amount of chloroform generated in the reaction is of the same order of magnitude as the amount of substrate cracked.

It is generally accepted that the cracking of hydrocarbons proceeds via the generation of carbonium ions. The formation of $CHCl_3$ from CCl_4 indicates that chloroaluminum hydride species are formed by substitution of Cl^- by H^-. These species react with CCl_4 to form $CHCl_3$ and regenerate the starting chloroaluminum species to make the process catalytic. An initiation step involving H_α elimination was not considered important, since no noble metals were present on the catalyst surface.

Table II. Products Obtained by Cracking Isobutane

Major Products	
propane	*n*-pentane
n-butane	3-methylpentane
2-methylbutane	
Minor Products	
methane	2,2,4-trimethylpentane
ethane	2,2,3-trimethylpentane
ethylene	2,2,4-trimethylhexane

In addition to catalytic cracking, hydrocarbons may undergo thermal cracking. Thermal cracking proceeds by the homolytic cleavage of carbon–carbon and carbon–hydrogen bonds, which generate hydrocarbon radicals that react by a radical mechanism.[2,3] The products generated by thermal cracking are vastly different from the products generated by catalytic cracking. For the cracking of *n*-hexadecane, the products characteristic of radical cracking include large amounts of C_1 hydrocarbons, C_2 hydrocarbons are the major products, olefins larger than C_4 are present in the product stream, and no branched chain hydrocarbons are present.[2] The products characteristic of carbonium ion type chemistry for the cracking of *n*-hexadecane are small amounts of C_1 and C_2 hydrocarbons, with C_3–C_6 hydrocarbons as the major products and no olefins larger than C_4 detected in the product stream. Branched chain paraffins are present in the product stream.[2,4]

When the product distribution for the cracking of *n*-pentane and *n*-heptane is examined, it is found that methane and C_2 hydrocarbons are present in small quantities. The major products are propane, isobutane, and *n*-butane (C_3–C_4 hydrocarbons) with minor amounts of C_5 and higher hydrocarbons present in the product stream. This type of product distribution is consistent with a carbonium ion mechanism and supports the mechanism proposed for the catalytic cracking of hydrocarbons. To further clarify the mechanism for the cracking of hydrocarbons, the cracking of isobutane was studied.

The cracking of isobutane provides mechanistic information concerning cracking reactions by a solid acid catalyst[36,37] by forming different products depending on the method of activation. Hydrogen atom abstraction leads to isobutylene, propylene, methane, and hydrogen. Hydride ion abstraction leads to isobutylene, *n*-butane, isomers of butene, propane, propylene, methane, hydrogen, and $C_5(+)$ hydrocarbons formed from the reaction of carbonium ions with the olefins in the reaction mixture. The presence of the $C_5(+)$ hydrocarbons is the best indication of a carbonium ion mechanism. When isobutane is reacted with the aluminum chloride treated silicon dioxide catalyst prepared in carbon tetrachloride, a complex mixture of hydrocarbons is identified by GC and GC/FTIR, which includes $C_5(+)$ hydrocarbons; see Table II. The products provide definitive evidence for a carbonium ion mechanism.

Some of the other substrates used in the fixed bed flow reactor include *n*-hexane, dodecane, *n*-hexadecane, pump oil, activated carbon (charcoal), Pennsylvania soft coal, and resid. The saturated hydrocarbons gave, as with heptane, C_3–C_4 hydrocarbons as major products with C_1 and C_2 hydrocarbons present in minor amounts. The temperatures employed for the reactions ranged from 110 to 250 °C, and catalyst activity increased with increasing temperature.

Activated carbon and soft coal reacted to give methane, methyl chloride, and ethyl chloride, which arise from the cracking of methyl and ethyl side chains in the structures of the two materials. Resid when reacted with the solid acid catalyst gave C_1–C_5 aliphatic hydrocarbons and various aromatic compounds. The major products obtained from the reaction include methane, ethylene,

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(37) Kramer, G. M.; McVicker, G. B. *Acc. Chem. Res.* **1986**, *19*, 78–84.

Table III. Activities for Different $AlCl_2$-Functionalized Supports

X[a]	propane[b]	isobutane[b]	*n*-butane[b]
SiO_2	4.2×10^{-3}	7.1×10^{-2}	5.4×10^{-6}
Al_2O_3	6.2×10^{-3}	5.3×10^{-2}	3.0×10^{-6}
silicalite[c]	1.8×10^{-2}	1.1×10^{-1}	3.3×10^{-1}
B_2O_3	1.1×10^{-2}	5.0×10^{-2}	1.5×10^{-5}
TiO_2	5.0×10^{-8}	5.0×10^{-4}	none
MgO	2.4×10^{-9}	7.8×10^{-5}	none
		Blanks	
SiO_2	8.0×10^{-12}	5.3×10^{-10}	2.2×10^{-9}
Al_2O_3	none	5.3×10^{-10}	1.0×10^{-9}
zeolite	none	none	none
TiO_2	none	none	none
B_2O_3	$<10^{-12}$	8.5×10^{-10}	$<10^{-10}$
MgO	none	none	none
$AlCl_3$	1.9×10^{-2}	8.9×10^{-2}	1.5×10^{-4}

[a] Made in CCl_4. [b] Units: moles of product/(moles of Al/18 h). [c] A high-silica zeolite.

methyl chloride, isobutane, ethyl chloride, chloropropane, isopentane, and benzene. Extensive investigations of these reactions were not conducted due to the complexity of the systems and are reported here only as examples of other substrates that can be cracked by our catalyst.

Comparison of Catalytic Activities. Several disadvantages arise from using our fixed bed flow reactor because quantitative control and measurement of the amounts of each reactant is difficult. The data obtained demonstrate the feasibility of using a catalyst for a particular reaction, but a detailed comparison of the activities of various catalysis is not feasible. To compare activities of catalysts, batch reactions were conducted in a 250-mL Parr pressure bottle apparatus.[38,39] The probe molecule used was *n*-hexadecane,[3,4] whose rate of cracking is affected by olefin impurities.[40,41] GC analysis indicates that 99+% *n*-hexadecane (Aldrich Chemical Co.) has only saturated branched chain isomers as impurities as reported.[41] The cracking reactions were conducted by using 50 mL of a 1.195 M *n*-hexadecane solution in carbon tetrachloride, 1–1.5 g of catalyst, and 25 psig H_2 for 18 h at 100 °C. For *n*-hexadecane the products characteristic of radical cracking involve large amounts of methane, with C_2 hydrocarbons the major products and olefins larger than C_4 present in the product stream. No branched chain hydrocarbons are present.[3] For *n*-hexadecane, carbonium ion cracking chemistry leads to small amounts of C_1 and C_2 hydrocarbons, C_3–C_6 hydrocarbons are the major products, no olefins larger than C_4 are detected, and branched chain paraffins are formed.[3,4] The results for the cracking of *n*-hexadecane at 100 °C by various aluminum chloride functionalized inorganic oxides prepared in carbon tetrachloride are presented in Table III.

The batch reactor is a closed system, and previous work[46] has shown that cracking approaches an equilibrium in this system which hinders the progress of the desired reaction. Accordingly, the extent of conversion to light hydrocarbon products is used as a measure of catalyst activity. When the solutions and atmosphere of the cracking reactions are analyzed after reaction (GC and GC/FTIR), it is found that the product selectivity for C_5 hydrocarbons was less than that for C_3–C_4 hydrocarbons with no C_6 or higher hydrocarbons being detected. Blank supports were prepared by refluxing the support materials in a carbon tetrachloride for 3 days without addition of Al_2Cl_6, and the results are reported in Table III.

Table IV. Activities for $AlCl_2$–SiO_2 Catalysts Prepared in Different Solvents

solvent[a]	propane[b]	isobutane[b]	*n*-butane[b]
CCl_4	4.2×10^{-3}	7.1×10^{-2}	5.4×10^{-6}
$CHCl_3$	6.0×10^{-9}	4.1×10^{-5}	4.1×10^{-5}
CH_2Cl_2	1.8×10^{-8}	7.1×10^{-7}	3.3×10^{-7}
$ClCH_2CH_2Cl$	2.4×10^{-8}	none	none
C_6H_6	1.0×10^{-8}	none	none

[a] All reactions run in 50 mL of 1.195 M *n*-hexadecane in CCl_4 at 100 °C and 25 psig H_2. [b] Units moles of product/(moles of Al/18 h).

Table V. Product Distribution for Catalysts with Varying Percents of Aluminum Chloride on Silicon Dioxide Cracking Hexadecane

	% product[a,b]			
product	SiO_2	9.1 wt % catalyst	16.7 wt % catalyst	33.3 wt % catalyst
methane	61.8	87.5	0.8	0.5
ethylene	none	5.5	0.2	0.1
ethane	21.8	none	none	trace
HCl	none	7.0	0.1	none
propane	0.1	none	2.4	6.7
MeCl	7.5	none	none	none
isobutane	2.3	none	70.3	75.5
n-butane	6.5	none	none	1.4
isopentane	none	none	26.2	15.9

[a] % product as represented by integrated areas of product peaks by using an integrating recorder. [b] The activity is represented by forming 1.5×10^{-3} mol of isobutane/mol of Al at the end of 18 h for the 16.7 wt % catalyst and 1.6×10^{-1} mol of isobutane after 1 h for the 33.3 wt % catalyst.

The three major products from the cracking of *n*-hexadecane are propane, isobutane, and *n*-butane. As shown in Table III, the most active catalysts are those prepared on silica gel, a high-silica zeolite, boron oxide, and alumina. The next most active catalyst after the alumina-based catalyst is the catalyst prepared on titanium dioxide. The least active catalyst is the magnesium oxide based catalyst. The observed order in activity is the same as the order in the strengths of the acid catalysts, as reflected in the frequency shifts for the Lewis acid band of adsorbed pyridine on the solid acid catalysts. This supports the carbonium ion mechanism for catalytic cracking.

A blank reaction using an amount of aluminum chloride equal to the amount of aluminum chloride used to prepare 1 g of catalyst led to comparable activity for the three major products as with our best catalysts, but the reaction was very unselective, leading to large amounts of C_5–C_{15} products and a high molecular weight tar. After one reaction using free aluminum chloride, the valves and pressure gauge of the pressure head were corroded to the point that they could not be used again. The reactions using the aluminum chloride funtionalized supports have been run in the same pressure reactor more than 100 times with no significant corrosion to the pressure head. It is also very significant that a typical fluid cracking catalyst (LZ-Y82 zeolite) run under the conditions employed here produces no observable cracking products.

The results for the catalytic cracking of *n*-hexadecane in carbon tetrachloride using catalysts prepared in different solvents with silicon dioxide as the support are also in Table IV. The catalyst prepared in carbon tetrachloride is the most active. Again, the catalyst activities follow the trend in the frequency shift for the Lewis acid band for pyridine.

Catalyst Optimization. Previous experiments varying the support and the solvent used to prepare the catalyst showed that the silicon dioxide based catalyst made in carbon tetrachloride produced the most active catalyst. The next experiments, which establish the uniqueness of our most active catalyst, focused on the variation of the weight percent of aluminum chloride and the surface area of the support.

Using 9.1, 16.7, and 33.3 wt % of aluminum chloride, various silicon dioxide supports were reacted in refluxing CCl_4 for 2–3

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(38) Nyberg, E. D. Ph.D. Dissertation, University of Illinois, Urbana-Champain, IL, 1982.

(39) Zuzich, A. H. Ph.D. Dissertation, University of Florida, Gainesville, FL, 1987.

(40) Morterra, C.; Chiorino, A.; Ghiotti, G.; Garrone, E. *J. Chem. Soc., Faraday Trans. 1* **1979**, *75*, 271.

(41) Ford, T. J. *Ind. Eng. Chem. Fundam.* **1986**, *25*, 240–243.

(42) Weast, R. C. *CRC Handbook of Chemistry and Physics*, 62nd ed.; CRC Press, Inc., Boca Raton, FL, 1981.

(43) Sinfelt, J. H. *Ind. Eng. Chem. Fundam.* **1986**, *25*, 2–9.

(44) Maier, W. F. *Nature* **1987**, *329*, 531.

(45) Thomas, J. M.; Klinowski, J. In *Advances in Catalysis*; Vol. 35, Eley, D. D.; Pines, H.; Weisz, P. B., Ed.; Academic Press, Inc.: Orlando, FL, 1987; Vol. 35, p 199.

(46) Hightower, J. W.; Emmett, P. H. *J. Am. Chem. Soc.* **1965**, *87*, 939.

Table VI. Hexadecane Cracking Activities for Aluminum Chloride Treated Catalysts with Varing Surface Areas of Silicon Dioxide[a]

	moles of product/moles of Al[b]			
product	215 m^2/g 33.3 wt %	690 m^2/g 33.3 wt %	340 m^2/g 16.7 wt %	340 m^2/g 33.3 wt %
propane	7.68×10^{-6}	1.82×10^{-6}	2.19×10^{-5}	1.64×10^{-2}
isobutane	1.4×10^{-3}	1.49×10^{-6}	1.50×10^{-3}	1.62×10^{-1}

[a] At the end of 18 h. [b] The 215 m^2/g and 690 m^2/g silicon dioxide supports were obtained from AESAR and have pore volumes of 1.0 cm^3/g at 0.4 cm^3/g with a mesh size of 60–325. The 340 m^2/g dioxide was Davison Grade No. 62 silica, which had a pore volume of 1.1 cm^3/g and a mesh size of 60–200.

days. All catalysts were compared in a Parr pressure reactor at 100 °C and 25 psig H_2 in 50 mL of a 1.195 M solution of *n*-hexadecane in carbon tetrachloride using 1–1.5 g of catalyst. The total product distributions for the catalysts are shown in Table V, and the activities for propane, isobutane, and *n*-butane production are shown in Table VI. Decreasing the loading of aluminum chloride from 33.3 to 16.7 wt % causes a slight shift in product distribution, which is most pronounced for the C_5 products. A further decrease in the loading from 16.7 to 9.1 wt % shows a drastic change in product distribution and a large decrease in activity. The major C_1 and C_2 products are obtained only in trace amounts at 9.1 wt % loading.

When the activities of the 33.3 and 16.1 wt % catalysts are compared (Table VI), it is seen that the former catalyst is 2 orders of magnitude higher in activity. Since the activities are corrected for the number of moles of aluminum chloride present, the same activity would result if there was a first-order dependence on the amount of aluminum chloride present. Other factors must be involved, and these observations suggest that the active sites are $-O-AlCl_2$ species and not just any chloroaluminum species. A significant number of $-O-AlCl_2$ groups bonded to the surface hydroxyl groups of the silicon dioxide would only be formed at the higher loadings. The catalyst made using a 9.1 wt % loading of aluminum chloride showed no activity for cracking, giving only trace amounts of methane, ethylene, and HCl, which is even less than the comparable blank reaction employing dried silicon dioxide that was refluxed in CCl_4.

Surface area variations were carried out by using silicon dioxide from AESAR of 215 and 690 m^2/g surface area in addition to our original 320 m^2/g silicon dioxide from Davison Chemical (Grade No. 62). Catalysts were prepared with 33.3 wt % aluminum chloride, and cracking was done under reaction conditions identical with those described for the experiments on the variation of catalyst loadings. The catalyst activities for the 215 and 690 m^2/g catalysts are given in Table VI.

The product distributions for each catalyst are very similar, and the activity of the 215 m^2/g catalyst is roughly 1 order of magnitude more active than the 690 m^2/g catalyst. A significant difference is observed in the 215 m^2/g silicon dioxide from AESAR and that from the 340 m^2/g Davison silicon dioxide. Thus, very subtle differences in either the support manufacture or surface cause dramatic differences.

The catalyst selectivities are similar for all of the catalysts and are indicative of a carbonium ion cracking mechanism. The 33.3 wt % loading on a 340 m^2/g silicon dioxide results in the most active catalyst. The coverage of aluminum chloride on this catalyst surface is approximately 80%, on the basis of the number of available surface hydroxyl groups.

Conclusion

The objective of this reasearch is to prepare a new solid acid with tetrahedral aluminum sites. Aluminum chloride reacts with silica gel to produce such a material that acid catalyzes cracking reactions. The characterization of the catalyst by IR spectroscopy demonstrates that both Brønsted and Lewis acid sites are present on the catalyst surface. In addition to the detection of acid sites by IR spectroscopy the relative strength of the Lewis acid sites present on the catalyst are measured. It is shown that the catalysts prepared by reacting silica gel, a high-silica zeolite, alumina, or boron oxide with aluminum chloride in carbon tetrachloride contain the strongest Lewis acid sites. When other solvents or inorganic oxides are used to prepare the catalyst, a solid with much lower Lewis acid strength results. The characterization of the catalysts by ^{27}Al and ^{29}Si solid-state MAS NMR spectroscopy demonstrated that our most active catalyst contains tetrahedral dichloroaluminum species that are stable under catalytic cracking reaction conditions.

From the cracking reactions it is concluded that the 33.3 wt % catalyst prepared on silica gel (340 m^2/g surface area) and a high-silica zeolite are the most active. Trends in the cracking activity of the catalysts parallel the order in Lewis acid site strengths, as determined by the infrared studies. It was also determined that in order to obtain long-term activity a chlorine source is needed. The formation of coke was detected during the cracking reactions and was the primary cause of catalyst deactivation when the chlorine source was not available.

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