Properties of Aluminum-Fluoride Catalysts Prepared by the Fluoridation of Aluminum Oxide with Trifluoromethane

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High-purity AIF₃ has been prepared by allowing γ -Al₂O₃ to react with gascous trifluoromethane at 670–770 K under 101 kPa total pressure. The use of gaseous trifluoromethane is a new, general method for preparing metal fluorides from metal oxides. AIF₃ prepared using this procedure retained the physical form of the starting γ -Al₂O₃. A $\frac{1}{16}$ -in. γ -Al₂O₃ extrudate, for example, yielded an AIF₃ extrudate with comparable physical dimensions and crush strengths. X-Ray diffraction, BET surface area, pore volume, and surface acidity measurements were employed to characterize various AIF₃ samples. Significant decreases in surface area and pore volume as well as surface acidity occurred upon increasing the concentration of AIF₃ from 90 to 100%. This behavior presumably results from the fluoridation of residual γ -Al₂O₃. AIF₃ extrudates were utilized as supports for Pt and Pd on γ -Al₂O₃. In a unique application, Pd/AIF₃ was used to hydrogenate *m*diethylbenzene in superacid (HF/TaF₅) solution.

I. INTRODUCTION

While studying the use of fluorocarbons as redispersion agents for agglomerated noble-metal-on-alumina catalysts, it was observed that under certain reaction conditions the alumina support was completely converted into aluminum fluoride (1). This observation prompted us to investigate the utility of fluorocarbons as metal-oxide fluorinating agents. Trifluoromethane (HCF₃) was found to be particularly effective. At 670-770 K and under 101 kPa total pressure HCF₃ readily transforms such diverse metal oxides as Al₂O₃, MgO, TiO₂, UO₂, and Ta₂O₅ into their corresponding fluorides or oxyfluorides (2). The nontoxic and noncorrosive nature of HCF₃ is an attractive feature since conventional HF fluoriding procedures present numerous safety hazards (3).

Although HCF₃ can be generally used to prepare metal fluorides from metal oxides, special emphasis will be placed here in describing the preparation of AlF₃ from Al₂O₃ and the use of AlF₃ as a support for noblemetal catalysts. The AlF₃ and noble-metal/ AlF₃ catalysts prepared in these studies were characterized by a combination of acidity, BET, pore volume, X-ray diffraction, and H₂-chemisorption measurements. Noble-metal/AlF₃ catalysts offer unique utility in strongly acidic solutions where common support materials such as Al₂O₃, SiO₂-Al₂O₃, and MgO readily solubilize. The hydrogenation of *m*-diethylbenzene, using Pt/AlF₃ and Pd/AlF₃ catalysts, in an HF/TaF₅ superacid solution provides an example of one such application.

2. EXPERIMENTAL SECTION

A. Materials

A $\frac{1}{16}$ -in. γ -Al₂O₃ extrudate with a BET surface area of 178 m²/g was used throughout these studies. Trifluoromethane (HCF₃) and tetrafluoromethane (CF₄) were used as supplied by the Matheson Gas Company. Hydrogen was passed through a Deoxo unit and a molecular sieve drier prior to use. Helium was dried by passage through a molecular sieve drier. Oxygen was used as supplied. Platinum and palladium salts were supplied by Engelhard Minerals and Chemicals Corporation. Aluminum-fluoride samples were obtained from the Allied Chemical Company.

B. Preparations

In a typical quartz tube furnace preparation of AlF₃ 100 g of γ -Al₂O₃ extrudate was allowed to react with 40% HCF₃/He (500 cm³/min, 101 kPa) at 773 K for 5.0 hr. A yield of 158 g (165 g theoretical yield) of AlF₃ was obtained. The progress of the reaction was followed by monitoring the evolution of H₂O vapor. Although no equipment corrosion was encountered, caution should be exercised, since the exit gases may contain trace quantities of HF.

Conventional fluorided-alumina catalysts were prepared by impregnating γ -Al₂O₃ with standardized aqueous HF solutions.

Platinum and palladium catalysts supported on γ -Al₂O₃ and AlF₃ were prepared by incipient wetness impregnations using aqueous noble-metal-acid choride solutions. The aqueous wettabilities of γ -Al₂O₃ and AlF₃ are near 0.65 and 0.3 cm³/g, respectively. Nonaqueous incipient wetness impregnations were carried out with acetone solutions of chloroplatinic acid and either acidified palladium chloride or palladium acetate. Impregnated catalysts were dried at 390 K under air for 16 hr prior to reduction.

C. Equipment and Procedures

A Thermcraft Inc. tube furnace, mounted in a horizontal position, was used in AlF_3 preparations and also in catalyst reductions and calcinations. Quartz reaction tubes (1.0 in. in diameter) were employed. Gas lines and fittings were constructed from 316 stainless steel.

X-Ray powder diffraction patterns were measured on a Philips Electronic Instruments diffractometer using nickel-filtered Cu K α radiation. Pt, Pd, and AlF₃ crystallite sizes were calculated from the widths of the X-ray reflection patterns, as described elsewhere (4). Noble-metal catalysts were reduced prior to X-ray diffraction measurements.

Thermal gravimetric analysis (TGA) experiments involving AIF₃ were carried out under Ar (40 cm³/min, 101 kPa) in a Fischer TGA apparatus employing a Cahn RG electrobalance. Samples were heated at 20 K/min to a maximum of 1500 K.

Hydrogen isotherms and nitrogen BET surface areas were determined on a conventional high-vacuum system utilizing a Texas Instruments fused quartz precision pressure gauge (5, 6). Pt and Pd catalysts were reduced *in situ* (20% H₂/He, 500 cm³/min, 101 kPa) at 773 and 390 K, respectively, for 2.0 hr prior to chemisorption measurements. A hydrogen adsorption-evacuation-readsorption procedure at room temperature was used to estimate supported Pd surface areas (7). BET surface area samples were dried under He (500 cm³/min, 101 kPa) at 773 K for 2.0 hr before measurement.

Benzene hydrogenations were carried out at 323–373 K in a fixed-bed stainlesssteel reactor. Prereduced catalysts were rereduced (373 K, 500 cm³ H₂/min, 101 kPa) *in situ* for 1.0 hr prior to introduction of feed. The feedstock was 10% benzene/hexane. The following hydrogenation conditions were employed: 101 kPa total pressure, 0.29 g catalyst, weight hourly space velocity (WHW) = 6.1, 340 cm³ H₂/min, H₂/benzene = 40. These conditions were chosen to minimize diffusion limitation effects (8). Benzene conversion to cyclohexane was determined by in-line gas chromatography.

Hydrogenations of *m*-diethylbenzene in superacid solution (HF/TaF₅) were carried out in an Autoclave Engineers 300 cm³, Hastelloy C, autoclave at 303 K under 1380 kPa total pressure. Prereduced catalysts were digested in anhydrous hydrofluoric acid for 2 days to convert the last trace of γ -Al₂O₃ to AlF₃, washed with fresh anhydrous hydrofluoric acid, and dried under a N₂ stream. The treated catalyst was charged in a basket attached to the impeller and placed in the autoclave under a N_2 atmosphere. The superacid solution and H_2 were brought to the reaction condition prior to introducing *m*-diethylbenzene. Hydrogenation rates were determined by measuring the uptake of hydrogen as a function of time.

Acidities of the fluorided-alumina supports were determined by titration of the solids with a standardized *n*-butylamine/ benzene solution in the presence of a series of Hammett indicators (9, 10).

Cyclohexene isomerization studies were carried out over fluorided-alumina supports in an attempt to ascertain the relative acidities of these materials. Prior to use, the solids were dried in situ under helium (500 cm³/min) at 773 K for 16 hr. The skeletal isomerization of cyclohexene to an equilibrium mixture of isomeric (1-, 3-, and 4-) methylcyclopentenes was performed at 623 K and 1380 kPa. The space velocity was 25 WHW and the hydrogen/cyclohexene mole ratio was held at 2.3. Preliminary studies established that under these conditions no mass or pore volume diffusion limitations occur. Product analyses were made by inline gas chromatography measurements.

3. RESULTS AND DISCUSSIONS

A. Preparation of Aluminum Fluoride

Anhydrous AlF₃ is a white crystalline solid which sublimes at 1560 K/101 kPa (11). It is normally prepared by either fluoriding Al₂O₃ with gaseous or aqueous HF (Eq. (1)),

$$Al_2O_3 + 6HF \rightarrow 2AlF_3 + 3H_2O, \quad (1)$$

or by allowing an aluminum hydroxide to react with ammonium bifluoride (Eq. (2)) in solution or in the solid state.

$$AI(OH)_3 + 3NH_4HF_2 \rightarrow AIF_3 + 3NH_4F + 3H_2O.$$
(2)

The reactions summarized in (1) and (2) are generally carried out at temperatures near 870 K. Anhydrous AlF_3 thus produced is in the form of a fine powder.

In contrast to the above preparations, the fluoridation of γ -Al₂O₃ with HCF₃ takes place at temperatures above 670 K. The nontoxic and noncorrosive nature of HCF₃ makes this fluoriding technique attractive from the point of view of convenience and safety (12). The formation of AlF₃ from γ -Al₂O₃ is consistent with Eq. (3). Gas chromatography and mass spectrometry measurements confirmed the generation of CO and H₂O.

$$\gamma$$
-Al₂O₃ + 2HCF₃ \rightarrow
2AlF₃ + 2CO + H₂O. (3)

The free energy of formation of AlF₃ according to Eq. (3) is favorable by 111 kcal/ mole (13–16). Table 1 illustrates the essentially stoichiometric fluoridation of γ -Al₂O₃ with HCF₃ at 723–823 K and at CHF₃ partial pressures of 11 to 33 kPa. The extent of fluoridation is easily monitored by measuring the gain in product weight. The BET surface areas of the fluorided aluminas systematically decreased with increasing aluminum-fluoride concentration.

Tetrafluoromethane (CF₄) is ineffective in fluoriding Al₂O₃ at temperatures as high as 900 K. Even in the presence of noble metals and/or oxygen no bulk fluoridation of Al₂O₃ occurs. The surface fluoridation of Al₂O₃ with CF₄ at 870 K has, however, been reported (17). The free energy of formation of AlF₃ via Eq. (4) is favorable by 258 kcal/ mole (13-16).

$$2AI_2O_3 + 3CF_4 \rightarrow 4AIF_3 + 3CO_2. \quad (4)$$

The failure of CF₄ to act as a bulk Al₂O₃ fluoriding agent suggests, therefore, a kinetic limitation. The CF₄ molecule which contains only strong C-F bonds (130 kcal/ mole) presumably does not decompose under these conditions (18). HCF₃, in contrast to CF₄, contains a relatively weak C-H bond (106 kcal/mole) which must rupture at temperatures above 670°C (18–20). Initial rupture of the C-H bond would lead to the formation of H₂O and ultimately to the complete degradation of HCF₃. The active

HCF ₃ ^b (cm ³ /min)	<i>T</i> (±4 K)	t (hr)	Product wt (g)		Percentage AlF_{3}^{c}		BET ^d (m ² /g)
			Theo.	Found	Theo.	Found	
25	773	0.13	20.3	20.3	3.46	3.52	175
25	773	0.25	20.5	20.5	6.86		171
50	773	0.25	21.1	20.8	13.3		165
50	723	0.50	22.2	22.1	25.4		144
50	773	0.50	22.2	21.6	25.4	24.8	146
50	823	0.50	22.2	22.2	25.4	-	144
50	773	0.75	22.8	22.8	36.2	-	135
50	773	1.00	24.4	24.3	46.1	44.8	96
50	773	1.50	26.6	26.2	63.5		79
50	773	2.00	28.8	27.9	78.2	79	47
50	773	3.00	32.9	31.7	100	94	8.7
100	773	1.50	32.9	32.6	100	99	8.9

TABLE 1

Fluoridation of y-Al₂O₃ with HCF₃^a

^a 20.0 g of dry γ -Al₂O₃ (178 m²/g) was employed in each treatment. The γ -Al₂O₃ extrudates were dried at 773 K prior to fluoridation.

^b 200 cm³/min of helium was used as diluent in each fluoridation, 101 kPa total pressure.

^c Fluorine analyses were carried out by the Analytical and Information Division, Exxon Research and Engineering Company, Linden, N.J.

^d Surface areas were determined by the nitrogen BET method.

fluoriding species produced upon degradation generate AlF₃. Higher-molecularweight perfluorocarbons are potential fluoriding agents since carbon-carbon bond rupture (F₃C-CF₃ = 93 kcal/mole) may occur at relatively low temperatures (21). Degradation of fluorocarbon radicals into active fluoriding species would likely follow an initial carbon-carbon bond dissociation.

B. Physical Properties of Aluminum Fluoride

The fluoridation of γ -Al₂O₃ extrudates with HCF₃ yields AlF₃ extrudates of comparable crush strength and physical dimensions. The starting $\frac{1}{16}$ -in. γ -Al₂O₃ extrudates have average dimensions of 0.073 in. \times 0.40 in. (22). The AlF₃ products exhibited average dimensions of 0.071 in. \times 0.40 in.; thus, no appreciable change in superficial extrudate volume occurred upon fluoridation. The absence of a volume change is surprising, since the crystal density of AlF₃ is less than that of γ -Al₂O₃ (3.2 vs 3.7 g/cm³, respectively) and also since twice as many fluoride ions as oxide ions (Al₂O₃ \rightarrow Al₂F₆) are required to complete the crystal lattice (23). It should be noted that the ionic radii of oxide and fluoride ions are similar, 0.136 and 0.140 nm, respectively. Retention of the original γ -Al₂O₃ extrudate volume upon fluoridation can, however, be rationalized by the following argument. The relationship among superficial extrudate, crystal, and pore volumes is given by Eq. (5).

Since the crystal volume can be calculated from the weight of a given extrudate particle and the known crystal density of the material, an apparent pore volume is then obtained in a straightforward calculation. The average pore volume of γ -Al₂O₃ (178 m²/g) was calculated to be 0.64 ± 0.04 cm³/g. This value agrees with the H₂O wettability (0.65 cm³/g) and N₂ isotherm pore volume $(0.51 \text{ cm}^3/\text{g})$ of this particular γ -Al₂O₃. The average pore volume of a series of HCF₃prepared AIF₃ extrudates (3.7 to 49.7 m^2/g) was calculated to be 0.29 ± 0.03 cm³/g. The calculated pore volume is consistent with the H₂O wettability (0.3 cm³/g) exhibited by these AlF₃ samples. Thus the apparent pore volume of γ -Al₂O₃ is reduced to about 50% of its original value upon fluoridation. The loss in pore volume results from fluoride ions occupying interparticle spaces in the expanding AlF₃ lattice. Since both Al_2O_3 and AlF₃ possess close-packed anion layers, the crystal volume occupied by fluoride ions is set by the conversion level (23). The above analysis suggests that the pore volume of the AIF₃ product may be systematically varied by utilizing aluminas with different initial pore volumes.

Table 2 summarizes the effect reaction conditions have on the surface area of HCF₃-prepared AlF₃. At a given HCF₃ partial pressure, the surface areas of the 90+% AlF₃ samples decrease upon increasing the treatment temperature from 673 to 773 K. Longer reaction times and/or higher HCF₃ concentrations at a given temperature also lowered the surface area. The decrease in surface area parallels increasing AlF₃ content within the range 90 to 100%. A significant fraction of the surface area displayed by the 90+% AlF₃ materials likely results from the presence of unreacted Al₂O₃ (24).

The observed decrease in the surface

TABLE 2

The Effect of Reaction Conditions on the Surface Area and Pore Volume of AlF₃ Prepared by Fluoriding γ -Al₂O₃ with HCF₃

T	Percentage	t	Minimum (%)	Surface area ^b	Pore volume ^b
(°K) HCF_3/He^a	(hr)	AlF_3	(m²/g)	(cm ³ /g)	
Starting	y-Al ₂ O ₃ ^c			178	0.513
673	20	3.0	90 ^d	49.7	0.232
723	20	2.0	90 ^d	32.9	0.198
723	20	2.5	95°	22.4	0.171
773	20	2.5	90 ^d	25.4	0.135
773	20	2.5	90^d	21.5	0.177
773	40	5.0	99 ^e	3.7	0.050
Aqueous	HF-treated Al ₂ O ₃		100	11.8	
Aqueous	HF-treated Al ₂ O _{3⁸}		100	6.9	
Aqueous	HF-treated Al ₂ O ₃		96	1.2	
Aqueous	HF-treated Al ₂ O _{3^h}		90 ^d	3.3	
Gaseous	HF-treated Al ₂ O ₃ ⁱ		94	10	
Gaseous HF-treated Al ₂ O ₃ ⁱ		86	22		
Gaseous	HF-treated Al ₂ O ₃ ⁱ		70	63	
Ammonia treated	acal aqueous NH4F-		71.4	45	

^a 500 cm³/min, 101 kPa total pressure.

^b Nitrogen isotherms.

- ^c Supplied by Engelhard Minerals and Chemicals Corporation.
- ^d Minimum AlF₃ content established by X-ray diffraction measurements.
- ^e AlF₃ content determined by TGA.
- ^f Abstracted from Ref. (25).
- ⁸ Abstracted from Ref. (28).
- * Supplied by Allied Chemical Company.
- ⁱ Abstracted from Ref. (29).
- ^j Abstracted from Ref. (30).

area of the 90+% AlF₃ samples with increasing AlF₃ content is consistent with the solid-state structure of AlF₃. In the solid state, AlF₃ exists as an infinite three-dimensional crystalline network wherein each aluminum atom is coordinated to six equivalent fluoride ions (23). Such a highly condensed, regular crystal structure would not be expected to exhibit a high surface area. Crystallite sintering at the high preparative temperatures would also favor the formation of a low-surface-area product.

A HCF₃-prepared AlF₃ sample (22.4 m²/ g) was subjected to a TGA study in an attempt to quantify the extent of fluoridation. A 95.1-mg sample decreased by 89.4 mg between 1300 and 1500 K. The weight loss results from the sublimation of AlF₃ (11, 25). The nonsublimable material was determined by X-ray powder diffraction measurements to be α -Al₂O₃. The fact that α -Al₂O₃ remains suggests that a sublimable aluminum oxyfluoride is not produced. From the weight of the recovered α -Al₂O₃ the concentration of AlF₃ in a typical HCF₃-prepared AlF₃ is near 95%.

A commercial AIF₃ obtained from Allied Chemical Company assayed as 61% AIF₃. The bulk of the remaining material is H_2O . A sample of the hydrated AIF₃ was calcined at 923 K for 5.0 hr under 20% O₂/He (500 cm³/min). The calcined sample was determined by X-ray measurements to be essentially pure rhombohedral AIF_3 (26) and exhibited a surface area of $3.3 \text{ m}^2/\text{g}$. Calcining the hydrated AlF₃ material at 823 K for 5.0 hr, however, produced a rhombohedral AlF₃ which was contaminated with an $AlF_{1.96}(OH)_{1.04}$ phase (27). This sample exhibited a surface area of $42.2 \text{ m}^2/\text{g}$. These results clearly demonstrate that the apparent surface area of AlF₃ is markedly increased by the presence of relatively small quantities of aluminum-oxide or aluminumhydroxide impurities.

Additional AlF₃ surface area data abstracted from the literature are presented in Table 2 for comparative purposes (25, 28– 30). Within the 90% and higher AlF₃ concentration range, the HCF₃-prepared samples generally exhibit somewhat higher surface areas than those prepared by fluoriding Al_2O_3 with either aqueous or gaseous HF. The aqueous HF-prepared AlF_3 samples do not exhibit a recognizable correlation between AlF_3 content and surface area. The gaseous HF-treated Al_2O_3 preparations do, however, demonstrate decreasing surface areas with increasing AlF_3 concentrations (29).

The pore volumes of the HCF₃-prepared AlF₃ samples decrease sharply with decreasing surface areas. The H₂O wettabilities of these samples are near 0.3 cm³/g; thus, a large fraction of the total adsorptive capacity must be associated with macropores (>120 nm) since pore volumes calculated from N₂ isotherms apply only to pores less than 120 nm in diameter (*31*). This situation can be contrasted with a typical γ -Al₂O₃ in which better than 95% of the total pore volume is associated with pores having diameters in the range 7–7.5 nm.

The physical form and surface characteristics of HCF₃-prepared AlF₃ suggest potential application as a catalyst support. The self-supporting extrudate form would allow usage in a fixed-bed operation. An active metal component supported on AlF₃ would reside primarily on the surface since the pore volume is composed of pores with diameters greater than 120 nm. The latter situation may be desirable in catalytic operations where pore blockage and/or diffusion limitations may be present.

The HCF₃-prepared AlF₃ products listed in Table 2 exhibit an X-ray powder diffraction pattern consistent with that reported for rhombohedral AlF₃ (26). The major diffraction lines of rhombohedral AlF₃ are summarized in Table 3. Only the highestsurface-area AlF₃ (49.7 m²/g) product exhibited discernible background diffraction lines from unreacted γ -Al₂O₃. Addition of incremental amounts of γ -Al₂O₃ to a highpurity AlF₃ (99%)-has set the minimum Xray-detectable Al₂O₃ concentration in AlF₃ to be between 5 and 10 wt%. The minimum

TABLE 3

Major X-Ray Diffraction Lines of Aluminum Fluoride^a

d ^b (nm)	I ^b	d ^c (nm)
0.352	100	0.355
0.212	19	0.212
0.176	24	0.177
0.159	14	0.159
0.156	7	0.157

^a Rhombohedral AlF₁.

^b Abstracted from Ref. (26).

^c This study.

AIF₃ content of the HCF₃-prepared samples summarized in Table 2 is thus estimated from X-ray data to be at least 90 wt%. The widths of the AlF₃ X-ray diffraction lines narrow with decreasing surface area. Apparent AlF₃ crystallite sizes calculated using the width of the $2\theta = 35.7^{\circ}$ X-ray line are summarized in Table 4. AlF₃ crystallite sizes calculated from X-ray diffraction and surface area data are in poor agreement (4,32). The disagreement arises primarily from the fact that the AIF_3 crystallites are strained and disordered (33). The nonregular AlF₃ crystallites vield broadened X-ray diffraction lines which translate into AlF₃ crystallite sizes smaller than they actually are. Crystallite sizes calculated from BET surface area measurements are therefore judged to be a more reliable estimate of the AlF₃ particle size. In contrast to the AlF₃ samples, the crystallite sizes of γ -Al₂O₃ calculated from X-ray and surface area data are in reasonable agreement. Such consistency suggests that γ -Al₂O₃ is not as severely strained and/or disordered as the AlF₃ samples.

A 71.4% AlF₃ sample studied by Reitsma and Boelhouwer exhibited X-ray diffraction linewidths indicative of 100-nm AlF₃ crystallites (30). The crystallite size calculated from the reported surface area is likely too small because of an enhancement from the Al₂O₃ phase present in their sample. The X- ray crystallite size data suggest that AlF₃ produced by treating Al(OH)₃ with an ammoniacal aqueous NH₄F solution contain larger crystallites than those obtained by fluoriding γ -Al₂O₃ with HCF₃. A commercial AlF₃ sample exhibited an apparent crystallite size (41 nm) in the same range as that found for the lowest-surface-area (3.7 m²/g) HCF₃-prepared AlF₃ sample.

The diffraction lines of HCF₃-prepared AlF₃ narrowed upon air calcination at elevated temperatures. An AlF₃ sample (25.4 m^2/g , 12 nm (X ray), 74 nm (BET)) calcined under air at 823 K for 2 and 6 hr exhibited crystallite sizes calculated from X-ray data of 18 and 26 nm, respectively. The apparent AlF₃ crystallite growth detected by X-ray measurements suggests that thermal treat-

TABLE 4

Apparent Crystallite Sizes of Aluminum Fluorides Prepared by Treating γ-Al₂O₃ with HCF₃

Minimum AlF3 (%)	Surface area (m²/g)	Apparent crystallite size (nm)		
		X ray ^a	BET ^b	
 90¢	49.7	12	38	
90°	32.9	14	57	
90°	25.4	12	74	
95 ^d	22.4	13	84	
90 °	9.8	18	191	
90 ^c	6.8	19	278	
99 ^d	3.7	46	501	
90 ^{c.e}	3.3	41	577	
71.4⁄	45	100	42	
0.0%	178	7 ^h	8.6	

^{*a*} Calculated from the width of the $2\theta = 35.7^{\circ}$ diffraction line.

^b Calculated using: $l = 6 \times 10^4/(S.A.)(d)$, where (S.A.) = surface area (m²/g) and d = crystal density (AlF₃ = 3.2, Al₂O₃ = 3.7 g/cm³).

 $^{\rm c}$ Minimum AlF3 content established by X-ray diffraction measurements.

^d AlF₃ content determined by TGA.

^e Supplied by Allied Chemical Company.

^f Abstracted from Ref. (30).

 ${}^{s}\gamma$ -Al₂O₃ supplied by Engelhard Minerals and Chemicals Corporation.

^h Calculated from the width of the $2\theta = 45.8^{\circ}$ diffraction line.

ment produces crystallites which are less strained and disordered. The crystallite size as estimated by X-ray diffraction linewidths could conceivably increase to 74 nm, the crystallite size calculated from the BET surface area, before sintering of the individual AlF₃ particles would be indicated.

C. Acidic Properties of Aluminum Fluoride

The acidities of various HCF₃-prepared AlF₃ samples have been estimated by titrating the solids with standardized *n*-butylamine/benzene solutions in the presence of a series of Hammett indicators (9, 10). The results of these studies are summarized in Table 5. An anthraquinone indicator ($H_0 \le -8.2$) was not converted into its acid form by any of the 90% and higher AlF₃ catalysts. Thus, these materials contain no acid sites equivalent to 90% H₂SO₄ (29). AlF₃-Al₂O₃ catalysts containing smaller quantities of AlF₃, 3.3 and 24.6%, respectively, have been reported by Reitsma and Boelhouwer to possess $H_0 \le -5.6$ (equivalent to 71% H₂SO₄) acid sites (30). These sites disappear, however, at higher AlF₃ concentrations. At the highest AlF₃ concentration (71.4%) studied by Reitsma and Boelhouwer only $H_0 \le -3.0$ (equivalent to

Acidities of a S	Series of HCI	F ₃ -Fluorided	Aluminas
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Percentage AlF ₃	Fluoriding agent	Acid	Acidity (≤ -3.0)		
		$\leq -8.2^{a}$	≤-5.6 ^b	≤-3.0 ^c	(µmole/m)
0		325	325	475	2.7
3.46	HCF ₃	325	375	375	2.1
6.86	HCF ₃	300	375	375	2.2
13.3	HCF ₃	275	325	325	2.0
25.4	HCF ₃	275	325	325	2.2
46.1	HCF ₃	175	225	225	2.4
63.5	HCF ₃	125	175	175	2.2
78.2	HCF ₃	75	125	125	2.7
90	HCF ₃	0	0	140	2.8
95	HCF ₃	0	0	70	2.8
100	HCF ₃	0	25	25	2.8
3.3 ^d	NH₄F	0	140	300	3.1
24.6 ^d	NH₄F	0	90	160	3.1
58.5 ^d	NH₄F	0	0	60	1.4
71.4 ^d	NH₄F	0	0	30	0.7
2.2	HF	375	375	375	2.5
4.4	HF	375	375	375	2.5
14.8	HF	125	175	175	1.3
29.6	HF	75	125	125	1.1
59.2	HF	75	125	125	1.4
100	HF	0	0	0	
90°	HF	0	0	0	_
94′	HF	0	0	0	

^a Anthraquinone indicator (acidic form requires 90% H₂SO₄).

^b Benzalacetophenone indicator (acidic form requires 71% H₂SO₄).

^c Dicinnamalacetone indicator (acidic form requires 48% H₂SO₄).

^d Abstracted from Ref. (30); ammoniacal aqueous NH₄F-treated Al₂O₃.

^e Abstracted from Ref. (34); aqueous HF-treated Al₂O₃.

^f Abstracted from Ref. (29); aqueous HF-treated Al₂O₃.

48% H_2SO_4) acid sites are present. AlF₃ catalysts containing greater than 90% AlF₃ have been reported to be devoid of acid sites equivalent to 48% H₂SO₄ (29, 34). The 3-100% AIF₃ catalysts prepared in this study using HCF₃ are consistently more acidic than the HF-prepared AlF₃-Al₂O₃ catalysts listed in Table 5. The differences in acidity between the HCF₃ and HF preparations are especially apparent when compared on a square-meter basis. The number of $H_0 \leq -3.0$ acid sites demonstrated by the HCF₃-prepared catalysts is linearly dependent upon the surface areas of the material. The higher number of acid sites demonstrated by the lower-weightpercentage AIF₃ catalysts may be associated with the Al₂O₃ component or possibly with an AlF₃-Al₂O₃ interface (30).

It is apparent that the HCF₃-prepared partially fluorinated Al_2O_3 catalysts retain higher acidities than conventionally (HF) fluorinated Al_2O_3 . Thus, HCF₃-prepared $AlF_3-Al_2O_3$ catalysts would be expected to be more active solid acids than materials of the same AlF₃ content prepared by conventional procedures. The acidity advantage predicted for HCF₃-prepared fluorided aluminas, when compared to aluminas fluorided with aqueous HF, is clearly demonstrated in Fig. 1 where cyclohexene isomerization activities are compared. The differences in isomerization activities are particularly apparent at higher AlF₃ concentrations where the HCF₃-fluorinated aluminas are markedly superior isomerization catalysts. The decreased isomerization activities at higher AlF₃ concentrations are consistent with other published studies (28, 30, 35, 36).

D. Catalytic Studies Employing Pt and Pd Catalysts Supported on AlF₃

Platinum and palladium catalysts supported on AlF₃ can be conveniently prepared using either aqueous or nonaqueous impregnations. Generally good agreement between metal surface areas determined by H₂-chemisorption and X-ray line-broadening techniques is found (see Table 6). The dispersion of Pt/AlF₃ is improved by impregnating AlF₃ with acetone rather than aqueous solutions of chloroplatinic acid. Palladium dispersion on a given-BET-sur-



FIG. 1. Cyclohexene isomerization over fluorided aluminas. Run conditions: 623 K, 1380 kPa, $H_2/$ cyclohexene = 2.3, WHW = 25, 15 min on feed.

Metal Surface Areas of Pt and Pd Catalysts Supported on γ -Al ₂ O ₃ and AlF ₃					
Catalyst	BET^a (m^2/a)	Impregnation	Metal surface area ^b (m ² /g)	Dispersion (%)	
	(m/g) media	media		X ray	H ₂ chemisorption
2% Pt/Al ₂ O ₃	178	H ₂ O	_		87
3% Pt/AlF	25.4	H ₂ O	6	2.6	4.0
2% Pt/AlF ₃	25.4	Acetone	36	15	19.5
5% Pt/AIF ₃	25.4	Acetone	39	17	20.0
3% Pd/Al ₂ O ₃	178	H ₂ O	137	34	32
3% Pd/AIF ₃	3.7	H ₂ O	19	4.4	_
3% Pd/AlF ₃	21.5	H ₂ O	57	13	6.3
3% Pd/AlF ₃	22.4	H_2O	50	12	11.3
3% Pd/AIF ₃	32.9	H ₂ O	57	13	15.1
3% Pd/AlF ₃	49.7	H ₂ O	76	18	_
3% Pd/AlF ₃	25.4	Acetone	83	19	18.9

TABLE 6

^a Initial surface area of support.

^b Determined by X-ray line broadening.

face-area AlF₃ is, in contrast, relatively insensitive to the impregnation media. The dispersion of Pd increased somewhat with increasing surface area of the AlF₃ support. Palladium and platinum catalysts supported on γ -Al₂O₃ exhibited normal dispersion levels (7, 37, 38).

The results of benzene hydrogenation studies carried out over Pt and Pd catalysts are summarized in Table 7. As is well documented in the literature, Pt catalysts are about an order of magnitude more active than Pd catalysts (39, 40). Within experimental error the specific activity of Pd is the same on γ -Al₂O₃ and AlF₃ supports. Platinum, however, is about three to four times more active on AlF₃ than on Al₂O₃. The higher specific activity exhibited by the Pt/AlF₃ catalyst may reflect the presence of larger Pt crystallites on this support compared to γ -Al₂O₃ (7.5- vs 1.5-nm crystallites).

 $HF-TaF_5$ -virgin naphtha isomerization systems are known to deactivate with time on feed. The major deactivation agents have been shown to be alkylbenzenes produced by alkylating trace quantities of benzene in the superacid solution (41, 42). Alkylbenzenes deactivate superacid solutions by forming stable protonated alkylbenzene-TaF₆⁻ complexes. To regenerate poisoned HF/TaF₅ isomerization catalysts alkylbenzenes must either be removed or rendered noncomplexing. Alkylbenzenes become noncomplexing by hydrogenating them to their corresponding saturates. Due to the highly reactive and corrosive nature of the superacid solution, a limited number of potential supported hydrogenation catalysts exist. Common catalyst supports such as Al₂O₃, SiO₂, and SiO₂-Al₂O₃ vigorously dissolve in HF/TaF₅ solutions. Carbon supports, although stable in superacid solution (43), are not commonly available in the form of self-supporting pellets which are required for fixed-bed operations. Carbonbased catalysts also cannot be regenerated (under O_2) upon deactivation and contain relatively high concentrations of oxygen functional groups which may generate secondary poisons (e.g., H₂O) in the superacid media. AlF₃ extrudates thus offer potential as a noble-metal support in a superacid regeneration scheme. AlF₃-based catalysts would be stable under normal oxygen regeneration procedures and could thus be re-

Catalyst	Metal surface area ^a (m ² /g)	<i>Т</i> (°К)	Percentage conversion	Specific rate × 10 ³ (mole/hr/m ²)
2% Pt/Al ₂ O ₃	204	323	29.4	5.6
2% Pt/A1F.	36	373	96.6	18.4
270 I UIMI 3	50	348	41.1	44.3
3% Pd/Al ₂ O ₃	137	348	5.6	1.1
		373	13.1	2.5
3% Pd/AIF ₃	57	348	2.2	1.0
		373	7.0	3.0

TABLE 7

Benzene Hydrogenation Using Pt and Pd Catalysts Supported on γ -Al₂O₃ and AlF

Note. Conditions: 101 kPa, S.V. = 6.1 WHW, H_2 /benzene = 40, feed = 10% benzene/hexane, 0.29 g catalyst. ^{*a*} Metal surface areas were determined by a combination of H_2 -chemisorption and X-ray line-broadening measurements.

cycled. An anhydrous AIF_3 support would also not likely generate secondary poisons within the superacid solution.

The results of *m*-diethylbenzene (model alkylbenzene) hydrogenation in HF/TaF5 solution are summarized in Table 8. Pd/carbon and Pd/AlF₃ catalysts demonstrated comparable hydrogenation rates. A 3% Pd/ AlF₃ catalyst displayed a constant hydrogenation rate through six cycles in batch autoclave operations. Each cycle was carried out to essentially complete hydrogenation of *m*-diethylbenzene. No detectable AlF₃ degradation or loss in Pd surface area occurred during the six catalytic cycles. A 2% Pt/AlF₃ catalyst exhibited an initial specific hydrogenation activity about two times greater than that of 3% Pd/AlF₃. The 2% Pt/ AlF₃ catalyst was, however, found to lose approximately 20% of its initial activity per cycle. The cause of Pt deactivation is not known. The HF/TaF_5-m -diethylbenzene hydrogenation studies thus indicate that Pd/ AlF₃ catalysts are stable and active hydrogenation catalysts in superacid solution.

4. SUMMARY

Relatively high purity (greater than 90%) and surface area (20–50 m²/g) AlF₃ was prepared by allowing γ -Al₂O₃ to react with

HCF₃ at 670–770 K under 101 kPa total pressure. On the basis of HCF₃ utilization, the yields of AlF₃ are essentially stoichiometric. The nontoxic and noncorrosive nature of HCF₃ makes this fluoriding procedure very attractive, especially, in light of the safety hazards present when using conventional gaseous or aqueous HF fluoriding procedure. The HCF₃-prepared AlF₃ products were found to retain the physical form of the starting γ -Al₂O₃. A $\frac{1}{16}$ -in. γ -Al₂O₃ ex-

TABLE 8

Hydrogenation of *m*-Diethylbenzene in HF/TaF₅ Superacid Solution

Catalyst	Metal surface area ^a (m ² /g)	Specific rate $\times 10^3$ (moles H ₂ /hr/m ²)	
5% Pd/carbon ^b	65	2.8	
3% Pd/AlF3	65	3.1	
2% Pt/AlF ₃	36	6.4	

Note. Conditions: 303 K, 1380 kPa total pressure, 1500 rpm, HF/TaF₅/m-diethylbenzene = 2/0.2/0.05 (moles).

^a Metal surface areas were determined by a combination of H₂-chemisorption and X-ray line-broadening techniques.

^b Granular carbon-supported catalyst was supplied by Engelhard Minerals and Chemicals Corporation. trudate, for example, yielded an AlF₃ extrudate with the same physical dimensions. This result is significant since AlF₃ powders cannot be compacted or extruded into selfsupporting pellets without an added binder.

The BET surface areas, pore volumes, and surface acidities of HCF₃-fluorided aluminas decrease with increasing AlF₃ concentration. The systematic reduction of these parameters with increasing AlF₃ content is likely associated with the removal of unreacted γ -Al₂O₃.

AlF₃ extrudates were employed as supports for Pt and Pd catalysts. These catalysts exhibit moderate metal dispersions of 15-20% and good benzene hydrogenation activities. Pd/AlF₃ was also found to be stable and an active alkylbenzene hydrogenation catalyst in HF/TaF₅ superacid solution.

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