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Activation of Chlorinated Methanes at the Surface of Nanoscopic Lewis Acidic Aluminium Fluorides

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We report on the activation of chlorinated methanes at the heterogeneous catalysts aluminum chlorofluoride (ACF) and high surface aluminum fluoride (HS-AIF₃) under moderate conditions. For comparison, chlorinated toluenes and 1,2-dichloroethane were also tested. The strong Lewis acids are able to promote the cleavage of C-Cl bonds in the presence of Et₃SiH. The C-Cl bonds were converted into C-H bonds via hydrodechlorination reactions or in the presence of benzene into C-C bonds via Friedel-Crafts type reactions. The catalytic reactions show high conversions.

Introduction

Chlorinated organic compounds are often used as starting materials for various Friedel-Crafts or hydrodechlorination reactions. Friedel-Crafts reactions of halogenated compounds are of current interest because they open up reaction routes to access pharmaceuticals, dyes, agro- and fine chemicals.¹ Various heterogeneous catalysts, such as zeolites, protonated titanate nanotubes, clays, nafion, resin–silica nanocomposites and heteropolyacids (HPAs) have been applied for Friedel-Crafts reactions.²

Hydrodechlorination reactions of chlorinated organic compounds are of interest because of environmental issues related to their "super greenhouse gas" behavior and ozone depletion potential.³ A wide range of heterogeneous catalytic reactions to achieve hydrodechlorination reactions is reported in the literature. For instance, Z. M. de Pedro et al., M. A. Álvarez-Montero et al., N. Chen et al., C. D. Thompson et al., Makkee et al. and Coq et al. described the application of palladium or platinum catalysts supported on carbon.⁴ Furthermore, palladium, platinum or ruthenium catalysts supported on alumina are known for their reactivity in the activation of C-Cl bonds.⁵ To improve the selectivity and activity, alumina-supported bimetallic systems like Pd/Pt, Pd/Cu, Pd/Ni, Ni/Au were investigated thoroughly as hydrodechlorination catalysts as well.⁶ In addition, Ni/C, Ni-Pd/C, Pt/Al₂O₃, Ag-Pd/ZrO₂ and Pd-Ag/Al₂O₃, have proven to be highly active, especially for the catalytic hydrodechlorination of 1,2 dichloroethane.⁷ However, the conditions for the depletion of chlorine-containing molecules in hydrodechlorination reactions

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using the above mentioned catalysts are fairly harsh; for all cases the temperatures exceed 100°C and are often higher than 250°C. Current research also focuses on the investigation of homogeneous catalysts immobilized on solid materials, such as rhodium(I) complexes supported on MCM-41.⁸

We recently reported on C-F bond activation reactions at nanoscopic solid Lewis acids like ACF.⁹ ACF (AlCl_xF_{3-x}, $x \approx 0.05-0.25$) is an amorphous strong Lewis acid, the acidity of which is comparable with that of SbF₅. In the presence of Et₃SiH, the fluorinated methanes CH₃F, CH₂F₂ and CHF₃ as well as C₆H₅CF₃ and C₆H₅CH₂F are converted into Friedel-Crafts or hydrodefluorination products.

The present paper focuses on the activation of C-Cl bonds in the presence of Et_3SiH . Microporous ACF and mesoporous HS-AlF₃ were studied as catalysts in the activation of chlorinated methanes, and for comparison toluenes and 1,2-dichloroethane.

Results and Discussion

The reactions of the chlorinated methanes CCl_4 , $CHCl_3$, CH_2Cl_2 , and CH_3Cl with Et_3SiH in the presence of the Lewis acid ACF in C_6D_6 as solvent at 24°C or 70°C led to the formation of both Friedel-Crafts and hydrodechlorination products. (Scheme 1, Table 1).



Scheme 1. ACF-catalyzed hydrodechlorinations and Friedel-Crafts reactions of chlorinated methanes in the presence of Et₃SiH.

Polychlorinated methanes in C_6D_6 yielded deuterated diphenylmethane as the main product, which is formed via two Friedel-Crafts reaction steps and up to two hydrodehalogenation reactions. Apparently, Friedel-Crafts-like reactions are favoured over hydrodechlorination steps. Deuterated toluene was also formed in small amounts in the reactions of polychlorinated methanes. For CH₃Cl, the main product is Ph^DCH₃ (Ph^D= C₆D₅) and considerable amounts of methane are also generated.

chlorinated	methane	s in the	presence of	of silane		
subs.	Т [°С]	t [d]	conv. [%] ^[a]	main product ^[b]	minor products	TON [c]
CCI ₄	24	3	12	Ph ^D ₂ CH ₂ (94%)	Ph ^D CH₃ (6%)	1
CCl ₄	70	3	90	Ph ^D ₂ CH ₂ (99%)	Ph ^D CH₃ Ph ^D ₃CH	7
CHCl₃	70	2	88	Ph ^D ₂ CH ₂ (98%)	Ph ^D CH₃ Ph ^D ₃CH	9
CHCl₃	24	3	13	Ph ^D ₂ CH ₂ (94%)	Ph ^D CH₃ (6%)	1
CHCl₃	70	3	>99	Ph ^D ₂ CH ₂ (99%)	Ph ^D CH₃ Ph ^D ₃CH	10
CH_2Cl_2	70	2	35	Ph ^D ₂ CH ₂ (95%)	Ph ^D CH ₃ (5%)	5
CH_2CI_2	70	3	46	Ph ^D ₂ CH ₂ (95%)	Ph ^D CH₃ (5%)	6
CH ₃ CI	70	2	35	Ph ^D CH₃ (51%)	CH ₄ (49%)	21
CH ₃ Cl	70	3	46	Ph ^D CH₃ (54%)	CH ₄ (46%)	27

Table 1. Conversions and product distributions for the catalytic activation of

Experiments for the activation of CH₃Cl were performed in JYoung NMR tubes whereas all the other reactions were carried out in standard NMR tubes. All reactions were carried out in 0.9 ml of C₆D₆ as solvent and using 25 mg of the catalyst ACF. Et₃SiH was added stoichiometrically to the number of chlorine atoms in the substrate [a] Based on the conversion of Et₃SiH into Et₃SiCl or the ratio products to substrate, if the signals overlapped in ¹H NMR spectrum. [b] Ph^D= C₆D₅ [c] Calculated based on the amount of products per number of active acidic sites at the ACF (1 g ACF contains 1 mmol of active sites determined by NH₃-TPD).¹⁰



Scheme 2. ACF-catalyzed Friedel-Crafts reactions of chlorinated methanes in the absence of $\mathsf{Et}_3\mathsf{SiH}$

Table 2	Conversions	and product	distributions	for the	catalytic activations
of chlori	nated methane	es in the abse	ence of silane		

subs.	т [°С]	t [d]	conv. [%] ^[a]	main product	minor products	TON [b]
CCI ₄	70	3		-		
CHCl₃	24	3	17	Ph ^D ₃CH (88%)	Ph ^D ₂ CH ₂ (12%)	2
CHCl₃	70	3	74	Ph ^D ₃CH (91%)	Ph ^D ₂ CH ₂ (7%), Ph'CH ₃	7
CH ₂ Cl ₂	24	3	65	Ph ^D ₂ CH ₂ (99%),	Ph ^D CH ₃ (1%)	9
CH ₂ Cl ₂	70	3	95	Ph ^D ₂ CH ₂ (99%)	Ph ^D CH ₃ (1%)	13
CH₃CI	24	3	27	Ph ^D CH₃	-	16
CH₃CI	70	3	79	Ph ^D CH₃	-	46

Experiments for the activation of CH₃Cl were performed in JYoung NM tubes whereas the other reactions were carried out in standard NMR tubes All reactions were carried out in 0.9 ml of C₆D₆ as solvent and using 25 mg c the catalyst ACF. [a] Based on the products to substrate ratio determined b ¹H NMR spectroscopy. [b] Calculated based on the amount of the product per number of active acidic sites at the ACF (1 g ACF contains 1 mmol c active sites determined by NH₃-TPD).¹⁰

For comparison, the C-Cl-bond activation was also investigated in the absence of silane (Scheme 2 and Table 2). CH₃Cl, CH₂Cl₂ and CHCl₃ reacted to give the deuterated mono-, di- and triphenylmethane as the main products, respectively. Note that CCl₄ was not activated in the reaction in the absence of silane. In contrast to the reactions with silane, CHCl₃ was converted mainly into Ph^D₃CH. Note that the generation of minor products which are formed via C-C coupling and hydrodechlorination steps was also observed. We tentatively suppose an occurrence of Cl/H exchange reactions at the Lewis acid ACF.¹¹

It can be assumed that in the Friedel-Crafts reactions of chlorinated methanes partially chlorinated toluenes are formed as intermediates. Therefore, chlorinated toluenes were treated with Et₃SiH in the presence of ACF (Scheme 3, Table 3). In all the transformations Ph^DPhCH₂ (Ph= C₆H₅) was formed as the main product. Small amounts of Ph^D₂PhCH were generated in the reaction of polychlorinated toluenes.

The activation of chlorinated toluenes was also investigated in the absence of silane (Scheme 4). Table 4 summarizes the results of these reactions. The activation of α -monochlorotoluene PhCH₂Cl and α, α -dichlorotoluene PhCHCl₂ led to the formation of diphenylmethane Ph^DPhCH₂ and triphenylmethane Ph^D₂PhCH as the main products, respectively. No activation of α, α, α -trichlorotoluene PhCCl₃ was observed.



Scheme 3. ACF-catalyzed hydrodechlorinations and Friedel-Crafts reactions of chlorinated toluenes in the presence of Et_3SiH .

 Table 3. Conversions and product distributions for the catalytic activations

 of chlorinated toluenes in the presence of silane

substrate	Т [°С]	t [d]	conv. [%] ^[a]	main product	minor product	TON [b]
PhCCl₃	24	1	82	Ph ^D PhCH ₂ (91%)	Ph ^D ₂PhCH (9%)	9
PhCCl₃	24	2	96	Ph ^D PhCH ₂ (91%)	Ph ^D ₂PhCH (9%)	9
PhCCl₃	70	3	95	Ph ^D PhCH ₂ (83%)	Ph ^D ₂PhCH (17%)	9
PhCHCl ₂	24	1	64	Ph ^D PhCH ₂ (82%)	Ph ^D ₂PhCH (18%)	5
PhCHCl ₂	24	3	66	Ph ^D PhCH ₂ (83%)	Ph ^D ₂ PhCH (17%)	5
PhCHCl ₂	70	2	84	Ph ^D PhCH ₂ (82%)	Ph ^D ₂ PhCH (18%)	6
PhCH ₂ CI	24	1	78	Ph ^D PhCH ₂ (>99%)	-	5
PhCH ₂ CI	24	2	88	Ph ^D PhCH ₂ (>99%)	4	5
PhCH₂CI	70	3	92	Ph ^D PhCH ₂ (>99%)		5

All reactions were carried out in 0.9 ml C₆D₆ as solvent and 25 mg ACF. Et₃SiH was added stoichiometrically to the number of chlorine atoms in the substrate. [a] Based on the conversion of Et₃SiH into Et₃SiCl or the ratio products to substrate, if the signals overlapped in ¹H NMR spectrum [b]. Calculated based on the amount of the products per number of active acidic sites at the ACF (1 g ACF contains 1 mmol of active sites determined by NH₃-TPD).¹⁰

The activation of chlorinated toluenes was also investigated in the absence of silane (Scheme 4). Table 4 summarizes the results of these reactions. The activation of α -monochlorotoluene PhCH₂Cl and α, α -dichlorotoluene PhCHCl₂ led to the formation of diphenylmethane Ph^DPhCH₂ and triphenylmethane Ph^D₂PhCH as the main products,

respectively. No activation of $\alpha,\alpha,\alpha\text{-trichlorotoluene PhCCl}_3$ was observed.



Scheme 4. ACF-catalyzed hydrodechlorination and Friedel-Crafts reactions of chlorinated toluenes in the absence of Et_3SiH .

 Table 4. Conversions and product distributions for the catalytic activations of chlorinated toluenes in the absence of silane

substrate	Т [°С]	t [d]	conv. [%] ^[a]	main product	minor products	TON [b]
PhCCl ₃	24	3	0	-	-	-
PhCCI ₃	70	3	0	-	-	-
PhCHCl ₂	24	3	22	Ph ^D ₂PhCH (87%)	Ph ^D PhCH ₂ (13%)	2
PhCHCl ₂	70	3	36	Ph ^D ₂ PhCH (88%)	Ph ^D PhCH ₂ (12%)	3
PhCH ₂ CI	24	3	93	Ph ^D PhCH ₂ (98%)	PhCH₃ Ph ^D ₂PhCH	6
PhCH ₂ CI	70	3	>99	Ph ^D PhCH ₂ (98%)	PhCH₃ Ph ^D ₂PhCH	6

All reactions were carried out in 0.9 ml C_6D_6 as solvent and using 25 mg ACF. [a] Based on the products to substrate ratio determined by ¹H NMR spectroscopy. [b] Calculated based on the amount of the products per number of active acidic sites at the ACF (1 g ACF contains 1 mmol of active sites determined by NH₃-TPD).¹⁰

Possible steric effects were further studied by using 1,2-dichloroethane CICH₂CH₂CI. The latter was activated both in the presence and absence of Et₃SiH in C₆D₆ as solvent at ACF (Scheme 5, Table 5). 1,2-Dichloroethane CICH₂CH₂CH₂CI reacted to the Friedel-Crafts products Ph^DCH₂CH₂Ph^D and Ph^DCH₂CH₃ and 1,1-diphenylethane Ph^D₂CHCH₃ in both the presence and absence of silane. In the absence of the solvent C₆D₆ and Et₃SiH, CICH₂CH₂CI undergoes a rearrangement to form exclusively 1,1-dichloroethane.

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Scheme 5. ACF-catalyzed hydrodechlorination and Friedel-Crafts reactions of 1,2-dichloroethane in the presence and absence of Et₃SiH.

 Table 5. Conversions and product distributions for the catalytic activations of 1,2-dicholoroethane in the absence and presence of silane

main products	minor product	Et₃SiH [mmol]	Т [°С]	conv. [%] ^[a]	TON [b]	
Ph ^D CH ₂ CH ₂ Ph ^D (74%)	Ph ^D CH ₂ CH ₃ (18%) Ph ^D ₂ CHCH ₃ (8%)	0.60	24	3	0.4	
Ph ^D CH ₂ CH ₂ Ph ^D (78%)	Ph ^D CH ₂ CH ₃ (13%) Ph ^D ₂ CHCH ₃ (9%)	0.60	70	63	8	
Ph ^D CH ₂ CH ₂ Ph ^D (93%)	Ph ^D CH ₂ CH ₃ (4%) Ph ^D ₂ CHCH ₃ (2%) Ph ^D ₂ CHCH ₂ Ph ^D (1%)	-	24	35	4	
Ph ^D CH₂CH₂Ph ^D (78%)	Ph ^D CH ₂ CH ₃ (9%) Ph ^D ₂ CHCH ₃ (12%) Ph ^D ₂ CHCH ₂ Ph ^D (1%)	-	70	60	7	
Ph ^D CH ₂ CH ₂ Ph ^D (68%)	Ph ^D CH ₂ CH ₃ (10%) Ph ^D ₂ CHCH ₃ (14%) Ph ^D ₂ CHCH ₂ Ph ^D (8%)		70	91	11	
CICHCHC	_		70	1	5	

All reactions were carried out in 0.9 ml of C_6D_6 as a solvent and using 25 mg of ACF. The reaction was carried on for 72 h. If adopted, Et₃SiH was added stoichiometrically to the number of chlorine atoms in the substrates [a] Based on the conversion of Et₃SiH into Et₃SiCl in the presence of silane or the ratio of products to the substrate if the signals overlapped, whereas in the absence of silane it was always calculated based on the ratio of products to the substrate; determined by ¹H NMR spectroscopy. [b] Calculated based on the amount of the products per number of active acidic sites at the ACF (1 g ACF contains 1 mmol of active sites determined by NH₃-TPD).¹⁰

Unlike ACF, which is microporous, $HS-AIF_3$ is mesoporous.¹² Table 6 shows the conversions of chlorinated

methanes with Et₃SiH at *HS*-AlF₃. Both, chlorinated methanes and chlorinated toluenes reacted to yield $Ph_2^DCH_2$ and Ph^DPhCH_2 as the main products. The conversions were higher for chlorinated toluenes at *HS*-AlF₃ in the presence of silane in comparison with the results achieved with ACF (Table 3). Literature data indicate that ACF is in liquid phase/solid state reactions slightly more reactive than *HS*-AlF₃, which might be an explanation for the higher reactivity of ACF towards chlorinated methanes.¹³ However, the lower activity of ACF towards chlorinated toluenes might, in contrast, be due to diffusionlimited accessibility which is related to the different porosity of the two catalysts.

Table 6. Conversions and product distributions for the catalytic activation with HS-AIF₃ of chlorinated methanes and toluenes in the presence of silane

					100	
substrate	T [°C]	T [d]	conv [%] ^[a]	main product	minor products	TON [b]
CCl ₄	70	3	28	Ph ^D ₂ CH ₂ (87%)	Ph ^D CH₃ (4%) CHCl₃ (9%)	2
CHCI3	70	2	43	Ph ^D ₂ CH ₂ (97%)	Ph ^D CH₃ (3%)	4
CH ₂ Cl ₂	70	2	6	Ph ^D ₂ CH ₂ (95%)	Ph ^D CH₃ (5%)	1
CH ₂ Cl ₂	70	3	7	Ph ^D ₂ CH ₂ (92%)	Ph ^D CH₃ (8%)	1
CH ₃ CI	70	2	7	CH4 (82%)	Ph ^D CH₃ (18%)	4
CH₃CI	70	3	10	CH ₄ (82%)	Ph ^D CH₃ (18%)	5
PhCCl ₃	24	2	>99	Ph ^D PhCH ₂ (79%)	-	10
PhCHCl ₂	70	2	>99	Ph ^D PhCH ₂ (98%)	Ph ^D ₂ PhCH (2%)	8
PhCH₂Cl	24	1	>99	Ph ^D PhCH₂ (>99%)	-	6

All reactions were carried out in 0.9 ml of C_6D_6 as a solvent and using 25 mg HS-AlF₃. Et₃SiH was added stoichiometrically to the number of chlorine atoms in the substrate [a] Based on the conversion of Et₃SiH into Et₃SiCl in the presence of silane or the ratio of products to substrate if the signals overlapped in ¹H NMR spectrum; determined by ¹H NMR spectroscopy. [b] Calculated on the basis of the amount of the products per number of active acidic sites at the HS-AlF₃ (1 g HS-AlF₃ contains 1 mmol of active sites determined by NH₃-TPD).¹⁰

To gain a better understanding about the interaction of the substrates with ACF, *Pulse*TA[®] (PTA) experiments were performed.¹⁴ PTA was successfully employed before for studying both reactivity and adsorption/desorption phenomena of solid fluorides.^{15,16} The experimental setup can be understood as an usual TA-MS device equipped with a gas dosing unit allowing for the injection of gases into the purge gas thus enabling an interaction with the solid. Evaporable liquids can be

pulsed as well by using a septum-tightened heated (120 °C) GC injector and ordinary μ L syringes. One obtains usual thermoanalytical curves (under heating or, as in the present case, isothermally) and additional information about adsorption processes being due the reactant injections. Isothermal PTA revealed to be of extraordinary sensitivity *vs.* enthalpic effects and mass changes. The injection pulses as well as changes of the product composition of the gas phase are monitored by the ionic current (IC) curves of pre-chosen characteristic mass numbers for the injected starting compound and for presumed reaction products.

Fig. 1 shows the loading of ACF with six pulses of 2 mL $CH_3Cl_{(g)}$. Chemisorption is indicated by comparably large exothermal DTA peaks and a (decreasing) persistent mass gain for each CH_3Cl pulse. The following two injections of 2 µL and one injection of 4 µL Et_3SiH did neither lead to significant DTA peaks nor to any persistent mass gain. On the contrary, the interaction of prior formed ACF°Et_3SiH did not show any remarkable interaction with CH_3Cl (Figure S11 in the ESI). Thus, both Et_3SiH and CH_3Cl adsorb at ACF in a first loading. Regardless of the sequence of pulsing the silane or CH_3Cl , no reaction at least at the solid/gas interphase was observed.



Figure 1. TA-MS curves of an isothermal (31°C) *Pulse*TA[®] experiment with thermally pretreated (200 °C) ACF (34.4 mg) under Ar with the IC curves for the mass numbers m/z= 50 (CH₃Cl⁺), and 59 (EtSiH⁺). ACF was preloaded with six pulses of 2 mL CH₃Cl. Next, Et₃SiH was added in 3 pulses.



Figure 2. TA-MS curves of an isothermal *Pulse*TA[®] experiment with thermally pretreated (180°C) ACF (35.1 mg) with the IC curves for the mass numbers m/z= 50 (CH₃Cl⁺), and 78 (C₆H₆⁺). The eight benzene pulses led to a constant loading of ACF. Pulsing then of 2 mL gaseous CH₃Cl led to further loading

which is then continued by further benzene pulses. Note that the weak m/z= 50 intensity for the benzene pulses belong to the mass spectrum of benzene, whereas for pulses 9-11 it represents CH_3CI .



Scheme 6. Proposed mechanism for ACF-catalyzed hydrodechlorination and Friedel-Crafts reactions of CH₃Cl in the presence of Et₃SiH.



Scheme 7. Proposed mechanism for ACF-catalyzed Friedel-Crafts reactions of $\mbox{CH}_3\mbox{Cl}.$

The mechanism for the hydrodechlorination might proceed via a similar reaction pathway as previously reported for hydrodefluorination reactions in the presence of silane.⁹ Initially, Et₃SiH can be adsorbed at the Lewis acidic sites of ACF which

results in a more electrophilic silicon atom in Et₃SiH (see Scheme 6 for CH₃Cl). As a result of this polarization, surfacebound species of silvlium-like character are generated, which can initiate a C-CI bond cleavage reaction to give the chlorosilane and formally a surface bound hydride. The generated carbenium-like species might react with the latter or initiates a Friedel-Crafts reaction. However, a reverse mechanism is also conceivable, which involves an initial formation of a carbenium ion by C-Cl bond cleavage and a subsequent reaction with a silane or benzene. For the reactions without silane we suggest a similar C-Cl activation, and Friedel-Crafts reaction pathway to give the C-C-coupling product and HCI (see Scheme 7).¹⁶ Note, that a PulseTA® experiment which involved alternating treatment of the surface with benzene, CH₃CI and again benzene indicated that both substrates can be adsorbed at the same time (see Figure 2).

Conclusions

In summary, we have demonstrated that nanoscopic aluminium fluorides, such as aluminium chlorofluoride (ACF) and high surface-aluminium fluoride (HS-AIF₃) are suitable catalysts for the activation of C-Cl bonds in the presence of Et₃SiH under mild reaction conditions. The C-Cl bonds are converted either into C-H bonds via hydrodehalogenation reactions or into C-C bonds via Friedel-Crafts type reactions. In the absence of silane, classical Friedel-Crafts reactions take place. Differences between ACF and HS-AIF₃ are mainly due to different porosities in both catalysts (micro- vs. mesoporosity).

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Keywords: heterogeneous catalysis, silane, activation of chlorinated compounds

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ACF ACF C₆D₆ DCI + HD + CH_4 Et₃SiCl

ACF and HS-AIF₃ as a powerful Lewis acid for Friedel-Crafts type and hydrodechlorination reactions.

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Activation of Chlorinated Methanes at the Surface of Nanoscopic Lewis **Acidic Aliminium Fluorides**

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