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# Friedel–Crafts catalysis using supported reagents. Synthesis, characterization and catalytic application of $ZnCl_2$ supported on fluoride-modified sol–gel-derived aluminosilicates

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$ZnCl_2$–aluminosilicate catalysts were prepared via a sol–gel route involving fluoride-catalyzed hydrolysis of aluminum and silicon alkoxides in the presence of NaF, KF, $NH_4F$ and $ZnF_2$. The catalysts were characterized by employing $^{29}Si$, $^{27}Al$ and $^{19}F$ solid-state MAS NMR. The dependence of the activities of the catalysts on the nature and amount of fluoride present in the catalysts were investigated using Friedel–Crafts alkylation reaction of benzene with benzyl chloride.

**Keywords:** alumina–silica sol–gel mixed oxide, fluoride additives, $ZnCl_2$, $ZnF_2$, catalysts, solid-state NMR, Friedel–Crafts alkylation

## 1. Introduction

Zinc chloride supported on montmorillonite clay, alumina, silica and aluminosilicates, has been extensively investigated in recent years as catalyst for Friedel–Crafts reactions [1–8]. Zinc chloride supported on montmorillonite K10 clay, "clayzic" reported by Clark and co-workers [1,2] is a useful alternative to traditional Friedel–Crafts alkylation catalysts such as $AlCl_3$ and HF. They have environmental drawbacks in addition to often poor selectivity and lack of re-usability. In our earlier investigations [6–8] on zinc chloride incorporated on sol–gel-derived silica, aluminosilicate and metal-diketonate-modified aluminosilicates for Friedel–Crafts alkylation reactions we observed higher activities in comparison to the $ZnCl_2$/montomorillonite clay catalysts. We have used a range of characterization techniques including solid-state NMR and infrared spectroscopy to determine the influence of various fluoride additives on alumina [9], silica [6,10] and commercial montmorillonite K10 clay [3,11].

Recently, fluorinated supports are receiving increasing attention as catalysts for acid- and base-catalyzed reactions. Pt supported on fluoride-modified alumina was used as a catalyst for the complete oxidation of benzene [12]. Fluoride-modified alumina is used for the acid-catalyzed isomerization of 1-butene, $n$-butene and isobutane [13–15]. KF supported on alumina catalyst has been employed for base-catalyzed reactions – both Michael addition, aldol condensation reactions, etc. [16]. The use of fluorinated alumina for various acid-catalyzed reactions has been discussed by Saniger et al. [17]. The fluorination of the supports was found to increase the total acidic sites and their strength up to a certain optimum concentration. Beyond this loading an increase in F content was found to result in a decrease in the Lewis acidic sites [18,19]. Various fluorinating agents such as KF, NaF, $NH_4F$, etc. have been found to reduce the gelation time of the silica sol [20]. In our previous work on $CdF_2$-, $ZnF_2$- and $CuF_2$-incorporated montmorillonite clay [3] we obtained higher activities for the Friedel–Crafts alkylation reaction for the $ZnF_2$/clay catalysts. We now report an investigation of the influence of fluoride content on the Friedel–Crafts alkylation activity and varying fluoride precursors of the $ZnCl_2$–aluminosilicate catalysts and also characterization of these materials by solid-state NMR.

## 2. Experimental

The aqueous solutions of the $ZnCl_2$ and various $F^-$ additives (KF, NaF and $NH_4F$) were added to the mixed alkoxide solution of aluminum trisecbutoxide (ATSB) and tetraethyl orthosilicate (TEOS). Aluminum trisecbutoxide (20.0 g, 0.08 mol) and TEOS (17.4 ml, 0.08 mol) and 1-butanol (200 ml) were stirred at 70 °C for 5–10 min until a clear solution was obtained. After cooling to room temperature, this solution was divided into five equal portions. The $ZnCl_2$ and fluoride salts were dissolved in separate portions of water and then added to the alkoxide mixture to avoid the precipitation of $ZnF_2$. The gelled samples were stirred for 10 min and left to stand overnight. Residual solvent was then removed by heating in an oven at 110 °C and then at 225 °C overnight. The amounts of $F^-$ salts used per (1/5) portion of the aluminosilicate sol are given in table 1. 1.5 g of $ZnCl_2$ (0.012 mol) was used in all samples, as this amount is the optimum loading for the Friedel–Crafts activity [8].

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Table 1
Amounts of $F^-$ in various Zn–Al–Si catalysts.

| Amount of KF (g) | Amount of NaF (g) | Amount of $NH_4F$ (g) | Amount of $ZnF_2$ (g) | |
|---|---|---|---|---|
| KF–Zn–Al–Si[a] | NaF–Zn–Al–Si[a] | $NH_4F$–Zn–Al–Si[a] | $ZnF_2$/Al–Si | $ZnF_2$/Al–Si(H-acac) |
| 0.05 | 0.04 | 0.03 | 0.1 | 0.1 |
| 0.10 | 0.08 | 0.06 | 0.3 | 0.3 |
| 0.15 | 0.12 | 0.09 | 0.4 | 0.4 |
| 0.21 | 0.15 | 0.12 | 0.5 | 0.5 |

[a] 1.5 g $ZnCl_2$ is used for all the catalysts.

A series of the catalysts using $ZnF_2$ as the active component on unmodified and 2,4-pentanedione (H-acac)-modified aluminosilicate sol–gel support was also prepared. The synthesis procedure for the H-acac-modified aluminosilicate sol–gel mixed oxide is described elsewhere [8]. The preparation procedure of the unmodified aluminosilicate sol–gel mixed oxide support is as follows. Aluminum trisecbutoxide (20.0 g, 0.08 mol) and TEOS (17.4 ml, 0.08 mol) and 1-butanol (200 ml) were stirred at 70 °C for 5–10 min until a clear solution was obtained. To this alkoxide mixture 37.5 ml (2.8 mol) water was added to form an aluminosilicate gel. The solvent was then removed by heating in an oven at 110 °C. $ZnF_2$/Al–Si catalysts were made by impregnating an aqueous solution containing calculated amount of $ZnF_2$ on the 1 g of the H-acac-modified and unmodified aluminosilicate mixed oxide as the supports. The amounts of $ZnF_2$ used in this series of catalysts were given in table 1.

The catalysts were characterized by solid-state NMR and the experiments were carried out on a Bruker DPX-300 multinuclear Fourier transform spectrometer using a Bruker narrow bore MAS probe with 4 mm zirconia rotors. $^{27}$Al spectra were obtained at 78.2 MHz with a 30° pulse and 250 ms delay between the pulses over a spectral window of 50 kHz. The spectra were referenced to external aqueous aluminum nitrate. $^{29}$Si CP-MAS spectra were obtained at 59.62 MHz using cross-polarization with proton decoupling during acquisition and referenced to external TMS. Samples were spun at 4 kHz in air. A 10 ms contact time was used with a 5 s delay between pulses. Between 5000 and 10000 FIDs were typically accumulated over a spectral window of 18 kHz. $^{19}$F MAS NMR spectra were obtained at 282.88 MHz and referenced to $CFCl_3$ using powdered Teflon as an external secondary standard ($-123.0$ ppm). The DEPTH pulse sequence was employed to remove background $^{19}$F signals from the probe [21]. Samples were spun at 14 kHz with air. 256 scans were typically accumulated over a 14 kHz spectral width with a 5 s delay between pulses.

The activities of the catalysts were tested in liquid-phase Friedel–Crafts alkylation of benzene with benzyl chloride. Benzene (Caledon Laboratories, 22.0 ml, 0.25 mol) was stirred vigorously in a 100 ml round-bottomed flask and freshly dried catalyst (typically 0.50 g) was added to the reactant. Benzyl chloride (5.8 ml, 0.05 mol) was then added in one aliquot and the reagents stirred at room temperature for 15 min. The catalyst was then filtered and the products were analyzed by a Perkin–Elmer Sigma 3B gas chromatograph interfaced to a Hewlett–Packard 3396 series II integrator. Analysis was carried out with the aid of packed columns containing 3% OV-17 on Gas Chrom Q. Products were identified by GC-MS using a Carlo Erba MFC 500 GC interfaced to a Kratos Concept 1S mass spectrometer. The % conversion was defined as the total conversion of benzyl chloride (to diphenylmethane and the *ortho*, *meta* and *para* isomers of dibenzylbenzene). The reproducibility of the activities were verified by testing each catalyst twice.

## 3. Results and discussion

The $^{29}$Si solid-state CP/MAS NMR spectra of the fluorinated Zn–Al–Si catalysts are broad indicating a range of $Q^n$ silanol and $Si(Oal)_n(Osi)_{4-n}$ sites, but no structural information can be obtained. The $F^-$ may attack the silica layer forming $SiF_6^{2-}$ which decomposes to $SiF_4$ and $F^-$ at elevated temperatures. As the Si atoms are removed, Al atoms replace them in the tetrahedral layer [7]. Evidence for this is also seen the $^{27}$Al spectra (vide infra), where the relative intensity of the tetrahedral species increases with increase in $F^-$ loading.

Figure 1 shows $^{27}$Al solid-state MAS NMR spectra of the fluorinated Zn–Al–Si catalysts, with the lowest fluoride loading in each series. There are three overlapping resonances: the octahedral $[Al(H_2O)_6]^{3+}$ species at approximately 0 ppm, the tetrahedral $AlO_4^-$ species at approximately 55 ppm and the Al“V” peak at 30 ppm. There is a controversy in the literature regarding the assignment of this peak to five co-ordinate aluminum [22]. As the amount of fluoride in the catalysts is increased the Al“V” peak decreased in intensity with a corresponding increase in the tetrahedral (framework) aluminum peak, in comparison to the same catalysts with low F loadings. The shift to lower field observed in the $^{29}$Si spectra of the KF- and NaF-loaded catalysts is consistent with an increase in the amount of framework Al species. In the case of $NH_4F$-modified catalysts the reduction in the intensity of the Al“V” signal with increasing fluoride is not as pronounced as with the KF- and NaF-modified catalysts, and there is only a slight increase in the tetrahedral intensity as the fluoride loading increases. In all cases, as the fluoride is introduced the 30 ppm peak decreases and the tetrahedral aluminum peak increases.

The $^{19}$F MAS NMR spectra of the unmodified and H-acac-modified $ZnF_2$/Al–Si catalysts are shown in fig-

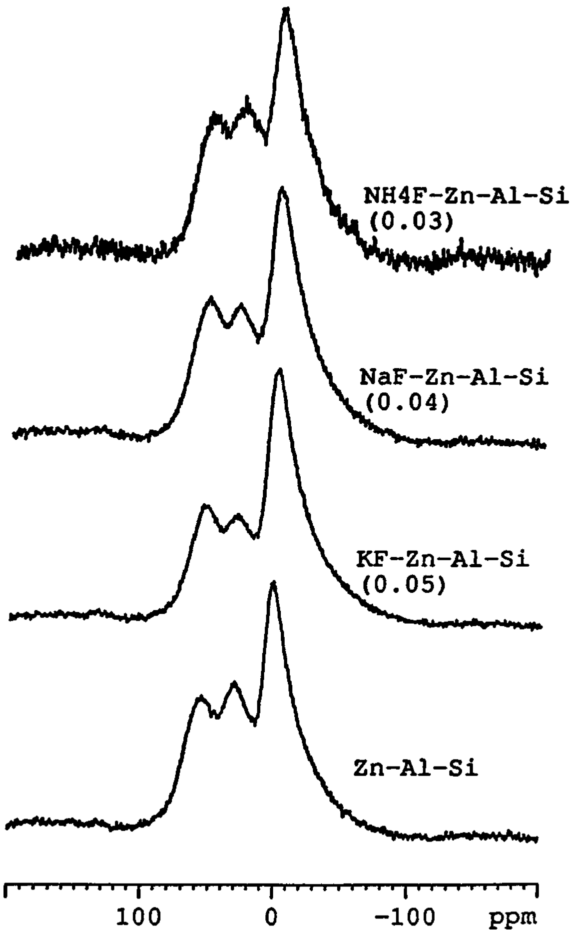

Figure 1. 78.2 MHz $^{27}$Al MAS NMR spectra of the Zn–Al–Si catalysts with low fluoride contents (the amount of fluoride in each catalyst is given in parentheses).

ures 2 and 3. The $^{19}$F resonance at $-155$ ppm may be attributed to the surface adsorbed $SiF_6^{2-}$ species. The peak at $-120$ ppm can be assigned to the free fluoride ion. We attributed a sharp intense $^{19}$F resonance at $-124$ ppm to free $F^-$ and a weak peak at $-149$ ppm to $SiF_6^{2-}$, as in our earlier $^{19}$F NMR studies on $ZnF_2/SiO_2$ catalysts [3]. $^{19}$F NMR spectra obtained at different spin rates of 10 and 15 kHz to determine isotropic chemical shifts are shown in figure 4. The peak at $-120$ ppm is partly a spinning side band but the spectrum of the sample spun at 15 kHz shows a small peak in this region. In both spectra there is a shoulder on the $-155$ ppm peak at approximately $-175$ ppm, which may be due to the presence of $F^-$ species since the intensity of this peak increases with increasing loadings [21].

In the case of KF-modified catalysts $^{19}$F signals could be detected only for the higher loadings of KF, perhaps due to some of the fluorine being lost as HF in the drying stages. There is one discernible peak at approximately $-140$ ppm due to the $AlF_4^-$ species which is tetrahedral and could account for the decrease in Al$^{\text{“V”}}$ observed in the $^{27}$Al spectra [21]. With the addition of the fluoride there is a decrease in non-framework species and an increase in tetrahedral aluminum from incorporation of the aluminum

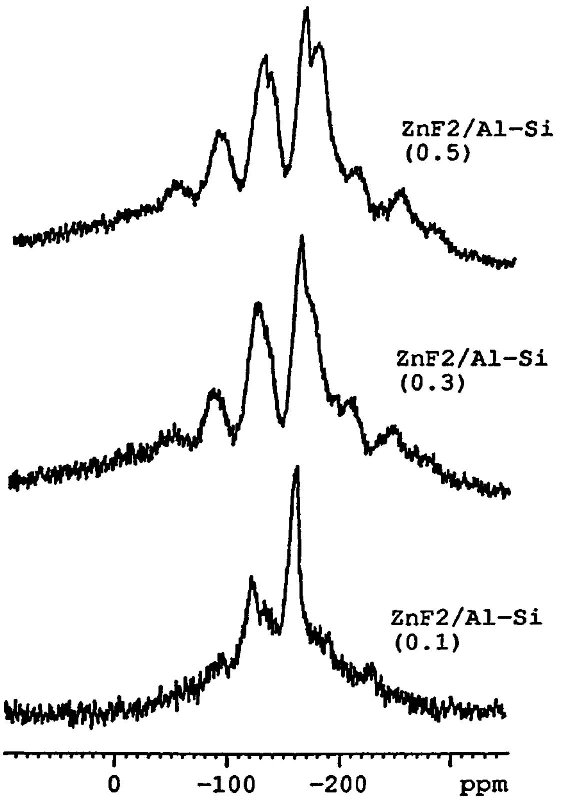

Figure 2. $^{19}$F MAS NMR spectra of the $ZnF_2$/Al–Si catalyst (the amount of $ZnF_2$ is given in parentheses).

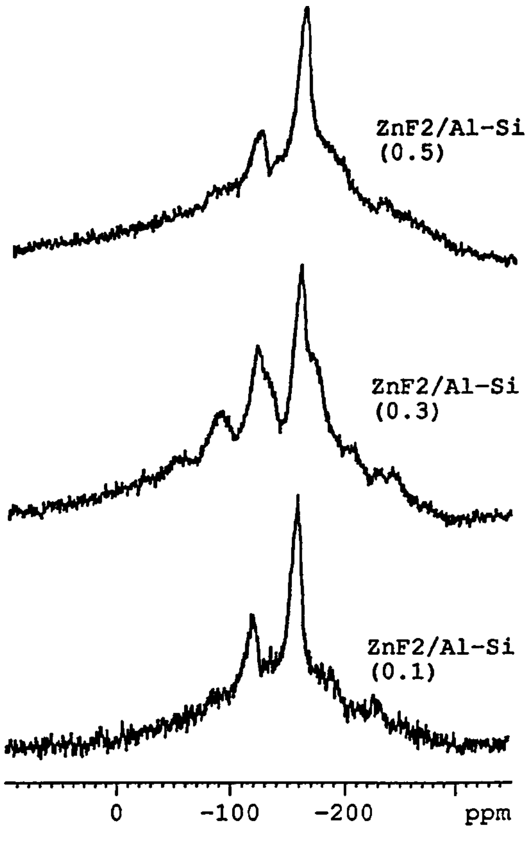

Figure 3. $^{19}$F MAS NMR spectra of the $ZnF_2$/Al–Si (H-acac-modified) catalyst (the amount of $ZnF_2$ is given in parentheses).

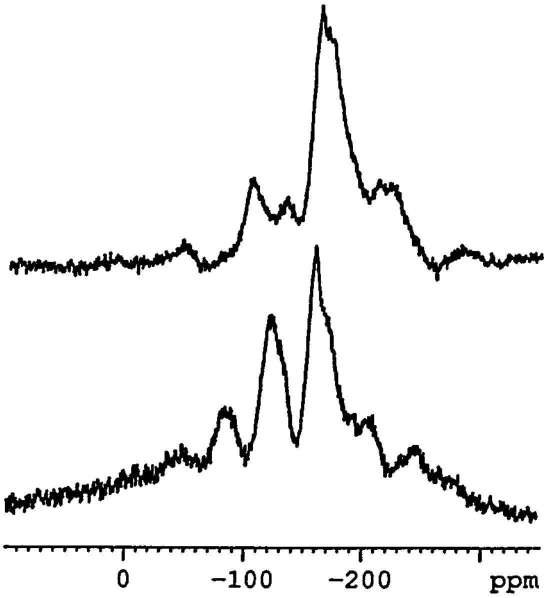

Figure 4. $^{19}F$ MAS NMR spectra of the $ZnF_2$/Al–Si (H-acac-modified) catalyst: (top) spin rate 10 kHz and (bottom) spin rate 15 kHz.

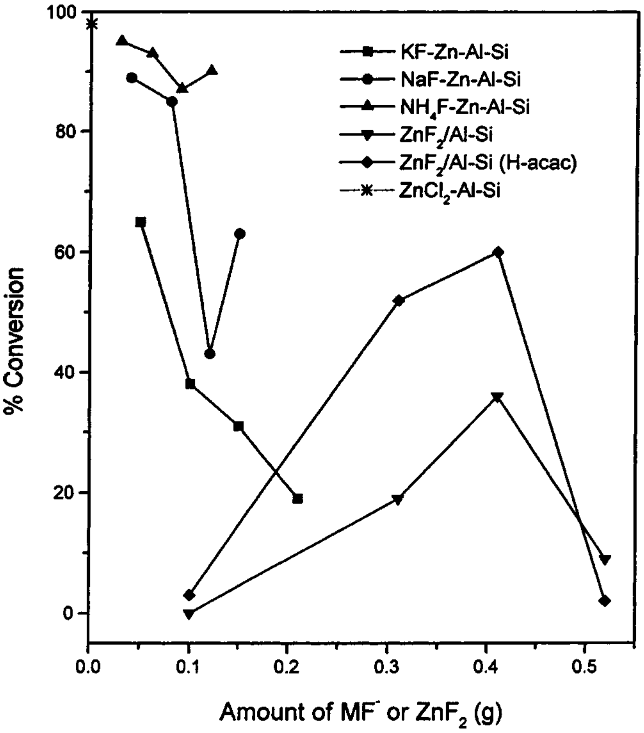

Figure 5. Friedel–Crafts alkylation activities of the $ZnCl_2$ and $ZnF_2$ catalysts.

into the aluminosilicate framework due to the formation of $AlF_4^-$ species. No $^{19}F$ NMR signal was detected in the case of NaF- and $NH_4F$-modified catalysts presumably due to the small amounts of fluoride used.

The Friedel–Crafts alkylation activities of the catalysts are shown in figure 5. The alkylation activities are in the order $ZnCl_2$–Al–Si $>$ $NH_4F$–Zn–Al–Si $>$ NaF–Zn–Al–Si $>$ KF–Zn–Al–Si $>$ $ZnF_2$–Al–Si(H-acac) $>$ $ZnCl_2$–Al–Si. The $ZnCl_2$–Al–Si is more effective than any of the fluoride-modified materials in the alkylation reaction, with the $NH_4F$–Zn–Al–Si series being almost as effective. Among the three fluorinating agents, KF is the least reactive, perhaps due to structural collapse as indicated by $^{19}F$ and $^{27}Al$ NMR. The activity of the 2,4-pentanedione (H-acac)-modified catalyst is higher than that of the corresponding unmodified $ZnF_2$–Al–Si catalyst. Optimum % conversions in both series were obtained with $ZnF_2$ loadings about 0.4 g, but these were significantly lower than those of $ZnCl_2$–Al–Si catalysts. Thus the present investigation shows that $ZnCl_2$ is a better active species for the alkylation reaction in comparison to the $ZnF_2$ precursor. Among the three fluorinating agents studied, $NH_4F$-modified Zn–Al–Si catalysts were found to be more active in comparison to NaF- and KF-modified Zn–Al–Si catalysts.

## 4. Conclusions

$NH_4F$ is an effective additive for improving the catalytic activity of the $ZnCl_2$–Al–Si catalysts in Friedel–Crafts catalysis, however, $ZnF_2$ supported on unmodified and 2,4-pentanedione-modified aluminosilicate is less effective than $ZnCl_2$ in Friedel–Crafts alkylation reaction. In some cases the added fluoride is not detected by $^{19}F$ MAS NMR following calcination, suggesting the removal of $F^-$ as HF.

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