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Effect of the support on the basic and catalytic properties of KF

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Abstract

KF supported by various supports was characterized by DTG-DTA coupled with mass spectral analysis of the gases evolved by the solid, in situ XRD, calorimetry, ^{19}F NMR spectroscopy, and tested in the Michael addition of cyclohexene-2-one with nitroalkanes. After dehydration at low temperatures, from ^{19}F NMR spectroscopy F is in part as KF when the support is α-alumina but only as K_3AlF_6 when the support is γ-alumina. During activation no fluorine is lost. On α-alumina KF is detected by XRD only after calcination at about 723 K and results in part of the decomposition of K_3AlF_6; it disappears with formation of K_2AlF_5 and $KAlO_2$ at higher temperatures. A comparison of the results obtained by XRD and NMR suggests that KF is well dispersed on α-alumina. KF/α-alumina is a strong base, stronger than KF on γ-alumina, and more active for Michael reactions. On KF/α-alumina the Michael condensation of 2-cyclohexen-1-one with nitroalkanes can be achieved in 5 min with an equimolar mixture of reactants. Solvent-free reactions can also be achieved reaching 75% yield in adduct after 8 h, and KF/α-alumina is also active after simple drying at 393 K, avoiding the usual activation at higher temperatures.

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Keywords: Activation of supported KF; Solid base; Thermal analysis; XRD; Basic strength; Michael addition; Solvent-free reactions

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1. Introduction

KF/alumina was introduced by Clark [1] as solid base and has been applied as catalyst to a wide variety of organic syntheses. Several recent articles have reviewed this field [2–4]. Conflicting conclusions have been reported on its base strength: most authors consider it to be weak or moderate, but some note high or even superbasicity. The conditions of activation and the loading seem to be critical to its properties. Supported KF needs, for instance, to be activated at about 650–700 K and the reason for this is not quite clear [4,5]. This is unfortunate since the requirement of activation at high temperatures is considered inconvenient for industrial applications in reactors designed for operation at low temperatures.

The identity of the active phase is also disputed: loadings higher than that required for monolayer coverage are usually needed for high activities. KF was not detected by X-ray diffraction at low loadings, while both KF and K_3AlF_6 were present at higher loadings. K_3AlF_6 pure or supported on alumina showed no catalytic activity for the base-catalyzed self-condensation of benzaldehyde to benzyl benzoate [5]. Furthermore, the catalytic activities of alumina-supported KOH and K_2CO_3 were lower than that of KF/Al_2O_3. These results suggest that the catalytic activity of KF/Al_2O_3 is associated with F^- ions rather than O^{2-} ions, which may be the active sites on KOH or K_2CO_3 supported on alumina. The identification of the active F^- species has been attempted by ^{19}F MAS NMR with controversial results. Several peaks at −123, −132, −157, and −166 ppm have been observed and identified to F^- in water, KF, K_3AlF_6, and AlF_3, respectively [6]. The active site has been related either to the species characterized by a peak at −135 ppm [5], or to the one at −150 ppm [4].

A variety of reactions have been investigated on these catalyst including the Michael [7], Knoevenagel and related

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addition reactions [8], aldol condensations [9,10], hydration of amides, alcoholysis of esters and epoxides [11], and the Darzens reaction [2]. In the Michael reaction, KF/alumina reached complete conversion for the reaction of nitroethane with 3-butene-2-one, in 3 min, using, however, a ratio of nitroethane/butanone = 20 [12,13]. With a ratio reduced to 4 the reaction time increased to 30 min [4]. Such high excess requires a large recycling of the unreacted product and a catalyst working with an equimolar ratio of reactants would be interesting. Another recent preoccupation for the chemical technology of the future is the avoidance of noxious and environmentally unacceptable organic solvents [14]. The aim of this work was then to investigate the effect of the support on the properties of KF in order to understand better its activation and to design a catalyst able to catalyze Michael reactions with a 1:1 ratio of reactants under solvent-free conditions.

2. Experimental

α-Alumina (SPH 512, 10.5 m^2/g) and γ-alumina (SCP 350, 400 m^2/g) from Rhone Poulenc were used as supports. Titanium oxides were supplied by Millenium Inorganic Chemicals. KF was supported onto these supports using impregnation. The precursor salt was $KF \cdot 2H_2O$ from Aldrich. For instance KF1α was supported on α-alumina: 15 g of alumina milled to a fine powder was poured into 150 mL of water containing the desired amount of KF (1 mmol KF/g of support for KF1). Water was evaporated at 323 K and then the solid was dried at 383 K. KFA was supplied by Aldrich, and KF/Al-MCM-41 was prepared by impregnating a solid prepared according to a published procedure and containing 0.15 wt% Al [15]. The characteristics of the supports are reported in Table 1. The different catalysts reported in Table 2 were thus obtained by changing the support and the amount of fluoride. The catalysts were either calcined at 723 K or evacuated at different temperatures in good vacuum just before use. K and F were analyzed in two separate experiments: K was analyzed first at IRC by ICP after dissolution of the solid, and F was determined in a second step by potentiometry using a specific electrode at SCA-Solaize. The F/K ratio of the impregnated solids lower than 1 is attributed to some rehydration of hygroscopic samples before the second analysis and to some heterogeneity induced by impregnation.

Table 1
Characteristics of the supports

Support	Origin	Reference	Surface area (m^2/g)
α-Alumina	Rhône-Poulenc	SPH 512	10.5
γ-Alumina	Rhône-Poulenc	SCP 350	400
Rutile	Millenium	RL11A	10
Anatase	Millenium	DT51	94
Al-MCM-41	home made	–	880

Table 2
Chemical composition and surface areas of the supported fluorides

Sample	K (%)	F (%)	K/F (atom/atom)	Surface area (m^2/g)	CO_2 adsorption ($\mu mol\ g^{-1}$)
KF1α	2.8	1.1	1.2	9.4	14
KF10α	14.4	5.5	1.2	4.8	10.6
KF1γ	4.03	1.25	1.5	234	98.9
KF10γ	14.4	5.2	1.3	35	92
KFA (10 mmol/g)	–	–		14.9	–
KF1-anatase	3.8	1.7	1.1	44	–
KF1-rutile	3.5	1.04	1.6	6	–
KF-Al-MCM-41	1.5	0.7	1	97	–

Two instruments were used for X-ray powder diffraction. For the standard measurements at room temperature under air, the patterns were recorded on a Philips PW1050 goniometer equipped with a diffracted-beam graphite monochromator (Cu-K_α radiation). The in situ patterns were performed on a Siemens D500 goniometer bearing a high-temperature camera [16] using Ni-filtered Cu-K_α radiation. A position-sensitive detector (Raytech) was used in step-scanning mode from 10 to 110° (2θ) (64 channels used, step size of 0.016° (2θ), 1 or 8 s/step). The data were processed with the DiffracPlus software (Bruker-Socabim). The phases were identified using the Powder Diffraction File (PDF) database (JCPDS, International Centre for Diffraction Data).

For calculating phase concentrations by the Rietveld method, diffraction peak profiles were modeled using the DBWS-9411 code [17] for structure refinement with a pseudo-Voigt function that had average crystallite size as a fitting parameter [18].

The isotherm for N_2 adsorption at 77 K was determined on solids activated at 723 K in N_2 or air and then desorbed in situ at 473 K in vacuum. A few samples were characterized by calorimetry using CO_2 adsorption at room temperature with a Tian–Calvet calorimeter on samples activated in vacuum at 673 K. The desorption of CO_2 was also investigated by programmed desorption using a Setaram DTA-DTG apparatus coupled with a mass spectrometer. ^{19}F MAS NMR spectra were recorded at 8.5 kHz on a DSX400 Bruker spectrometer, with a 2.5-mm NMR probe from Bruker. The chemical shifts were referenced relative to external $CFCl_3$.

The Michael additions of nitroalkanes to 2-cylohexen-1-one were investigated at 323 K in batch conditions using a three-neck glass reactor equipped with a condensor. The ratios of reactants 3 and 1 were used, with dimethylformamide (10 mL) as solvent and 0.1 or 0.3 g of catalyst. Decane (0.1 mL) was used as internal standard for the chromatographic analysis. The solvent and the substrates were mixed, then the catalyst freshly activated under vacuum was rapidly introduced (under an inert Ar atmosphere), and the measurement was started. Reactants and products were analyzed by gas chromatography (Perkin-Elmer) using a polar capillary column.

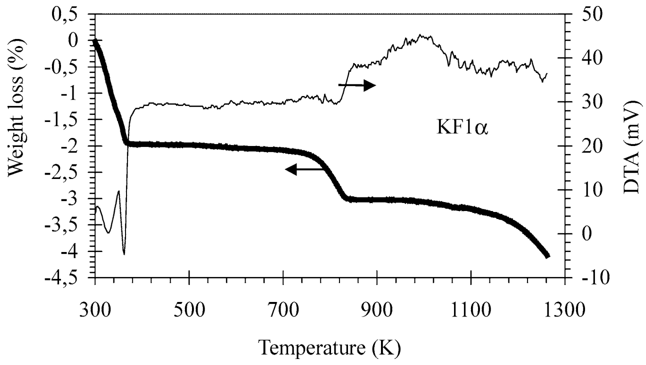


Fig. 1. DTG- DTA trace of KF1α.

3. Results

3.1. Thermal analysis of supported KF

The DTA trace of KF1/α-alumina is reported in Fig. 1 and shows two weight losses: one in the range 400–750 K corresponding to an endothermic event, and the second one to a broad exothermic peak above 800 K. The gases evolved by the solid during thermal analysis were analyzed by mass spectrometry recording the characteristic masses of water, fluorhydric acid, and CO_2 as a function of temperature. The first weight loss is composed of loosely adsorbed water. Above 750 K the solid loses mainly water, but a very small peak of CO_2 (not shown) could be observed at about 813 K. No HF was detected in this analysis on KF1α, so that the broad exotherm is attributed to a solid-state reaction of the fluorides with the support. No HF evolution was detected with KF5α and only a small peak was observed on KF10α, with a concomitant loss of water, suggesting that HF is produced by hydrolysis of the fluoride at about 813 K. With KF/γ-alumina a regular weight loss was observed corresponding to water, with no F evolution.

3.2. XRD analysis

The XRD pattern of α- or γ-alumina-supported samples, as prepared (without calcination), shows the K_3AlF_6 phase. After calcination at 723 K, only the K_3AlF_6 lines are observed on the samples supported by γ-alumina (Fig. 2) whereas on the α-alumina support, the KF phase appears but only for samples with higher loading (Fig. 3). The mixture of the two phases K_3AlF_6 and KF is present in the commercial sample KFA as reported earlier [4]. Weak lines corresponding to carbonated or hydrated phases ($KHCO_3$, $K_2CO_3(H_2O)_{1.5}$, $K(H_2O)OH$) were also seen on the patterns.

In order to avoid the formation of these phases and to determine those existing under conditions close to those of the catalytic reaction, a thorough investigation was performed using in situ measurements in a controlled atmosphere in flowing He from room temperature up to 1000 K. The low loaded sample 1 mmol KF/α-alumina was chosen to investigate the presence of the KF phase after treatment.

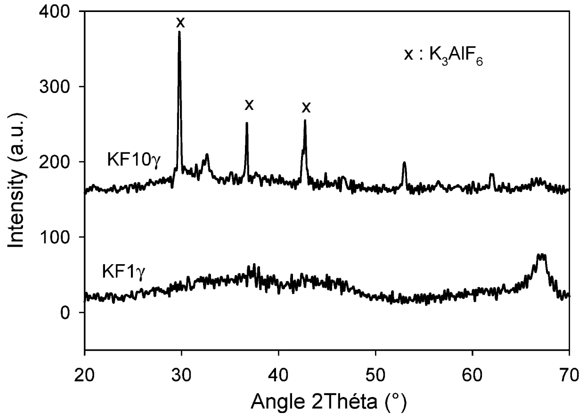


Fig. 2. XRD pattern of γ-alumina supported KF after calcinations at 723 K and transfer in air.

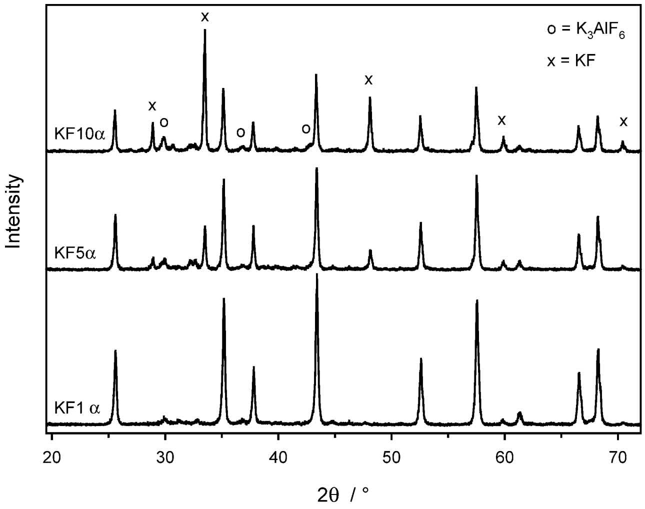


Fig. 3. X-ray patterns recorded in air of KF supported on α-alumina for different loadings after calcination at 723 K. On KF1α, only the alumina phase is detected.

The XRD patterns were continuously recorded during the increase of temperature (0.15 K/min) which corresponds to a 16 K temperature increase during the pattern recording. The most significant patterns are shown in Fig. 4. The XRD patterns of KF1α as prepared at room temperature contain only weak reflections of K_3AlF_6 in addition to those of α-alumina and $KHCO_3$. The carbonate is decomposed above 400 K, the temperature at which K_3AlF_6 begins to sinter. Around 723 K, the diffraction lines of K_3AlF_6 decrease in intensity and the characteristic reflections of KF appear, showing its presence and crystallization on the sample containing 1 mmol KF/α-alumina. Beyond 773 K, K_3AlF_6 disappears, and KF stabilizes reaching a maximum and then starts to decrease and disappears around 900 K. At these temperatures, new phases K_2AlF_5 (PDF 46-1013) and $KAlO_2$ (PDF 2-897 and 45-849) are formed.

The phases present at 723 and 773 K were specially studied. Two batches of as-prepared KF1α were heated up to

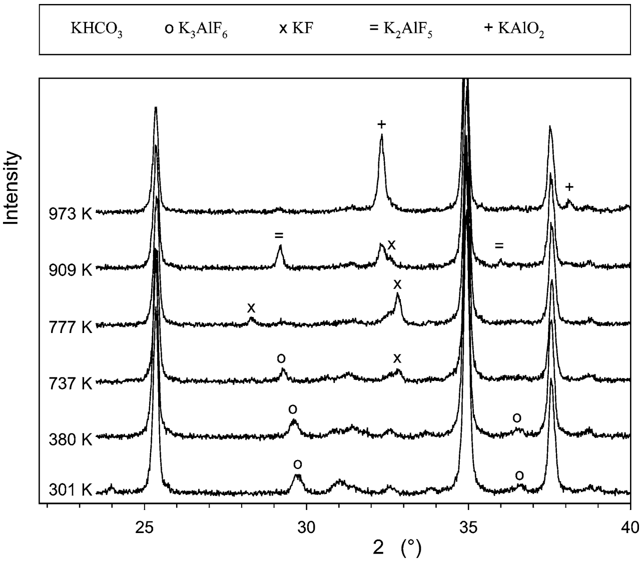


Fig. 4. Evolution of the X-ray pattern of the KF1α catalyst as a function of temperature. The KF phase is clearly present at 777 K.

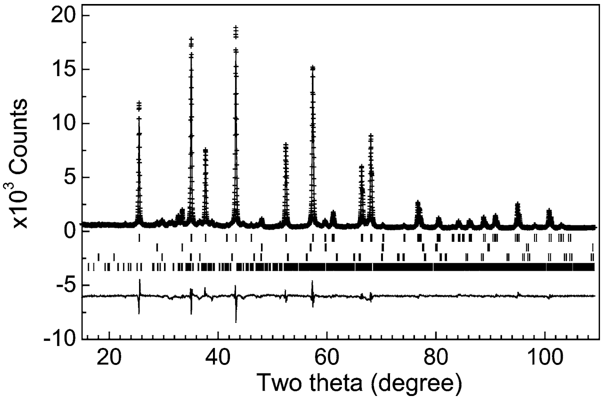


Fig. 5. Plot for the Rietveld refinement of a X-ray pattern measured under a controlled atmosphere on KF1α cooled to room temperature after activation to show the presence of KF. Marks from up to down correspond to reflections of αAl_2O_3, KF, K_3AlF_6, and $KALO_2$ in this order. Rwp = 0.10 and Rf = 0.9 for KF.

Table 3
Phase concentrations (wt%) estimated by Rietveld refinement of the in situ XRD pattern (recorded at room temperature) of the sample KF1α

	α-Al_2O_3	KF	$K_3AlF_6 + KAlO_2$
Calcined to 723 K	96 (1)	1.9 (3)	2.3 (2)
Calcined to 773 K	95 (1)	2.3 (1)	2.4 (2)

these temperatures and cooled down to room temperature always under controlled atmosphere. High-quality patterns were recorded at these temperatures and at room temperature to estimate the phase concentration by Rietveld analysis. The patterns obtained at room temperature showed that the KF phase observed between 723 and 900 K was retained, so that it is believed that the phases observed by this in situ XRD investigation are those present in the working catalyst. It is well known that KF is hygroscopic, so that when the sample is put to air, it is rehydrated, probably carbonated, and the phase KF disappears.

For phase refining, α-alumina was simulated by a crystalline structure of rhombohedral symmetry with spatial group *R-3c* [19], K_3AlF_6 by a cubic structure with spatial group *Fm3m* [20], and KF also by a cubic structure with spatial group *Fm3m* [21]. An orthorhombic symmetry with spatial group *Pbca* was utilized for simulating the phase $KAlO_2$ [22]. An example of the refinements is shown in Fig. 5. The results of the Rietveld refinement are reported in Table 3. K_2AlF_5 formed above 773 K has been reported in the phase diagram KF-AlF_3 [23] in the same temperature range and could not be quantified precisely. Standard deviations, given in parentheses, correspond to the variation of the last figures of the corresponding number. Since they corresponded to refined parameters, they are not estimated of the analysis as a whole, but only of the minimum probable errors based on the parameters normal distribution [24].

3.3. Infrared analysis of the solid

It has been proposed [25] that KF could simply introduce hydroxyls at the surface of alumina, and this hypothesis was investigated by infrared spectrometry on samples first calcined at 473 K and then evacuated at the same temperature (Fig. 6). KF10α has practically no hydroxyls, whereas KF10γ has a strong OH band at about 3500 cm^{-1}, even after evacuation at 573 K. Therefore hydroxyls can be the active sites when KF is supported on γ-alumina but not on α-alumina.

3.4. Surface areas of supported KF

The changes of surface area of the materials are reported in Tables 1 and 2, and also support the occurrence of a modification of the support either by the basic solution of KF or by a solid-state reaction. The addition of 10 mmol/g of KF to α-alumina induces a decrease of the area from 9 to 5 m^2/g. The magnitude is larger when γ-alumina is used as support with a 10-fold decrease. This is consistent with a reaction between the fluoride and the γ-alumina consuming KF. These simple characterizations are evidence that fluorides interact strongly with γ-alumina which has an acid character and much less with α-alumina which is neutral.

3.5. Basicity of the solid

The calorimetric results determined on samples evacuated at 673 K are reported in Fig. 7 in terms of differential heats of adsorption as a function of the surface concentration of CO_2 in order to take into account the different surface areas of the samples. A larger heat of adsorption and a larger number of basic sites are noted on the sample KF1α, compared to KF1γ. At 10 mmol/g loading the difference is smaller. About 0.1 mmol/g of basic sites is measured by adsorption of CO_2 on KF10α. This number of basic sites

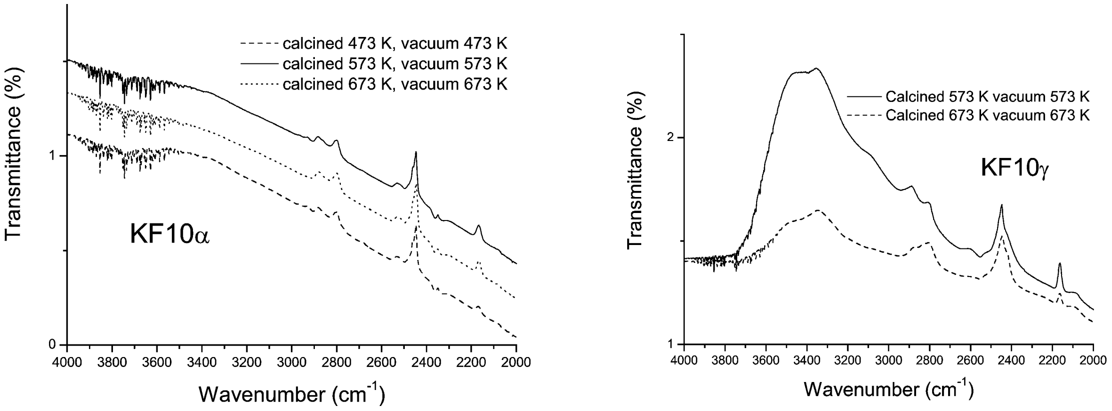


Fig. 6. Infrared spectra of supported KF after calcination and vacuum treatments at different temperatures.

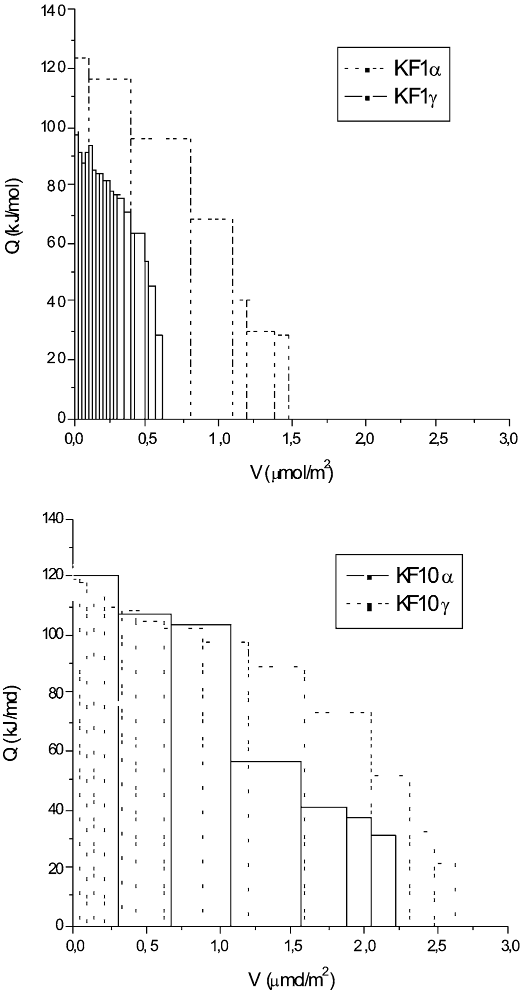


Fig. 7. Enthalpies of CO_2 adsorption on KF supported by α- or γ-alumina.

represents only 1% of the original F atoms, suggesting that the basic sites have a very specific environment.

3.6. ^{19}F NMR investigation

The nature of F species was investigated by MAS NMR: the spectra obtained with KF1α and KF5α stored in air are reported in Fig. 8. These spectra show three different species with different relaxation times T1, and different intensities: a narrow line at −118 to −121 ppm, attributed to free liquid-like F^- anions, which is indeed the main line in KF5α sample, a line at −158 ppm attributed to K_3AlF_6 observed on both samples, with higher intensity at low KF content, and a line at −133 ppm attributed to KF, very weak for KF1α (spectrum b), and more intense for KF5α (spectrum a). After vacuum treatment at 623 K and transfer of KF1α under argon (Fig. 8c) the line at −118 ppm disappears and three lines are visible: the −158 ppm signal due to K_3AlF_6, and two weak lines at −168 and −174 ppm. The signal at −168 ppm has been earlier assigned to F in AlF_3. The species at −174 ppm is observed on the KF1α sample only and not on the KF10α sample after evacuation at 623 or 923 K. Since the size of the crystals of KF increases with the loading, as seen from the evolution of the XRD lines of Fig. 2, the signal at −174 ppm, indicative of a F bearing a higher negative charge, could be tentatively assigned to F linked to defects of the small crystals of KF.

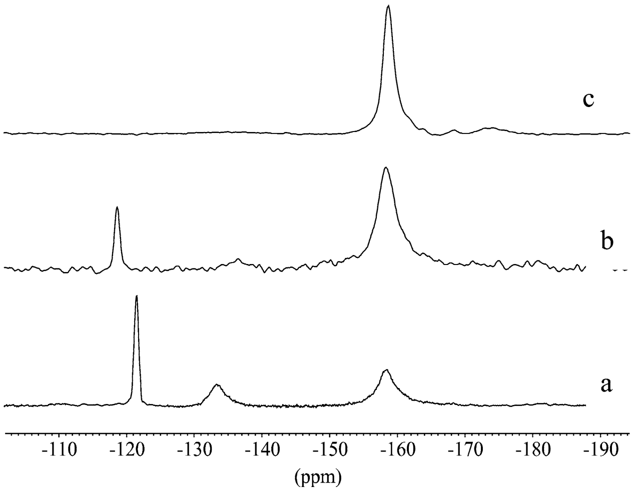


Fig. 8. F NMR spectra of KF5α and KF1α after storage at room temperature (a and b) or evacuation at 623 K (c).

Fig. 9 reports the spectra of KF10α treated at 623 or 923 K. It appears clearly that the line at −134 to −136 ppm

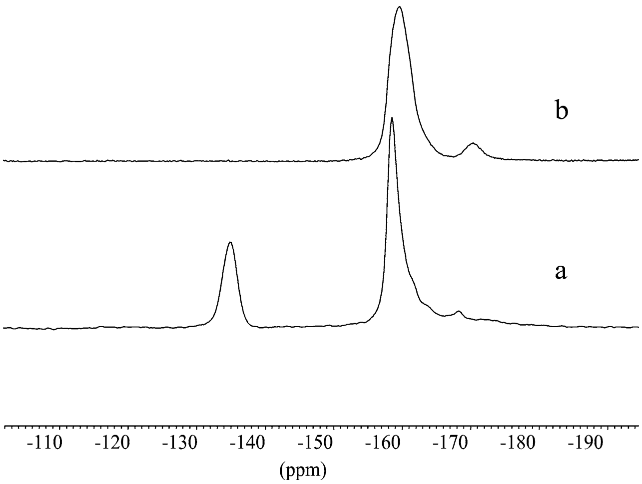


Fig. 9. F NMR spectra of KF10α after dehydration at (a) 623 K or (b) 923 K.

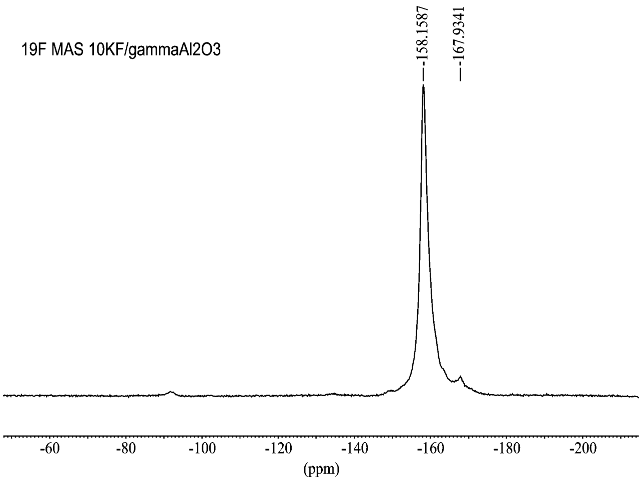
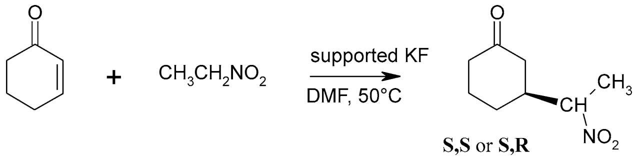


Fig. 10. ^{19}F MAS NMR spectrum of KF10γ after drying overnight at 393 K.



Scheme 1. Michael reaction of nitroethane and 2-cylohexen-1-one.

related to KF is strong on this sample after dehydration at 623 K and then disappears at 923 K. At this high temperature the sharp peak assigned to F in K_3AlF_6 decreases in intensity and is broadened. This broad peak then contains several components and can account for the observation by XRD of different fluorinated phases K_3AlF_6 and K_2AlF_5.

The spectrum of KF10γ after drying at oven temperature is reported in Fig. 10. This solid exhibits a strong line at -158 ppm due to K_3AlF_6 and a weak line at -118 ppm of liquid-like F^- anions. In that case nearly all KF has reacted with the support.

3.7. *Catalytic properties*

The Michael condensation of 2-cylohexen-1-one and nitroethane (Scheme 1) yields two isomers which can be separated by gas chromatography. The catalytic properties are reported in Table 4. The reaction is limited to Michael addition, and reaches high conversions, however, after quite different times. KF supported on α-alumina is more active with both nitro compounds. The difference in activity is small for a loading of 10 mmol/g but reaches a factor of 6 at low loading. It is interesting to note that high conversion can also be reached with a catalyst just dried at oven temperature. This property is specific to the sample supported by α-alumina and is not reproduced on γ-alumina. The kinetics of the reaction has not been investigated in detail but it is clear that the effect of the ratio nitro compound/ketone is very different when changing the support: decreasing this ratio from 3 to 1 the rate is maintained at the same level with KF1α. With KF1γ the rate with a ratio of 3 is low and the ratio was not decreased further.

Different supports, including acid and basic forms of titania and one Al-MCM-41, are compared in Fig. 11. Rutile which has basic properties is a good support, but anatase and Al-MCM-41 are not suited as supports. The aqueous solution of KF used for impregnation is strongly basic and attacks both solids as evident by the decrease of surface after impregnation.

Table 4
Catalytic activities of supported fluorides for Michael condensations of 2-cyclohexen-1-one with nitromethane (NM) or nitroethane (NE)

Sample	Nitroalkane	Ratio nitro/ketone	Treatment temperature (K)	Final conversion (%)	Time (min)	Initial rate (10^{-3} mol min^{-1} g^{-1})
KF1α[a]	NM	3	623	95	180	0.73
KF10α[a]	NM	3	623	99	240	1.21
KF10γ[a]	NM	3	673	98	220	0.78
KF1α[a]	NE	3	623	97	30	1.2
KF1γ[a]	NE	3	623	71	375	0.2
KF1α[a]	NE	1	623	85	300	1.4
KF1α[b]	NE	1	Not activated	75	120	1.5
KF1γ[b]	NE	1	Not activated	39	480	0.4

Pretreatments are in vacuum at the specified temperature, weight of catalyst: [a]0.3 g, [b] 0.1 g.

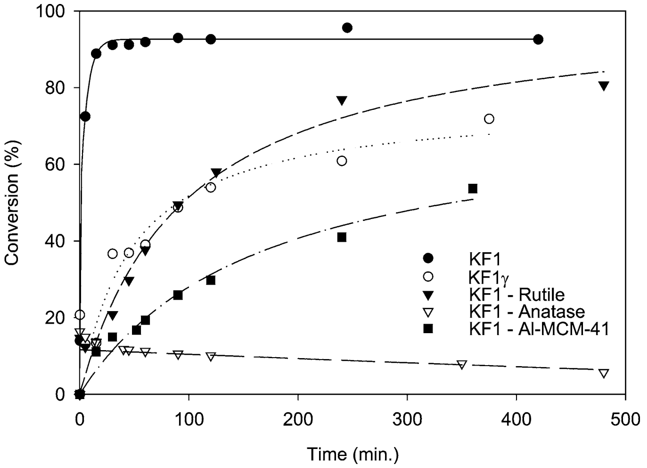


Fig. 11. Catalytic activities of KF-supported catalysts at room temperature for the Michael addition of 2-cyclohexen-1-one on nitroethane starting with an equimolar ratio of reactants.

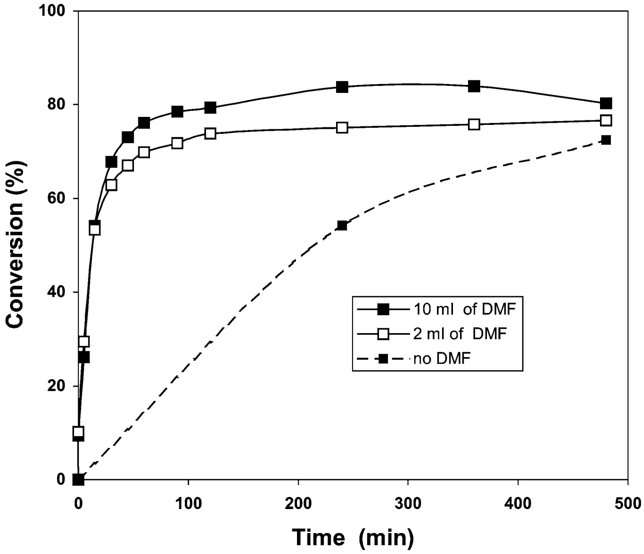


Fig. 12. Effect of the amount of solvent on the conversion of cyclohexenone (2.5 mmol) and nitroethane (2.5 mmol) catalyzed by KF1α.

4. Discussion

The support effect is clearly evident both on catalytic properties and on the basic strength measured by the adsorption of CO_2. It can be first remarked that whereas KF/γ-alumina exhibits a strong OH infrared band, KF/α-alumina shows no OH band (Fig. 6); therefore if both OH and F^- can be considered as active sites on KF/γ-alumina, there exists only one possible association of fluorine on KF/α-alumina. Moreover the low activity (Table 4) of KF10γ dehydrated at oven temperature and consisting mainly in K_3AlF_6 suggests that this phase is not active, as suggested earlier by Handa et al. [5].

It appears clearly that the intermediate phases observed on the solid are completely different when the support is changed. On KF/α-alumina stored at room temperature XRD is unable to detect KF whatever the loading. However KF is detected in small concentrations by NMR by the peak at −133–136 ppm at 1 mmol/g, and more clearly at 5 and 10 mmol/g, and therefore exists as a well-dispersed phase. It must be considered that the species of liquid F is also potentially a source of KF upon dehydration. After treatment at about 723 K, KF is detected by XRD even at a low loading of 1 mmol/g, with a low concentration of about 2 wt%. Activation above 723 K results in the progressive disappearance of KF with the formation of other phases. The evolution of the XRD patterns of Fig. 4 shows the growth of KF crystals. They can be formed in part by decomposition of K_3AlF_6 observed simultaneously, and also probably by sintering of a preexisting dispersed/hydrated KF phase.

A quite different situation is found in the case of KF/γ-alumina in which both XRD and NMR detect only K_3AlF_6 as a fluorine-containing phase. Many authors [4–6] have pointed out that KF/γ-alumina shows a significant activity only after activation at higher temperatures. The decomposition of K_3AlF_6 with formation of KF occurs in the temperature range of activation, about 723 K, and accounts for the promotion of high basicity on KF10γ. The maximum of activity as a function of temperature can also be attributed to the consecutive disappearance of KF with formation of $KAlO_2$ (the corresponding loss of fluorine has been detected above 800 K by mass spectrometry). On both supports strong basicity appears when KF is formed and this is an argument for proposing the fluoride as the active phase. The difference between the two supports is that on α-alumina, KF can be formed at low temperatures by simple dehydration, i.e., reaction of the liquid-like F^- species with adsorbed K, whereas on our γ-alumina this fluorine species is lacking and KF results mainly from the decomposition of K_3AlF_6 at higher temperatures.

The use of different supports suggests that neutral or basic supports are preferred, since acid supports react with the basic solution of KF: this is true for γ-alumina but can be extended to titania and Al-MCM-41. KF/γ-alumina gives good yields for the Michael addition of cyclohexenone on nitroalkanes only with high nitroalkane/olefin ratios and high KF content, but is much less active at low KF content or with the stoichiometric mixture. KF/α-alumina is much less sensitive to the ratio nitroalkane/olefin and reaches high conversions with the equimolar mixture of reactants. An attempt was made to decrease the amount of solvent, with the same equimolar mixture: a more concentrated solution (2 mL of solvent) does not change the results, but under solvent-free conditions at 323 K, a lower rate is observed and the yield reaches 75% in adduct in about 8 h (Fig. 12). This result must be optimized but illustrates the possibility of obtaining relatively high yields in the absence of solvent. The longer reaction times when the nitroalkane/olefin ratio or the amount of solvent decreases suggests an inhibition of the reaction by the olefinic ketone.

The reaction rate is controlled by the basic strength and is not directly related to the total number of basic sites reported in Table 2. Fig. 7 shows a heterogeneity of the surface with a large variation of the enthalpy of adsorption as a function of coverage: in this case, it is expected that the active sites are related to the stronger bases. KF1γ, with the lower activity, also shows the lower basic strength corresponding to an enthalpy of adsorption of CO_2 of about 90 kJ/mol. It can then be supposed that this basic strength is close to the minimum required to initiate the reaction by formation of the intermediate carbanion. It is interesting to remark that KF1α contains about 2 wt% KF (Table 3); therefore about 40% of the original KF loading remains as KF on this support. As remarked above, the total number of basic sites measured by adsorption of CO_2 represents at most 1% of the F atoms on KF10α or KF1α. If we consider that only the sites which adsorb CO_2 with an enthalpy of adsorption > 90 kJ/mol are active, we conclude that less than 0.5% of the F atoms are active sites. This proportion is quite consistent with the idea that the active sites are F species of low coordination linked to defects.

A very interesting point is the high activity of KF/α–alumina just dried at 393 K, in which KF must be well dispersed. The thermal analysis of Fig. 1 shows that oven temperature is enough to dehydrate the solid, and the high activity then observed suggests that this catalyst is less sensitive to the atmosphere and therefore recyclable. Oven temperature is clearly not enough to induce a decarbonation of the catalyst and its high activity must be assigned to fluoride anions.

In conclusion, the basicity of supported KF can be significantly increased by a proper choice of support. This higher basicity is probably due to the dispersion of KF in small crystals, which can be formed by two different paths on aluminas: dehydration of hydrated KF or decomposition of K_3AlF_6. In the second case strong basic properties and activity are observed only after activation at about 700 K. KF on α-alumina gives a more basic solid which is a much better catalyst for Michael condensation performed with an equimolar mixture of reactants avoiding recycling, and even under solvent-free conditions. Another important property from a practical point of view is the possibility of bypassing the activation procedure which can be reduced to drying at oven temperature.

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