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KF on γ-alumina: An efficient catalyst for the aldol condensation to pseudoionones

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ABSTRACT

KF/γ-alumina is an effective catalyst for the aldol condensation of citral with acetone. Even at a relatively low acetone/citral ratio of 1–10, the selectivity to pseudoionones was high, ranging between 82% and 97%. X-ray diffraction shows the presence of KF and K_3AlF_6 crystallographic phases on the supported catalyst. At KF loadings of 3–6.75 mmol g^{-1}, a pretreatment of the catalyst by heating to 450 °C was necessary to obtain an active catalyst. However, samples with KF loadings of 8.5 mmol g^{-1} and higher were active even without pretreatment, facilitating handling and use of the catalysts. The development of (1 1 1) planes revealed by *in situ* XRD during the thermal activation process correlates with the activity for aldol condensation.

1. Introduction

The aldol condensation of citral with acetone gives pseudoionones which are important as precursors for vitamin A and fragrances (Scheme 1). Industrially, this reaction is catalyzed by sodium hydroxide with typical pseudoionone yields of 60–80% [1]. The yield is reduced by various side reactions arising from the self-condensation of acetone and of citral and by secondary reactions of the pseudoionones, so that further purification becomes necessary. The substitution of homogeneous bases by solid catalysts is highly desirable as the use of aqueous alkali leads to large amounts of wastes and fast corrosion of the reactor. Solid base catalysts such as alkaline earth metal oxides, modified alumina, clays and hydrotalcites have been studied for aldol condensation reactions [2–4]. Climent et al. [4] reported good activity over pure MgO for the liquid phase condensation at 60 °C, but the selectivity to pseudoionones was only about 68% at an acetone/citral ratio of 2.7. Calcined hydrotalcites containing aluminium and magnesium were more active and showed a higher selectivity than MgO. By raising the acetone/citral ratio from 2.7 to 19, the selectivity to pseudoionones could be increased from 79% to 99%. The controlled addition of water to the calcined hydrotalcite further improved the rate of reaction. Magnesium oxide doped with 0.5 wt% Li formed an active catalyst which yielded 93% pseudoionones at 80 °C; however, a rather high acetone:citral ratio of 49 was used [3]. The presence of lithium has been correlated with an increase in the density of strongly basic sites in the form of low-coordination oxygen anions. These sites are proposed to be responsible for the abstraction of an α-proton from the acetone molecule, forming a carbanion intermediate in the rate-determining step.

Alumina-supported KF has been extensively used as a base catalyst for many organic reactions such as aldol and Michael condensations, carbon–carbon and carbon–oxygen bond formation, and elimination reactions [5–8]. It is easily prepared and is also available commercially. Despite its wide applications, the nature of the active sites on the catalyst is still unknown. The interaction of alumina with KF leads to the formation of K_3AlF_6 and KOH according to the following equation:

$$12KF + Al_2O_3 + 3H_2O \rightarrow 2K_3AlF_6 + 6KOH$$

Using ^{19}F MAS NMR, Kabashima et al. [9] identified several F-containing species including KF, KF associated with water, K_3AlF_6 and AlF_3. The dominant species was K_3AlF_6 but its concentration did not correlate with the catalytic activity for the Tishchenko reaction of pivaldehyde or the double bond isomerization of 1-pentene. Instead, the activities were linked to a fluoride-containing species with a peak at −150 ppm. The hydroxide ion was ruled out as the active species because the activity of KOH/alumina for the Tishchenko reaction was lower than that of KF/alumina. Clacens et al. [10] found that KF supported on α-alumina is a stronger base than KF/γ-alumina. Despite the much lower surface areas of the α-alumina supported KF (4.8–9.4 m^2/g) as compared to the γ-alumina samples, the samples were more active for Michael reactions. Activation of the catalysts could be carried out by simply drying at oven temperature instead of high temperature calcination. Using XRD and NMR results, the authors proposed that on α-alumina, KF can be formed at low temperatures (120 °C) by reaction of a liquid-like F^--species which then reacts with adsorbed K^+. However, on

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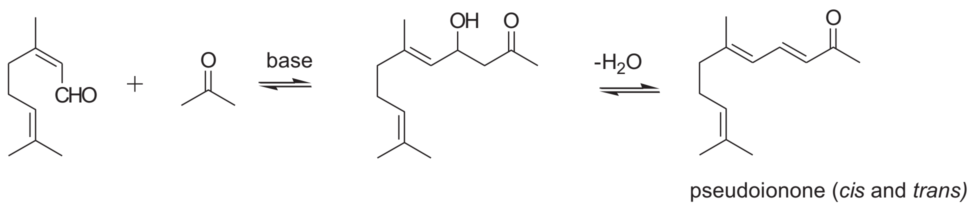

Scheme 1. Cross-aldol condensation between citral and acetone to pseudoionones.

γ-alumina, KF reacts completely with the support forming K_3AlF_6 and activation at 450 °C is necessary to decompose K_3AlF_6 to the active KF phase.

In this work, we investigated the use of KF/γ-alumina in the aldol condensation of citral with acetone. *In situ* powder X-ray diffractometry was used to follow any phase changes on heating in *vacuo*.

2. Experimental

2.1. Preparation of supported KF catalyst

Supported KF on γ-alumina with loadings of 3–15 mmol KF/g was prepared by the wet impregnation method. γ-Alumina was added to a solution of KF in water and the suspension was stirred at room temperature for 2 h. Water was evaporated at 60 °C under reduced pressure using a rotary evaporator. Teflon apparatus was used throughout the preparation as KF attacks laboratory glass. The catalyst was dried at 100 °C overnight, and pretreated in vacuum at the desired temperature before testing for any catalytic activity. A commercial sample KF/alumina (Fluka, 5.5 mmol KF/g) was also tested for comparison. Nitrogen adsorption–desorption isotherms were measured using a Micromeritics Tristar 3000. X-ray diffraction measurements were carried out using a Siemens D5005 as well as a Bruker D8 equipped with a high temperature stage. In both instruments, a Cu anode was used. *In situ* X-ray patterns were recorded as the sample was heated from 100 °C to 700 °C under evacuation.

2.2. Catalytic measurements

Commercial citral consisting of a mixture of *cis* and *trans* isomers (35:65) was used without purification. Typically, citral (7.6 mmol), acetone (45 mmol) and nitrobenzene (10 μl) as internal standard were added to a two-necked round-bottomed flask equipped with a condenser system. The solution was heated under stirring to 45 °C in nitrogen before addition of the catalyst (0.25 g). Aliquots were taken at regular time intervals and analyzed by gas chromatography using a FID detector and HP-5 column. The products were identified by GC–MS (Shimadzu). The effective carbon number was calculated for the individual compounds and taken into account for calculating conversion and selectivity. The effect of varying acetone/citral was carried out by keeping the amount of citral at 7.6 mmol and varying the amount of acetone.

3. Results and discussion

3.1. Textural properties

γ-Alumina, has a surface area of 111 $m^2 g^{-1}$ (Table 1). Increasing the KF loading from 3 to 15 mmol g^{-1} alumina resulted in lower surface areas. The pore size distribution curve for γ-alumina falls in the range of 2.7–10 nm (Fig. 1). After loading with KF, there was a shift to bigger pores along with a decreased pore volume. This shows that the smaller pores become blocked upon impregnation.

Table 1
Textural properties of alumina-supported KF.

Sample (mmol KF g^{-1})	Surface area (m^2/g)	Pore volume (cm^3/g)
γ-Alumina[a]	111	0.21
3 KF/γ-alumina	67.1	0.14
6.75 KF/γ-alumina	45.7	0.11
8.5 KF/γ-alumina	33.2	0.09
8.5 KF/γ-alumina[a]	27.9	0.08
10 KF/γ-alumina	28.8	0.08
10 KF/γ-alumina[a]	26.6	0.07
12.5 KF/γ-alumina[a]	26.4	0.07
15 KF/γ-alumina[a]	19.8	0.05
Fluka[a]	16.1	0.06

[a] Degassed at 300 °C under N_2 flow for 4 h; rest degassed at 100 °C.

The surface area also decreased slightly when the sample was pretreated to higher temperatures. For example, the surface area of 8.5 mmol g^{-1} KF/γ-alumina, was 33.2 $m^2 g^{-1}$ when the sample was degassed at 100 °C but decreased to 26.6 $m^2 g^{-1}$ after degassing at 300 °C. It appears that degassing at 300 °C can already cause some sintering of the material.

3.2. Aldol condensation of citral and acetone

A commercial KF/γ-alumina (Fluka, 5.5 mmol g^{-1}) was initially used as catalyst for the formation of pseudoionones. The catalyst was pretreated in vacuum at 450 °C. The influence of the reaction temperature was investigated using an acetone/citral molar ratio of 2.5 (Table 2). At 25 °C, a conversion of 77% with a selectivity of 93% to pseudoionones was obtained after 6 h. With increase of the reaction temperature to 50 °C, the selectivity to pseudoionones decreased slightly to 89%. Other products were due to the self-condensation of citral and of acetone. Despite the excess acetone used, mesityl oxide constituted only 0.8% of the reaction mixture. From the temperature dependence of the reaction rate, an apparent activation energy of 32 kJ mol^{-1} was determined. This is comparable to the 25 kJ mol^{-1} reported for hydrotalcites, where the low

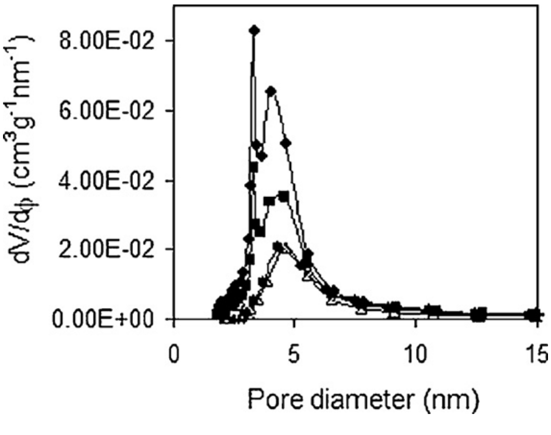

Fig. 1. Pore size distribution of (◆) γ-alumina (■) 3 mmol g^{-1} (●) 8.5 mmol g^{-1} and (△) 10 mmol g^{-1} KF/γ-alumina.

Table 2
Influence of reaction temperature on the formation of pseudoionones.

Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)	Initial rate[a] (mmol g^{-1} min^{-1})
25	6	77	93	0.41
30	6	83	93	0.40
40	6	90	91	0.58
50	6	94	89	1.26

Reaction conditions: citral (7.6 mmol), acetone (19.1 mmol), Fluka–KF/alumina (0.22 g).

[a] With respect to citral consumed.

value was attributed to strong adsorption of the reagents on the catalyst surface [11].

To assess the influence of the reagent concentrations on the selectivity to pseudoionones, the acetone/citral ratio was varied from 1 to 10 at a reaction temperature of 40 °C (Table 3). The rate of reaction was lowest for an acetone/citral ratio of 1. After 6 h, the conversion was 62% and the selectivity to pseudoionone was 82%. At this high citral concentration, self-condensation of citral is significant. The reaction was faster when the acetone/citral ratio was increased. Using a ratio of 6–10, the selectivity to pseudoionone was 95–97% and the self-condensation of citral was greatly reduced. These results show that KF/γ-alumina is an effective catalyst for the aldol condensation of citral and acetone. The yield of pseudoionones is high even when using a moderate excess of acetone. In comparison, Roelofs et al. [12,13] required an extremely high acetone/citral mole ratio close to 250 to obtain a pseudoionone selectivity of 90% over activated hydrotalcite catalysts. In this case, the reaction was conducted at 0 °C using 1 wt% of citral. After 24 h, the citral conversion reached 65%. However, no reaction was observed when the acetone/citral ratio was reduced to 20. The authors postulated that the inhibition of the reaction could be due to strong adsorption of citral on the catalyst surface. This trend is also observed in our data: the initial rate increases 10-fold when the concentration of citral is reduced by a factor of 3.3 (Table 3). The use of KF/γ-alumina for aldol condensation of methylpseudoionones from citral and butanone has been reported previously [14]. However, the selectivity was only 50% as oligomers of citral were formed. It was postulated that despite excess butanone, citral could not be effectively desorbed from the surface of the catalyst. In this study, the high selectivity to pseudoionones obtained may be attributed to the higher polarity of acetone as compared to butanone. Hence, the surface concentration of citral is kept low, thus minimizing self-condensation of citral.

At KF loadings of 3–5 mmol g^{-1} KF, the conversion was <10% even after pretreatment at 450 °C in vacuum. The activity for cross-aldol condensation of citral and acetone increased with KF loading. The conversion was 53% after 1 h over a 6.75 mmol g^{-1} KF/γ-alumina sample that had dried at 100 °C (Table 4). Pretreatment at a higher temperature, 450 °C, produced a more active catalyst that was able to convert 80% citral after the same time. At KF loadings of 8.5 and 10 mmol g^{-1}, as-synthesized samples showed already comparable activity to those pretreated to 450 °C. The selectivity to pseudoionones was ~94–95%, with little difference between untreated and pretreated catalysts. In contrast, hydrotalcites need to be carefully rehydrated under CO$_2$-free conditions or to have an optimum amount of water added to the reaction medium for better activity [11,13]. Climent et al. [4] reported that the initial rate of pseudoionone formation over Al–Mg hydrotalcite was 0.87–0.92 mmol g^{-1} min^{-1} for acetone/citral ratio of 5–20. These values are lower than those found for KF/γ-alumina in this work (Table 3).

Table 3
Influence of acetone/citral ratio on the aldol condensation of citral and acetone.

Acetone/citral ratio	Time (h)	Conversion (%)	Selectivity (%)	Initial rate (mmol g^{-1} min^{-1})
1	6	62	82	0.20
1.5	6	85	87	0.48
2	6	87	89	0.52
3	6	88	90	0.61
4.3	6	98	91	1.27
6	2	98	95	1.81
10	2	99	97	2.00

Reaction conditions: citral (7.6 mmol), acetone (7.6–76 mmol), Fluka–KF/alumina (0.22 g), 40 °C.

Table 4
Effect of pretreatment on activity for pseudoionone formation.

KF loading (mmol g^{-1})	Time (h)	Conversion (%)	Selectivity (%)	Initial rate (mmol g^{-1} min^{-1})
6.75[a]	1	53	94	0.36
6.75[b]	1	80	94	0.53
8.5[a]	0.5	81	94	1.70
8.5[b]	0.5	83	95	1.75
10[a]	0.5	82	93	2.2
10[b]	0.5	85	94	2.1

Reaction conditions: citral 7.6 mmol, acetone (45 mmol), catalyst (0.25 g), 45 °C.

[a] Dried at 100 °C for 4 h.

[b] Pretreatment at 450 °C under vacuum for 2 h.

The leaching of KF was investigated by hot filtration of a 8.5 mmol g^{-1} KF/γ-alumina catalyst from the reaction mixture after 10 min. No further conversion was observed in the catalyst-free reaction mixture. Furthermore, the catalyst could be reused for subsequent batch reactions after recalcining at 450 °C.

The dependence of the catalytic activity on the pretreatment conditions has been reported previously. Hattori and co-workers [7,9] observed that the catalytic activity of KF/alumina for the isomerisation of pent-1-ene, Michael addition of nitromethane to buten-2-one and Tischenko reaction of pivalaldehyde reached a maximum when the catalyst had been pretreated at 450 °C. The authors proposed that the increase in activity with pretreatment temperature up to 450 °C is caused by the removal of adsorbates such as water and carbon dioxide which initially cover the basic sites, while the decrease after heating above 450 °C may be due to structural changes in the surface leading to elimination of basic sites. Some hints towards the active species came from ^{19}F NMR, where a signal at about −150 ppm was observed whose inten-

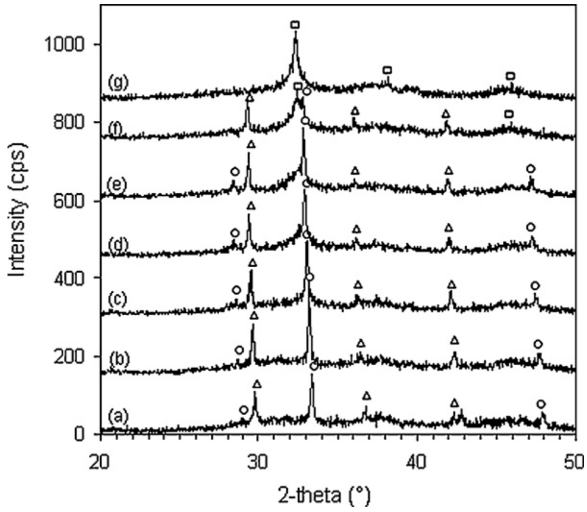

Fig. 2. X-ray diffractograms of 6.75 mmol g^{-1} KF/γ-alumina at (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 450 °C, (f) 500 °C and (g) 600 °C. (○) KF (△) K_3AlF_6 (□) Al_2O_3.

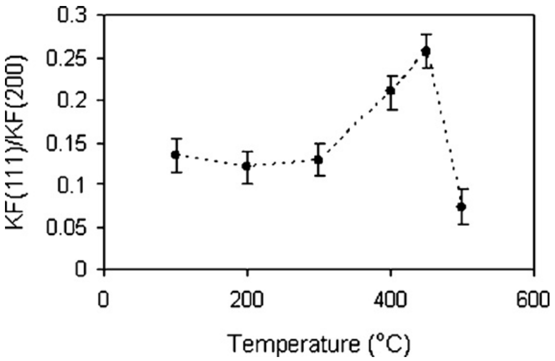

Fig. 3. Ratio of KF(1 1 1)/KF(2 0 0) peak intensity as a function of temperature.

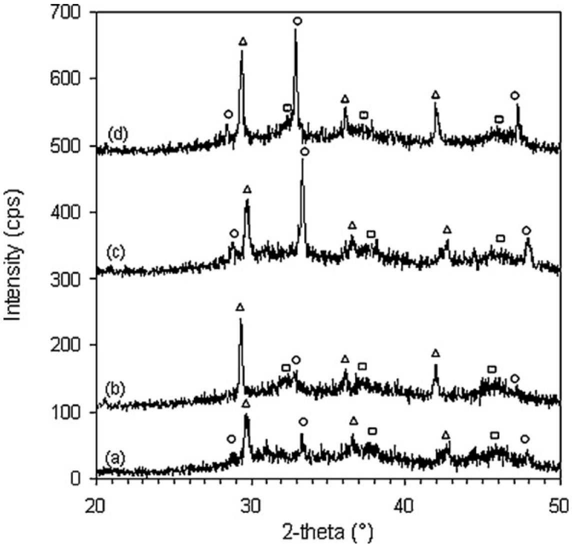

Fig. 4. X-ray diffractograms of 5 mmol g^{-1} KF/γ-alumina at (a) 100 °C, (b) 450 °C and 10 mmol g^{-1} KF/γ-alumina at (c) 100 °C and (d) 400 °C. (○) KF (△) K_3AlF_6 (□) Al_2O_3.

sity correlated with the activity for double bond isomerisation and Tishchenko reaction.

In order to elucidate the nature of the activity for aldol condensation, we recorded the powder X-ray diffractograms *in situ* during heat treatment and determined the phases present on the alumina-supported KF samples as the temperature was raised. For 6.75 mol g^{-1} KF/γ-alumina (Fig. 2), both KF (ICCD 00-036-1458) and K_3AlF_6 (ICCD 00-003-0615) phases could be observed in the as-synthesized sample. The presence of K_3AlF_6 suggests that the KF interacts strongly with the alumina support. The presence of the KF phase is indicated by peaks at 2θ ~28.9°, 33.6° and 48.1°, corresponding to diffraction from the (1 1 1), (2 0 0), and (2 2 0) planes, respectively. Upon heating, the (1 1 1) peak increased in intensity and reached a maximum at 400–450 °C (Fig. 3). At 500 °C, only the most intense peaks of KF (2θ ~33.6° and ~48.1°) and K_3AlF_6 (2θ ~29.7°, ~36.6° and ~42.5°) can still be observed. These peaks were no longer observable on further heating to 600 °C. As samples treated to 500 °C were no longer catalytically active, neither K_3AlF_6 nor the exposed (2 0 0) and (2 2 0) planes of KF can be the active phases. For the 5 mmol g^{-1} sample, the (1 1 1) peak was very small at 100 °C and not observed after heating to 450 °C (Fig. 4). In contrast, for 10 mmol g^{-1} KF/γ-alumina, this peak is observed already at room temperature. The correlation with conversion measurements suggests that the (1 1 1) planes of KF is responsible for the catalytic activity in the aldol condensation. With high KF loadings, more of these planes are present from the beginning, while at low KF loading, decomposition of the K_3AlF_6 phase during pretreatment at 450 °C may give rise to the formation of KF with more (1 1 1) planes exposed.

4. Conclusions

γ-Alumina-supported KF is an active catalyst in the cross-aldol condensation between citral and acetone. The selectivity to pseudoionones is >93% for acetone/citral ratios above 6. For KF loadings below 6.75 mmol g^{-1}, pretreatment at 450 °C resulted in a significant increase of the activity compared to the untreated sample. For KF loading above 8.5 mmol g^{-1}, the activity of the pretreated catalyst was similar to that of the untreated catalyst. The catalytic activity was correlated with the appearance of a strong KF (1 1 1) reflection in the X-ray diffractogram. Considering the ease of preparation, handling, good activity and selectivity coupled with the lack of leaching, KF/γ-alumina is an effective catalyst in the synthesis of pseudoionones.

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