

Highly efficient self-condensation of benzaldehyde to benzyl benzoate over KF-loaded alumina

Haruhisa Handa ^a, Toshihide Baba ^a, Hisashi Sugisawa ^b, Yoshio Ono ^{a,*}

^a Department of Chemical Engineering, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

^b Analytical Instrument Division, JEOL, 1-2 Musashino 3-Chome, Akishima-shi, Tokyo 196, Japan

Received 15 September 1997; accepted 20 October 1997

Abstract

The self-condensation of benzaldehyde to benzyl benzoate was carried out over KF-loaded alumina. The catalytic activity strongly depends on the loading amount of KF. The pretreatment of the catalyst at high temperature under vacuum is essential for the high catalytic activity. When KF (5 mmol/g-alumina) loaded alumina was evacuated at 673 K, the catalyst gave selectively benzyl benzoate, whose yield was 94.2% in 3 h at 323 K. © 1998 Published by Elsevier Science B.V. All rights reserved.

Keywords: Self-condensation; Benzaldehyde; Benzyl benzoate; KF-loaded alumina; Solid base

1. Introduction

It has been reported that KF-loaded alumina (KF–Al₂O₃) shows an efficient solid base catalyst for promoting versatile chemical transformations [1–11], such as the Michael addition [1–6], C-, N-, O- and S-alkylation reactions [7,8], the Knoevenagel condensation [2,9], Wittig–Horner reactions [10] and alkene isomerization [11].

It is known that the catalytic activity of KF–Al₂O₃ depends very much on the drying conditions of alumina after loading KF by impregnation or loading amount of KF [3,12]. In general, drying temperature is, at its highest, 473 K under reduced pressure. Recently, Hattori and coworkers reported that treating KF–Al₂O₃ at

high temperature (573–673 K) under high vacuum is essential for obtaining the high catalytic activity for double-bond isomerization of 1-pentene [13].

In this work, we report the catalytic activities of KF–Al₂O₃ for the self-condensation of benzaldehyde into benzyl benzoate.



It will be emphasized that the high temperature pretreatment of the catalyst under vacuum is indispensable for the condensation.

The catalytic self-condensation of aldehydes to esters, catalyzed by aluminum alkoxide is known as Tishchenko-reaction [14]. The condensation of benzaldehyde to benzyl benzoate is also catalyzed by various homogeneous [15–19] and heterogeneous catalysts [20–22]. For example, transition metal complexes such as di-

* Corresponding author.

sodium tetracarbonyl-ferrate(II) [15] are very active. Solid base catalysts are also active for the self-condensation. Thus, alkaline earth metal oxides are reported to catalyze the condensation. The catalytic activity of CaO catalysts is proportional to the number of basic sites [20].

Here, KF–Al₂O₃ is a highly active and selective catalyst for the self-condensation of benzaldehyde to benzyl benzoate. The effects of the reaction conditions and the pretreatment temperature on the catalytic activities are studied. The characterization of KF–Al₂O₃ by XRD, IR and ¹⁹F MAS NMR are also described.

2. Experimental

2.1. Catalyst preparation

The Alumina used had a surface area of 141 m² g⁻¹ and an average diameter of 15 nm. KF, KOH and K₂CO₃ loaded on alumina were prepared through an impregnation method of their aqueous solutions then left to dry for 12 h at 393 K. Prior to the reaction, the catalyst was evacuated under 10⁻³ Pa at a prescribed temperature for 3 h.

KNH₂ loaded on alumina was prepared by impregnation from its ammoniacal solution as follows: alumina and a small amount of Fe₂O₃ (2 wt.% g-alumina⁻¹) was placed in a quartz reactor and then heated under vacuum at 673 K for 3 h. Fe₂O₃ was a catalyst in converting K metal into KNH₂ in liquid ammonia. A piece of K metal (2.6 mmol g-alumina⁻¹) was added into the reactor under nitrogen. After the evacuation, ammonia was liquefied to dissolved the K metal. The blue color due to solvated electrons disappeared in about 10 min, indicating the formation of KNH₂. After 1 h, the reactor was warmed to room temperature removing most of the ammonia and then heated under vacuum at 573 K for 1 h.

2.2. Reaction of benzaldehyde

Benzaldehyde purified by distillation was placed into a glass tube, which was attached to

the side arm of the quartz reactor and degassed through a freeze–thaw method. The reaction started as benzaldehyde was transferred into the reactor containing a catalyst prepared (as described above) without solvent. The products were identified with ¹H NMR and GS-MAS. The conversion of benzaldehyde and the yields of the products were determined by gas-chromatograph (a OV 101 glass column) using toluene as an internal standard.

2.3. XRD and IR measurements

XRD spectra of KF–Al₂O₃ were recorded on RIGAKU DENKI RINT2000 spectrometer after exposing the sample to air.

IR spectra of KF–Al₂O₃ were recorded on JEOL JIR-WINSPEC50 spectrometer at room temperature by using the self supporting disk (10 mg g⁻¹) evacuated at an elevated temperature for 3 h.

2.4. Sample preparation for ¹⁹F MAS NMR measurements

KF–Al₂O₃ (0.30 g) was packed in a glass tube with side arms; each connected to a glass capsule used for ¹⁹F MAS NMR measurements. KF loaded on alumina was heated under vacuum at an elevated temperature for 3 h. After cooling the sample to room temperature, it was transferred into a glass capsule under vacuum, so as to fill the capsule completely and evenly. The neck of the capsule was then sealed, while the sample itself was maintained at 77 K.

2.5. ¹⁹F MAS NMR measurements

¹⁹F MAS NMR spectra were recorded on a Chemagnetics CMX-Infinity spectrometer operating at 282.4 MHz. A sealed sample in a glass tube was inserted into a zirconia rotor. The spinning rate of the sample was 12 kHz. The chemical shifts were referenced relative to external CFCI₃ (0.0 ppm).

3. Results and discussion

3.1. Time course of the yield of benzyl benzoate

The reaction of benzaldehyde was carried out with KF (5 mmol/g-alumina)–Al₂O₃ without using any solvent at 323 K. The catalyst weight was 0.25 g and the amount of benzaldehyde was 29.5 mmol (3.0 cm³). Fig. 1 shows the change in the yield of benzyl benzoate with the reaction time. The yield increased with the reaction time and reached 94.2% in 180 min. When the reaction was carried out for 20 h, the yield was 98%. The analysis of the time course led to the second order kinetics with respect to the concentration of benzaldehyde.

KF–Al₂O₃ is a very selective catalyst for the self-condensation of benzaldehyde. The selectivity to benzyl benzoate was 100%, and the other products such as benzyl alcohol and benzoic acid, which are Cannizzaro reaction products, were not detected.

3.2. Catalytic activities of various solid bases

The reaction was carried out with various solid base catalysts at 323 K for 3 h, and the yield of benzyl benzoate are listed in Table 1. KF–Al₂O₃ showed the highest catalytic activity. The activity of KNH₂ loaded on alumina was lower than that of KF–Al₂O₃, though it is a

strongly basic catalyst [23]. The activity of KF–Al₂O₃ was much higher than that of KCO₃–Al₂O₃ or KOH–Al₂O₃. Thus, KF–Al₂O₃ has seemingly, the highest activity among the base catalysts reported so far.

Al₂O₃ and KF, when separately used, showed no catalytic activity. Moreover, KF supported on SiO₂, TiO₂, and activated carbon showed no catalytic activity. Thus, it is essential to support KF on alumina to generate catalytic activity in agreement with the results of a previous work [1], indicating that the active sites are generated by the reaction of KF with alumina.

3.3. Influence of the amount of KF supported on alumina

The dependence of the amount of KF-loaded alumina on the yield of benzyl benzoate was examined at 273 K (Fig. 2). The yield increased with increasing KF content, a maximum yield of 46.4% was observed at 5 mmol/g-alumina, corresponding to 0.5 mol KF/mol Al₂O₃. Further increase of the loading amount of KF beyond 5 mmol/g-alumina, led to the decrease of the catalytic activity. The selectivity to benzyl benzoate was always 100%, independent of the loading amount of KF.

3.4. Influence of evacuation temperature

As described earlier, it has been reported that the catalytic activity of KF–Al₂O₃ depends very much on the drying conditions of alumina after loading KF by impregnation or loading amount of KF [3,12]. Recently, Hattori and coworkers reported that treating KF–Al₂O₃ at high temperature (573–673 K) under high vacuum is essential in obtaining the high catalytic activity for double-bond isomerization of 1-pentene [13]. Therefore, we examined the dependence of the catalytic activity of KF–Al₂O₃ for self-condensation of benzaldehyde on the heating temperature of the catalyst under vacuum.

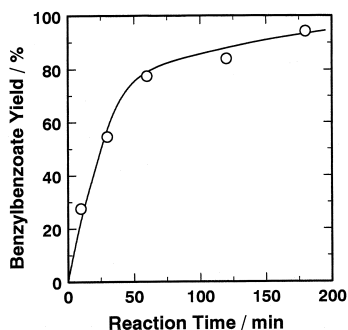


Fig. 1. Time course of the yield of benzyl benzoate over KF–Al₂O₃. KF–Al₂O₃: 0.25 g, reaction temperature: 323 K, benzaldehyde: 29.5 mmol. The amount of KF was 5.0 mmol/g-alumina. The catalyst was evacuated at 673 K for 3 h.

Table 1

Catalytic activities of various solid base catalysts for the self-condensation of benzaldehyde to benzyl benzoate

Catalyst	Evacuation temperature (K)	Yield of benzyl benzoate (%)
KF/Al ₂ O ₃	673	98.8 ^a
	673	94.2
KNH ₂ /Al ₂ O ₃ ^b	573	75.5
K ₂ CO ₃ /Al ₂ O ₃	673	22.6
KOH/Al ₂ O ₃	673	1.4
Al ₂ O ₃	673	0

Reaction temperature: 323 K, reaction time: 3 h, the amount of benzaldehyde: 29.5 mmol (3.0 cm³), catalyst weight: 0.25 g, the amount of base: 5.0 mmol/g-alumina.

^aReaction time: 20 h.

^bAmount of KNH₂: 2.6 mmol/g-alumina.

Fig. 3 shows the influence of the evacuation temperature on the catalytic activities of KF–Al₂O₃ at 273 K. The catalytic activity strongly depended on the evacuation temperature. The yield of benzyl benzoate sharply increased with increasing evacuation temperature and reached around a maximum temperature of 670 K. At higher evacuation temperature, the catalytic activity declined and almost disappeared by evacuating the catalyst at 873 K. The product was only benzyl benzoate, whose selectivity was 100%, independent of the evacuation temperature.

The influence of the evacuation temperature on the catalytic activity for the isomerization of 2,3-dimethyl-1-butene was examined at 313 K and is also shown in Fig. 3. The similar dependence of the evacuation temperature on the catalytic activity to that on the benzaldehyde

reaction was observed, though the temperature giving the highest activity is slightly shifted. The evacuation temperature dependence shown in Fig. 3 is almost the same as the results reported by Hattrori and co-workers for the isomerization of 1-pentene [13].

It should be noted that the high-temperature pretreatment is indispensable for getting high catalytic activity for both self condensation of benzaldehyde and alkene isomerizations. No catalytic activities were observed when the pretreatment temperature was below 473 K under the reaction conditions.

The surface area of KF–Al₂O₃ did not change much in the pretreatment temperature range of 523 to 773 K, being constant (ca. 90 m²/g).

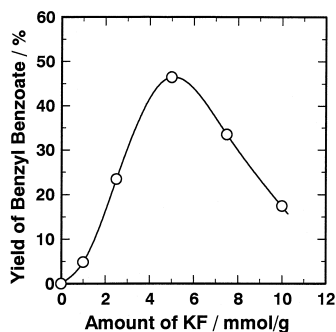


Fig. 2. Influence of the amount of KF-loaded alumina on the yield of benzyl benzoate. Reaction temperature: 273 K, reaction time: 3 h, benzaldehyde: 29.5 mmol, catalyst weight: 0.25 g. The catalyst was evacuated at 673 K for 3 h.

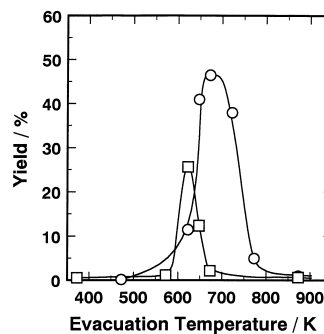
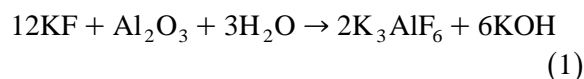


Fig. 3. Influence of evacuation temperature of KF (5 mmol/g-alumina)–Al₂O₃ on the yield of benzyl benzoate. (○): Self-condensation of benzaldehyde. Reaction temperature: 273 K, reaction time: 3 h, benzaldehyde: 29.5 mmol, catalyst weight: 0.25 g. (□): Isomerization of 2,3-dimethyl-1-butene. Reaction temperature: 313 K, reaction time: 20 h, 2,3-dimethyl-1-butene: 24 mmol, catalyst weight: 0.25 g.

This result indicated that the sharp decrease in the activity of KF–Al₂O₃ above 673 K is not caused by the decrease in the surface area, and that the surface chemical state of the KF–Al₂O₃ changes with thermal treatment. The same result was also reported by Hattori and co-workers [13].

3.5. Basic sites on KF / Al₂O₃

As for the basic sites on KF–Al₂O₃, several proposals has been made [3,12,24]. It is known that K₃AlF₆ is formed by the reaction of aqueous KF and alumina.



Weistock et al. also found the formation of carbonate ions by IR spectroscopy [24]. Based on these results, they concluded that the high reactivity of KF–Al₂O₃ was a consequence of potassium hydroxide and/or carbonate formation by the reaction of KF with Al₂O₃ and that fluoride ion has little or no direct role in the catalytic activity of KF–Al₂O₃ [24]. The carbonate was supposed to be formed by the reaction of carbon dioxide and KOH formed by reaction (1) during the drying procedure. On the other hand, Ando et al. stressed the importance of coordinatively unsaturated F[−] ions, though they did not deny the participation of the hydroxide species [3,12].

We have examined the surface property of KF–Al₂O₃. The formation of K₃AlF₆ was confirmed by XRD in the sample upon loading KF on Al₂O₃ by impregnation. K₃AlF₆ still existed after heating the sample at 673 K. Fig. 4 shows the ¹⁹F MAS NMR spectrum of KF–Al₂O₃ evacuated at 673 K. The major band was observed at −157 ppm, beside two bands at −135 ppm and −166 ppm. The major peak is assigned to K₃AlF₆ because of the agreement of the chemical shift value with the authentic sample. This shows the most of fluorine atoms exist

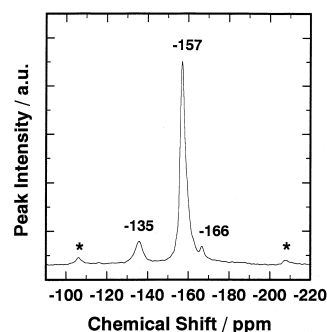


Fig. 4. ¹⁹F MAS NMR spectrum of KF (5 mmol/g-alumina)–Al₂O₃ evacuated at 673 K for 3 h. (*): Spinning side bands.

as K₃AlF₆. Duke and Miller have already reported that ¹⁹F MAS NMR of KF-loaded alumina is observed at −155 ppm and assigned the peak to K₃AlF₆ [25].

To check the catalytic activity of K₃AlF₆, the reaction was carried out by using neat K₃AlF₆ and K₃AlF₆ which had been loaded on Al₂O₃ by impregnation and heated under vacuum at 673 K. Both catalysts showed no catalytic activity.

The XRD pattern due to K₃AlF₆ was observed after pretreatment at 873 K, where the catalytic activity of KF–Al₂O₃ was completely lost. These results confirmed that K₃AlF₆ is not a catalytically active species.

The small peak at −135 ppm is assigned to F[−] species on the surface. The intensity of this band increases with evacuation temperature and through a maximum at 673 K, it decreased. The peak was not observed when the sample was evacuated at 873 K. The intensity change with evacuation temperature parallels with the change in the catalytic activity for benzaldehyde self-condensation. This indicates that the F[−] species giving this ¹⁹F NMR signal is directly related to the catalytic activity.

The chemical shift values of alkaline metal fluorides, MF (M = Li, Na, K, Rb Cs) ranges from −130 ppm to −79 ppm [26]. The value of −135 ppm for F[−] species on the surface of KF–Al₂O₃ indicates that this F[−] species is more electron-rich than F[−] ions in solid MX.

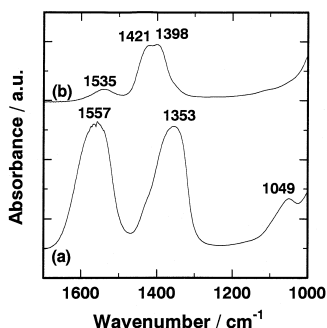


Fig. 5. IR spectrum of KF–Al₂O₃. (a) KF (5 mmol/g-alumina)–Al₂O₃ evacuated at 473 K for 3 h. (b) KF (5 mmol/g-alumina)–Al₂O₃ evacuated at 673 K for 3 h.

This may account for the high activity of KF–Al₂O₃ treated at 673 K.

3.6. Role of carbonate and hydroxide species

The IR spectra of KF–Al₂O₃ evacuated at 473 K showed two bands at 1557 and 1353 cm⁻¹. These bands are assigned to bidentate-type CO₃²⁻ [27] Fig. 5. When evacuated at 673 K, the bands were observed at 1535, 1421, and 1398 cm⁻¹, indicating that both bidentate- and monodentate-type carbonate species exist on the surface of KF–Al₂O₃. However, the catalytic activity of K₂CO₃–Al₂O₃ for the self-condensation of benzaldehyde was much lower than KF–Al₂O₃, as shown in Table 1. Therefore, it is unlikely that the carbonate species is a catalytically active species for this reaction.

Furthermore, the catalytic activity of KOH–Al₂O₃ was very low (Table 1), while the surface area of KOH–Al₂O₃ was 121 m²/g, which is larger than that of KF–Al₂O₃ (92 m²/g). These results indicated that the hydroxide is not responsible for the catalytic activity.

We compared the catalytic activities of three catalysts, KF–Al₂O₃, K₂CO₃–Al₂O₃, and KOH–Al₂O₃ for isomerization of 2,3-dimethylbut-2-ene to 2,3-dimethylbut-1-ene. Table 2 shows that the catalytic activity of KF–Al₂O₃ is much lower than those of K₂CO₃–Al₂O₃ and KOH–Al₂O₃. Thus, the order of the catalytic

Table 2

Isomerization of 2,3-dimethylbut-1-ene to 2,3-dimethylbut-2-ene

Catalyst	Evacuation temperature (°C)	Conversion (%)
K ₂ CO ₃ –Al ₂ O ₃	673	89
KOH–Al ₂ O ₃	673	86
KF–Al ₂ O ₃	623	26
	673	2

Reaction temperature: 313 K, catalyst: 0.25 g, reaction time: 20 h, 2,3-dimethylbut-1-ene: 24 mmol (3 cm³), the amount of base: 5.0 mmol/g-alumina.

activity for benzaldehyde self-condensation is different from that of alkene isomerization.

4. Conclusion

KF (5 mmol/g-alumina)–Al₂O₃ heated under vacuum at 673 K catalyzes highly efficient self-condensation of benzaldehyde to benzyl benzoate. It follows that the active sites on KF–Al₂O₃ is different from those of K₂CO₃–Al₂O₃ and KOH–Al₂O₃. This again suggests that carbonate or hydroxide species is not responsible for the catalytic activity on KF–Al₂O₃.

References

- [1] J. Yamawaki, T. Ando, Chem. Lett. (1979) 755.
- [2] J. Yamawaki, T. Kawata, A.T. Hanafusa, Bull. Chem. Soc. Jpn. 56 (1983) 1885.
- [3] T. Ando, S.J. Brown, J.H. Clark, D.G. Cork, T. Hanafusa, J. Ichihara, J.M. Miller, M.S. Robertson, J. Chem. Soc. Perkin Trans. 2 (1986) 1133.
- [4] D. Villemin, J. Chem. Soc., Chem. Commun. (1983) 1092.
- [5] P. Laszlo, P. Penntreau, Tetrahedron Lett. 26 (1985) 2645.
- [6] J.H. Clark, D.G. Cork, M.S. Robertson, Chem. Lett. (1983) 1145.
- [7] J. Yamawaki, T. Ando, Chem. Lett. (1980) 533.
- [8] J. Yamawaki, T. Ando, T. Hanafusa, Chem. Lett. (1981) 1143.
- [9] T. Ando, J. Yamawaki, T. Kawata, S. Sumi, T. Hanafusa, Bull. Chem. Soc. Jpn. 55 (1982) 2504.
- [10] F. Texier-Boullet, D. Villemin, M. Ricard, H. Moison, A. Foucaud, Tetrahedron 41 (1985) 1259.
- [11] A.S. Radhakrishna, S.K. Suri, K.R.K. Prasad Rao, K. Sivaprakash, B.B. Singh, Syn. Commun. 20 (1990) 345.
- [12] T. Ando, J.H. Clark, D.G. Cork, T. Hanafusa, J. Ichihara, T. Kimura, Tetrahedron Lett. 28 (1987) 1421.

- [13] H. Tsuji, H. Kabashima, H. Kita, H. Hattori, *React. Kinet. Catal. Lett.* 56 (1995) 363.
- [14] V.C. Tishchenko, *J. Russ. Phys. Chem. Soc.* 38 (1906) 355 and 485.
- [15] M. Yamashita, Y. Watanabe, T. Mistudo, Y. Tagegami, *Bull. Chem. Soc. Jpn.* 49 (1976) 3597.
- [16] H. Horino, T. Ito, A. Yamamoto, *Chem Lett.* (1978) 17.
- [17] K. Yokoo, N. Mine, H. Taniguchi, Y. Fujiwara, *J. Organomet. Chem.* 255 (1983) 71.
- [18] G.M. Villacorta, J.S. Filippo Jr., *J. Org. Chem.* 48 (1982) 1151.
- [19] P.R. Stapp, *J. Org. Chem.* 38 (1973) 1433.
- [20] K. Tanabe, K. Saito, *J. Catal.* 35 (1974) 247.
- [21] H. Tsuji, F. Yagi, H. Hattori, H. Kita, *J. Catal.* 148 (1994) 759.
- [22] F. Scott, F.R. van Heerden, H.G. Ranbenheimer, *J. Chem. Res.* (1994) 144.
- [23] T. Baba, H. Handa, Y. Ono, *J. Chem. Soc., Faraday Trans.* 90 (1994) 187.
- [24] L.M. Weinstock, J.M. Stevenson, *Tetrahedron Lett.* 27 (1986) 3845.
- [25] C.V.A. Duke, J.M. Miller, *J. Mol. Catal.* 62 (1990) 233.
- [26] J.H. Clark, E.M. Goodman, D.K. Smith, S.J. Brown, J.M. Miller, *J. Chem. Soc., Chem. Commun.* (1986) 657.
- [27] J.V. Evans, T.L. Whateley, *Trans. Faraday Soc.* 63 (1967) 2769.