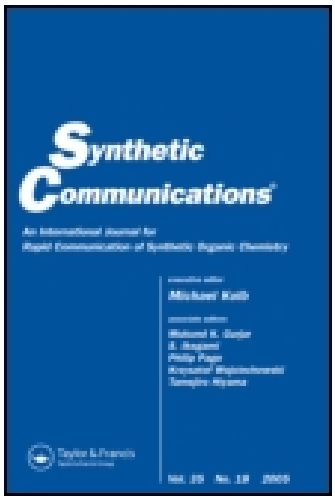

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KF-Al_2O_3 MEDIATED CROSS-CANNIZZARO REACTION UNDER MICROWAVE IRRADIATION*

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$KF\text{-}Al_2O_3$ MEDIATED CROSS-CANNIZZARO REACTION UNDER MICROWAVE IRRADIATION*

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ABSTRACT

Aromatic aldehydes are selectively converted to the corresponding alcohols in high yields by cross-Cannizzaro reaction using $KF\text{-}Al_2O_3$ under microwave irradiation in solvent-free condition.

Surface mediated solid state reactions coupled with mircrowaves[1] have received much attention due to their operational simplicity, enhanced reaction rates, greater selectivities, cleaner reaction products and simple experimental/isolation procedures. Organic transformations which normally require longer reaction times at reflux temperature can be achieved conveniently and rapidly by microwave irradiation. The Cannizzaro reaction is an important inexpensive process[2] for the preparation of alcohol and acid

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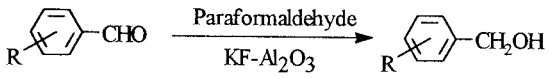
from aromatic aldehydes. This reaction is normally carried out in solution phase employing strong bases[3–5] like NaOH, KOH and $Ba(OH)_2 \cdot 8H_2O$ etc.

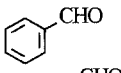
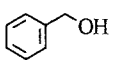
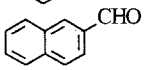
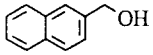
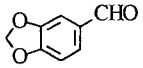
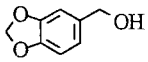
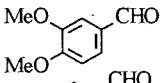
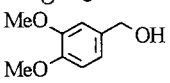
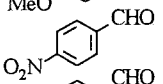
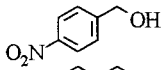
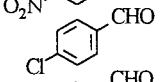
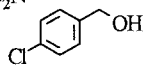
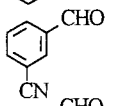
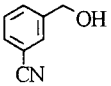
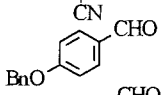
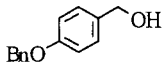
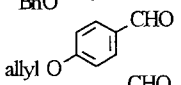
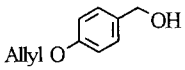
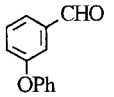
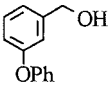
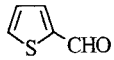
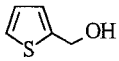
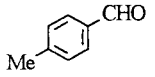
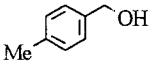
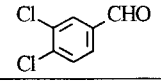
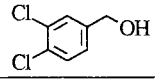
Recently, cross-Cannizzaro reactions have been reported[6] by using NaOH and $Ba(OH)_2 \cdot 8H_2O$ as bases formaldehyde as hydride source to produce alcohols in good yields from the corresponding aromatic aldehydes. Such strongly basic conditions promote substantial amounts of byproducts due to the side reactions associated with strong bases. Existing processes for this conversion involve harsh conditions and environmentally unfavourable solvents. Further, there is an advantage in developing an efficient and rapid method for the preparation of alcohols using inexpensive and recoverable catalysts under solvent-free conditions.



Scheme.

In continuation of our interest on microwave-assisted solid state reactions,[7] herein we report a rapid, efficient and practical method for cross-Cannizzaro reaction to produce alcohols in higher yields. The reaction proceeds efficiently in excellent yields under microwave irradiation in the absence of solvent. Several substituted aromatic aldehydes underwent clean and remarkably fast cross-Cannizzaro reaction with paraformaldehyde in presence of $KF\text{-}Al_2O_3$ under microwave irradiation. The reactions are quick and clean, and afford exclusively alcohols in excellent yields without the formation of undesirable side products. It is remarkable to observe that the reactions are slow and afford moderate yields of the products when unsupported KF is employed in place of $KF\text{-}Al_2O_3$. Further, several undesirable side products were formed along with required alcohols when basic alumina was used for this transformation under similar reaction conditions. High conversions were obtained with KF supported on basic alumina. To confirm the rate enhancement, benzaldehyde was reacted with paraformaldehyde in the presence of 37% KF on Al_2O_3 (3 wt equiv. of aldehyde) under microwave irradiation for 5 min to afford benzyl alcohol in 92% yield, whereas the same reaction under thermal conditions in refluxing dioxane requires a longer reaction time of 7 h and gave 85% yield of benzyl alcohol. This clearly shows the role of microwave irradiation in enhancing reaction rates and yields of the products. Aromatic aldehydes bearing electron withdrawing substituents are rapidly converted to the corresponding alcohols in high yields when compared to those possessing electron releasing

Table. KF-Al_2O_3 Mediated Cross-Cannizzaro Reaction Under Thermal and Microwave Irradiation

Entry	Aldehyde	Alcohol	Reaction Time (Yield)[c]	
			Microwave Irradiation[a]	Conventional Heating[b]
a.			5 min (92)	7 h (85)
b.			8 min (85)	12 h (80)
c.			7 min (88)	9 h (78)
d.			6 min (83)	10 h (83)
e.			3 min (95)	6 h (90)
f.			3 min (92)	8 h (87)
g.			3 min (94)	6 h (89)
h.			5 min (89)	9 h (77)
i.			5 min (86)	10 h (75)
j.			3 min (88)	8 h (80)
k.			3 min (94)	5 h (89)
l.			4 min (87)	7 h (78)
m.			4 min (93)	10 h (73)

[a] Pulsed irradiation (1 min with 30 sec interval) operating at 650 W.

[b] Refluxed in dioxane.

[c] Isolated yields after purfication. 5 to 12% corresponding acids were isolated.

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substituents in the ring. The reactions are very clean and free from aromatic by-products which are normally formed in Cannizzaro reactions under conventional conditions.

In conclusion, the letter describes a rapid and efficient procedure for the preparation of alcohols by cross-Cannizzaro reaction using an inexpensive and surface bound reagent KF-Al_2O_3 under microwave irradiation in solvent-free conditions.

EXPERIMENTAL

Method A – Microwave Irradiation: A mixture of benzaldehyde (5 mmol) and paraformaldehyde (10 mmol) was admixed with 37% KF on Al_2O_3 (3 wt. equiv. of aldehyde) in a pyrex test tube and subjected to microwave irradiation at 650 W for an appropriate time. On completion of the reaction, as indicated by TLC, the reaction mass was directly charged on a silica gel column (Aldrich, 100–200 mesh) and eluted with ethyl acetate–hexane (2 : 8) to afford benzyl alcohol in 91% yield.

Method B – Conventional Heating: A mixture of benzaldehyde (5 mmol), paraformaldehyde (10 mmol) and KF-Al_2O_3 (3 wt. equiv. of aldehyde) was refluxed in dioxane for a specified time as required to complete the reaction. After complete conversion as indicated by TLC, the reaction mass was filtered and concentrated in vacuo. The resulting product was purified as above to afford benzyl alcohol in 85% yield.

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