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Short communication

Fly-ash:H_2SO_4 catalyzed solvent free efficient synthesis of some aryl chalcones under microwave irradiation

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ABSTRACT

Some 2*E* aryl chalcones have been synthesized using greener catalyst Fly-ash:H_2SO_4 assisted solvent free environmentally benign Crossed-Aldol reaction. The yields of chalcones are more than 90%. The synthesized chalcones are characterized by their physical constants and spectral data.

1. Introduction

Heterogeneous catalytic Aldol and Crossed-Aldol condensation is a powerful tool for formation of carbon–carbon bond in many kinds of carbonyl compounds [1]. Also microwave assisted solvent free Aldol and Crossed-Aldol condensation were useful synthesis of carbonyl compounds [2]. Thermal aldol reaction is found to be sluggish and took longer time with low yields. However in the microwave heating conditions, the rate of reaction is fast as a result the reaction times are shorter and yield are high with easy isolation of products. Numerous green catalysts have been used for synthesizing chalcones such as silica-sulphuric acid [1,3], anhydrous zinc chloride [4], clay [5], ground chemistry catalysts-grinding the reactants with sodium hydroxide [6], aqueous alkali in lower temperature [7], solid sulphonic acid from aqueous alkali in lower temperature [7], solid sulphonic acid from bamboo [8], barium hydroxide [9] anhydrous sodium bicarbonate [10], microwave assisted synthesis [11], Fly-ash:water [12] and sulphated titania [13]. Chalcones possess various multi-pronged activities such as antimicrobial [14], antidepressants [15], antiplasmodial [16], anti-aids [17] and insect antifeedant activities [18,19]. In the present investigation, the authors wish to report a new versatile catalyst Fly-ash:H_2SO_4 for efficient synthesizing chalcones by Crossed-Aldol condensation reaction. The yields of chalcones are more than 96%. The synthesized chalcones are characterized by their physical constants, mass, IR and NMR spectral data as they are unknown compounds so far. The purities of the known synthesized chalcones have been checked by their physical constants and their spectral data earlier published in the literature.

2. Experimental

2.1. Materials and methods

All chemicals were procured from E-Merck brand. Fly ash was collected from Thermal Power Plant-II, Neyveli Lignite Corporation (NLC), Neyveli, Tamil Nadu, India. Melting points of all chalcones were determined in open glass capillaries on Mettler FP51 melting point apparatus and are uncorrected. Infrared spectra (KBr, 4000–400 cm^{-1}) were recorded on an Avatar-300 Fourier transform spectrophotometer. The NMR spectra of unknown compounds were recorded in Bruker AVIII 5000 spectrometer operating at 500 MHz for ^1H NMR spectra and 125.46 MHz for ^{13}C NMR spectra in $CDCl_3$ solvent using TMS as internal standard. Electron impact (EI, 70 eV) and chemical ionization mode FAB^+ mass spectra were recorded with a Varian 500 spectrometer.

2.2. Preparation and characterization of catalyst

In a 50 mL Borosil beaker, 1 g of Fly-ash and 0.8 mL (0.5 mol) of sulphuric acid were taken and mixed thoroughly with glass rod. This mixture was heated on a hot air oven at 85 °C for 1 h, cooled to room temperature, stored in a Borosil bottle and tightly capped. This was characterized by infrared spectra and SEM analysis.

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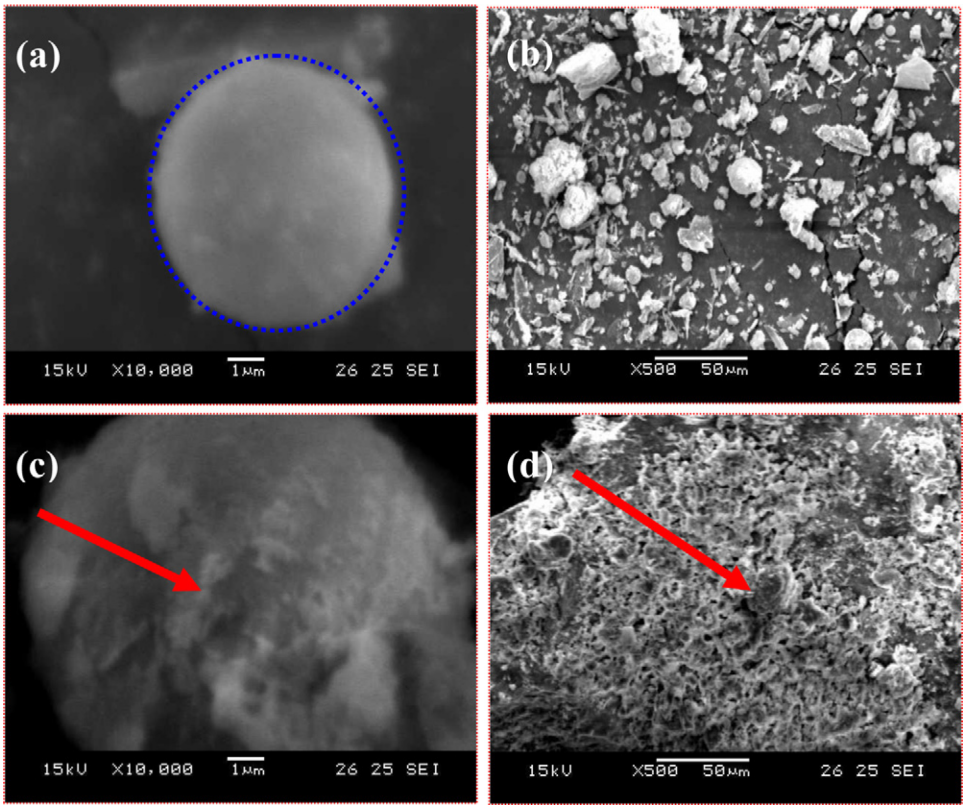


Fig. 1. SEM images of pure fly ash and Fly-ash:H_2SO_4: (a) Pure Fly-ash (1 µm); (b) pure Fly-ash (50 µm); (c) Fly-ash:H_2SO_4 (1 µm) (⇒ – corroded); (d) Fly-ash:H_2SO_4 (50 µm) (⇒ – corroded).

Infrared spectral data of Fly-ash:H_2SO_4 is ν (cm^{-1}): 3456 (OH); 3010 (C—H); 1495, 1390 (C—S); 1336, 1154 (S=O); and *out of plane* modes: 1136, 1090, 976, 890, 850, 820, 667, 658, 620, 580, 498, 425.

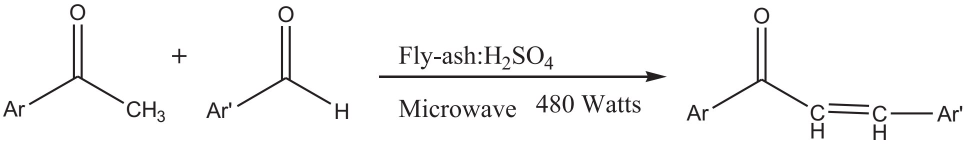
The SEM images of pure Fly-ash and Fly-ash:H_2SO_4 at two different magnifications are shown in Fig. 1a–d. Fig. 1a and b depicted that the crystallinity is found to be more in pure fly ash. The spherical shaped particles are clearly seen at both magnifications in Fig. 1a and b. Fig. 1a reveals that the globular structure of pure fly ash (round shaped particle). This also seen from Fig. 1c and d that some of the particles are slightly corroded by H_2SO_4 (indicated by arrow mark) and this may be due to dissolution of Fly-ash by H_2SO_4. This will further confirmed by Fig. 1d, the well-shaped particles of pure Fly-ash. Fig. 1b is aggregated to Fig. 1d due to presence of H_2SO_4.

2.3. Synthesis of chalcones

An appropriate equi-molar quantities of aryl methyl ketones (2 mmol), substituted benzaldehydes (2 mmol) and Fly-ash:H_2SO_4 (0.75 g) were taken in Borosil tube and tightly capped. The mixture was subjected to microwave heated for 5–6 min in a microwave oven (Scheme 1) (LG Grill, Intellowave, Microwave Oven, 160–800 W) and then cooled to room temperature. The organic layer was separated with dichloromethane and the solid product was obtained on evaporation. The solid, on recrystallization with benzene–hexane mixture gave glittering pale yellow solid. The insoluble catalyst was recycled by washing the solid reagent remained on the filter by ethyl acetate (8 mL) followed by drying in an oven at 100 °C for 1 h and it was made reusable for further reactions.

3. Results and discussion

Fly ash is a waste air-pollutant and it has many chemical species [10,12,20] SiO_2, Fe_2O_3, Al_2O_3, CaO, MgO and insoluble residues. The waste Fly-ash is converted into useful catalyst Fly-ash:H_2SO_4 by mixing Fly-ash and sulphuric acid. The sulphuric acid group and chemical species present in the Fly-ash have enhanced the catalytic activity. During the course of the reactions these species are responsible for the promoting effects on condensation between the aryl ketone and aryl aldehydic groups leading to the formation of unsaturated ketone. The proposed general reaction mechanism is shown in (Fig. 2). For this condensation, generally a base is used as a catalyst. In the case of base catalyzed aldol condensation, the mechanism generally involves the formation of anion of ketone. Whilst in our case Fly-ash:H_2SO_4 act as a solid acid catalyst, it is protonating the aldehyde. The protonated aldehyde attached by the enolic



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Scheme 1. Synthesis of chalcones by Fly-ash:H_2SO_4.

Table 1

Analytical and mass spectral data of chalcones synthesized by Fly-ash:H_2SO_4 catalyzed aryl methyl ketones and substituted benzaldehydes reaction of the type $Ar{-}CO{-}CH_3 + Ar'{-}CHO \rightarrow Ar{-}CO{-}CH{=}CH{-}Ar'$ under microwave irradiation.

Entry	Ar	Ar′	Product	M.W.	Yield (%)	M.p. (°C)	Mass (*m*/*z*)
1	C_6H_5	C_6H_5	$C_6H_5COCH{=}CHC_6H_5$	208	93	55–56 (55–58) [20]	–
2	4-$N(CH_3)_2C_6H_4$	C_6H_5	4-$N(CH_3)_2C_6H_4COCH{=}CHC_6H_5$	294	94	87–88 (87–88) [20]	–
3	C_6H_5	$C_{10}H_7$(1-Naph)	$C_6H_5COCH{=}CHC_{10}H_7$	273	95	104–105 (104–105) [21]	–
4	C_6H_5	C_8H_6N(3-Indole)	$C_6H_5COCH{=}CHC_8H_6N$	262	92	140–141 (140) [23]	–
5	C_6H_5	4-OHC_6H_4	$C_6H_5COCH{=}CHC_6H_4OH$	291	94	122–123 (122) [22]	–
6	C_6H_5	4-$OCH_3C_6H_4$	$C_6H_5COCH{=}CHC_6H_4OCH_3$	291	94	164–165 (164) [21]	–
7	4-$NH_2C_6H_5$	C_4H_3(3-Furyl)	$C_6H_5COCH{=}CHC_4H_3$	213	92	120–121 (119–120) [22]	–
8	4-$NH_2C_6H_4$	C_6H_5	4-$NH_2C_6H_4COCH{=}CHC_6H_5$	223	92	98–99 (98–99) [20]	–
9	4-$NH_2C_6H_4$	4-$N(C_2H_5)_2C_6H_4$	4-$NH_2C_6H_4COCH{=}CHC_6H_4N(CH_3)_2$	294	92	90–91	294[M+], 256, 222, 165, 146, 144, 133, 124, 111, 92, 35, 16
10	4-$NH_2C_6H_4$	2,6-$Cl_2C_6H_3$	4-$NH_2C_6H_4COCH{=}CHC_6H_3Cl_2$	291	90	98–99	291[M+]
11	4-$NH_2C_6H_4$	$C_{10}H_7$(1-Naph)	4-$NH_2C_6H_4COCH{=}CHC_{10}H_7$	273	93	124–125	273[M+]
12	4-F-C_6H_4	C_6H_5	4-$FC_6H_4COCH{=}CHC_6H_5$	226	90	49–50 (49–50) [20]	–
13	2,4-$Cl_2C_6H_3$	C_6H_5	2,4-$Cl_2C_6H_3COCH{=}CHC_6H_5$	276	94	80–82 (80–81) [24]	–
14	3,4-$Cl_2C_6H_3$	C_6H_5	3,4-$Cl_2C_6H_3COCH{=}CHC_6H_5$	276	94	100–101 (100–101) [16]	–
15	4-$(OH)C_6H_4$	C_6H_5	2,5-$(OH)C_6H_3COCH{=}CHC_6H_5$	226	90	63–64 (63–64) [20]	–
16	$C_{10}H_7$(1-Naph)	C_6H_5	$C_{10}H_7COCH{:}CHC_6H_5$	258	94	100–102 (100–102) [23]	–
17	4-$BrC_{10}H_6$(1-Naph)	C_6H_5	4-$BrC_{10}H_6COCH{=}CHC_6H_5$	396	95	103–104 (103–104) [20]	–
18	4-$ClC_{10}H_6$(1-Naph)	C_6H_5	4-$ClC_{10}H_6COCH{=}CHC_6H_5$	292	94	122–123 (122–123) [20]	–
19	4-$OCH_3C_{10}H_6$(1-Naph)	C_6H_5	4-$OCH_3C_{10}H_6COCH{=}CHC_6H_5$	310	93	113–114 (113–114) [20]	–
20	4-$CH_3C_{10}H_6$(1-Naph)	C_6H_5	4-$CH_3C_{10}H_6COCH{=}CHC_6H_5$	284	94	98–99 (98) [20]	–
21	$C_{10}H_7$(2-Naph)	C_6H_5	$C_{10}H_7COCH{:}CHC_6H_5$	258	94	104–105 (104–105) [20]	–
22	6-$OCH_3C_{10}H_6$(2-Naph)	C_6H_5	6-$OCH_3C_{10}H_6COCH{=}CHC_6H_5$	310	95	67–68 (67–68) [20]	–
23	6-$CH_3C_{10}H_6$(2-Naph)	C_6H_5	6-$CH_3C_{10}H_6COCH{=}CHC_6H_5$	284	94	123–124 (123–124) [20]	–
24	$C_{13}H_9$(2-Fluorene)	C_6H_5	$C_{13}H_9COCH{=}CHC_6H_5$	296	90	150–151 (150–151) [20]	–
25	$C_{12}H_9$(Biphenyl)	C_6H_5	$C_{12}H_9COCH{=}CHC_6H_5$	284	95	153–154 (153–154) [20]	–
26	C_4H_3O(2-Furyl)	C_6H_5	$C_4H_3OCOCH{=}CHC_6H_5$	198	95	80–81 (80–81) [20]	–
27	5-$CH_3C_4H_2N$(2-Pyrrole)	C_6H_5	5-$CH_3C_4H_2NCOCH{=}CHC_6H_5$	210	94	137–138 (137–138) [20]	–
28	C_4H_3S(2-thienyl)	C_6H_5	$C_4H_3SCOCH{=}CHC_6H_5$	204	95	112–113 (112–113)[20]	–
29	$C_{14}H_{10}$(Anthracene)	C_6H_5	$C_{14}H_9COCH{=}CHC_6H_5$	308	92	124–125 (124–125)[20]	–
30	5-BrC_4H_2S(2-thienyl)	C_6H_5	5-$BrC_4H_2SCOCH{=}CHC_6H_5$	292	96	107–110	292[M+], 294[M+2], 214, 201, 160, 131, 90, 82, 78
31	5-BrC_4H_2S(2-thienyl)	4-BrC_6H_4	5-$BrC_4H_2SCOCH{=}CHC_6H_4Br$	371	94	173–174	371[M+], 373[M+2], 375[M+4], 290, 214, 188, 180, 160, 82, 78
32	5-BrC_4H_2S(2-thienyl)	2-ClC_6H_4	5-$BrC_4H_2SCOCH{=}CHC_6H_4Cl$	326	94	143–145	326[M+], 328[M+2], 290, 165, 160, 82, 78
33	5-BrC_4H_2S(2-thienyl)	4-ClC_6H_4	5-$BrC_4H_2SCOCH{=}CHC_6H_4Cl$	326	95	155–157	326[M+], 328[M+2], 290, 214, 188, 180, 160, 82, 78, 77
34	5-BrC_4H_2S(2-thienyl)	4-$N(CH_3)_2C_6H_4$	5-$BrC_4H_2SCOCH{=}CHC_6H_4N(CH_3)_2$	335	92	142–143	335[M+], 337[M+2], 319, 304, 290, 214, 174, 160, 120, 82, 78 30, 15
35	5-BrC_4H_2S(2-thienyl)	4-FC_6H_4	5-$BrC_4H_2SCOCH{=}CHC_6H_4F$	309	90	164–165	309[M+], 311[M+2], 290, 231, 214, 160, 149, 95, 82, 78, 18
36	5-BrC_4H_2S(2-thienyl)	4-IC_6H_4	5-$BrC_4H_2SCOCH{=}CHC_6H_4I$	416	91	184–185	416[M+], 418[M+2], 420[M+4], 338, 290, 256, 228, 214, 203, 188, 160, 126, 82, 78
37	5-BrC_4H_2S(2-thienyl)	4-$OCH_3C_6H_5$	5-$BrC_4H_2SCOCH{=}CHC_6H_4OCH_3$	322	93	148–149	322[M+], 324[M+2], 306, 290, 243, 214, 161, 160, 107, 91, 82, 78, 55, 31, 15
38	5-BrC_4H_2S(2-thienyl)	4-$CH_3C_6H_5C_6H_5$	5-$BrC_4H_2SCOCH{=}CHC_6H_4CH_3$	306	92	151–152	306[M+], 308[M+2], 290, 214, 160, 145, 91, 82, 78, 15

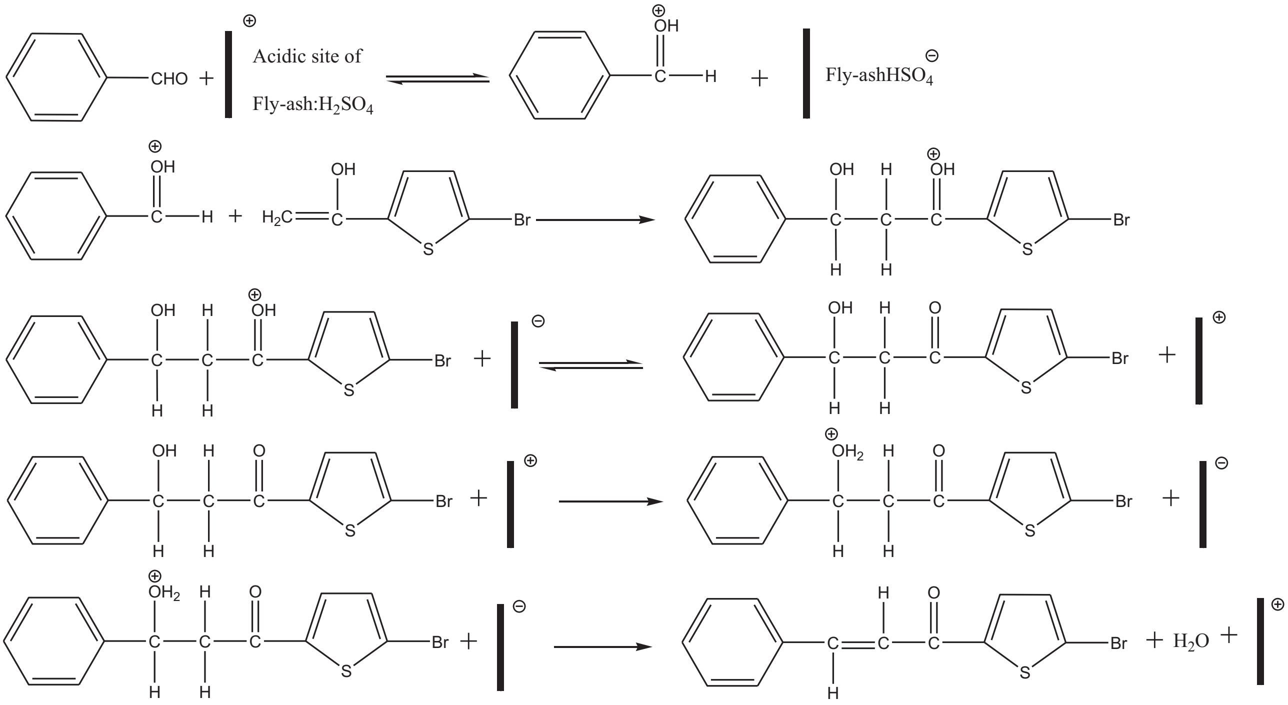

Fig. 2. Proposed mechanism for crossed-aldol reaction of benzaldehydes and 5-bromo-2-thienyl ketone in presence of Fly-ash:H_2SO_4 catalyst.

form of the ketone. This catalyst also initializes the dehydration of the aldol condensed product to form chalcones. A similar mechanism has been proposed for this condensation with the catalyst [13]. In these experiments the products were isolated and the catalyst was washed with ethyl acetate, heated to 100 °C then reusable for further five run reactions. There was no appreciable change in the percentage of yield of chalcones. In this protocol the reaction gave better yields of the chalcones during the condensation without any environmental discharge. The analytical and mass spectral data are presented in Table 1. The IR and NMR spectral data of unknown chalcones are presented in supplementary data (Tables S1–S3).

We have investigated the catalytic effect of Fly-ash:H_2SO_4 on the synthesis of substituted styryl-5-bromo-2-thienyl ketone (Entry **30**) by varying the catalyst quantity from 0.5 g to 1.5 g. As the catalyst quantity is increased from 0.5 g to 0.75 g, the percentage of yield of product is increased from 95 to 96%. Further increase the catalyst amount there is no significant increasing of the percentage of product. This catalytic effect is shown in (Fig. 3). The optimum quantity of catalyst loading was found to be 0.75 g. We have carried out this reaction with various substituted ketones and benzaldehydes. The results, analytical and mass spectral data are summarized in Table 1. There is no significant effect of substituents on the condensation reaction. This reaction mechanism was proposed based on Krishnakumar et al. and Climent et al. [13]. The reusability of this catalyst was studied the reaction of 5-bromo-2-thienyl ketone and benzaldehyde. The reusability of catalyst on crossed-aldol reaction of 5-bromo-2-thienyl ketone and benzaldehydes is given in Table 2. From Table 2, first two runs gave 96% product. The third, fourth and fifth runs of reactions gave the yields 95.8%, 95.7% and 95.5% of chalcones. There was no appreciable loss in its effect of catalytic activity was observed up to fifth run.

Table 2
Reusability of catalyst on condensation of 5-bromo-2-thienyl ketone (2 mmol) and benzaldehydes (2 mmol) under microwave irradiation.

Run	1	2	3	4	5
Yield	96	96	95.8	95.7	95.5

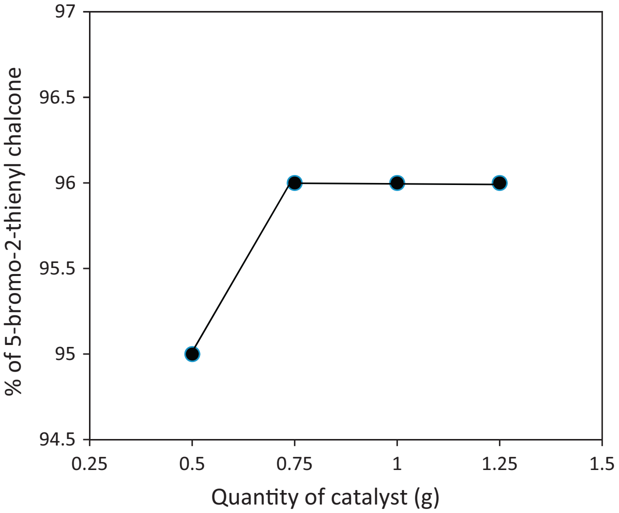

Fig. 3. Effects of catalyst loading.

4. Conclusion

We have developed an efficient catalytic method for synthesis of chalcones by Crossed-Aldol reaction using a solvent free environmentally greener catalyst Fly-ash:H_2SO_4 under microwave irradiation between aryl ketones and aldehydes. This reaction protocol offers a simple, economical, environmentally friendly, non-hazards, easier work-up procedure and good yields.

Supplementary data

The IR and NMR spectral data of unknown chalcones are presented in supplementary data (Tables S1–S3, see supplementary data).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2012.01.054.

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